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CICLO XXIV

SUSTAINABLE DESIGN OF BIOFUEL SYSTEMS: A MODELLING APPROACH FOR THE FINANCIAL AND ENVIRONMENTAL OPTIMISATION OF FIRST AND SECOND GENERATION ETHANOL SUPPLY CHAINS

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To my family
To Stefano

In memory of my little Elsa

As the sun comes up, as the moon goes down
These heavy notions creep around
It makes me think, long ago
I was brought into this life a little lamb, a little lamb
Courageous, stumbling
Fearless was my middle name.
But somewhere there I lost my way
Everyone walks the same
Expecting me to step
The narrow path they've laid
They claim to Walk unafraid
I'll be clumsy instead
Hold me love me or leave me high.
Say "keep within the boundaries if you want to play.
Say "contradiction only makes it harder."
How can I be
What I want To be?
When all I want to do is strip away
These stilled constraints
And crush this charade
Shred this sad masquerade
I don't need no persuading
I'll trip, fall, pick myself up and Walk unafraid
I'll be clumsy instead
Hold me love or me leave me high.
If I have a bag of rocks to carry as I go
I just want to hold my head up high
I don't care what I have to step over
I'm prepared to look you in the eye
Look me in the eye
And if you see familiarity
Then celebrate the contradiction
Help me when I fall to Walk unafraid
I'll be clumsy instead
Hold me love me or leave me high.

(from the album *UP*, R.E.M.)

Foreword

The fulfilment of the research project presented in this Thesis has involved the financial and intellectual support of many people, to whom the author is most grateful.

Most of the research activity that led to the results and achievements summarised in the Thesis has been developed at the Department of Chemical Engineering Principles and Practice of the University of Padova (DIPIC), under the supervision of Prof. Fabrizio Bezzo. Part of the work has been carried out at the Centre for Process Systems Engineering, Chemical Engineering Department, Imperial College London (UK), under the supervision of Prof. Nilay Shah.

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All the material presented in this Thesis is original, unless explicit references provided by the author. The full list of publications drawn from this research project is reported below.

<u>Publications in International Journals</u>

Giarola, S.; A. Zamboni; F. Bezzo (in press). Environmentally conscious capacity planning and technology selection for bioethanol supply chains. *Renewable Energy* doi:10.1016/j.renene.2011.12.011

Giarola, S.; N. Shah; F. Bezzo (in press). A comprehensive approach to the design of ethanol supply chains including carbon trading effects. *Bioresource Technology,* doi:10.1016/j.biortech.2011.11.090.

Giarola, S.; A. Zamboni; F. Bezzo (2011). Spatially explicit multi-objective optimisation for design and planning of hybrid first and second generation biorefineries. *Computers and Chemical Engineering*, **35**, 1782-1797

Khor, C.S.; S. Giarola; B. Chachuat; N. Shah (2011). An optimization-based framework for process planning under uncertainty with risk management. *Chemical Product and Process Modeling*, **6**(2), Article 4

Dal Mas, M.; S. Giarola; A. Zamboni; F. Bezzo (2011). Strategic design and investment capacity planning of the ethanol supply chain under price uncertainty. *Biomass and Bioenergy*, **35**, 2059-2071

<u>Papers Submitted for Publication in International Journals</u>

Giarola, S.; F. Bezzo, N. Shah. A risk management approach to the economic and environmental strategic design of ethanol supply chains. *Biomass and Bioenergy.*

Publications/Abstracts in Conference Proceedings

Khor, C.S.; S. Giarola; B. Chachuat; N. Shah (2011). An optimization-based framework for process planning under uncertainty with risk management. Presented at: *AIChE 2011 Annual Meeting*, Minneapolis, U.S.A., 16th-21st October.

Giarola, S.; N. Shah; F. Bezzo (2011). Assessing the economic and environmental performance of ethanol supply chains under market uncertainty. Presented at: *ISAF XIX*, Verona, Italy, 10th-14th October.

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Giarola, S.; A. Zamboni; F. Bezzo (2011). Supply chain design and capacity planning: From first to second generation biofuel systems. In: *Chemical Engineering Transactions 24, ICheaP-10* (S. Pierucci, Ed.), AIDIC, Milan, Italy, 253-258

Dal Mas, M.; S. Giarola; A. Zamboni; F. Bezzo (2010). Capacity planning and financial optimization of the bioethanol supply chain under price uncertainty. In: *Computer Aided Chemical Engineering 28, European Symposium on Computer Aided Process Engineering* (S. Pierucci, G. Buzzi-Ferraris, Eds.), Elsevier, Amsterdam (The Netherlands), 97-102

Chapters/Sections in Textbooks and Volumes

Giarola, S.; A. Zamboni; F. Bezzo (in press). Environmentally Conscious Supply Chain Design and Capacity Planning: from First to Second Generation Biofuel Systems. In: *AIDIC Conference Series* Vol.10.

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Abstract

During recent years, biofuels have been encountering a particular interest as a means to address the increasing global energy demand reducing the dependency on fossil fuels and mitigating global warming potentials. Among biofuels, biomass-based ethanol has been assuming a leading position in substituting petroleum-based gasoline: even if its actual carbon footprint is still debated, it is generally acknowledged a reduction in net greenhouse gas (GHG) emissions with respect to oil.

Bioethanol current production is based on the so-called first generation conversion technologies, using the products of conventional food crops as feedstocks, as starchy-, sugar- and oil-based resources (e.g., corn, wheat and sugarcane). The enthusiastic support these biofuels were given at the earlier beginning, has eroded more recently as new studies have highlighted their competition with food crops. Thus, the promotion of biofuels produced from cellulosic biomass (second generation biofuels), which does not have any food value, has been strongly recommended. However high capital expenditures and production costs still hinder the establishment of second generation facilities at a commercial scale. In this context, the main question concerns the identification of the most proper strategies (on both economic and environmental terms) to pave the way for a more sustainable transport system.

In light of this complex background, a well-advised transition towards a more sustainable transport system, requires an integrated analysis based on several issues involving the supply chain (SC) as a whole, that may help defining a more comprehensive view of biofuels. In tackling such high-level decision problems, analytical modelling has been recognised as the best optimisation option especially in the early stage of unknown structures design to address the full management of production systems considering all the stages of the production and distribution SC. Mixed Integer Linear Programming (MILP) in particular, represents one of the most suitable tools in determining the optimal solutions of complex SC design problems where multiple alternatives are to be taken into account.

Notwithstanding biorefineries represent an important part of the literature and biofuels have been gaining ever greater attention, strategic biofuels SC design is dealt with in a still limited number of works and some topics need to be properly discussed. Accordingly, the main purpose of this Thesis is to cover this gap of knowledge in the literature. In the context of bioenergy systems development and deployment, the general aim of this work is to provide quantitative and deterministic tools analysing and optimising the overall supply chain, so as to define the most convenient strategies for the development of the future road transport systems. The MILP, often moMILP, (multi-objective Mixed Integer Linear Programming) modelling frameworks developed, enable simultaneous consideration of conflicting criteria (i.e., financial, environmental, economic) to assist the stakeholders' decisions on biofuels industry at strategic and tactical levels. The analysis, in particular, has been approached effectively embodying the Life Cycle Analysis (LCA) principles within the SC Analysis (SCA) techniques aiming at a quantitative assessment of the environmental burdens of each SC stage (i.e., biomass production and transport; fuel production and distribution). In addition, financial assessment has been integrated within the formulation involving properly devised risk indices measuring the trade-off between profitability and the risk the investors might be willing to accept for the business to be established.

The attention has been devoted, in particular, to the identification of the suitable strategies to pave the way for the most sustainable technologies for ethanol production. First, a broad range of processes (belonging to both first and second generation) has been dealt with, considering also the possibility of integrating multiple feedstocks within properly devised hybrid technologies using both starchy- and cellulose-rich materials. Then, the analysis has been focused on the general interactions of market policies (i.e., carbon trading, subsidies) on ethanol market development trends to boost sustainable production of ethanol.

Models capabilities in steering decisions on investments for bioenergy systems are evaluated in addressing real world case studies referring to the emerging bioethanol production in Northern Italy.

Riassunto

Le preoccupazioni crescenti degli effetti delle modificazioni climatiche e l'incertezza dell'approvvigionamento energetico esprimono l'importanza cruciale della necessità di ridefinire il sistema di approvvigionamento energetico globale. L'urgenza della questione è legata ad un disaccoppiamento tra la prospettiva di una crescita costante della domanda di combustibili, ed il loro approvvigionamento, che ci si aspetta divenire sempre più incerto e costoso. Il fenomeno del cambiamento climatico è ampiamente riconosciuto essere una conseguenza dell'accresciuta concentrazione di gas serra in atmosfera dovuti all'attività antropogenica ed il trasporto ne è uno dei principali responsabili.

Negli ultimi anni, l'interesse per le energie rinnovabili è aumentato notevolmente per rispondere alla crescita della domanda di energia e cercare allo stesso tempo sia di ridurre la dipendenza da combustibili fossili che di contribuire alla mitigazione del riscaldamento globale. Alla biomassa è stata attribuita una particolare attenzione perché può essere sfruttata non solo per produrre energia elettrica, meccanica e termica, ma anche come fonte primaria di biocombustibili liquidi per autotrazione. Allo scopo di realizzare un sistema di trasporti più sostenibile, l'Unione Europea ha svolto un ruolo fondamentale nella promozione di biocombustibili fissando immissioni obbligatorie di fonti rinnovabili rispetto all'energia complessiva impiegata nei trasporti (5.75% entro il 2010 e 10% entro il 2020). I biocombustibili devono anche rispettare dei requisiti di sostenibilità ambientale nel loro impatto sul suolo, sull'acqua, sull'aria. Va tutelata, inoltre, la biodiversità e deve essere garantita una riduzione crescente delle emissioni di gas serra nella produzione di biocombustibili rispetto allo stesso quantitativo energetico di combustibile fossile che andranno a sostituire (35% dal 2009, 50% dal 2017 e 60% dal 2018).

Tra le alternative possibili, il bioetanolo è generalmente considerato la soluzione più pratica e perseguibile nel breve-medio periodo per sostituire la benzina. Nonostante il suo impatto sul ciclo del carbonio (la cosiddetta *carbon footprint*) sia stato e sia attualmente argomento molto dibattuto, si riconosce che la produzione ed impiego di questo biocombustibile possa risultare in una riduzione netta delle emissioni di gas serra rispetto alla benzina. Questo genere di investimento su larga scala porterebbe, inoltre, una crescita delle economie rurali grazie all'aumento ed alla segmentazione dei filoni di mercato tipicamente ascritti all'agricoltura.

L'attuale produzione di bioetanolo si basa sulla cosiddetta tecnologia di prima generazione, così chiamata perché sfrutta coltivazioni convenzionali come materie prime: si tratta di risorse ricche di sostanze amidacee, zuccherine od oleose, come mais, grano e canna da zucchero. Tuttavia l'iniziale entusiasmo di cui inizialmente godette questa tecnologia, si è recentemente affievolito a causa delle emergenti problematiche legate alla competizione della destinazione

finale delle coltivazioni tra uso energetico ed alimentare. Inoltre, sono emerse preoccupazioni in merito al degrado ambientale per effetto di pratiche monocoltura e la deforestazione necessarie per lo sviluppo su larga scala di tale tecnologia. In generale, dubbi sulla sostenibilità energetica e sulla profittabilità economica del processo, troppo legata al costo di approvvigionamento della biomassa, hanno minato in parte lo sviluppo dell'industria del bioetanolo e la sua accettazione sociale. Alla luce di tutto questo, è emersa la convenienza a promuovere i cosiddetti biocombustibili di seconda generazione, ottenuti cioè a partire da materiale cellulosico e sostanzialmente privi di valore alimentare. Tuttavia, gli elevati costi di capitale e di produzione ostacolano attualmente lo sviluppo di tali tecnologie su scala commerciale, tanto che recentemente sono divenute operative solo strutture su scala di impianto pilota e dimostrativa.

La complessità del contesto impone che la transizione verso un sistema di trasporti più sostenibile sia opportunamente guidata dall'adozione di efficaci strumenti quantitativi in grado di analizzare il problema esteso all'intera filiera produttiva (*Supply Chain*, SC). La ridefinizione del sistema di approvvigionamento energetico nel trasporto richiede un'analisi integrata il più comprensiva possibile delle intrecciate problematiche coinvolte nella produzione di biocombustibili. Le strategie d'investimento richiedono complessi processi decisionali, per i quali la modellazione analitica risulta essere una delle migliori opzioni metodologiche per garantire l'ottimizzazione delle scelte che coinvolgono l'intero sistema produttivo. I modelli a variabili miste lineari e intere (*Mixed Integer Linear Programming*, MILP), in particolare, costituiscono uno degli strumenti più adatti nel determinare le soluzioni ottimali a complessi problemi di ottimizzazione tipicamente legati alla progettazione di filiere produttive in cui vengano prese in considerazione configurazioni alternative ed esclusive.

La ricerca bibliografica ha evidenziato alcune lacune nella letteratura in merito alle questioni di progettazione strategica di filiere produttive di biocombustibili, nonostante il concetto di bioraffineria costituisca già un argomento ampiamente trattato ed i biocombustibili stiano riscuotendo un interesse sempre crescente. Tutto ciò ha dato l'impulso per lo svolgimento di questa Tesi. Nel contesto generale dello sviluppo di sistemi bioenergetici, lo scopo generale di questo lavoro è quello di fornire degli opportuni strumenti decisionali per affrontare la transizione verso un sistema di trasporto più sostenibile, muovendo dalla prima alla seconda generazione di bioetanolo. Le metodologie adottate devono essere in grado di abbracciare l'intero problema analizzando tutti gli stadi della filiera, evidenziando aspetti positivi e negativi che provengono da un'ottimizzazione sia di tipo economico che ambientale. I modelli MILP proposti mirano ad essere strumenti di progettazione e pianificazione industriale nel settore dei biocombustibili in grado di contemperare aspetti economici ed ambientali. In effetti, essendo le infrastrutture produttive di biocombustibili ancora ad uno stadio immaturo, un loro studio preliminare rappresenta un'opportunità importante per analizzare la configurazione della filiera prima del suo sviluppo organico, consentendo di individuare gli investimenti ottimali e le opportune scelte di natura politica nazionale ed internazionale. Gli stadi della filiera di biocombustibili (produzione e distribuzione della biomassa; produzione e trasporto del bioetanolo) sono analizzati ed inseriti in modo integrato all'interno della modellazione matematica MILP proposta. L'attenzione è stata focalizzata in particolare sull'identificazione delle strategie opportune atte a favorire lo sviluppo delle più sostenibili tecnologie di produzione del bioetanolo. Innanzitutto, è stata considerata un'ampia gamma di processi, sia di prima che di seconda generazione, ed è stata altresì inclusa la possibilità di integrare opportunamente le due tecnologie all'interno di strutture ibride che ricevano sia materia prima amidacea che cellulosica. Infine, l'analisi si è focalizzata sull'interazione tra le politiche di mercato e lo sviluppo del mercato del bioetanolo, con particolare riguardo alle potenzialità di promuoverne una produzione sostenibile. Sono stati pertanto analizzati meccanismi di mercato cosiddetti flessibili, previsti dal Protocollo di Kyoto, come il *carbon trading*, ovvero lo scambio di permessi ad emettere gas serra, e potenziali effetti legati all'introduzione di sussidi pubblici.

In generale, l'analisi delle filiere (*Supply Chain Analysis*, SCA) di biocombustibili affrontata in questo lavoro di Tesi mira a fornire una valutazione integrata di aspetti economici, finanziari ed ambientali valutati lungo l'intera rete produttiva. Questo approccio alla progettazione valuta la responsabilità ambientale come un obiettivo della modellazione e non semplicemente come vincolo, secondo l'approccio della cosiddetta *Green Supply Chain Management* (GrSCM). L'approccio integra i principi del *Life Cycle Assessment* (LCA) con le tecniche SCA per ottenere una valutazione quantitativa dell'impatto ambientale arrecato da ogni singola fase della filiera. L'analisi finanziaria inoltre necessita di essere integrata attraverso l'introduzione di opportune misure di rischio finanziario in grado di descrivere il compromesso tra profittabilità e rischio che l'investitore decide di accettare. Per affrontare queste questioni, sono introdotte tecniche di programmazione multi-obbiettivo (*Multi-objective Mathematical Programming*, moMP), capaci di includere aspetti ambientali, finanziari ed economici nella progettazione di processi chimici.

I modelli sviluppati sono stati applicati ad un caso studio reale che affronta la possibile organizzazione della produzione di bioetanolo in Nord Italia sfruttando la disponibilità di molteplici biomasse sia di prima che di seconda generazione.

Il lavoro di Tesi è organizzato secondo il seguente schema concettuale.

Nel capitolo 1, dopo aver descritto il panorama bibliografico di riferimento, vengono illustrati gli approcci metodologici e modellistici alla base del lavoro, che prevedono l'integrazione di tecniche LCA ed SCA in analisi multi obiettivo secondo tecniche MILP.

Nel capitolo 2 viene trattato l'approccio modellistico alla base della descrizione tecnologica e dell'analisi economica per i sistemi di produzione considerati. Vengono studiati processi di prima e seconda generazione, che ottengono bioetanolo a partire rispettivamente da materiale amidaceo (mais) e lignocellulosico (residui e biomasse coltivate a scopo energetico, e*nergy* *crops*). L'aspetto peculiare della trattazione riguarda, inoltre, la modellazione di un processo di tecnologie ibride che utilizzano sia la parte amidacea che il residuo cellulosico del mais per la produzione di biocombustibili.

Nel capitolo 3 viene condotta la progettazione di filiera di bioetanolo attraverso la formulazione di un problema di ottimizzazione bi-obbiettivo (simultanea minimizzazione delle emissioni di gas serra e massimizzazione del profitto) con lo sviluppo di un modello MILP multi-periodo e georeferenziato. Il modello MILP formulato sfrutta tecniche moMP per l'implementazione di criteri di ottimizzazione ambientale ed economico. Sono considerate diverse configurazioni tecnologiche e vengono prese in esame più soluzioni per lo sfruttamento dei sotto-prodotti del processo di produzione di bioetanolo come possibili alternative tecnologiche per l'abbattimento di costi ed emissioni. Il modello costruito viene poi applicato all'analisi di una possibile filiera di bioetanolo in Nord Italia.

Nel capitolo 4 si studiano gli effetti dell'applicazione di strumenti finanziari sul *design* di filiere bioenergetiche nelle loro capacità di promuovere tecnologie più sostenibili per la produzione di bioetanolo. Nel modello viene implementato un meccanismo di *carbon trading* che prevede la commercializzazione di permessi ad emettere gas serra (CO_2-equivalenti) rispetto a dei valori soglia stabiliti secondo la normativa ambientale per la sostenibilità dei biocombustibili. La trattazione modellistica esamina anche le dinamiche dei fattori d'incertezza del mercato di riferimento con particolare riguardo all'acquisto della biomassa utilizzata. In questo caso, sono stati ignorati gli aspetti legati alla georeferenziazione, per esaltare invece la questione rilevante legata alla scelta tecnologica sulle prestazioni della filiera. Si descrive, pertanto, lo sviluppo di un modello MILP multi-periodo con un approccio stocastico per la pianificazione della produzione di bioetanolo. La filiera viene progettata seguendo l'ottimizzazione di indici finanziari di investimento nel quale un ulteriore termine di profitto/perdita proviene dalla commercializzazione di permessi di emissione.

Il capitolo 5 estende la trattazione del modello descritto nel capitolo 4, inglobando una più ampia modellazione della pianificazione d'investimento in condizioni di incertezza che abbraccia il processo decisionale con considerazioni di gestione del rischio d'investimento. In particolare, il modello MILP stocastico viene esteso secondo una formulazione multi-obbiettivo permettendo la simultanea ottimizzazione di profitto ed emissione di gas serra. Sono inoltre inclusi dei vincoli sul livello massimo di rischio finanziario sostenibile nell'investimento. Si mostra in questo modo come la diversa attitudine al rischio dell'investitore (propensione o avversione) modifichi la strategia d'investimento in termini di scelte tecnologiche e biomasse trattate, anche alla luce di vincoli ambientali e di profittabilità economica.

Il capitolo 6 conclude la discussione della ricerca sviluppata con la presentazione dei principali risultati conseguiti e l'analisi di alcuni dei potenziali sviluppi futuri per proseguire la ricerca sull'argomento.

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List of symbols

Sets

$c \in C$	coefficients for costs linearisation, $C = \{1, 2\}$
$g \in G$	grid squares, $G = \{1,\ldots,60\}$
$g' \in G$	set of square regions different than g
$i \in I$	biomass types as addressed in chapter 3, I = {*corn, corn stover*}
$i \in I$	biomass types as addressed in chapter 4 and 5, I = {*corn, poplar, willow, miscanthus, corn stover, wheat straw, barley straw, switchgrass*}
$j \in J$	product types, J = {*ethanol, DDGS, power*}
$k \in K$	production technologies as addressed in chapter 3, $K = \{1,2,3,4,5,6,7,8,9,10\}$
$k \in K$	production technologies as addressed in chapter 4 and 5, K = {*DGP, DGP-CHP, DAP, SEP, GBP*}
$p \in P$	discretisation intervals for plant size linearisation, $P = \{1,\ldots,6\}$
$s \in S$	life cycle stages as addressed in chapter 3, S = {*bp, bpt, bt, fp, fd, ec*}
$s \in S$	life cycle stages as addressed in chapter 4 and 5, S = {*bp, bpt, bt, fp, ec*}
$s \in S$	life cycle stages as addressed in appendix D, S = {*bp, bpt, bt, fp*}
$sc \in Sc$	probability discretisation scenarios, $Sc = \{1,\ldots,NS\}$
$t \in T$	time periods as addressed in chapter 3, $T = \{1,\ldots,5\}$
$t \in T$	time periods as addressed in chapter 4, 6 and appendix D, $T = \{1,\ldots,20\}$
$t \in T$	time periods as addressed in chapter 5, $T = \{1,\ldots,6\}$

Subsets

$tech_k \subset K$	subset of technologies producing DDGS to be sold, $tech_k = \{1,3,5,6,7\}$
$fratio_k \subset K$	subset of technologies using corn and stover for ethanol production, $fratio_k = \{5,6,7,8,9,10\}$
$sub_p \subset P$	subset of discretisation intervals, $sub_p\ P = \{1,\ldots,5\}$
$FTL_{g,l,g'}$	subset of feasible transport links for each product *i* via mode *t* between *g* and *g'* $FTL_{g,l,g'} = (g,l,g') = FRL_{g,l,g'} + FBL_{g,l,g'} + FSL_{g,l,g'} + FTSL_{g,l,g'}$

$FRL_{g,l,g'} = (g,rail,g') \Leftrightarrow g$ can be connected with g' by rail

$FBL_{g,l,g'} = (g,barge,g') \Leftrightarrow g$ can be connected with g' by barge

$FSL_{g,l,g'} = (g,ship,g') \Leftrightarrow g$ can be connected with g' by ship

$FTSL_{g,l,g'} = (g,t\text{-}ship,g') \Leftrightarrow g$ can be connected with g' by t-ship

$Local_{g,l,g'}$	feasibility limitation of local transport links via mode *l* between *g* and *g'* $Local_{g,l,g'} = (g,l,g') \Leftrightarrow LD_{gg'} < 72$ km
$Total_{g,l,g'}$	total transport links allowed for each product *i* via mode *l* between *g* and *g'* $Total_{g,l,g'} = (g,l,g') = Local_{g,l,g'} + FTL_{g,l,g'}$

Scalars

b	experience index
dk	depreciation charge constant per each time *t*
ε	tolerance value
ER	ethanol rate [t/y]
ER^0	reference ethanol rate for capital cost estimation [t/y]

ζ	interest rate
δ	conversion factor specific for DDGS
ϕ	fixed costs % over incomes, 0.15
L	lower limit for expansion number over time
LA	land surface availability [ha]
LHV_e	ethanol lower heating value
$LowerLimit$	lower limit for capacity expansion [t/time period]
μ	risk-attitude
M	maximum profit value [€], s.t. M>>PBT
N	maximum NPV value [€], s.t. N>>NPV
n	NPV lower limit [€]
NS	number of scenarios
$PCap^{\min}$	minimum ethanol production capacity [t of ethanol/time period]
$PM_{ethanol}$	ethanol molecular weight [g/mol]
PR	progressive ratio for technological learning
r	scaling exponent for capital cost
ρ	ethanol density
θ	facility operating capacity flexibility
TCI^0	total capital investment for a facility of reference scale ER^0
tf	final time period
Tr	taxation rate
t_ref	reference time for capital costs update
U	upper limit for expansion number over time
$UpperLimit$	allowable ethanol production variation [t/y] or [t/time period]

Ω	target profit for risk calculation [€]

Parameters

α	feedstock intermediate compounds involved in ethanol production
$a_{i,k}$	coefficient for capital cost estimation for conversion technology k and biomass i
a_k	coefficient for capital cost estimation for conversion technology k
AD_g	arable land density [km^2 of arable/km^2 of grid surface]
$\beta_{i,k}$	fraction of ethanol rate from biomass type i for each technology k
$BA_{g,i}$	biomass i availability for ethanol production in region g [t/time period]
$BA_{i,t}$	biomass i available for ethanol production at time t [t/y]
BCD_g^{max}	maximum cultivation density in region g [km^2 of cultivation/km^2 of arable land]
$BN_{i,k,p}$	biomass i needs for technology k at each linearisation interval p [t/y] or [t/time period]
$BNexp_{i,k,p}$	biomass i needs to the power of the scaling factor for technology k at each linearisation interval p [t/time period]
$BNexp_{i,k,p}^{0}$	biomass i needs to the power of the scaling factor for technology k at the linearisation interval $p = 2$ [t/time period]
$burn_{i,k}$	fraction of biomass i fed to CHP for each technology k
BY_i	biomass yield of product i [t/ha]
$BY_{i,g}$	biomass yield of product i in region g [t/time period km^2]
$BY_{i,t}$	cultivation yields for each biomass i at time t [t/ha]
$CapMax_{i,k}$	maximum capacity in terms of biomass i for conversion technology k [t/y]

$CapMin_{i,k}$	minimum capacity in terms of biomass i for conversion technology k [t/y]
$CI_{i,k,p}$	capital investment at each linearisation interval p for the conversion technology k and biomass i [€]
$CI_{p,k}$	capital investment at each linearisation interval p and for technology k [€]
CI_{p,k,t_ref}	capital investment at each linearisation interval p and for technology k at reference time t_ref [€]
$CI^{0}_{i,k}$	capital investment for biomass i technology k at size $p = 2$ [€]
CI_{p,k,t_ref}	capital investment at each linearisation interval p, for technology k at the year of interest t [M€]
$coef_{c,i,k}$	coefficients (slope [€/t], intercept [€/y] or [€/time period]) for linear regression of production costs for technology k and biomass i
$coef_{k,c}$	coefficients for the linear regression of production costs for each technology k, slope ($c = 1$) [€/t] and intercept ($c = 2$) [€/time period]
$CR_{k,t}$	cost reduction for biomass i technology k at time t
df_t	discount factor at time t
$dfCF_t$	discount factor for cash flow at time t
$dfTCI_t$	discount factor for investments at time t
dk_t	depreciation charge at time t
$etperc_t$	ethanol blending percentage at time t
$E\_EPC_{i,k,p,t}$	ethanol production cost for biomass i technology k size p and time t [€/time period]
ER_p	ethanol production rate for each plant size p [t/y]
φ_α	concentration of the intermediate compound α in the feedstock for the black-box model
f_s	emission factor for life cycle stage s [kg CO_2-eq/unit]

$f_{i,k,s,t}$	emission factors for life cycle stage s time t technology k and biomass i [kg CO_2-eq/unit]
$fbp_{i,g}$	emission factor for biomass i production in grid g and biomass [kg CO_2-eq/t of biomass]
$fbpt_i$	emission factor for biomass i pre-treatment [kg CO_2-eq/t of biomass]
fbt_l	emission factor for biomass supply via mode l [kg CO_2-eq/t of biomass · km^2]
$fbtl*$	emission factor for local biomass transport [kg CO_2-eq/t of biomass · km^2]
fec_k	emissions credits for each technology k [kg CO_2-eq/unit]
ffd_l	emission factor for ethanol distribution via mode l [kg CO_2-eq/t of ethanol · km^2]
ffp_i	emission factor for ethanol production from biomass i [kg CO_2-eq/t of ethanol]
γ_i	conversion of biomass i to ethanol [t of ethanol/t of biomass]
$\gamma_{i,j,k}$	conversion of biomass i to product j through technology k [t of ethanol/t of biomass] or [kWh/L of ethanol]
GHG_{red}	GHG emissions savings required to biofuels
$GHG_{red,t}$	GHG emissions savings required to biofuels at time t
GS_g	grid surface [km^2]
IBF_g	internal biomass production feasibility, binary parameter
$LD_{g,g'}$	local delivery distance between grids g and g' [km]
MP_j	market price for ethanol product j
$MP_{j,t}$	market price of product j at time t [€/t] or [€/MWh]
$MP\_All_{sc,t}$	market price for traded emissions [€/kg CO_2-eq]
$M\&S_t$	Marshall and Swift at time t
$M\&S_{t\_ref}$	Marshall and Swift at the base time for capital cost estimation t_ref
η_{rec}	ethanol recovery efficiency for the technologies considered

π_{sc}	probability related to scenario sc
$PC_{p,k}$	production costs linearised for size p and conversion technology k [€/time period]
$PCap_p$	plant capacity of size p used for cost linearisation [t/time period]
PR_k	progress ratio for technology k
q_i	maximum quota of collectable biomass i for ethanol production
r_k	power factor for capital cost estimation for conversion technology k
$S_{\alpha/fuel}$	selectivity of reactant α for the technologies considered for ethanol production
$\tau_{g,l,g'}$	tortuosity factor of transport mode l between g and g'
$UEPC_{i,k,p,t}$	unitary ethanol production cost for biomass i technology k size p at time period t [€/t]
UPC_i	unit production costs for biomass type i [€/t]
$UPC_{i,g}$	unit production costs for biomass type i in grid g [€/t]
$UPC_{i,sc,t}$	unit purchase cost for biomass i at scenario sc and time t [€/t]
$UPC_{min,i}$	minimum bound for unit production costs of biomass type i [€/t]
$UPC_{max,i}$	maximum bound for unit production costs of biomass type i [€/t]
UTC_i	unit transport cost for biomass i [€/t]
$UTCb_l$	unit transport costs for biomass via mean l [€/t]
$UTCf_l$	unit transport costs for ethanol via mean l [€/t]
$UTCl$	unit transport cost for biomass transfer within g [€/(t · km)]
W_e	ethanol fuel rate from technology k in the black-box model [t/time period]
W_f	feedstock rate in the black-box model [t/time period]
ω_k	exceeding electricity production specific for each conversion technology k [kWh/L of ethanol]
$\chi_{\alpha/fuel}$	conversion of reactant α for the technologies considered for ethanol production

Continuous variables

$BA_{i,k,t}$	biomass i available for ethanol production with technology k at time t [t/time period]
BPC_t	biomass production costs at time t [€/time period]
$BPC_{i,k,sc,t}$	biomass purchase cost for biomass i technology k scenario sc at time t [€/y] or [€/time period]
$Cap_{i,k,t}$	nominal capacity of biomass i for technology k at time t [t/time period]
$Cap_{i,k,sc,t}$	biomass i rate for technology k scenario sc at time t [t/y]
CCF	discounted Cumulative Cash Flow [€]
$CF_{k,t}$	cash flow for technology k at time t [€/y]
CF_t	cash flow at time t [€/time period]
$CF_{i,k,sc,t}$	cash flow for biomass i technology k scenario sc at time t [€/y] or [€/time period]
D_t	depreciation at time t [€/time period]
$D_{i,k}$	depreciation charge for biomass i technology k [€/time period]
$D_{i,k,t}$	depreciation charge for biomass i technology k at time t [€/y]
$D\_Cap_{i,k,t}$	decrease of installed capacity for biomass i facility k at time t [t/time period]
$D\_Cap_{i,k,sc,t}$	inlet of biomass i decrease for facility k at time t and scenario sc [t/y]
$Db^T_{i,g,t}$	biomass i demand in region g at time t [t/time period]
$dev_{i,k,sc}$	deviation from the target profit for biomass i technology k scenario sc [€]
$Df^T_{g,t}$	ethanol demand in region g at time t [t/time period]
$EBR_{i,k,p,sc,t}$	actual operating capacity for biomass i technology k at time t scenario sc and size p [t/time period]

$E\_Cap_{i,k,sc,t}$	effective facility biomass *i* rate for technology *k* scenario *sc* at time *t* [t/time period]
eDR	expected Downside Risk [€]
eDR_{max}	maximum expected Downside Risk [€]
$eNPV$	expected net present value [€]
EPC_t	ethanol production cost at time *t* [€/time period]
$EPC_{i,k,sc,t}$	ethanol production cost for biomass *i* technology *k* scenario *sc* at time *t* [€/y] or [€/time period]
$eTIOT$	expected total impact over time [kg CO_2-eq]
$F_{s,t}$	reference flow for life cycle stage *s* and time *t* [units/tome period]
$F_{i,k,s,t}$	reference flow for life cycle stage *s*, biomass *i*, technology *k* and time *t* [units/y]
$F_{i,k,s,sc,t}$	reference flow for biomass *i*, technology *k*, life cycle stage *s*, scenario *sc* and time *t* [units/y] or [units/time period]
FCC	discounted facilities capital costs [€]
FCC_t	facilities capital costs at time *t*, €/time period
$FixC_t$	fixed cost at time *t* [€/time period]
$I\_BN_{i,k,p,t}$	biomass *i* needs for technology *k* at each linearisation interval *p* at time *t* [t/time period]
$I\_BNexp_{i,k,t}$	biomass *i* needs raised to the power of the scaling factor for technology *k* at time *t* [t/time period]
$I\_Cap_{i,k,t}$	increase of installed capacity for biomass *i* technology *k* at time *t* [t/time period]
$I\_Cap_{i,k,sc,t}$	inlet of biomass *i* increase for facility *k* at time *t* and scenario *sc* [t/y]

$Imp_{i,k,s,sc,t}$	impact of life cycle stage *s* for biomass *i* technology *k* scenario *sc* at time *t* [kg CO_2-eq/time period]
$Imp_{s,t}$	impact for life cycle stage *s* at time *t* [kg CO_2-eq/time period]
$Imp^{\sigma}_{k,s,t}$	impact either on global warming (σ = GHG) or water resource (σ = WF) for technology *k* life cycle stage *s* at time *t* [kg CO_2-eq/y] or [$\mathrm{m}^3_{\mathrm{H_2O}}$/y]
Inc_t	gross earnings at time *t* [€/time period]
$Inc_{i,k,sc,t}$	gross earnings for biomass *i* technology *k* scenario *sc* at time *t* [€/y] or [€/time period]
$In\_Cap_{i,k}$	initial installed capacity for biomass *i* for facility *k* at time *t* = 1 [t/y]
$\lambda_{p,k,g,t}$	linearisation variables for TCI at interval *p* and for technology *k*, in region *g* at time *t*
$\lambda_{i,k,p}$	linearisation variables for TCI for biomass *i* at interval *p* and for technology *k*
$\lambda^{plan}_{p,k,g,t}$	linearisation variables for TCI at interval *p* and for technology *k*, in region *g* at time *t*
$LA\_crop_{i,k,t}$	land devoted to supplying biomass *i* for technology *k* at time *t* [t/time period]
$MaxCO2_{i,k,sc,t}$	emissions cap for biomass *i* technology *k* scenario *sc* at time *t* [kg CO_2-eq/y] or [kg CO_2-eq/time period]
NPV	net present value [€]
$NPV_{i,k,sc}$	net present value for using biomass *i* technology *k* at scenario *sc* [€]
NPV_{sc}	net present value at scenario *sc* [€]
Obj_{eco}	economic objective function [€]
Obj_{env}	objective environmental impact [kg CO_2-eq]
$Obj_{env,2}$	objective environmental impact [$\mathrm{m}^3_{\mathrm{H_2O}}$]

$P^{T}_{j,k,g,t}$	total production rate for product j through technology k in region g at time t [t/time period or MWh/time period]
$P^{T}_{i,j,k,sc,t}$	total production rate for product j from biomass i technology k scenario sc at time t [t/y] or [€/time period]
$P_{ethanol}$	annual ethanol production rate [t/time period]
$P\_All_{i,k,sc,t}$	purchased permit for biomass i technology k scenario sc at time t [kg CO_2-eq/y] or [kg CO_2-eq/time period]
$Pb_{i,g,t}$	production rate of biomass i in region g at time t [t/time period]
PBT_{t}	profit before taxes for production technology k at time t [€/time period]
$PBT_{i,k,sc,t}$	profit before taxes for biomass i technology k scenario sc at time t [€/y] or [€/time period]
$Pf_{i,k,g,t}$	ethanol production rate from biomass i through facility k in region g at time t [t/time period]
$q_{i,k,sc}$	supporting variable for *eDR* linearisation for biomass i technology k scenario sc [€]
$Qb_{i,g,l,g',t}$	flow rate of biomass i between g and g' via transport mode l at time t [t/time period]
$Qf_{g,l,g',t}$	ethanol flow rate between g and g' via transport mode l at time t [t/time period]
$S\_All_{i,k,sc,t}$	sold permits for biomass i technology k scenario sc at time t [kg CO_2-eq/y] or [kg CO_2-eq/time period]
$TAR_{j,k,t}$	gross profit from product j related to production technology k at time t, €/time period
TAX_{t}	tax amount at time t [€/time period]

$TAX_{i,k,sc,t}$	tax amount for biomass *i* technology *k* scenario *sc* at time *t* [€/y] or [€/time period]
$TC_{i,k,sc,t}$	transport cost for biomass *i* technology *k* scenario *sc* at time *t* [€/y] or [€/time period]
TCb_t	biomass transport cost at time *t* [€/time period]
TCf_t	ethanol transport cost at time *t* [€/time period]
TCI	total capital investment for a processing facility
$TCI_{i,k}$	total capital investment for biomass *i* and technology *k* [€]
$TCI_{i,k,t}$	total capital investment for biomass *i* technology *k* and time *t* [€]
TCI_k	total capital investment for technology *k* [€]
TCI_t	total capital investment at time *t* [€]
TI_t	total impact at time *t* [kg CO_2-eq/time period]
$TI_{i,k,sc,t}$	total impact for biomass *i* technology *k* scenario *sc* at time *t* [kg CO_2-eq/y] or [kg CO_2-eq/time period]
$TI^{*}_{i,k,sc,t}$	gasoline total impact equivalent to biofuels pathway for biomass *i* technology *k* scenario *sc* at time *t* [kg CO_2-eq/y] or [kg CO_2-eq/time period]
$TI^{\sigma}_{k,t}$	total impact either on global warming (σ = GHG) or water resource (σ = WF) for technology *k* life cycle at time *t* [kg CO_2-eq/y] or [$m^3_{H_2O}$/y]
$TI^{GHG}_{k,t}$	yearly total impact on global warming technology *k* life cycle at time *t* [kg CO_2-eq/y]
$TI^{WF}_{k,t}$	yearly total impact on water resources technology *k* life cycle at time *t* [$m^3_{H_2O}$/y]
$TIOT$	total impact over time [kg CO_2-eq]
$TIOT^{GHG}$	total impact on global warming over time [kg CO_2-eq]

$TIOT^{WF}$	total impact on water resources over time [$m^3_{H_2O}$]
$TPot_{i,t}$	total potential production of biomass *i* at time *t* [t/time period]
$VarC_t$	variable costs at time *t* [€/time period]
$VarC_{i,k,sc,t}$	variable costs for biomass *i* technology *k* scenario *sc* at time *t* [€/y] or [€/time period]
W_e	bioethanol rate in the black-box model [t/y]
W_f	feedstock rate in the black-box model [t/y]

Binary variables

$\delta_{i,k,sc}$	1 if a technology *k* using biomass *i* under scenario *sc* is established, 0 otherwise
$\delta 1_{i,k,sc}$	indicator variable for *eDR* linearisation for technology *k* using biomass *i* under scenario *sc*
$\delta 2_{i,k,sc}$	indicator variable for *eDR* linearisation for technology *k* using biomass *i* under scenario *sc*
$V_{i,k,sc,t}$	1 if taxation has not to be applied for facility *k* biomass *i* at time *t* and scenario *sc*, 0 otherwise
$W_{i,k,p,sc,t}$,	1 if facility size of plant adopting technology *k* biomass *i* at time *t* and scenario sc belongs to linearisation interval *p* of the actual production rate, 0 otherwise
$y_{p,k,g,t}$	1 if a production facility *k* of size *p* is to be established in region *g* at time *t*, 0 otherwise
$y_{i,k,p}$	supporting variable for linearisation of plant scale
$Y_{i,k}$	1 if a production facility *k* treating biomass *i* is to be established, 0 otherwise
$Y_{i,k,p,t}$	1 if facility size of plant adopting technology *k* biomass *i* at time *t* belongs to linearisation interval *p* of the installed capacity, 0 otherwise

$Y_{k,g,t}$	1 if a production facility *k* is already established in region *g* at time *t*, 0 otherwise
$Y^{plan}_{k,g,t}$	1 if the establishment of a new conversion facilities *k* is to be planned in region *g* during time period *t*, 0 otherwise
$Y^{start}_{k,g}$	1 if the establishment of a new conversion facilities *k* is to be planned in region *g* at the beginning, 0 otherwise
$Z_{i,k,sc,t}$	1 if a facility of technology *k* with biomass *i* at scenario *sc* and time *t*, has to be enlarged, 0 otherwise
$Z_{i,k,t}$	1 if a facility of technology *k* with biomass *i* at time *t*, has to be enlarged, 0 otherwise

Acronyms

CAPM	Capital Asset Pricing Model
CHP	Combined Heat and Power
COD	Chemical Oxygen Demand
CTS	Cooling Tower System
CVaR	Conditional Value at Risk
DAP	Dilute Acid Hydrolysis Process
DDGS	Distiller's Dried Grains with Solubles
DGP	Dry-Grind Process
DGP-CHP	Dry-Grind Process with CHP station
EISA	Energy Independency and Security Act
eNPV	expected Net Present Value
eDR	expected Downside Risk

EPA	Environmental Protection Agency
EU	European Union
EU ETS	European Union Emission Trading Scheme
FCI	Fixed Capital Investment
FFV	Flexible-Fuel vehicles
GAMS	General Algebraic Modeling System
GBP	Gasification Biosynthesis Process
GBP_{high}	Gasification Biosynthesis Process (more optimistic yield values)
GBP_{ave}	Gasification Biosynthesis Process (average yield values)
GBP_{low}	Gasification Biosynthesis Process (more cautionary yield values)
GC	Green Credit
GDP	Gross Domestic Product
GHG	Greenhouse Gas
GrSCM	Green Supply Chain Management
HHV	Higher Heating Value
Hybrid	Integrated process using corn and stover feedstocks with DDGS sold
Hybrid-CHP	Integrated process using corn and stover feedstocks with DDGS burnt
IFPRI	International Food Policy Research Institute
iLUC	indirect Land Use Change
ISO	International Organization for Standardization
LCA	Life Cycle Analysis
LCEP	Ligno-Cellulosic Ethanol Process
LHV	Lower Heating Value
MILP	Mixed Integer Linear Programming
MIP	Mixed Integer Programming

M&S	Marshall and Swift Equipment Cost Index
moMILP	Multi-objective Mixed Integer Linear Programming
moMP	Multi-objective Mathematical Programming
MP	Mathematical Programming
MPC	Model Predictive Control
MTBE	Methyl tertiary butyl ether
NEB	Net Energy Balance
NPV	Net Present Value
NYMEX	New York Mercantile Exchange
OECD	Organisation for Economic Cooperation and Development
OPEC	Organization of the Petroleum Exporting Countries
OV	Opportunity Value
PDVSA	Petróleos de Venezuela S.A
PR	Progressive Ratio
PSE	Process System Engineering
RAR	Risk Area Ratio
RFS	Renewable Fuels Standard
ROI	Return On Investment
SC	Supply Chain
SCA	Supply Chain Analysis
SCM	Supply Chain Management
SEP	Steam Explosion Process
SHF	Separate Hydrolysis and Fermentation
SM	Simulation Model
SOC	Soil Organic Carbon

SRF	Short Rotation Forestry
SSCF	Simultaneous Saccharification and Co-Fermentation
SSF	Simultaneous Saccharification and Fermentation
TCI	Total Capital Investment
TPC	Total Product Cost
TTW	Tank-To-Wheel
URR	Ultimately Recoverable Reserves
VaR	Value at Risk
WF	Water Footprint
WTT	Well-To-Tank
WWT	Waste Water Treatment
USDA	U.S. Department of Agriculture
USDOE	U.S. Department of Energy

Chapter 1

Motivations and Literature Survey

Energy enables life on earth and is also a driving force for economy development. Societal evolution has been driven by the revolutionary changes in energy cost and effectiveness occurred throughout the history. In particular, social and economic progression has always come with an increase of energy demand and at the same time technological breakthrough has provided greater amount of energy at higher efficiency.

The economic and financial crisis we are now witnessing, although being related to different and interlinked causes, is in many ways strongly connected to energy supply security and costs. Bad energy management can lead to social disruption and to worsening of the state of the planet. Recent events having had planetary consequences (i.e., the Libyan War, the oil spill in the Gulf of Mexico, the Fukushima incident) are jeopardising the reliance on the current energy provision system as a whole. The unbalancing trends between energy demand and supply characterising current economies and level of life, pervading the society with a sense of uncertainty, are calling for a challenging shift towards sustainable energy production and consumption. In fact, a general paradigm shift in societal, economic and technological choices is advocated, where sustainable development, as well as energy and resource conservation thinking plays a major role. The so-called Green Economy, however, not only is supposed as changes in the production techniques (e.g., adoption of cleaner technologies, transports and agricultural practices), but needs embracing and modifying deeply each human behaviour. Current society is asked to follow a sustainable development, providing goods and services for people, at the same time using earthly resources without damaging future generations quality of life. Future societal and economic development needs being encouraged according to the principle of optimisation in resources and energy usage, representing now the binding approach to support and analyse complex decisions or allocation problems occurring both in the design of future production systems as well as in the upgrading the existing processing structures. Policy makers need to be provided with proper multi-criteria decision analysis tools in order to identify the pathway towards the establishment of future energy supply systems optimising them along each step of their supply chain, from feedstocks supply up to energy delivery, and complying with a complex set of constraints in terms of environmental, social and economic performance. Mathematical modelling frameworks might help the identification of the best routes aiming at the design and planning of sustainable (e.g., low-carbon content, low-water requirement) energy infrastructures and biorefineries. In particular, some mathematical techniques (e.g., mathematical programming, MP) have the ability to allow for making decisions embracing a large number of alternative design configurations in order to identify the best investment strategies.

The work presented in this Thesis aims at showing the suitability of MP in leading the transition towards more sustainable energy systems. In particular, such high-level decisions to be taken in almost undetermined infrastructures (e.g., new biofuels supply systems) require properly devised design tools.

This chapter aims at providing a general overview of the motivations supporting the research project. Current energy provision system shortfalls are first presented with a particular view on fossil fuels consumption, peak of production and environmental sustainability concerns. Then the role of biomass in driving the transition towards a more sustainable energy supply system is discussed within the general context of the European policy framework; particular attention is focused on the deployment of biomass-based fuels. Then, biofuels production status and technologies are dealt with along with their potentials and main drawbacks in substituting conventional fuels in the market. The discussion next develops the main aspects concerning the most suitable engineering approaches to cope with high-level decisions involved in new biofuels infrastructures design. In particular, biofuels network planning process having to be based upon holistic and comprehensive evaluations of their performance, needs for properly devised engineering approaches based on mathematical programming tools Motivations and aim of the work are then presented and a general overview about the structure of the Thesis conclude the introduction.

1.1 Energy: increasing demand but limited resources

Energy is the backbone of present human societies but the consciousness of an important role in both everyday life and social development has pervaded common sense since ancient times. The original Greek word (*energeia*) from which the term energy was derived, was coined by Aristotle during the 4th century BC, with the meaning of ‘force of expression’, suggesting something which is wrought. In the 17th century, the concept of energy was embedded in the idea of living force (*vis viva*). It was thank to the Industrial Revolution and the spread of working machines during the 19th century, that a new consciousness of the energy concept has emerged as deprived of the original philosophical meanings and achieving its modern sense.

The events of History has been teaching how energy consumption and economic growth are closely interrelated. On the one hand, progressive improvements in energy technologies have enabled the process of development for centuries, through technical revolutions innovations (e.g., steam engine, electricity, internal-combustion engine), as well as more modest steps forward. On the other hand, economic development has induced a surge in energy demand, especially when the mass consumption imposed itself in western countries (Lescaroux, 2011). The growth in per-capita income has allowed satisfying, progressively, a series of ‘needs’, from home and food heating to cooling through energy-consuming capital goods like boilers, passengers cars and electronic devices. According to some economic analyses (Lescaroux, 2011), energy consumption for any end-usage (residential, road transportation, industry and services) behaves as a function of the income. This means, in particular, that the wealth is the main driver of energy consumption, even if its influence varies in the course of economic development.

Nowadays, we are witnessing a period of high energy demand increase and the supply reliability is forecast to fall, particularly in view of population growth expectations. According to the International Energy Outlook (EIA, 2011) forecasts, world energy consumption is expected to increase by 53% between 2008 and 2035 (1.6% per year), stimulated in particular by the industrial and transportation sector. Future energy consumption growth will be driven by non-OECD Countries (see Figure 1.1) (e.g., China and India), at an average of 2.3% per year (well above the 0.6% growth rate in the OECD economies). The main problem revealed by the EIA forecasts, relates fossil fuel use, accounting for more than 80% of the total world energy consumption up to now (Figure 1.2). This strongly reliance of economies on non renewable energies is projected to increase (by 1.0%, 1.5% and 1.6% per year for liquid fuels, coal and natural gas respectively, from 2008 to 2035) (EIA, 2011).

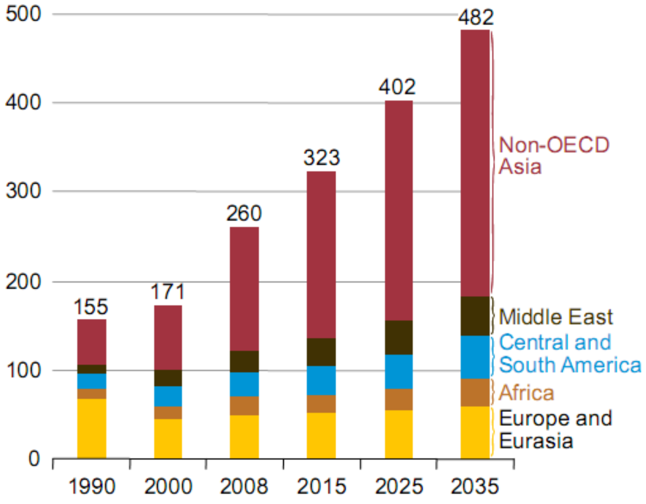

Figure 1.1 *World energy consumption projections between 1990-2035 (EIA, 2011).*

Even if it is acknowledged an ongoing rising share of renewable sources up to a 23% contribution on the total energy required in 2035, thus reducing coal and liquid fuels contributions, this mainly concerns the electric power generation sector, thanks to hydroelectricity and wind energy (EIA, 2011). Furthermore, such a transition might take largely variable economic efforts (e.g., the excess cost for reaching the target of 20% in renewable energy in EU, could range between 0.02% up to 0.08% of national income) (Boeters and Koorneef, 2011).

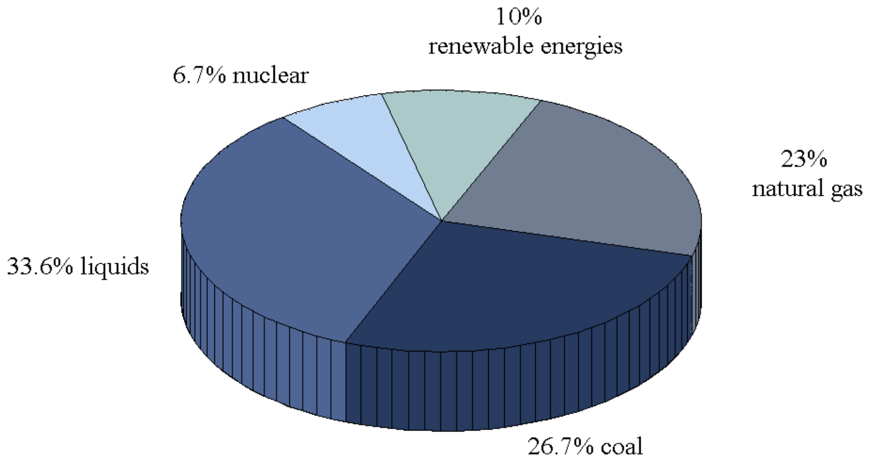

Figure 1.2 *World energy consumption by fuel in 2008 (EIA, 2011).*

Italy, in particular, is by far the EU member with the largest fossil fuel, particularly oil and gas, supply (GSE, 2011) (Figure 1.3), although, during recent years we have witnessed to a rapidly increasing share of renewable energy sources in power generation abiding by the regulation limits, as discussed later on.

In view of the above, forecasts of future energy supply show a wide variety of promising approaches to address the energy problem in the power sector. However, the knotty issue refers to the transportation sector, relying almost completely on oil and where complexities in establishing new logistics are likely to be the major hurdles to develop alternative fuels as well as more efficient technical devices (EIA, 2011).

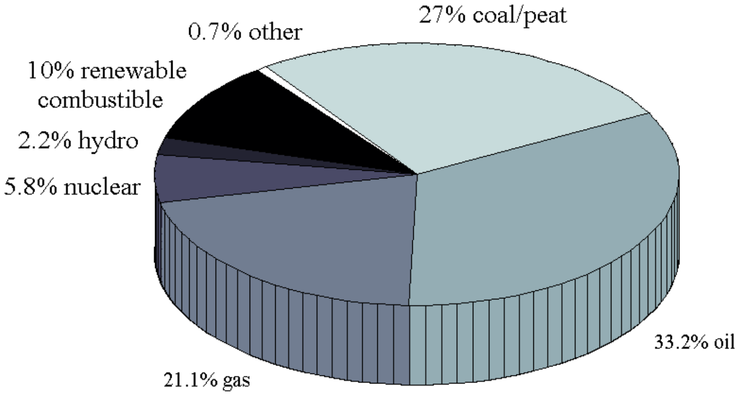

Figure 1.3 *Italian energy balance in power generation (GSE, 2011).*

1.2 Fossil fuels: supply and concerns

Energy provision system almost complete dependence on fossil fuels and on oil in particular, represents just the ultimate development of a situation far from sustainability already started in the 20th century and going on during the 21st century. Any sorts of social disruption (e.g., wars, economic depressions) was caused by countries' strategic imperatives of ensuring continued oil supplies and possibly the access to them (Figure 1.4).

The Oil Crisis of 1973 was only exacerbated by the Yom Kippur War, but it became apparent earlier when the first episodes of imbalance between supply and demand occurred. After, the U.S. had lost its predominance of world oil production, other producers entered the market in a predominant way (e.g., the Middle East, Libya, Algeria and Nigeria). The world oil prices fall during the 1960s due to the supply increase, was stopped through the new agreements negotiated in Tehran and Tripoli (1970-1971), introducing limitation to oil output of OPEC (The Organization of the Petroleum Exporting Countries) countries. At that time, the demand for oil exceeded predictions and some episodes of political instability causing supply intermittence (e.g., continued closure of the Suez Canal after the 1967 war between Israel and Egypt) began jeopardising the energy provision system. After the outbreak of the Yom Kippur War in October 1973, the limitation to crude oil output continued and a unilateral price rise was also imposed in some cases by the oil producing countries. A second wave of rapid increase in 1979 occurred after the Iranian revolution, to reach a new maximum in 1981. However, oil price trends have always been subjected to complex policy and social dynamics taking place worldwide and the Yom Kippur War Oil Embargo was just the first signal underlying the inherent level of uncertainty in the world energy supply. In the 1970s, the industrially developed states of the Organisation for Economic Cooperation and Development

(OECD), tried to react to the economic depression due to oil price shock by becoming more oil-efficient. Total OECD gross domestic product (GDP) increased by 19% between 1973 and 1980; total oil imports fell by 14%, and the oil use to produce each unit of GDP fell by 20% (increasing coal and nuclear energy source utilisation) (Mousdale, 2008). Geopolitical unpredictability and instability of oil suppliers represents even today a great threaten to the markets. Recently, the 2011 Libyan civil war (the so-called Libyan Revolution) along with the general political instability taking place in North Africa, has caused a new growth of crude oil prices.

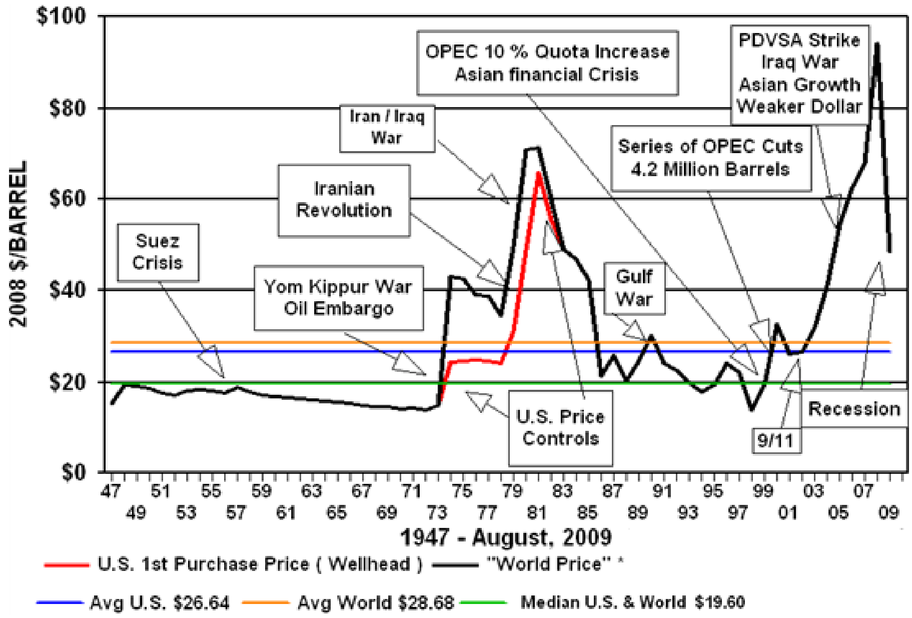

Figure 1.4 *Evolution of crude oil prices between 1947 and 2009 (WRTG, 2011) (PDVSA is Petróleos de Venezuela S.A).*

Recent crude oil evolution trends shows a high variability during the 21st century: after one of the most relevant increase of price ever happened (2004-2007), in 2008 a rapid collapse took place, then leading to a growing trend for almost all 2009-2010.

Price shocks which have taken place between 2004 and 2008 were due to market fundamentals (Kaufmann, 2011) concerning supply and/or demand unbalances related to the changes in OPEC and non-OPEC production. In particular, non-OPEC production stopped growing after 2004, thus leading global oil demand to be satisfied by OPEC nations (at growth rate lower than the demand) with subsequent oil prices rise. 2008 oil prices decline, instead, was due to a reduction of the demand caused by the financial crisis. Moreover, within these complex interlinked causes, speculations of private investors are likely to have played an important role (Kaufmann, 2011).

1.2.1 Peak of production: the problem of resource depletion

The high volatility shown in current oil prices trend also reveals worries about future energy supply, up to now mainly based on non-renewable sources. On the one side, there is a growing consciousness that present levels of oil production rate will probably be insufficient to match the rapidly growing consumption in countries (e.g., China, India). On the other side, concerns have been arising about the so-called peak of conventional fuels production. According to Hubbert's theory (Hubbert, 1949), fossil fuels are supposed to approach a maximum (peak of production) and then begin to decline, with the associated price increase and social effects. The problem is particularly alarming when speaking about peak oil production (Hubbert, 1949), currently being the main energy source (Figure 1.2). However, there might be similar trends for other fossil fuels: Hubbert (1971) also predicted a more distant peak coal; recently, several authors are warning about a relatively near-term peak gas (Simmons, 2007), as well.

Hubbert proposed a prediction technique, which is based on the fitting of a bell-shaped curve to the historical production and to the ultimately recoverable reserves (URR) and still represents the most used approach to forecast production of fossil resources. Through this technique, he suggested the peak of the world conventional crude oil production around 2000 (Hubbert, 1971).

The general idea of a future peak of oil production is now rather accepted. The time frame for this to happen, however, is still under discussion. Campbell and Laherrère (1998), derived a near-term expected peak before 2010 and most of the relevant published research on this subject points to a significant probability of the peak oil occurring prior to 2020 (de Almeida and Silva, 2009; Sorrell *et al.*, 2010). According to recent analysis (de Almeida and Silva, 2009), the evolution of the NYMEX (New York Mercantile Exchange) future prices for crude oil seems to reveal the expectation of the market participants (e.g., oil production companies, the largest fuel users, investors) about a continued price strength. This trend is likely to agree with the prediction about the occurrence of peak oil around the beginning of the next decade. Some authors, instead, state that the peak of oil production is very far away in time (Jackson, 2006) and many of the oil producers still maintain a public denial of near-term production problems. Apart from the fierce debate about the actual time for the maximum of production to come, it is widely acknowledged that many countries, among them some important producers (e.g., U.S.A. and Indonesia) had their individual peaks years ago. Venezuela, Nigeria, Norway, and Mexico have entered an initial phase of diminishing supply. The two most important producers in the world, Russia and Saudi Arabia, seem to be near the peak production or even already at their peaks. Thus, current oil supply strongly relies on permanent efforts just to maintain the present level of oil production and to offset the depletion rates (ranging between 2% and 4% in big onshore oil fields and up to 18% in some deep-water fields) by adopting energy-consuming technologies for exploration and extraction (e.g., new oil wells in presently producing fields, increased water injection, horizontal and multilateral wells). New potential oil fields lie in extremely hard to explore places (e.g., deep-sea offshore, the Artic), while some alternative fossil products (as the Alberta tar sands and the Orinoco bitumen), either face a very slow increase in the production rates, or have at present no viable producing technology (e.g., oil shale) (de Almeida and Silva, 2009).

The problem of energy supply unveils the radical crisis of the current economies as a whole and needs urgent solutions to set a new era where energy provision systems are asked to be first of all sustainable, not only in terms of durability and stability (to prevent resource depletion) but also in its environmental performance (to preserve the state of the planet).

1.3 Climate Change

There is scientific, social and political recognition now about the fact that climate change, referring to a change in the state of the climate (whether due to natural variability or as a result of human activity) is actually occurring. It can be identified using statistical tests by changes in the mean and /or the variability of climate properties that persists for an extended period (e.g., decades or longer). Climate change driver is the alteration in global atmosphere composition, particularly related to the so-called GHG concentration (e.g., CO_2, CH_4, N_2O) (IPCC, 2007). The main interest, however, is about the influences related (directly or indirectly) to human activity, which are recognised as responsible over the last 150 years for changes in the climate at an upper rate than those due to natural climate variability alone, as observed over comparable time periods. Climate change is widely accepted as very likely a result of increasing anthropogenic GHG emissions (The Royal Society, 2008). The consequences are also evident from observations of increases in global average air and ocean temperatures, widespread melting of snow and ice, rising global average sea level as well as the increased frequency and/or intensity of some extreme weather events (e.g., heavy precipitations, rainfalls) (IPCC, 2007).

Global CO_2 emissions increased by 0.4 Gt CO_2 between 2007 and 2008 at a growth rate of 1.5% (IEA STATISTICS, 2008), reaching about 30.2 billion t CO_2 (EIA, 2011). However, trends varied greatly between developed and developing countries (Figure 1.5). In 2008, non-OECD emissions exceeded OECD ones by 24% and if strong economic growth in developing countries will continue to rely on fossil fuels, they will be probably responsible for much of the projected growth of CO_2 emissions up to 2035, when an increase of about 43% of GHG amounts in the atmosphere is expected (EIA, 2011).

Among human activities, electricity and heat generation represents by far the largest producer of CO_2 emissions with 41% share of the world CO_2 emissions (Figure 1.6). This is due to the strong reliance of the sector worldwide on coal, the most carbon-intensive of fossil fuels. The second-largest share of global CO_2 emissions (22% in Figure 1.6) is due fossil fuels burning for transportation.

The future development of the world emissions intensity (as the amount of carbon dioxide emitted per unit of economic output) strongly depends on the fuels, used to generate the electricity (e.g., the share of non-emitting sources, such as renewable and nuclear) and to support people and goods transportation. On the one side, even if coal is expected to account for the largest share of carbon dioxide emitted for long (accounting for 43% of the total in 2008 as it is reported in Figure 1.7), it is forecast an emissions reduction related to the energy sector (1.8% and 2.4% respectively for OECD and non-OECD economies up to 2035). Some improvements have already been implemented through fuel switching away from carbon-intensive sources or from energy efficiency, but more has to be done in promoting renewable energies. On the other side, transportation sector is projected to rely almost completely on fossil fuels for a very long time, and this might have consequences on the state of the planet (EIA, 2011).

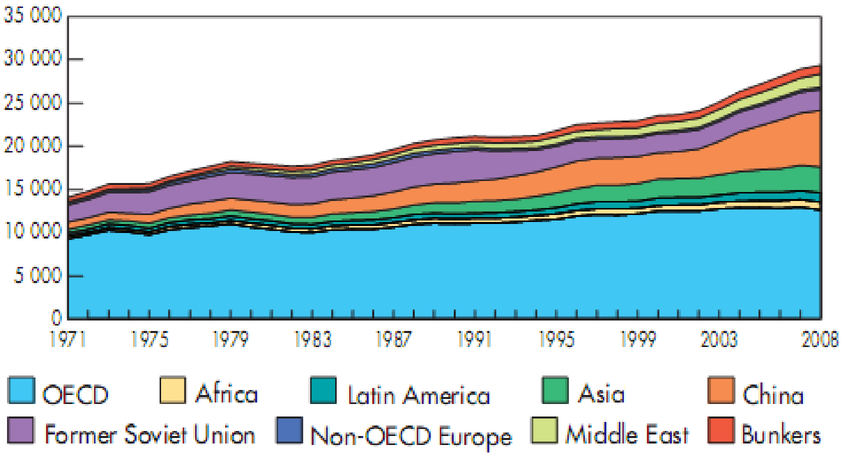

Figure 1.5 *Evaluation from 1971 to 2008 of world CO2 emissions by region in* $MtCO_2$ *(IEA, 2010).*

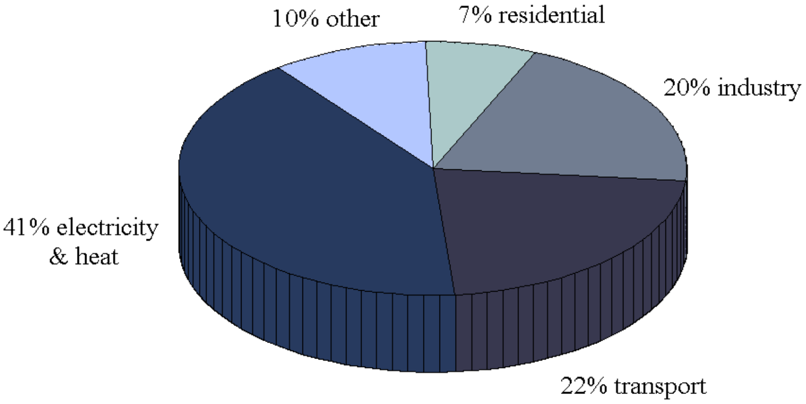

Figure 1.6 *World CO_2 emissions by sector in 2008 (IEA STATISTICS, 2010). 'Other' includes commercial/public services, agriculture/forestry, fishing, energy industries other than electricity and heat generation.*

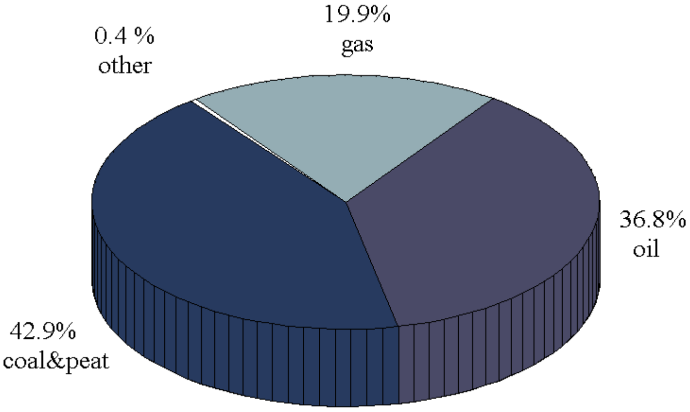

Figure 1.7 *World CO_2 emissions from fuel combustion by fuel in 2008 (IEA STATISTICS, 2010). 'Other' includes industrial and nonrenewable municipal waste.*

1.4 Policy and sustainable development

The continuation of the current energy trends would have profound implications for environmental protection (e.g., resource decline), energy security and economic development, as well as for climate change (IEA, 2009). Policy-makers design strategies should rely on decision-guiding tools addressing sustainable development, aiming at satisfying 'the needs of the present without compromising the abilities of future generations to meet their own needs' (WCED, 1987).

In particular, there has been a growing awareness that environmental protections purposes should have been pursued through an international approach in an ever more globalised world. The Kyoto Protocol (UNFCCC, 1992), which entered into force in February 2005, is by far the most comprehensive multinational effort to mitigate climate change. The Protocol committed industrialised countries to curb domestic GHG emissions by 5.2% (relative to 1990) by 2008-2012 (the first commitment period), and made carbon a tradable commodity by developing emissions trading schemes as cost-effective tools to abide by emissions limits. In the European Union, the largest scheme in operation is the EU ETS (European Union Emissions Trading Scheme), which covers emitters in the energy and industrial sectors (aviation will be added from 2012). These ‘flexible mechanisms’ permit industrialised countries to transfer emission allowances among themselves and to earn emission credits from investments for emissions reduction taking place in participating developed and developing countries. However, the Protocol has been limited in its potential effect on emissions control, since it does not imply action on the total amount of global emissions (e.g., U.S. still remains outside of its jurisdiction).

High oil prices and the ratification of the Kyoto Protocol in 2005 have provided incentives to promote in the EU the use of alternative energy sources, transportation fuels in particular. In the EU, a broad range of policies was developed aiming at reducing its dependence on external energy sources, and at creating a new stimulus for the rural economy, (Vertés *et al.*, 2010; Hugé *et al.*, 2011), as reported in Figure 1.8.

In particular, the first impulse towards the promotion of alternative energies came from the 2001 Green Paper (EC, 2001), which, by stressing the strong dependence of European energy provision from fossil fuels, highlighted the crucial need to face supply security and environmental sustainability issues. Later on, the Biomass Action Plan (EC, 2005) attempted to increase the transformation of various biomass feedstocks into energy (e.g., feedstocks derived from forestry or agriculture as well as waste materials). The 2006 Green Paper on Energy, (EC, 2006) aiming at implementing a European energy policy, was focused on emphasising sustainability, competitiveness and supply security of the energy system to actively combat climate change and to promote efficiency. Conservation of energy, priority to renewable and deployment of low carbon technologies at reduced environmental impacts were set as the pillars of the EU policy.

The transition towards a low-carbon economy is even more difficult for the transport sector, which requires the most costly measures to establish new infrastructures (Turk *et al.*, 2008) due to the current complete dependence on oil and the absence of structural pathways for more sustainable provision systems. Notwithstanding this, several alternatives have been outlined recently and biofuels represent one of the most viable solutions. Despite several and ongoing debates about the effective GHG emissions savings, biofuels are highlighted to as being carbon neutral because the carbohydrates used originate from atmospheric carbon fixed photosynthesis (Vertés *et al.*, 2010). Biofuels penetration in the market has been boosted by policy framework based upon tax exemption and subsidies in many countries, as discussed later on in this chapter.

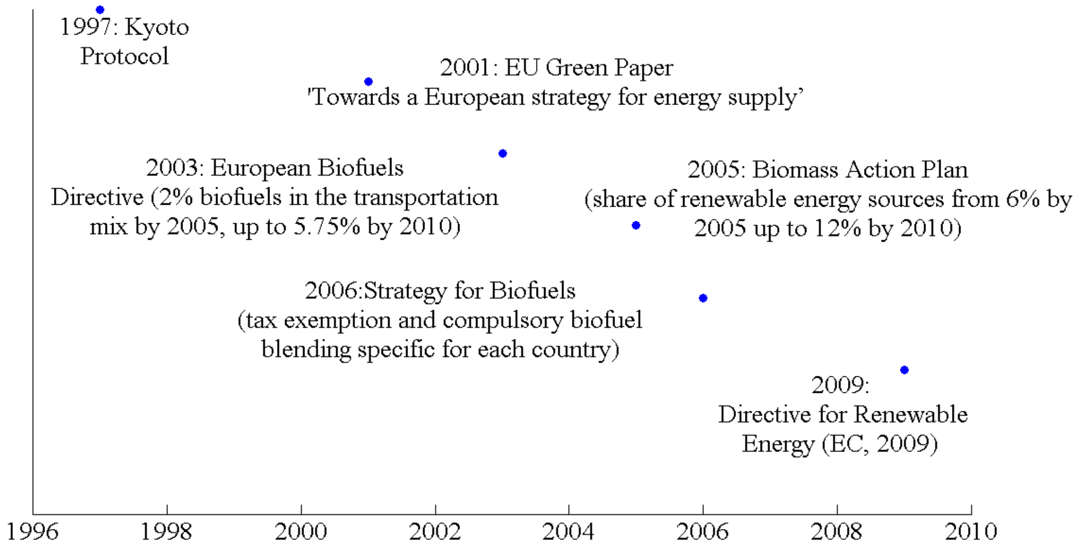

Figure 1.8 *European policies: a roadmap towards more sustainable and renewable energy production technologies.*

1.5 Renewable fuels in the transportation sector

Most studies on energy use in the transportation sector emphasise the growing importance of automobiles in individual transportation, and the continued dependence on fossil fuels.

The transportation sector has been relying for about 97% of the supply on fossil fuels (IEA, 2011) so far accounting for 27% of total world delivered energy consumption (IEA, 2010) and 22% of the overall GHG emissions in 2008 (IEA STATISTICS, 2010) (see Figure 1.6). Global demand for transport appears unlikely to decrease in the foreseeable future; the world energy outlook 2009 (IEA, 2009) projects that transport will grow by 45% by 2030. Increasing demand for personal travel in the growing economies, freight and goods transportation system expansion along national and international routes are the main drivers of the utilisation growth rate, which is expected to increase by 1.4% per year from 2008 and 2035 (EIA, 2011). The transportation energy demand projection is largely a result of an increase in non-OECD nations (by about 2.6% per year), where fast-paced gains in GDP raise standards of living and, correspondingly, the demand for personal travel and freight transport. Transportation energy use for the OECD nations, where consuming patterns are already well established and characterised by a slower growth, is supposed to have a rather stable growth with 0.3% rate per year projected (EIA, 2011).

To limit the emissions from this sector, policy makers should first and foremost consider measures to encourage (or require) improved vehicle efficiency, to increase the share of public transportation and, finally, to promote new low-carbon fuels. These include electricity, hydrogen and greater use of biofuels (e.g., as a blend in gasoline and diesel fuel).

The search for alternatives to fossil fuels first came from the OPEC embargoes and subsequent price shocks of the 1970s, when several major oil-importing countries (e.g., the Unites States and Brazil) implemented a series of incentive programs to encourage the production of transportation fuels made from organic matter instead of petroleum. Conventional biofuels such as ethanol and biodiesel and their various blends with fossil fuels have the advantage that a large-scale implementation can be built on the fleet and infrastructure of existing vehicles, including gas stations. Thus, they can represent a viable solution for energy security and fossil fuels depletion in the nearest time. During recent years, the production of biofuels has known a huge growth. Between 2001 and 2005, the global biofuels production doubled and then more than tripled until 2007, reaching 170 million litres per day. Of the 45 GL ethanol produced in 2005, about 3 GL was consumed for fuel use and the remainder for beverages and industrial purposes. About 60% of the world ethanol was derived from sugar crops (cane), 30% from grains (mostly corn), 7% was synthetic ethanol (produced from ethylene, coal, etc.), and 3% was produced by the bioconversion of other feedstocks (Vertès *et al.*, 2010). Unfortunately, the growth of the biofuel industry has faded in 2008, due partly to concerns regarding unsustainable practices in biofuel production, and partly to the economic crisis which culminated in autumn 2008 with a significant drop in petroleum prices (Figure 1.4). However, a wide range of fuels can be produced from biomass resources including liquid vectors (e.g., ethanol, biodiesel, Fischer-Tropsch diesel) and gases (e.g., hydrogen, methane). Biofuels production is a rapidly growing industry in many parts of the world and great attention is devoted to the development of the most feasible solutions to convert biomass into energy carriers.

At present, ethanol and biodiesel are the primary alternatives to gasoline for spark ignition engines or diesel for compression-ignition engines, respectively. Among the different biofuels, ethanol production more than doubled during the last four years, reaching over 85.6 billion litres in 2010 (Farrell *et al.*, 2006; Carriquiry *et al.*, 2011), thus assuming a leading position among biofuels in substituting petroleum-based gasoline. Growth of the ethanol manufacturing capacity and market is largely driven by blending mandates, subsidies and tax incentives enacted at the government level (e.g., EC, 2009). Different ethanol-gasoline blends are suitable within the fuel market, ranging from E10 (10% ethanol-90% gasoline by volume) to E85 (85% ethanol-15% gasoline by volume). Importantly, low ethanol concentration does not require significant changes in the car engine design characteristics, although this is needed for higher ethanol concentrations. Ethanol, in comparison with the typical hydrocarbon components of refined oils, is more oxygenated; its combustion is cleaner but generates less energy compared with either a pure hydrocarbon or a typical gasoline and an increased volume of combustion products (gases) per energy unit burnt. However, the higher octane number, leads to higher engine efficiencies.

1.5.1 Ethanol as a fuel

The production of ethanol has been known for a very long time, in terms of practical operations: although China was probably the first to develop alcoholic beverages (in 7000 BC ca.) from the fermentation of a mixture of fruits, winemaking can date back as early as 5400-5000 BC in western Asia (McGovern, 2003). The evolution of the chemical technology at the core of ethanol production, covered a very long timeframe, too. The earliest and simplest apparatus for distilling (alembics) were found in the Fertile Crescent dating back to around 500 BC, although it seems that such practices were derived from skills developed even before in China. Modern alembics were produced only later thanks to scientific studies on distillation by Arab alchemists around 700 AD (Simmonds, 1919). Since then the technology kept on improving. It was during the Industrial Revolution that one of the more relevant impetus than ever to the development of this technology came: the twin-column distillation apparatus devised in 1826 in the United Kingdom constituted the basic design for the following larger scale equipment leading, after many modifications, to azeotrope ethanol-water mixture.

Apart from being used as beverage and widely approved in both religion and worship practices, ethanol has been recognised several usages, throughout all history, (e.g., as solvent for material insoluble or poorly soluble in water, medicinal, antiseptic and general anaesthetic). Recently the high flammability of this product (the flash point is at 13°C) has turned to be a key property for other applications, particularly referring to the fuels market.

By 1905, ethanol was emerging as the fuel of choice for automobiles, opinion being heavily swayed by fears about oil scarcity and rising gasoline prices. Henry Ford planned to use ethanol as the primary fuels for his Model T in 1908. However, price competition between ethanol and gasoline had a crucial role and cars industry soon opted for the less expensive fossil alternative. Such an industry change was also due to the dominance of U.S. domestic production of oil, which was more than 60% of the worldwide total in 1913. Nevertheless, Henry Ford kept going on sponsoring agricultural mass products (grain, soybeans, etc) for industrial uses (e.g., his Model A was also equipped with a carburettor allowing for the use of gasoline, alcohol, or a mixture of the two).

During the wars and economic depressions occurred in the 20th century, several attempts were made to substitute ethanol for gasoline (e.g., alcohol-fuelled vehicle became predominant in Germany during World War II; in 1944, the U.S. Army had developed a nascent biomass-derived alcohol industry). Those programs were of such a contingency nature and so highly subsidised that once oil began flowing in increasingly large amounts, they were generally abandoned (Mousdale, 2008).

Until 2005, Brazil was the world's largest producer of ethanol, which was mainly derived from sugarcane and represented the most exported Brazilian commodity. Although since 1931 compulsory additions of ethanol to gasoline were set, the Oil Crisis in 1973 had severe consequences in Brazil. To meet the challenges of energy costs, the govern promoted hydroelectric as well as nuclear power and alcohol production so that a dual-fuel economy has evolved where motorists made rational choices based on the relative prices of gasoline, ethanol and blends. Brazilian automobile producers also introduced flexible-fuel vehicles (FFVs) in 2003, with engines capable of being powered by gasoline, 93% aqueous ethanol, or by a blend of gasoline and anhydrous ethanol.

For much of the 20th century in the U.S., ethanol production as intermediate for a large number of chemicals and products was dominated by synthetic routes from ethylene as a product of the petrochemical industry. The oil price shocks of the early 1970s made govern focus the attention on increasing market penetration of alternative fuels and oxygen-rich additives (oxygenate). Among the oxygenate candidates for gasoline, methyl tertiary butyl ether (MTBE) was first appointed as fuel additive by the Clean Air Act of 1990 and approved by the Environmental Protection Agency (EPA), but banned during 2002, recognising its high environmental pollution effects. It was necessary therefore the development of a second major fuel market by using alternative routes and bioethanol was chosen to replace MTBE. Fuel ethanol production in the United States has been almost exclusively produced from corn, adapting and developing the starchy seeds typically used in the production of malt and grain spirits. However, biofuel market development will in the long run depend on the use of cellulosic materials as primary feedstocks, given the high and ambitious targets set within a policy framework, having been focused on biomass-based fuels penetration for several years.

General incentives for agricultural producers operating within any small rural businesses were first introduced in U.S. in 2002 and later, tax refunds were provided for ethanol blenders and for small ethanol producers. However, the earliest regulation act aiming at increasing biomass-based fuels share was the U.S. Energy Policy Act of 2005, which established a national Renewable Fuels Standard (RFS) creating a framework of incentives for biofuel production and use, as well as supporting research on new biofuels technologies and cellulosic feedstocks. In 2007 the Department of Energy initiative on biomass research and development, within its annual Roadmap for Bioenergy and Bio-based Products in the United States, advocated an implementation of policy measures to advance biomass technologies and the bio-based industry. Moreover, the impetus to drive the implementation of biofuels was expressed by the U.S. President announcement about the need of an increase to 133 billion litres of renewable fuels by 2017 (nearly five times the 2007 level) at the 2007 State of the Union addresses. Finally, the 2007 Energy Independency and Security Act (EISA) established specific tax credits and incentives for promoting the implementation of biofuels, including targets for a greater market penetration of ethanol, fuel efficiency standards for passengers automobiles, minimum GHG emissions reductions for biofuels production technologies. Furthermore, individual states have tried to outpace the federal government in moving biofuels forward and reducing GHG emissions (e.g., Californian Low-Carbon Fuel Standard). As a result, the biofuel component of motor fuels is projected to grow substantially, making the United States, the world largest consumer and producer of fuel ethanol since 2005 (Mousdale, 2008).

Contrary to the case of the U.S., where biofuels have been promoted within a systematic governmental framework including extensive investments on research and subsidies, in Europe the necessary R&D efforts for developing more sustainable technologies remain fragmented, notwithstanding the great role given to biofuels within the EU energy agenda (see Figure 1.8). In particular, the so-called European Biofuels Directive (2003/30/EC) set several measures for boosting biofuels in transportation sector committing Europe to transform itself into a highly-efficient, low carbon economy. A more comprehensive approach to the problem related to energy supply, came from the so-called ‘20-20-20 Directive’ (EC, 2009). It established a reduction in EU greenhouse gas emissions by at least 20% below 1990 levels, a share of 20% of EU energy consumption from renewable resources and a 20% reduction in primary energy use compared with projected levels. In addition, targets were set in terms of biofuels market penetration and a 10% share of biofuels in total energy of the transportation sector was put as minimum threshold. Due to the general uncertain acceptance about biofuels during the coming into force of the Directive, the interest was devoted in particular to the promotion of more sustainable technologies: biofuels market share to be reached by a combination of domestic production and imports, is eligible for public incentives only abiding by proper sustainability criteria, including preservation of bio-diverse area and forests as well as minimum emissions savings with respect to fossil fuels (35% from 2009, 50% from 2017 and 60% from 2018 onwards). Contrary to the general trend of the world, biodiesel production in Europe is by far more important (about 56.1% of the world production in 2008, (Gnansounou, 2010)). European bioethanol production reaches about 5% of the global amount, but the situation differs greatly among the countries: some of them are characterised by a well-established ethanol market (e.g., its market share is about 5.41% in France), others instead will probably meet several difficulties in reaching the EU mandates (e.g., in Italy only about 0.25% of ethanol market share has been reached) (Gansounou, 2010).

1.5.2 Ethanol production technologies

Fermentation is the primary method for the production of beverage alcohol and much of the alcohol used in the industry; the approach based upon the reaction of ethylene with steam, is much more energy-consuming (Surisetty *et al.*, 2011). Fermentation may be applied on a wide variety of feedstocks and is based upon the enzymes (usually microscopic yeasts, such as

Saccharomices cerevisiae) action in the absence of oxygen to convert carbohydrates to ethanol according to the following reactions:

$$n(C_6H_{10}O_5) + n(H_2O) \rightarrow n(C_6H_{12}O_6)$$
$$C_6H_{10}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$$

The processes to convert biomass into ethanol may be classified according to the feedstock and the adopted technology into first and second generation. On the one hand, technologies that normally utilise the sugar or starch portion of plants to produce ethanol are known as first generation ones. On the other hand, second generation technologies convert lignocellulosic biomass into ethanol. These biomass could include: logging residues; forest thinning; wood mill residues; urban waste (paper, tree trimming, grass clipping); energy crops (switchgrass, woody plants); and agricultural residues such as sugar cane waste, corn stover, wheat straw, and rice straw.

1.5.2.1 First generation technologies

Current bioethanol production is mainly achieved from first generation technologies. Feedstock is generally derived from food crops (e.g., sugarcane, sugar beet, maize, sorghum and wheat).

Sugar crops are the main source of Brazilian fuel, favoured by climate conditions, and are processed with an easier and cheaper technology where sugars are extracted, yeast-fermented, and the resulting wine distilled into ethanol.

Starch crops require an additional step, which increases the cost of production. First they are converted into simple sugars through enzymatic process of ground kernels of the plants under high heat, then they might be fermented into fuel. The two main process designs for ethanol production from starch are the wet and the dry route but this second alternative (called dry-grind process) is usually the preferred technological choice (Kwiatkowsky *et al.*, 2006).

As the general purposes of this introduction, here just an overview of the main technological options to produce ethanol, is given. A more technically-detailed description of the process will be provided in chapter 2.

1.5.2.2 Second generation technologies

Cellulose is essentially a structural polymer in plants, highly insoluble, organised into crystalline macroscopic fibres, mixed with other polysaccharides (hemicelluloses), and protected from enzyme attack in native woods by the lignin. While hemicelluloses result from elaborated structures with several types of sugar (e.g., pentoses: xylose and arabinose; the hexoses: glucose, galactose and mannose), lignins are polyphenolic polymers, rather inert to enzyme-catalysed degradation. Among tree species, hardwoods and softwoods differ in their composition, hardwoods having less lignin; in general, cellulose content varies between 38-57% and lignin between 17-37% by weight (Mousdale, 2008).

Production of biofuels from lignocellulosic substrates does not represent a mature technology yet, even if some pilot plants have been brought into operation; the process may be realised through different processing routes (for a deep review of the production technologies, see the work by Piccolo (2010)).

In particular, one technological possibility is represented by the biochemical route, where enzymes and other microorganisms are used to convert cellulose and hemicellulose components of the feedstocks to sugar prior to their fermentation to produce ethanol. Lignin is removed and used as a fuel for heat and power generation. Such a process is possibly the most mature for the transformation of lignocellulosic materials into ethanol (Piccolo and Bezzo, 2009). A bioprocess for producing ethanol from a lignocellulosic substrate could be modelled either considering only cellulosic glucose as a feedstock or utilising both celluloses and hemicelluloses. It includes five main steps: biomass pretreatment, cellulose hydrolysis, fermentation of hexoses (or co-fermentation of pentoses and hexoses), product recovery. Even in the case of second generation technologies, as stated earlier for starchy-based ethanol, a more detailed description of the process is provided in chapter 2.

The most critical step, however, is the pretreatment, which is asked to remove as better as possible, the lignin and hemicellulose protective structure on the cellulose to increase accessibility of the enzymes, at the same time, providing high concentration and recovery of cellulose and hemicellulose sugars at low cost. Physical, biological, chemical treatment or a combination of these might ensure a good pretreatment. In particular, steam explosion (Sassner *et al.*, 2008) and dilute acid hydrolysis (USDOE, 1999) are among the most common methods.

One other possible route for lignocellulose transformation into ethanol is given by the hybrid thermochemical-biological process. This is quite a new processing method based on pyrolysis/gasification technologies to produce synthesis gas ($CO+H_2$) which can be converted in bioethanol through microbial fermentation (gasification biosynthesis process) (NREL, 2002). A number of microorganisms are able to utilise the gaseous compounds resulted from biomass gasification as substrates for growth and production. The process mainly consists of a preliminary pretreatment step, followed by gasification, syngas cleanup, cooling and fermentation as well as product recovery (a more detailed description and characterisation of the process will be given in chapter 2). Even if the process is acknowledged to have potentially great advantages (e.g., high efficiency in the biomass use, wide variability of substrates), uncertainty surrounds the effective technological performance of the technology in terms of product yields and rate. It is based on the adoption of several acetogenic microbes capable of metabolising cleaned syngas into ethanol. One of the most promising strains is represented by the *Clostridium ljungdahlii*, an anaerobic bacterium which converts CO, H_2

and CO_2 into a mixture of acetate and ethanol, according to ratios largely dependent on the pH and following the pathways reactions:

$$\begin{aligned} &6CO + 3H_2O \leftrightarrow C_2H_5OH + 4CO_2 \\ &6H_2 + 2CO_2 \leftrightarrow C_2H_5OH + 3H_2O \end{aligned}$$

A third technological option is the indirect gasification and mixed alcohol synthesis: gasification technologies produce a synthesis gas from which a wide range of long carbon chain biofuels can be reformed through a catalytic reaction (Phillips *et al.*, 2007). This conversion route was disregarded in Thesis.

1.5.3 Advantages and disadvantages of using ethanol

1.5.3.1 First generation ethanol

Several reasons exist to promote bioethanol development and deployment: economists and socioeconomists tend to emphasise the peak oil concerns and the related energy security issues, whereas scientists are far more interested in environmental sustainability and global warming problems. Even if its actual carbon footprint is still debated (Fargione *et al.*, 2008), it is generally acknowledged that ethanol fuel can achieve a reduction in net greenhouse gas emissions with respect to oil (Mussatto *et al.*, 2010). Moreover, the manufacture of this fuel at a large scale would have the advantage of improving rural economies, as well as increasing and diversifying the employments in the farming lands (Petrou and Pappis, 2009).

Bioethanol current production is mainly based on the first generation conversion technologies (e.g., sugarcane-based and corn-based ethanol fuel), representing up to now the most well-entrenched production processes. In fact, these production technologies can provide ethanol at relatively low costs: Brazilian sugarcane-based ethanol is available at about $0.20 per litre and U.S. corn-based ethanol costs about 50% more (Timilsina and Shrestha, 2011). Notwithstanding this, first generation ethanol is now incurring increasing discredits related to the effective economic sustainability, due to the high dependence on feedstocks supply costs sharing between 40-80% of the total operating costs (Petrou and Pappis, 2009). Food crops, which serve as raw material for biofuels production, have experienced so high price volatility, that significant uncertainties remain about future projections of the biofuels market (Dal-Mas *et al.*, 2011).

Furthermore, one of the most debated points refers to global energy supply issues and corn-based bioethanol capability of actually displacing fossil fuels, as formulated in terms of net energy balance (NEB), the ratio between energy in the ethanol produced and the one consumed in input conversion into products. Contradictory estimates has appeared (as reported in Table 1.1), but the published accounts displayed very different methodological approaches and quantitative assumptions (Bordin, 2007).

Even if the presence of different assumptions about relevant input parameters at the basis of the procedure could affect the results, the spread of energy balances around 1.0, with none of them greatly exceeding such a threshold, means that only a highly efficient production process (e.g., maximal utilisation of by-products, optimisation of each supply network step) could deliver a net energy gain. Furthermore, there is some debate about the effectiveness of NEB as a measure of biofuel performance. For instance, Dale (2008) advocated the need for more exhaustive metrics since the absolute value of the NEB interpretation might be misleading as it generally assumes that all energy carriers are equally valuable, without including decreased fossil fuel usage and GHG emissions reduction in the assessment.

Recently, new studies have highlighted debate and controversial results also in terms of environmental sustainability, affecting first generation ethanol industry growth and social perception (Londo *et al.*, 2010). In particular, ethanol from maize has greatly variable performance in terms of GHG emissions reduction, with results ranging from zero savings up to 86% savings compared to fossil gasoline, underlying uncertain assumptions on system boundaries, co-product allocation, and energy sources used in the production of agricultural inputs and feedstock conversion to biofuels (Kim and Dale, 2005; Delucchi, 2006; Farrell *et al.*, 2006; Davis *et al.*, 2009; Timilsina and Shrestha, 2011). More recent studies (Zamboni *et al.*, 2011a; OECD-FAO, 2008) show that the GHG emissions reduction potential could be significantly improved for first generation biofuels through enhanced yields and crop management, biorefinery operation and co-product utilisation.

Table 1.1 *Debated net energy balance of corn ethanol. Results may refer to either higher or lower heating value (respectively, HHV or LHV) of the input parameters.*

Source	**Energy Balance (HHV-based)**	**Energy Balance (LHV-based)**
Ho (1989)		0.96
Marland and Turhollow (1991)	1.25	
Pimentel (1991)		0.74
Keeney and DeLuca (1992)		0.92
Lorenz and Morris (1995)	1.38	
Shapouri *et al.* (1995)	1.20	
Levelton Engineering Ltd *et al.*(2000)		1.32
Wang *et al.* (1999)		1.33
Shapouri *et al.* (2002)	1.27	
Berthiaume *et al.* (2001)	0.79	

In addition, there is a wide awareness that first generation biofuels alone will not be able to satisfy the world growing energy needs. For instance, even if all US corn production was to be dedicated to ethanol, only 12% of the national gasoline demand would be met (Hill *et al.*, 2006). Large scale first generation deployment, requiring so extensive amount of lands, is often thought to be accompanied by environmental degradation (e.g. potential contribution to monoculture and deforestation). This means in particular that the displacement of existing agricultural production, due to biofuel demand, leading to land-use change (Gallagher, 2008), if left unchecked, might reduce biodiversity and even increase GHG emissions.

Finally, one of the most debated points generating great apprehension around first generation technologies deployment, concerns the direct competition with food crops which might occur when first generation ethanol is developed on a large scale (Carriquiry *et al.*, 2011). In fact, the high figure of undernourished people worldwide represents an urgent issue to be faced (FAO, 2008) and the demand of some agricultural commodities are claimed to have the potential to affect national food security. Most studies agree that expanded biofuel production would raise demand for feedstock commodities, moving upwards food price, even if there is considerable uncertainty in the estimated of the magnitude of this effect (Timilsina and Shrestha, 2011). For instance, the International Food Policy Research Institute (IFPRI) has forecast price increase for corn in the range of 23-72%, wheat of 8-30% and sugar of 11.5-66% in response to the implementation of national plans for biofuels by 2020 (ODI, 2008). However, these results exhibiting significant oscillations show that impact on the price of agricultural commodities due to first generation biofuels greatly differs in the assumptions made (e.g., whether by-products are either incorporated or not in the models (Tahehipour *et al.*, 2010); and whether the relation between industrial sectors is modelled or not, e.g., general or partial equilibrium model). However, notwithstanding the apparently high effect on crops price, the impact of biofuels on global or aggregated food prices seems to be smaller (Baier *et al.*, 2008).

1.5.3.2 Second generation ethanol

Cellulosic biomass is the most abundant biological material on earth. Therefore, the development of commercially available second generation bioethanol is not only important for greatly enlarging the volume and variety of feedstocks, but it turns out to be fundamental to support the ongoing increased biofuels market (Londo *et al.*, 2010; Dwivedi *et al.*, 2009). Future potential availability of biomass energy crops as well as wood industry, agricultural, and municipal solid waste in U.S. would lead to a total 1.3-2.3 billion tons of cellulosic biomass potentially equivalent to a biofuel supply matching 30-50% of current U.S. gasoline consumption (Mousdale, 2008). Moreover, second generation biofuels may cease diverting food agricultural commodities to fuel production and even enable the utilisation of waste material from agricultural production (Timilsina and Shrestha, 2011). However, although the cost of the feedstock is lower than that used for first-generation ethanol, cellulosic biomass is more difficult to break down than starch, and the conversion into liquid fuels more expensive (about \$1.00 per litre on a gasoline-equivalent basis, but are anticipated to drop to \$0.50 per litre in the long term (Timilsina and Shrestha, 2011)).

In comparison with first generation, biomass-derived ethanol is expected to require minor input of fossil fuels (Farrell *et al.*, 2006). Notwithstanding the variability of cellulosic ethanol NEB values (suggested to be around 2.0 (de Oliveira *et al.*, 2005; Pimentel and Patzek, 2005) or between 4.40-6.61 (Mousdale, 2008; Hammerschlag, 2006; Luo *et al.*, 2009a)), the process seems to have a profitable energy balance. This large discrepancy with the energy analysis of corn-derived ethanol, derives from the possibility for lignocellulosic processes to produce electricity on-site from the combustion of components of biomass not used for the fermentation (mainly lignin) in combined heat and power plants (CHP).

In addition, second generation biofuels from cellulosic feedstocks, are expected to have typical life cycle GHG reductions in the range of 70-90% relative to gasoline. Their improved environmental performance compared to first generation biofuels relies on higher biomass yields per hectare. Furthermore, emissions reductions potential comes from energy recovery realised through lignin valorisation for power generation. The overall savings estimation also might vary according to the share of conventional energy to produce the electrical power which is substituted (Timilsina and Shrestha, 2011).

In view of the above, the promotion of biofuels produced from cellulosic biomass (second generation biofuels) is clearly advocated. However, high capital expenditures and production costs hinder the establishment of second generation facilities at a commercial scale and only pilot or demonstrative plants have been brought into operation (Gnansonou *et al.*, 2009; Piccolo and Bezzo, 2009). First lignocellulosic crop residues, being the cheapest and most readily available feedstocks, may greatly extend the potential of ethanol industry (Mabee *et al.*, 2011), thus paving the way to the processing of dedicated energy crops. In particular, corn crop residues (corn stover) with a relatively high abundance and a composition rich in cellulose and hemicellulose are one of the most favourable feedstocks (Petrolia, 2008). Besides, their availability in the same areas as corn grain might ease the revamping of already existing corn conversion plants to a hybrid corn- and stover-based technology. This could represent a great benefit in the way that capital equipment, operating expenses and co-products could be shared to achieve overall savings in comparison with an ex novo second generation plant (USDA, 2005).

1.5.4 Future challenges for bioethanol

Many of the issues associated with first generation biofuels can be addressed by the production of second generation biofuels manufactured either from agricultural and forest residues or from non-food crop feedstocks.

However, great care should be taken in leading the transition towards more sustainable energy systems. In particular, one of the major issues associated with large-scale expansion of biofuels refers to the release of GHG emissions to the atmosphere through land-use change as farmers might clear existing forests to meet increased crop demand to supply food and feedstock for biofuels (indirect Land Use Change, iLUC (Delucchi, 2006)). In this context, GHG emissions savings of biofuels might disappear once the release of carbon stored in forests or grasslands during land conversion to crop production is taken into account. Several studies (Fargione *et al.*, 2008; Danielsen *et al.*, 2008) suggested that if emissions related to land-use change caused by biofuels expansion are included, the emissions would be so high that it would take hundreds of years to offset them. GHG balances are not favourable for any biofuels when cultivation of feedstocks causes the conversion of native ecosystems rich of biodiversity, such as forests, to crop lands. However, it is still difficult to manage the indirect effect on land use (Gnansonou *et al.*, 2009) and the procedure might be highly controversial for many reasons because it would make biofuels industry responsible for decisions over which they have no control (Searchinger *et al.*, 2008). A viable solution for both land competition and iLUC, might rely on the adoption of poorer quality land (marginal lands) which could be realised for lignocellulosic biomass, even if requiring more intense agricultural practices might be required to ensure an adequate level of crop production (Timilsina and Shrestha, 2011). The exploitation of crop residue also seems a viable choice, although the removal of residue should be carried out carefully in order to conserve soil organic carbon, nutrients level as well as to preserve the soil from erosion (Reijnders, 2008). On the other side, it would have the great advantage of becoming a brand new revenue for rural areas, without competing with any land use for feed/food production.

Furthermore, the potential impact of biofuels both on water supply and pollution, is another serious concern (The Royal Society, 2008). Approximately 70% of the freshwater around the world is already dedicated to agriculture (Timilsina and Shrestha, 2011). Some of the main bioethanol feedstocks (e.g., sugarcane and maize) need of relatively plentiful water and the amount of fertilisers and agrochemicals required to promote crop yields might result in greater environmental pollution. This issue represents one more reason for boosting a wide variety of cellulosic feedstocks for ethanol production, considering and assessing their constraints in soils, water supply and temperature. Moreover, as outlined above, biofuels production should focus on degraded and marginal lands which are ill suited for agriculture, and typically lack water and nutrients. It is important, therefore, for future biofuels infrastructures development to rely, on the one side, on the strategic adoption of the suitable cellulosic feedstocks capable of withstanding droughts and low nutrients quantities; and on the other side on the promotion of better agricultural practices for irrigation and fertilisers supply.

In addition, one of the major obstacles to make second generation bioethanol develop on a commercial scale relies on high investment and operating costs, thus representing a business even more affected by changing market conditions (An *et al.*, 2011). The competitiveness of ethanol production needed for the global implementation of the fuel, will depend on significant technological improvements along the production and distribution chain, the development of new co-products and the increase in biorefinery efficiency and cost-effectiveness (Vertés *et al.*, 2010).

Concluding, as energy issues are at the top of the policy agenda worldwide, policy-makers increasingly need better decision-supporting processes to assist them in fostering a sustainable energy future. This is even more important for establishing new biofuels infrastructures, considering the limited share of renewable energy in the transportation sector. The establishment of future biofuels systems is challenged by several and interlinked framework of causes and effects, such as energy, water, resource depletion, food production, climate change mitigation efficiency. The most important thing is that biofuels assessment has to encompass all of these aspects to get a sustainable trajectory. It is necessary therefore that the transition from an oil-based fuel system to a biomass-based one, representing a complex design problem, should be supported by properly devised mathematical modelling tools. There is the need for holistic analyses covering each aspect of the provision network (by adopting Supply Chain Management techniques (SCM)) and capable of evaluating several alternative configurations that may help defining a more comprehensive view of the biofuels production systems. The preliminary assessment of such systems is of crucial importance in order to overcome the drawbacks affecting the biofuels production practice particularly at the early stage of their industrial development.

1.6 Supply chain management

A supply chain is an integrated manufacturing process wherein a number of various entities (e.g., suppliers, manufacturers, distributors, retailers) work together to convert raw materials into final products, and deliver them to customers. For years each step of the chain has been seen and optimised individually. Recently there has been an increasing attention on the assessment and optimisation of the supply chain as a whole entity, characterised by forwards flow of materials and backwards flow of information (Beamon, 1998).

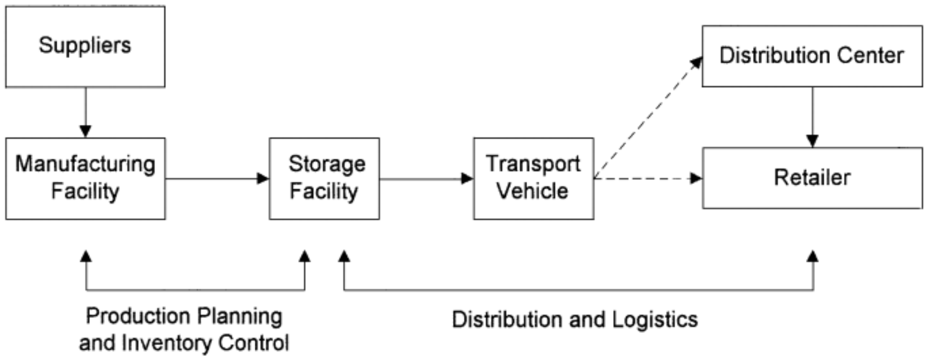

Figure 1.9 *Relation between Supply Chain and Supply Chain management (Beamon, 1998).*

A SC comprises two basic integrated processes (see Figure 1.9): the Production Planning and Inventory Control Process (upstream SC) and the Distribution and Logistics Process (downstream SC). In particular, the former describes the management of the entire manufacturing process (e.g., raw material scheduling and acquisition, manufacturing process design and scheduling, material handling design and control) as well as of the storage policies (raw materials and intermediates as well as final product inventories). The latter determines how products are retrieved and transported from the warehouse to retailers directly or indirectly by using distribution facilities (Beamon, 1998). The two processes interact with one another to produce an integrated SC.

The concept of supply chain management first appeared in the literature in the mid-1980s (Oliver and Webber, 1982), but its fundamental assumptions are significantly older. They include: managing inter-organisational operations, which can be traced back to channels research in the 1960s (Bucklin, 1966); systems integration research in the 1960s (Optner, 1960; Forrester, 1968) and the more recent idea of sharing information and exchange of inventory for information (La Londe, 1984). The earlier literature did not show a consistent view of what SCM was and frequently the concept was confused with logistics (Cooper *et al.*, 1997). Actually, the original use of the term emphasised the reduction in inventory within and across firms, just almost overlapping it with the logistics. Oliver and Webber (1982) stated that SCM covered the flow of goods from supplier through manufacturing and distribution chains to the end user. Stevens (1989) expanded this scope further upstream to the source of supply and down to the point of consumption. In 1994, SCM was more conceptualised and it was defined by the International Center for Competitive Excellence (University of North Florida) as ‘the integration of business processes from end user through original suppliers that provides products, services and information that add value for customers’. In view of the above, it is clear that a supply chain needs a deeper level of integration than logistics. If we consider a new product development as an example, all the aspects of business are ideally involved: marketing, research and development, manufacturing, logistics and finance. In addition to these internal functions, however, there is a need to include external organisations in the product development process in order to reduce the time-to market of new product introductions. The early supplier involvement is important in the product development process, but consumer and customer's participation is also necessary (in this distinguishing itself from logistics). Eventually, a more comprehensive definition of SCM was given by Cooper *et al.* (1997) as the integration of business processes across the supply chain. Since it transcends firms, functions and business processes, almost all functions and business processes are involved to achieve the objective of integrated SCM. Again, SCM is the network of organisations that are involved through upstream and downstream linkages, in the different processes and activities that produce value in the form of products and services in the hand of the ultimate consumer (Christopher, 1992). In particular, a conceptualisation of SCM as a three-part framework has been proposed which integrates the potential structures of supply chains (the configuration of companies within the supply chain), the business processes (the activities that produce a specific output of value to the customer), and the key components for management attention (by which the business processes are structured and managed) (Cooper *et al.*, 1997). In order to minimise inventory in the supply chain, information systems must be able to track and communicate production and customer requirements at different levels in the chain (e.g., marketing and customer must know what the product availability is). Thus, all functions or business processes need some level of upstream and/or downstream coordination.

Modern views of SCM can be classified on different levels, according to the following categories (Papageorgiou, 2009):

i. strategic and tactical level: SC design (infrastructure)
ii. tactical and operational level: SC planning and scheduling
iii. operational level: SC control (real-time management)

each one of the above characterised by a well determined time horizon as well as a precise detail level.

Management of supply chains is a complex task, because of the large size of the physical supply network and inherent uncertainties (Papageorgiou, 2009). Since the high competitive market in which they operate, improved decisions are required for efficient supply chain management. Depending on the level, one or more of these decisions are taken:

- number, size and location of manufacturing sites, warehouses and distribution centres
- production planning and scheduling
- allocation decisions (e.g., suppliers to plants; warehouses to markets)
- management of inventory levels
- transportation decisions (e.g., modes of transportation, freight size)

Appropriate performance measures might be assessed to estimate efficiency and effectiveness of SC (Beamon, 1998). Such measures can be used to either design a system with appropriate level of performance or to compare alternative systems. Suitable quantitative performance measures might be based on financial flow (e.g., cost minimisation, profit maximisation); on customer responsiveness (fill rate maximisation, product lateness minimisation, lead time minimisation). Moreover, the process industries might adopt SCM tools to undertake significant transformations such as changing market circumstances and increased competition, improved sustainability, environmental and social impacts; future regulation and compliance requirements (Papageorgiou, 2009).

SC models may be distinguished between two categories depending on the modelling task. On the one hand, Simulation Models (SM) can be used to study the detailed dynamics operation of a configuration under operational uncertainty, and to evaluate expected performance measures for the fixed configuration to a high level of accuracy (Beamon, 1998; Shah, 2005). On the other hand, they can be Mathematical Programming (MP) models, to optimise high-level decisions involving unknown configurations, taking an aggregate view of the dynamics and detail of operation (e.g., SC network design, medium term production and distribution planning).

1.7 Process industry supply chain

In the following a literature survey is presented about MIP modelling framework for SC modelling in the context of both SM and MP. More detailed discussions about multi-stage SC modelling are provided by Beamon (1998). Recently Shah (2005) and Papageorgiou (2009) have offered a review of the relevant associated research.

1.7.1 Supply chain simulation and policy analysis

A simulation engine needs to replicate or incorporate algorithms used at certain parts of the SC, producing agent- or object-oriented frameworks, both of which are suited to modelling complex systems with decentralised decisions. This makes supply chain simulation as a popular tool to formulate policy, because the processes used at different nodes of the SC result in a variety of different dynamic behaviours (often to the detriment of overall performance). Hence, simulation is useful in identifying the potential dynamic performance of the SC as a function of different operating policies, ahead of actual implementation of any one policy.

Bose and Pekny (2000) used a model predictive control (MPC) framework to understand the dynamic behaviour of a consumer goods SC.

A centralised approach where all decisions are taken simultaneously by a coordinator usually contrasts the results achieved with a decentralised approach where each entity makes decisions independently. SC can be thought of as distributed systems with somewhat decentralised decision-making (Gjerdrum *et al.*, 2000) to assess, for instance, scheduling strategies. The multi-agent approach is an effective technique for simulating this sort of system: the different players in the SC are represented by agents (e.g., warehouses, customers, plants and logistics functions) who are able to make autonomous decisions based on the information they have available and messages they receive.

Hung *et al.* (2006) developed a flexible object-oriented approach to the modelling of dynamic SC. Each node is characterised by physical and business properties, aiming at replicating decision-making within the simulation tool, including a stochastic simulation to account for uncertainties.

1.7.2 Mixed Integer Linear Programming

MP approaches to design problems traditionally belong to Process System Engineering (PSE) community. Even though first strictly focused on the company-centric view of the production stage level, the rising awareness of higher economic benefits coming from an integrated management of the interacting actors of the entire production system, has led to the inclusion of a more comprehensive optimisation approach. As a result, SCM has recently emerged as active area of research (Shapiro, 2001) in order to provide sophisticate decision-making supporting tools within the scope of SCM.

The full management of production systems is a critical aspect of modern enterprises development (Papageorgiou, 2009) and needs adopting a comprehensive approach considering all the stages belonging to the entire production and distribution SC. In particular, as stated by Kallrath (2000), MILP represents one of the most suitable tools in determining the optimal solutions of complex SC design problems where multiple alternatives are to be taken into account.

In dealing with SC networks design and planning, many of the decision that must be taken might be represented through discrete variables. Thus, MILP problems might capture investors’ decisions through purposed devised Boolean variables (i.e. representing whether an activity exists within a SC node, or a transportation link has to be established between different nodes). If this task is addressed through algorithmic approaches, it raises the need to represent these discrete choices, along with the continuous ones (e.g., production rate, profits, taxes...). Hence, a combination of discrete and continuous variables must be embodied within the general mathematical formulation, and the Mixed-Integer Programming (MIP) form may be expressed as:

$$\begin{aligned} \min\ & f(\mathbf{x},\mathbf{y}) \\ \text{s.t. } & h(\mathbf{x},\mathbf{y}) = 0 \\ & g(\mathbf{x},\mathbf{y}) \leq 0 \\ & \mathbf{x} \in \Re^{n},\ \mathbf{y} \in \{0,1\}^{m} \end{aligned} \tag{1.1}$$

where **x** still represents the *n*-set of continuous variables, whilst **y** is the *m*-set of discrete variables (which generally are binary variables that take 0-1 values to define the design decisions). MIP models refer to as MILP models when all the algebraic equations and inequalities (objective function and constraints defining the feasibility region) are linear (for a deep description of the MIP modelling framework and solution algorithm, see Dantzig and Thapa (1997); Dantzig and Thapa (2003); Williams (1993)).

The applications of MP for SC problems cover a wide variety of fields which can be subdivided into the following categories:

(i) supply chain infrastructure (network) design;
(ii) supply chain planning and scheduling.

The former is related to activities associated with establishing the best way to configure and manage the SC network. The latter involves deciding how to operate the network to respond best to the external conditions faced by the SC.

SC modelling might involve either deterministic or stochastic mathematical framework depending on whether the variables are given only fixed values or are assumed to follow a probabilistic distribution.

Finally, one key aspect which makes MP a suitable tools for supporting decision-making for selecting upon several alternatives, refers to the possibility of performing multiple criteria optimisation frameworks.

1.7.2.1 Supply chain network design

Supply chain network design covers a very broad range of topics. It generally refers to a strategic activity concerning one or more of the following decisions:

- where to create new facilities (e.g., production, storage logistics facilities)
- significant changes to existing facilities (e.g., expansion, contraction or closure)
- sourcing decisions (e.g., identifying what suppliers per each facility)
- allocation decisions (e.g., what products to be produced at each production facility; which market served by which warehouse)

Research in this field started very early on, with location-allocation problems as part of the set of operations research problems. Geoffrion and Graves (1974) considered the problem of a distribution system layout, sizing and allocation optimisation. Other works referring to production-distribution network optimisation (e.g., including aspects as opening or closing of plants, the assignment of facilities to plants and the assignment of production to facilities) have been reviewed by Vidal and Goetschalckx (1997). Kallrath (2002a) described a tool for the simultaneous strategic and operational planning in a multi-site production network, where minor changes to the infrastructures may happen during time.

All the above works rely on the concept of fixed ‘echelons’ in the way they assume a given fundamental structure for the network in terms of the echelons involved (e.g., suppliers, manufacturing plants, warehouses, distribution centres, customers). However, changes in the fundamental structure of the SC may sometimes lead to great economic benefits and this may be modelled by integrating the component of a system without any a priori assumption.

Another topic dealt with in the PSE community refers to long-term capacity planning of one production site, represented by a network of processes interconnected by material streams. In particular, it refers to an initial capacity associated with each process of the production site and the objective is to determine which processes to operate in the future as well as where and when to expand capacity. Sahinidis *et al.* (1989) described an MILP modelling framework, which selects processes to operate from an integrated network, and optimises net present value. Liu and Sahinidis (1996) extended the problem to include multiple product demand scenarios in each period, proposing also efficient solution algorithms.

1.7.2.2 Supply chain planning and scheduling

SC planning and scheduling determines the optimal infrastructure and seeks to identify how best to use the production, distribution and storage resources in the chain to respond to orders and demand forecasts in an economically efficient manner.

Optimisation methods have found considerable application here, particularly for the so-called ‘recipe-based’ representations, where processes are operated at fixed conditions and to fixed recipes and the modelling framework aims at optimising production, distribution and storage across multiple sites, using typically MILP modelling frameworks. A number of multi-period mathematical models have been proposed for process industry SCs. Wilkinson *et al.* (1996) described a continent-wide industrial case study, involving optimal planning in terms of production and distribution for a system including several entities as factories, markets, warehouses and products. Kallrath (2002b) presented a comprehensive review on planning and scheduling in the process industry. He identified the need for careful model formulation to reach the solution problems in reasonable computational times. Timpe and Kallrath (2000) presented a MIP framework aiming at optimal planning of multi-site networks with an accurate description of production capacities.

A relatively new field is represented by the so-called property-based planning. Business with slimmer margins (e.g., refining, petrochemical) are moving towards ‘property-based’ representations, where process conditions and models are implemented, and stream properties are inferred from process conditions and mixing rule. This approach turns out to involve complex non-linear modelling frameworks (Jackson and Grossmann, 2003).

1.7.2.3 Dealing with uncertainty

In order to assess future performance of a SC, uncertainty needs to be taken into account, usually about product demands, process yields, processing times, transportation lead times. A large number of problems in production planning and scheduling, location, transportation, finance, and engineering design require that decisions be made in presence of uncertainty. Uncertainty, for instance, governs the process of fuels, the availability of inputs, the demand and price of products. The need to account for uncertainty has widely been recognised an important issue, indeed, to facilitate calculations of expected return and evaluation of associated risks.

Decision-making under uncertainty is often further complicated by the presence of integer decision in a multi-period or multi-stage setting; this results in large problems difficult to solve. Sahinidis (2004) proposed an overview of the main approaches to optimisation under uncertainty for process system engineering applications: stochastic programming (recourse models, robust stochastic programming and probabilistic models), fuzzy programming (flexible and possibilistic programming), and stochastic dynamic programming. It is clear from the above that optimisation under uncertainty is a relatively new research branch on SCs and methodologies are still emerging. One of the most common approaches adopts stochastic programming formulations and, in particular, two-stage mathematical models with recourse. These mathematical frameworks involve two types of decisions variables: 'here-and-now' (design) variables of the first stage and 'wait-and-see' (control) variables of the second stage, which are determined before and after the realisation of the uncertain parameters, respectively. The first-stage decisions mainly pertain to raw material requirements and nominal production levels of the sealable products while the second-stage decisions are primarily corrective actions with respect to the first-stage decisions after the uncertain data are completely revealed. Uncertainty might be modelled either by a discrete number of scenarios or by probability distributions. Scenario-based two-stage or multi-stage stochastic programming with recourse is based on the seminal work by Dantzig (1955). Usually the expectations of second-stage variables (e.g., costs, profits...) are included in the objective functions, although, some works properly introduce some kind of variability metrics (Eppen *et al.*, 1989; Ahmed and Sahinidis, 1998) in the model.

For long-range planning of process networks, uncertainty in demands and prices were modelled in Liu and Sahinidis (1996) and Iyer and Grossmann (1998) by using a number of scenarios per each time period thus, resulting in multi-scenario, multi-period optimisation models. They also proposed algorithms to improve the solution procedure of such a large-scale problems. The exploitation of brand new and robust solution algorithms, usually based on decomposition techniques, is a main topic for great part of the academic research. Gupta and Maranas (2000) considered the problem of mid-term SC planning under demand uncertainty. They utilised a two-stage stochastic programming approach, where production is a here-and-now decisions, while distribution is optimised in a wait-and-see fashion (in fact, production tends to be the main contributor to led times). Sabri and Beamon (2000) also developed a combined strategic-operational design and planning model treating uncertainties in lead times. Tsiakis *et al.* (2001) showed how demand uncertainty can be introduced in a multi-period model for multi-echelon pharmaceutical SCs design. Future uncertainties were captured through a scenario tree, where each scenario represents a different discrete future outcome. A multistage stochastic model, where structural decisions are considered as recourse actions, was proposed by Guillén-Gosàlbez *et al.* (2006) for the SC design problem under demand uncertainty by integrating strategic and tactical/operational levels and solved using a properly devised decomposition solution strategy.

Within the chemical PSE domain related to optimisation under uncertainty, risk management is becoming a common topic for driving high-level decisions within the process of SCs strategic design and planning. In particular, it is usually referred to as financial risk, which might be expresses in the context of planning projects, as the probability of not reaching certain targets (e.g., profits, costs). In this perspective, when starting new business, investors might be willing to take a certain level of risk, meaning that they might accept to undergo some probability of failing the targets. Several risk measures have been used to address financial risk: eDR (expected Downside Risk (Eppen *et al.*, 1989)), VaR (Value at Risk, (Guldimann, 2000)) and CVaR (conditional Value at Risk, (Rockafellar and Uryasev, 2000; Verderame and Floudas, 2010).

1.7.2.4 Green Supply Chain Management

Recently there have been new pressures towards environmental sustainability due to restricting regulation imposed by governments. This has determined an increasing attention towards the inclusion of pollution mitigation as part of the optimisation criteria in the design of process systems. In fact, as pointed out by Cano-Ruiz and McRae (1998), a new approach in chemical plants design that considers the environmental performance as a design objective may lead to the discovery of unexplored solutions that not only minimise ecological damage but might also lead to overall economic benefits. However, each entity of the SC (e.g., suppliers, manufacturers, distribution/retailers and customers) is associated with products, processes and/or transportation activities which affect environment. Thus, limiting the scope of the analysis to a company-centric view of the production system may result in misleading solutions (e.g., a decrease of the local impact might determine an increase in the overall ecological damage). As a result, there has been a growing interest for the incorporation of environmental aspects within the economic-based framework of SCM. This requires the quantification of sustainability or environmental impact of a SC, preferably using life cycle-based indicators (Azapagic, 1999) and the use of these measures in the optimisation models. By including environmental responsibility principles within a more comprehensive approach analysing the performance of a production system across the entire SC a new branch of SCM has been developed, namely, the Green Supply Chain Management (GrSCM).

In an extensive review, Srivastava (2007) remarks the importance of a more extensive use of MP to contribute to major advance in an environmentally conscious SCM. In fact, MP might perform simultaneous optimisation of different issues, leading to multicriteria frameworks (Guillén-Gosálbez and Grossmann, 2009), through the incorporation of multiple criteria decision-making techniques within the modelling framework, namely, Multi-objective Mathematical Programming (moMP). This enables the simultaneous exploration of a balanced trade-off between conflicting objectives, improving decision-making progress particularly at the early stage of process development (Grossmann and Guillén-Gosalbéz, 2010).

According to Mavrotas and co-workers (Mavrotas *et al.*, 2008), the methods for solving moMP problems can be classified into three categories according to the phase in which the decision maker is involved in the decision process with respect to the moment of the set of feasible Pareto solutions being provided: the *a priori*, the interactive and the *a posteriori* methods.

The application of moMP within the specific field of GrSCM is further motivated by the approach used which is based on the evaluation of the SC performance in terms of ecological damage covering all the stage of the life cycle of the product (Bojarski *et al.*, 2009). GrSCM peculiarity is to effectively embody the Life Cycle Analysis (LCA) approach within the SC Analysis (SCA) techniques aiming at a quantitative assessment of the environmental burdens of each SC stage. LCA techniques has been broadly acknowledged as the best methodology to rigorously quantify the environmental burdens and their potential impact of a process, product or activity (Azapagic, 1999). However, including LCA techniques within a moMP framework poses the problem to find the most appropriate approach to evaluate the ecological damage of the system.

1.8 Biofuels: a new frontier for supply chain management

Biofuels infrastructures represent an opportunity to explore the configuration of the SCs before they develop organically and this would allow national and international policies as well as strategic decisions in industry to steer investments on optimal networks design and planning. As recently observed (Petrou and Pappis, 2009), there is a need for an integrated analysis based on several issues that may help defining a more comprehensive view of biofuels production systems. Moreover, biomass-based biofuels might rely upon complex logistics, making the collection phase unfavourably costly (Petrolia, 2008; Sokhansanj *et al.*, 2010; Sultana and Kumar, 2011).

In tackling high-level and multi-faceted decision problems such as planning and design of future biofuels supply chains, analytical modelling has been recognised as one of the best optimisation option especially in the early stage of unknown structures design (Beamon, 1998). Some works have proposed MP to address optimal process design for first and second generation ethanol production (Ahmetović *et al.*, 2010; Grossmann and Martìn, 2010). Plant topology issues were dealt with concerning decisions about unit connections (flows and potential recycles) and material balances, devised in the proper way to minimise the energy and water requirements of the overall plant. A relatively large number of recent works have proposed a comprehensive optimisation approach in the design of bioenergy supply chains (e.g., Bruglieri and Liberti, 2008; Rentizelas *et al.*, 2009). Other studies have focused on the adoption of techno-economic drivers in facing the design of the whole biofuel system. Dunnett *et al.* (2008) first proposed a steady-state spatially explicit MILP model to determine the cost optimal configuration for a lignocellulosic bioethanol SC. Zamboni *et al.* (2009a) and later Akgul *et al.* (2011) presented a spatially-explicit MILP model for the integrated management of the key issues affecting corn-based ethanol SCs such as biomass suppliers and production facilities allocation as well as transport logistics. More recently, Zhu *et al.* (2011) provided a decision-making tool to support strategic supply chain design and tactical scheduling for converting switchgrass to biofuel. Later Zhu and Yao (2011) presented a multi-feedstock network flow model for biomass-to-biofuels SC considering optimal strategic logistics design and tactical scheduling within an MILP framework. Papapostolou *et al.* (2011) presented an MILP mathematical model for the optimisation of biodiesel network using SC income maximisation as a driver. They developed a tool to support decision-making at strategic and operational level of integrated biofuels SC, considering contrasting issues such as feedstocks and biofuels provision geographical location (e.g., domestic production or imported supply) and adding some constraints in terms of water availability to biorefinery. Finally, Marvin *et al.* (2012) developed an MILP modelling framework for the economic optimisation of an ethanol fuel SC at a strategic and planning level using lignocellulosic residues as feedstocks for ethanol production and accounting for biomass spatial availability.

The possibility of performing moMP techniques addressing simultaneous optimisations of different issues (Guillén-Gosálbez and Grossmann, 2009), enables the exploration of a balanced trade-off between conflicting objectives (e.g., economic, environmental, social, risk-management). This might give invaluable insights on the pathways for driving and steering decisions on biofuels SC deployment, since the earlier stage of such structures design involves conflicting aspects to be evaluated. Decision makers should be provided with tools for analysing the overall supply chain, not only assessing the economic, but also the environmental pros and cons so as to define the most convenient strategies concerning the development of the future road transport systems. In fact, biofuels SC analysis should integrate economic aspects along with the environmental responsibility of the production network. Such a design process considers environmental concern as a new design objective and not merely as constraints in operations, according to the GrSCM concept. These moMP approaches encompassing LCA features within SC optimisation framework have already been applied to energy sector in general. Hugo and Pistikopoulos (2005) proposed a modelling framework combining plant location and capacity planning features with the principles of

LCA for long-range planning of multi-enterprise fuels SCs. Relatively few works have been addressing analytical programming to the environmentally conscious planning at a strategic or tactical level for biofuels SCs. Zamboni *et al.* (2009b) developed a static spatially explicit moMILP framework which minimises both the operating costs and the GHG emissions of a corn-based ethanol SC. Mele *et al.* (2011) proposed a bi-criteria model addressing both profit and environmental impacts of combined sugar/ethanol SCs by adopting the eco-indicator 99 and global warming potentials. Recently, multiple criteria decision-making tools have been proposed considering also the social effects of biofuels SC deployments. You *et al.* (2011) proposed a more comprehensive approach, where apart from economic and environmental impact, the social effect is also assessed for a cellulosic ethanol SC, even though it is evaluated only accounting for the accrued number of jobs such a business would create.

All these approaches to optimal biofuel SC design are deterministic. Unfortunately, the biofuels industry is more vulnerable to risk than many other industries because of feedstocks cost and competition with the established petroleum-based fuels (An *et al.*, 2011; Awudu and Zhang, 2012). Even if process systems engineering researchers have considered uncertainty (Liu and Sahinidis, 1996; Sahinidis, 2004) and the management of financial risk within the general context of process industry (You *et al.*, 2009; Verderame and Floudas, 2010; Khor *et al.*, 2011) relatively few studies have been able to address uncertainty related to biofuels SCs. Dal-Mas *et al.* (2011) proposed a multi-period and stochastic modelling framework accounting for uncertainties in product price and raw materials costs. The investment analysis has been assessed in terms of financial criteria such as the expected Net Present Value (eNPV) and the conditional Value at Risk. Kim *et al.* (2011) developed an optimisation model enabling decision making for the infrastructure of biofuel conversion processing. The design of a biofuels network encompasses the effect of uncertainty through a multi-scenario approach based on some dominant parameters such as biomass availability, demand, products sale price and yields. Kostin *et al.* (2011) have proposed a two-stage stochastic MILP modelling approach for optimal planning of integrated ethanol-sugars supply chains under product demand uncertainty. The modelling framework aims at steering strategic level decisions on the production network optimising the expected performance of the business under different risk mitigation options (Value at Risk; Opportunity Value, OV; Risk Area Ratio, RAR).

1.9 Motivation of the work

In view of the above, there are several topics still lacking a more comprehensive discussion to support a rational deployment of biofuels.

First, a smooth and rational transition towards the establishment of low-carbon fuels advocates a comprehensive view of the integration between starch- and cellulose-based ethanol fuel through the development of hybrid processes. The exploitation of both starchy feedstocks (corn) and their residues (stover) for ethanol production might ease the revamping of already existing first generation facilities. Although several plant topologies alternatives of integration between corn and stover feedstocks have been assessed by the US Department of Agriculture (USDA, 2005), a holistic approach to optimal planning of biofuels SCs is advocated. Multicriteria decision-making tools (moMILP models) addressing multi-echelon SC strategic planning and design (Sahinidis *et al.*, 1989; Tsiakis *et al.*, 2001) are advocated. Both environmental and economic performance (Hugo and Pistikopoulos, 2005) of a hybrid infrastructures are needed to be simultaneously addressed in order to assess the ability of such a system to pave the way for more sustainable second generation bioethanol.

Another gap of the literature concerns the effects on the promotion of biofuels SCs due to energy policy: the attribution of a value to carbon emissions, for instance, might significantly affect biofuels infrastructures (e.g., selection among several technological options, including both first and second generation production, and feedstocks). In fact, extensive market-based tools, such as emissions trading integrated with regulation targets, might play a key role for managing high costs related to the innovation within biofuels market (Turk *et al.*, 2008) and delivering a sustainable transport systems at lower costs. Even if the road transport sector is currently excluded from the EU ETS, several institutions have adopted market-based tools addressing the issue of biofuels sustainability to help accelerating the implementation of new technologies (e.g., the Californian ‘Low Carbon Fuel standard’ (ARB, 2011)). Thus, the implementation of this flexible mechanisms has to be addressed by adopting multicriteria decision making tools assessing strategic design and planning on ethanol fuel SC. Moreover, in studying the integrated long-term vision for biofuels development and deployment, carbon market volatility and the crucial role of technological learning in determining costs reduction, should be implemented (Hettinga *et al.*, 2009; de Wit *et al.*, 2010). In such a context decisions about optimal supply chain configurations need to carefully include risk-mitigation constraints, since investment strategies might rather change according to investor’s attitude towards risk (e.g., risk-taking or risk-averse).

The objective of this Thesis is to propose a comprehensive methodology and a general modelling approach to bridge the research gaps discussed in the above. Accordingly, the economics of the system will be assessed by means of SCA techniques, focusing on biomass cultivation size, technology selection and plant capacity. The environmental performance of the system will be evaluated in terms of GHG emissions, by adopting a Well-to-Tank (WTT) approach to LCA analysis (CONCAWE, 2007).

1.10 Thesis roadmap

A basic roadmap to this Thesis is presented in Figure 1.10. The Thesis structure is as follows.

Chapter 2 discusses the approach to techno-economic modelling and environmental assessment of the advanced technologies here chosen for ethanol production (e.g., hybrid processes operating with both corn stover and grains; second generation technologies).

Chapter 3 aims at delivering an environmentally conscious decision-making tool for the design of corn grain- and stover-based bioethanol production systems, considering possibilities of their mutual integration. It is based on a multi-period multi-objective MILP modelling framework for the design and the optimisation of bioethanol SCs where economics and environmental sustainability (GHG emissions reductions potential) for first and second generation ethanol are addressed.

Chapter 4 deals with the effect of energy policy on ethanol SC design and planning with particular regard to best processing pathways. The model is capable of assessing the effect of CO_2-equivalent emissions allowances trading and their inherent volatility level to boost investments on sustainable ethanol production.

Chapter 5 extends the MILP modelling framework presented in the chapter 4. Here a multicriteria decision making tool is proposed encompassing also risk management issues to support strategic design and planning on ethanol fuel SC under market uncertainty, arising from feedstocks and carbon cost within an emission allowances trading scheme.

Chapter 6 finally gathers together the main achievements of the research also outlining the main shortfalls and the main objectives to be carried out in the future work.

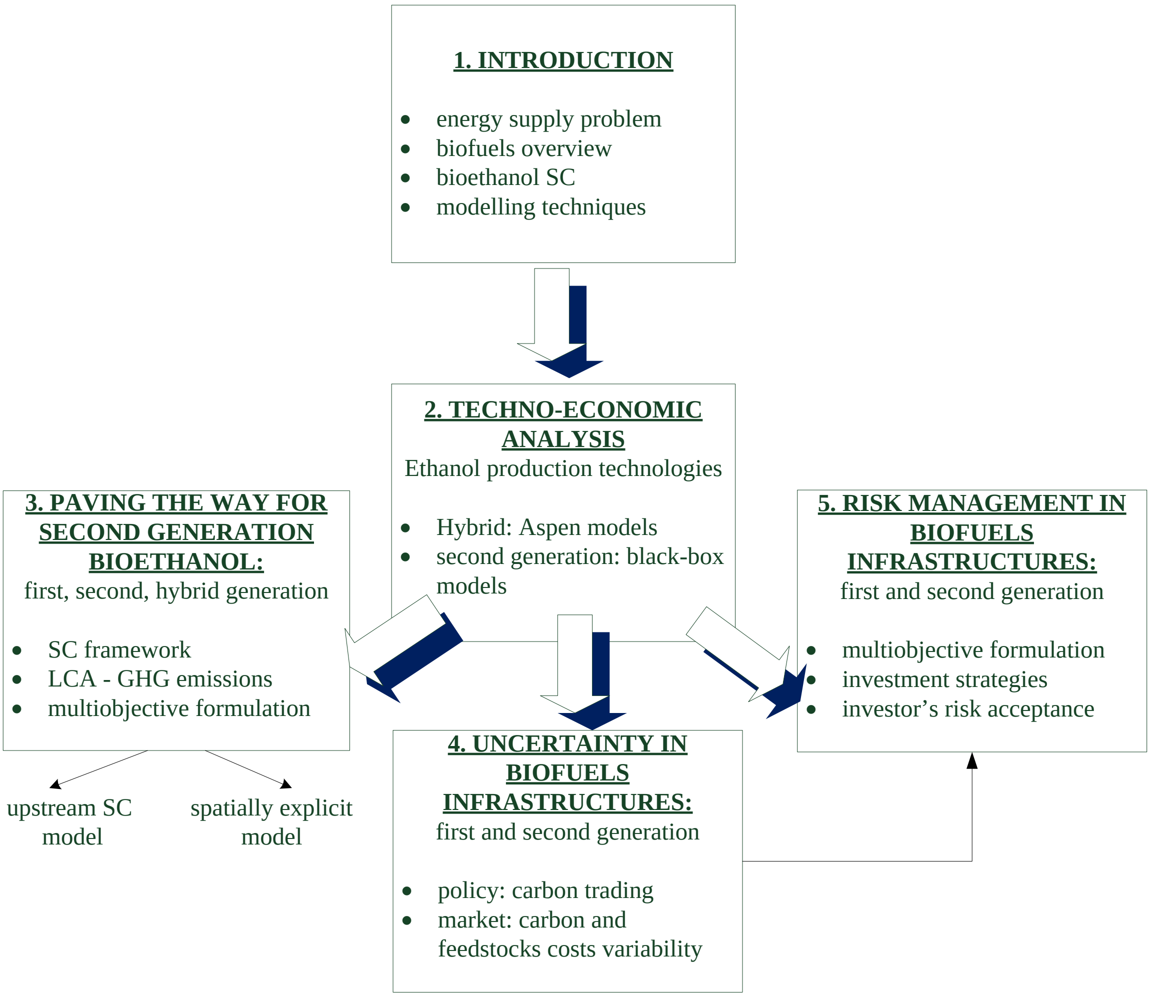

Figure 1.10 *Overview of the Thesis.*

Chapter 2

Analysis of ethanol production processes

Bioethanol supply chains design relies on the technical and economic characterisation of each network step, from biomass cultivation, transport and conversion into ethanol up to fuel distribution.

After a literature survey about computer simulation modelling and optimisation of bioethanol processes, the focus of this chapter is to provide an overview of the conversion technologies here addressed for ethanol production, offering also a techno-economic evaluation for the processes considered. The attention is focussed on the corn-based dry grind process and on a wide variety of cellulose-based generation technologies operating with different pre-treatment steps. In addition, the opportunity of integrating both corn grain and its residue (e.g., corn stover) for ethanol generation within a hybrid production process is considered.

The techno-economic characterisation has been approached adding the information available in the literature background and process simulation at various levels of integration. On the one hand, the Dry Grind process from corn is characterised collecting information from the literature and proposing several configurations by varying the services and power provision source to the plant (e.g., either supplied by the grid, or by using a DDGS- or a stover-fed CHP stations). On the other hand, the wide availability of technical and financial considerations about lignocellulosic production processes in the literature is used to set up a general framework to determine technical performance and economic assessments of second generation bioethanol processes. Several technological options are considered (e.g., dilute acid hydrolysis, steam-explosion and gasification-based fermentation) and a wide range of starting biomass feedstocks (e.g., poplar, willow, miscanthus, corn stover, wheat and barley straw, as well as switchgrass). Finally, since the literature is lacking about technologies embedding both first and second generation systems, a more rigorous study is carried out: a process simulation model is developed to assess the technical feasibility and to support the economic evaluation of a hybrid process, where both starchy (e.g., corn) and cellulosic (e.g., stover) feedstocks are converted into ethanol.

2.1 Corn-based ethanol production

Two processes are commonly available for corn-based ethanol production, differing in the way starch is released from corn: the dry grind (DGP) and wet mill processes. Being the DGP the industrially preferred technological choice, it is used as a reference in this work (Kwiatkowski *et al.*, 2006).

The industry of corn-based ethanol production has continued to improve its energy efficiency profile (Shapouri *et al.*, 2002) and new technological solutions for heat and power generation were explored over time, too (Morey *et al.*, 2006). Those technological improvements have definitely made first generation ethanol from corn a mature process (Bothast and Schlicher, 2005). Notwithstanding this, the process optimisation potential has become an imperative issue recently to address the great prices variability, since feedstocks and production costs have the largest share of the total costs.

The use of process simulators (e.g., NREL, 2000; Taylor *et al.*, 2000; Kwiatkowski *et al.*, 2006; De Kam *et al.*, 2009) and optimisation techniques (Karuppiah *et al.*, 2008) have therefore been applied to assess new processing alternatives and products form starch-based commodities. Franceschin *et al.* (2008) proposed a snapshot on the present business situation for DGP-based ethanol evaluating a number of potential short-term scenarios. They used process simulation to describe the standard production process, then pinch technology to identify some limiting operating conditions and a sensitivity analysis to a number of critical variables. A financial analysis was then carried out to evaluate present profitability of ethanol production from corn.

2.1.1 Corn-based Dry Grind Process

The DGP process comprises five main sections:

1. Grinding, cooking and liquefaction
2. Saccharification and fermentation
3. Distillation and dehydration
4. Water evaporation and recycling
5. Drying of the non-fermentable fraction

The modelling approach as provided by Franceschin *et al.* (2008) is taken as technological reference for the standard DGP (see Figure 2.1).

Starting from standard DGP process, three instances are discussed according to how power is supplied to the plant:

- by the grid (Franceschin *et al.*, 2008);
- by using DDGS as a fuel for the CHP station (Franceschin *et al.*, 2008);
- by using stover to feed a CHP generation system. Technical and economic analysis of this configuration has been determined according to information retrieved from the literature. The stover logistics assessment (Sokhansanj *et al.*, 2010) as well as the techno-economic evaluation of the stover-based CHP system supplying an ethanol plant (Mani *et al.*, 2010) have been integrated within the costs framework outlined by

Franceschin *et al.* (2008). Modelling parameters in terms of total capital investment (*TCI*, [€]) and operating costs (total product cost, *TPC* [€/t]) are collected in Table 2.1.

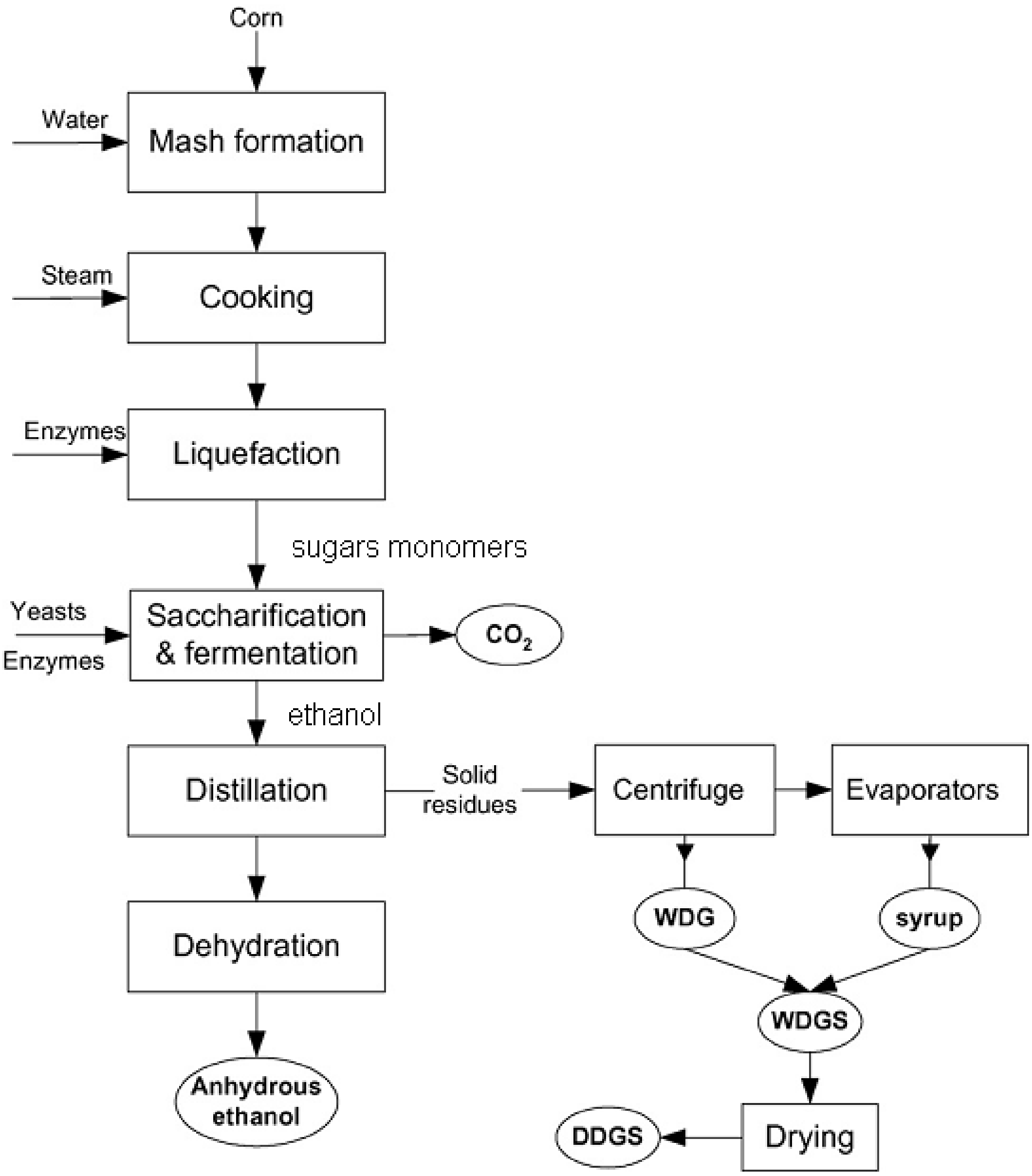

Figure 2.1 *Block flow diagram of the dry grind process.*

Table 2.1 *Operating and total capital investment (TCI) for a DGP plant with a stover-fed CHP station.*

	Technical data (Franceschin *et al.*, 2008)		
	ethanol plant nominal capacity	110	kt of ethanol/y
	electricity requirements	0.407	kWh/L of ethanol
	steam requirement	26.6	MW
	stover/corn	0.991	weight basis
	Operating costs	**[€/t]**	**reference**
A	CHP operating and management cost	18.76	Mani *et al.* (2010)
B	on-site stover preparation	17.30	Sokhansanj *et al.* (2010)
C	ash disposal	0.93	Mani *et al.* (2010)
D	ethanol production costs (standard DGP)	159.40	Franceschin *et al.* (2008)
E	utilities costs (standards DGP)	69	Franceschin *et al.* (2008)
F	**DGP with stover-fed CHP station†**	**127.39**	**F = A+B+C+D-E**
	TCI	**[€]**	**reference**
G	ethanol plant (standard DGP)	$70 \cdot 10^6$	Franceschin *et al.* (2008)
H	CHP station capital cost	$12 \cdot 10^6$	Mani *et al.* (2010)
I	**DGP with stover fed CHP station**	$82 \cdot 10^6$	I = G + H

†Feedstocks costs is not included.

2.2 Biomass-based ethanol production

This section is devoted to second generation technologies for ethanol production. After a literature survey about the stage of process development, a spreadsheet tool operating as a black-box model is performed by gathering information from the literature, to provide a techno-economic assessment of a wide variety of second generation technologies. An accurate and flexible assessment of the technology options performance (e.g., dilute acid hydrolysis, steam explosion, gasification biosynthesis), supports a detailed economic evaluation. The tool is general enough to be broadly extended accomplishing a large variety of technical options and feedstocks.

2.2.1 Lignocellulose-based process

Differently from first generation, the complexities of lignocellulosic feedstocks has led to a wide variety of processes for the production of ethanol (see Figure 2.2), which have been studied and are currently under development. The early stage of development of this large amount of technologies and processing options advocates for a more diffuse application of the process engineering modelling, design and optimisation. In particular, their large number of strongly interdependent steps encourages the adoption of proper tools for the simulation of the overall process, to investigate various process configurations and to retrieve information about which areas and conditions must be further investigated.

In the early 1990s, the first efforts were made for the study of biomass-to-ethanol conversion under the sponsorship of the International Energy Agency (Saddler, 1992). In particular, the first steps of the research were moved towards the identification of the key equipment and process steps (Galbe and Zacchi, 1994).

The significant variety of pretreatment methods of biomass, recently reviewed by Kumar *et al.* (2009), has led to the development of many flowsheet options for ethanol production. Von Sivers and Zacchi (1995) analysed three pretreatment process for the ethanol production from pine using commercial process simulators like Aspen Plus®: concentrated acid hydrolysis, two-stage hydrolysis by steam explosion using SO_2 and dilute acid, and steam explosion using SO_2 followed by enzymatic hydrolysis.

One of the main steps towards the process understanding, is represented by the pilot plant designed for the conversion of lignocellulosic biomass into ethanol built by the NREL. In this plant, tests in continuous regime for the utilisation of lignocellulosic residues of low cost and great availability like corn fibre were carried out. This allowed the acquisition of valuable experience considering the future implementation of the industrial process as well as feedback of the models utilised during the design step. Along with the experience gained in the pilot plant runs, NREL has developed an exhaustive model for the design and costing of biomass-to-ethanol process (USDOE, 1999). The model designed by NREL comprises a hydrolysis of wood with dilute acid followed by simultaneous saccharification and co-fermentation (SSCF) process utilising *cellulases* produced *in situ* by genetically engineered *Z. mobilis* with the ability of transforming both glucose and xylose into ethanol. A heat and power recovery scheme is considered, exploiting the residual lignin and methane from anaerobic treatment of wastewater. In 2002, a detailed report was proposed by NREL (USDOE, 2002) dealing with corn stover-based ethanol production modelling. Several technological assumptions change from the previous work due to the adoption of a different feedstock: the conditioning and the reaction step, which is now a two-step configuration using purchased *cellulases*, arise as the main modifications.

Hamelinck *et al.* (2005) provided a technical and economic assessment of a wide variety of second generation technologies, offering the state of the art of hydrolysis-fermentation-based ethanol and an overview of the perspectives for technological development in the short-, medium- and long-term horizons. Other works have adopted the Aspen Plus® simulator for comparing different technical options for design integration (Cardona and Sanchez, 2006), or to perform a sensitivity analysis of important process parameters to evaluate potential costs reduction effects for the process (focusing on pretreatment as well as saccharification and fermentation steps) considering several biomass (Sassner *et al.*, 2008). Piccolo and Bezzo (2009) analysed two different process alternatives (i.e., enzymatic hydrolysis and fermentation process as well as gasification and fermentation process) for the production of fuel ethanol from lignocellulosic feedstock. After a rigorous mass and energy balance, design optimisation as well as a financial analysis were carried out.

2.2.2 Black-box modelling

The wide availability of model-based results dealing with second generation ethanol, outlined in the comprehensive survey by Hamelinck *et al.* (2005), supports the approach to a techno-economic analysis set up by gathering the information from the literature.

Notwithstanding the high figure of technologies for converting cellulosic feedstocks into ethanol, they might be grouped into two broad categories: the biochemical and the thermochemical conversion, as shown in Figure 2.2.

The biochemical process comprises eight main sections:

1. Feed cleaning and milling;
2. Pretreatment and conditioning (e.g., dilute acid hydrolysis; steam explosion)
3. Saccharification and fermentation (SHF; SSF; SSCF)
4. Distillation and dehydration
5. Evaporation and water recycling
6. Drying of non-fermentable fraction
7. Wastewater treatment
8. CHP system.

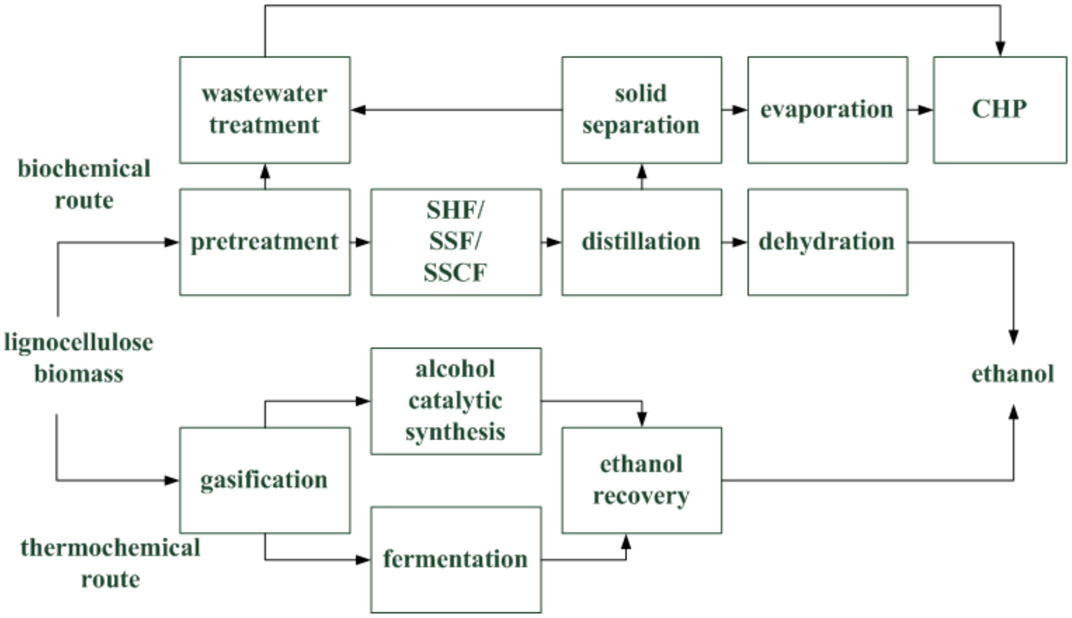

Figure 2.2 *Overview of second generation processes.*

As it is evident from Figure 2.2, the third step of the process involves several integration options. Enzymatic hydrolysis performed separately from the fermentation step is known as separate hydrolysis and fermentation (SHF). Cellulose hydrolysis carried out in the presence of the fermentative microorganism is referred to as simultaneous saccharification and fermentation (SSF). The key of the SSF of biomass is its ability to rapidly convert the sugars into ethanol as soon as they are formed, thus diminishing their inhibitory accumulation in the medium, achieving higher rates and yields with respect to SHF. Simultaneous saccharification of both cellulose (to glucose) and hemicellulose (to xylose and arabinose) and co-fermentation of both glucose and xylose (SSCF) is carried out by genetically modified microbes (*Z. mobilis*) that ferment xylose and glucose in the same broth as the enzymatic hydrolysis of cellulose and hemicellulose.

The thermochemical route involves three main steps:

1. Gasification;
2. Alcohol catalytic synthesis or syngas fermentation (biosynthensis);
3. Ethanol recovery.

The spreadsheet here tool here proposed deals with:

- the techno-economic assessment of the biochemical route involving SSCF reaction embedding several pretreatment options (e.g., dilute acid hydrolysis, steam explosion);
- the thermochemical technological option encompassing syngas conversion into ethanol according to a fermentation pathway.

A general framework is delivered allowing for the detailed technical and economic assessment of a wide set of second generation technologies and dealing with the variability of compositions among several feedstocks.

The following technical alternatives are taken into account: *i)* the Dilute Acid Process (DAP), where cellulosic feedstock is hydrolysed with dilute sulphuric acid (USDOE, 1999); *ii)* the Steam Explosion Process (SEP), where the cellulosic biomass is pre-treated with high pressure steam before being converted into ethanol (Sassner *et al.*, 2008); *iii)* the Gasification Biosynthesis Process, where biomass-based syngas is fermented to ethanol (GBP). Since the great uncertainty surrounding the thermochemical pathway (Munasinghe and Khanal, 2010), the process has been dealt with by producing several modelling scenarios representing different technological evolution. Several lignocellulosic feedstocks are accounted for: poplar, willow, miscanthus, stover, barley straw, wheat straw, and switchgrass. Dry biomass compositions are reported in Table 2.2.

A black-box system model is proposed as a platform for analysing the mass balance of converting feedstock into ethanol from a technology selected. The overall framework used to determine biomass yields into products (e.g., ethanol, power) is built according to the approach by Wei *et al.* (2009). The main idea relies on the assumption that the theoretical maximum ethanol yield from biomass and technology chosen, can be estimated by tracking the carbon balance of the process. In particular, biofuel rate W_e [t of ethanol/y] is related to feedstock W_f , [t of biomass/y] through the biomass composition described in terms of the intermediate compounds α involved in the reactions leading to ethanol (i.e., $\alpha = \{glucan, xylan\}$ if either DAP or SEP are the processes considered, while $\alpha = \{CO, H_2\}$ if GBP is selected). The core of the black box model relies on Eq. 2.1, which links biofuels rate with the starting biomass and is applied per each of the technologies available:

$$W_e = W_f \eta_{rec} PM_{ethanol} \sum_{\alpha} \chi_{\alpha/fuel} S_{\alpha/fuel} \varphi_{\alpha} \tag{2.1}$$

where η_{rec} is the recovery efficiency [w/w] for the technology chosen and $PM_{ethanol}$ is ethanol molecular weight (46 g/mol). The concentration of the intermediate compounds in the feedstock, φ_{α} ([mol/mol] or [w/w]) has been retrieved from the literature (see Table 2.2 and 2.3). The conversion $\chi_{\alpha/fuel}$ of reactant α and the selectivity $S_{\alpha/fuel}$ of α into ethanol have been obtained from the literature, too (see Table 2.4).

Table 2.2 *Dry biomass compositions.*

components	**poplar**	**willow**	**mischantus**	**corn stover**	**wheat straw**	**barley straw**	**switchgrass**
glucan	42.67	42.5	45	37.4	35.5	34.4	34.38
hemicellulose	24.01	22	30	27.6	24.2	27.7	27.11
acetate	4.64	3		2.9	2		2.05
lignin	27.68	26	21	18	26.5	25	26.14
ash	1	2		5.2	4.6	6.8	7.78
other insoluble solids		4.5		3.1	3.3		0.59
other soluble solids			4	5.8	3.9	6.1	1.96
moisture	47.9	50	9.6	15	12	15	20
reference	USDOE (1999)	Sassner *et al.* (2008)	Collura *et al.* (2006)	USDOE (2002)	Linde *et al.* (2007)	Viola *et al.* (2008)	Laser *et al.* (2009)

The GBP technology seems very promising from the environmental standpoint (EUNOMIA, 2010), but the business is surrounded by a high level of uncertainty on both technical and economic feasibility. In determining GBP ethanol yield, several scenarios representing different stage of technological development, have been modelled:

- GBP_{high}: gasification biosynthesis process where syngas composition, φ_{α} (see Table 2.3), is retrieved from experimental values obtained from operating a pilot scale indirect dual-bed gasification (Carpenter *et al.*, 2010). Conversion and selectivity are retrieved from the work by Wei *et al.* (2009);
- GBP_{ave}: thermochemical process for ethanol production based on the work by Piccolo and Bezzo (2009), biomass yields into products are collected in Table 2.4;

- GBP_{low}: thermochemical process for ethanol production where syngas composition, φ_α has been referred to a typical downdraft oxygen-blown gasifier operating at 1000°C (Bridgwater, 1995) in order to achieve 48% of CO and 32% of H_2 on a volumetric base. Concerning the syngas conversion into ethanol, the more conservative values have been adopted, retrieved from the work by NREL (2002), representing one of the most complete work on this topic so far.

Table 2.3 *Gas composition (%volume) obtained from fluidised-bed reactor at 650°C and a thermal cracker at 875°C (Carpenter et al., 2010).*

component	corn stover	vermont wood	wheat straw	switchgrass
H_2	26.9	28.6	25.4	23.5
CO	24.7	23.5	27.5	33.2
CO_2	23.7	24	22	19.4
CH_4	15.3	15.5	16.3	17
He	1.6	1.2	1.6	1.6
C_2H_4	4.2	3.9	4.3	5.1
C_2H_2	0.45	0.38	0.31	0.34
C_3H_8	0.4	0.61	0.81	0.82
C_3H_6	0.12	0.09	0.1	0.1
C_4H_8	0.1	0.07	0.08	0.08
H_2S	0	0	0.08	0.02

Final biomass yields into ethanol are determined as the ratio between W_e and W_f (Table 2.4). The economic assessment of each cellulose-based ethanol technologies has been dealt with focusing in particular on the fixed and total capital investment (*FCI* and *TCI*, [€]) assessment, according to the literature (Peters *et al.*, 2003). *FCI* involves direct costs (e.g., purchased equipment, purchased-equipment installation, instrumentation and controls, piping, electrical systems, buildings, yard improvements, service facilities, land) and indirect costs (e.g., engineering and supervision, construction expenses, legal expenses, contractor's fee, contingency). *TCI* is calculated just adding up the working capital term.

Each piece of equipment cost has been first determined according to the rigorous economic analysis by Hamelinck *et al.* (2005). The gasifier cost estimation is carried out according to the approach by Bridgwater (1995). Costs are then updated accounting for inflation effects through Marshall & Swift equipment cost index of the process industry. *FCI* and *TCI* are calculated according to the factored estimate approach by Peters *et al.* (2003) and USDOE (2002), as percentages related to the total installed equipment cost.

TPC has been evaluated by coupling information about current chemicals prices market and process rates estimated according to the literature (USDOE, 1999; Hamelinck *et al.*, 2005; Sassner *et al.*, 2008). Results are collected in Table 2.5.

Table 2.4 *Black-box model parameters per each technology: conversion of compound α into fuel* $\chi_{\alpha/fuel}$, *selectivity* $S_{\alpha/fuel}$ *of compound α into fuel and ethanol recovery efficiency* η_{rec}.

			DAP			
α	$\chi_{\alpha/fuel}$ [mol/mol]	Reference	$S_{\alpha/fuel}$ [mol/mol]	Reference	η_{rec} [w/w]	Reference
glucan	0.7958	USDOE (1999)	1.6115	USDOE (1999)	0.992	USDOE (1999)
xylan	0.6375	USDOE (1999)	1.4283	USDOE (1999)	0.992	USDOE (1999)
			SEP			
α	$\chi_{\alpha/fuel}$ [mol/mol]	Reference	$S_{\alpha/fuel}$ [mol/mol]	Reference	η_{rec} [w/w]	Reference
glucan	0.8603	Sassner *et al.* (2008)	1.6115	USDOE (1999)	0.992	USDOE (1999)
xylan	0.6120	Sassner *et al.* (2008)	1.4283	USDOE (1999)	0.992	USDOE (1999)
			GBP$_{high}$			
α	$\chi_{\alpha/fuel}$ [w/w]	Reference	$S_{\alpha/fuel}$ [w/w]	Reference	η_{rec} [w/w]	Reference
CO	0.2740	Wei *et al.* (2009)	0.8682	Wei *et al.* (2009)	0.95	Wei *et al.* (2009)
H_2	3.8462					
			GBP$_{low}$			
α	$\chi_{\alpha/fuel} \cdot S_{\alpha/fuel}$ [w/w]			Reference	$\eta_{rec,}$[w/w]	Reference
CO	0.5318			NREL (2002)	0.992	USDOE (1999)
H_2	0.1880			NREL (2002)	0.992	USDOE (1999)

2.3 Integration between corn and corn stover

The focus of this section is on the processing technologies description integrating the use of both corn stover and corn grain for bioethanol production within the same plant flowsheet.

After presenting the motivation of the modelling approach involving process simulation to describe the integration between the two feedstocks, a brief overview of the process is presented. Two alternative configurations are considered, depending on the DDGS destination (e.g., either selling or thermal valorisation). The main results of the economic analysis is carried out from the rigorous simulation of the process (*FCI*, *TCI*, and *TPC* determination). All the hypotheses about the operating conditions, and the results of the simulation model for the integrated flowsheet are presented in appendix A.

Table 2.5 *Ethanol generation technologies addressed in the study: technical properties and costs referred to corn, poplar, willow, miscanthus; corn stover, wheat straw, barley straw, switchgrass.*

poplar	**DAP**		**SEP**		**GBP$_{high}$**		**GBP$_{ave}$**		**GBP$_{low}$**	
product	ethanol	power	ethanol	power	ethanol	power	ethanol	power	ethanol	power
yields[a]	0.2296	0.4619	0.2390	0.3556	0.2252	1.2706	0.1608	1.0636	0.1510	1.1800
TCI[b]	361		327		366		394		399	
TPC[c]	181.37		243.71		154.89		164.75		167.15	
willow	**DAP**		**SEP**		**GBP$_{high}$**		**GBP$_{ave}$**		**GBP$_{low}$**	
product	ethanol	power	ethanol	power	ethanol	power	ethanol	power	ethanol	power
yields	0.2226	0.4605	0.2323	0.3537	0.2252	1.2706	0.1608	1.0636	0.1510	1.1800
TCI[b]	364		330		366		394		399	
TPC[c]	184		247.58		154.90		164.76		167.15	
miscanthus	**DAP**		**SEP**		**GBP$_{high}$**		**GBP$_{ave}$**		**GBP$_{low}$**	
product	ethanol	power	ethanol	power	ethanol	power	ethanol	power	ethanol	power
yields[a]	0.2568	0.4648	0.2662	0.3607	0.2252	1.2706	0.1608	1.0636	0.1510	1.1800
TCI[b]	329		299		366		393		398	
TPC[c]	158.82		223.63		154.81		164.65		167.04	
corn stover	**DAP**		**SEP**		**GBP$_{high}$**		**GBP$_{ave}$**		**GBP$_{low}$**	
product	ethanol	power	ethanol	power	ethanol	power	ethanol	power	ethanol	power
yields[a]	0.2219	0.4666	0.2363	0.3523	0.1613	1.4830	0.1608	1.0636	0.1479	1.0066
TCI[b]	344		308		382		393		389	
TPC[c]	168.8		238.78		164.50		164.66		163.95	
wheat straw	**DAP**		**SEP**		**GBP$_{high}$**		**GBP$_{ave}$**		**GBP$_{low}$**	
product	ethanol	power	ethanol	power	ethanol	power	ethanol	power	ethanol	power
yields[a]	0.2043	0.4652	0.2192	0.3485	0.1627	1.6397	0.1608	1.0636	0.1440	1.1534
TCI[b]	368		328		390		393		399	
TPC[c]	178		253.87		167.05		164.65		167.54	
barley straw	**DAP**		**SEP**		**GBP$_{high}$**		**GBP$_{ave}$**		**GBP$_{low}$**	
product	ethanol	power	ethanol	power	ethanol	power	ethanol	power	ethanol	power
yields[a]	0.2113	0.4682	0.2266	0.3512	0.1627	1.6397	0.1608	1.0636	0.1440	1.1534
TCI[b]	359		320		390		393		399	
TPC[c]	174.95		247.47		167.06		164.66		167.55	
switchgrass	**DAP**		**SEP**		**GBP$_{high}$**		**GBP$_{ave}$**		**GBP$_{low}$**	
product	ethanol	power	ethanol	power	ethanol	power	ethanol	power	ethanol	power
yields[a]	0.2094	0.4678	0.2246	0.3503	0.1937	1.2151	0.1608	1.0636	0.1389	1.0547
TCI[b]	366		326		364		393		394	
TPC[c]	178.79		250.38		156.24		164.68		166.38	

[a] Ethanol yields are expressed as [t of ethanol/t of dry biomass]. Power yield is expressed as [kWh/L of ethanol]

[b] *TCI* (Total Capital Investment) is evaluated for a facility of medium capacity (100000 t of ethanol/y).

[c] TPC (Total Product Cost) [€/t] represents ethanol production costs for a facility of medium capacity (i.e., 100000 t of ethanol/y); biomass feedstocks cost is not included.

2.3.1 Motivation

As broadly discussed in the previous chapter, the lignocellulosic bioethanol technology is characterised by so high costs that a preliminary analysis of integrated first and second generation technologies (e.g., hybrid processes) is suggested to lessen both production and hauling costs. Residues availability in the same areas as crop from which the fuel is derived, might ease the revamping of already existing plants producing ethanol from first generation technologies and pave the way towards commercial scale cellulosic bioethanol facilities (USDA, 2005). One of the most obvious options for connecting first and second ethanol production is represented by the exploitation of both the starchy feedstocks and its crop residue, e.g., the non-edible plant parts left on the field after the harvest. The amount of crop residue varies a lot in relation to the type of crop considered and one of the most copious is corn stover (Blanco-Canqui and Lal, 2007) (e.g., the non-grain part of a corn plant: stalks, husks, leaves and cobs).

The importance of corn stover as a biofuel feedstock is firstly due to its composition, denoted by a great abundance of cellulose and hemicellulose (USDA, 2005). While both of these sugar polymers can be fermented to bioethanol, lignin, the third most important component, does not contain sugars and mainly has a fuel value. Furthermore, corn stover is one of the most widely available crop residues (e.g.,: United States currently produce 68 Tg/y of dry corn stover (Petrolia, 2008)). Generally, estimates of crop residue production are made on the basis of site-specific production data of different crops by applying the straw/grain ratio (Lal, 2005), which varies among the different crop types. Relatively to the case of *Zea Mays* the ratio between grain and stover ranges between 0.55-1.50 (Gupta *et al.*, 1979; Larson *et al.*, 1982; Stout, 1990; Lal, 1995). In North Italy, large amounts of corn grain are yearly produced (about 9 t/ha) and a consistent quantity of stover is available, which is primary used either as soil amendment or as fodder, but very rarely sold, because of the low cost (about 30 €/t (EEN, 2007)).

2.3.2 Hybrid ethanol production modelling

A joint study between the U.S. Department of Energy (USDOE) and U.S. Department of Agriculture (USDA) in 1999 was the first to investigate synergies between commercial starch to ethanol technologies and cellulosic biomass to ethanol technologies. Then, the investigation turned to identify scenarios where capital equipment, operating expenses and co-products could be shared in order to find an overall savings compared to stand-alone cellulosic facility using corn stover feedstock (USDA, 2005). Among the scenarios investigated, the integration between the processes occurred in the following areas: combined utilities, combined ethanol purification, combined product processing and combined fermentation. Notwithstanding the technical and economic advantages reported by the USDA, the possibility of integration between first and second generation technologies in a unique facility where both the starchy and cellulosic feedstocks are exploited to produce ethanol, has not been investigated any further in the literature, and only a few demonstration scale plants have been brought into operation (Solomon *et al.*, 2007).

Thus, this work proposes a rigorous mass and energy balance analysis of the most convenient process configuration (i.e., utility and product processing integration) as outlined in the research previously led by USDOE and USDA (USDA, 2005). In order to describe the impact of increasing stover to grain ratio on costs, three instances are studied consisting in simulations with growing stover to grain ratios (1:1 in Instance A, 2:1 in Instance B, 3:1 in Instance C). In addition, the effects due to by-products destination are accounted for and per each instance the alternative use of DDGS is studied (e.g., either sold or burned in a CHP station). The commercial software package Aspen Plus® is used for modelling ethanol production process devised according to a suitable integration of starch- and cellulose-based feedstocks. The obtained cost framework allows the MILP optimisation to use more accurate economic evaluations of different process configurations solutions on the stover amount to be used.

The integration option is shown in the block flow diagram of Figure 2.3. Modelling assumptions, process simulation and economic assessment are approached as reported in appendix A.

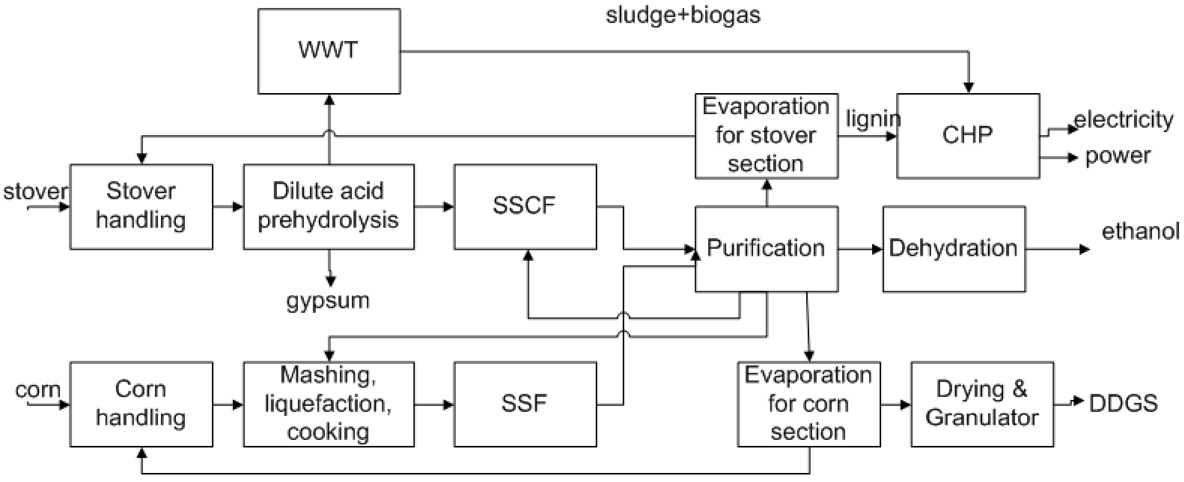

Figure 2.3 *Hybrid process: combined utilities and ethanol purification.*

2.3.3 Capital and operational costs

The most significant outcomes of economic assessment for the hybrid technologies are reported in terms of both capital (*FCI* and *TCI*) and operational (*TPC*) costs. Results are shown (Table 2.6) considering that:

- Configuration I represents a hybrid process where DDGS is sold to the cattle feed market;
- Configuration II takes into account the possibility of burning DDGS in a CHP station to deliver steam and electricity to the process;
- Per each of these configurations, three instances are studied. Instance A, B, C are characterised by an increasing stover to grain ratios entering as feedstocks for ethanol generation (respectively 1:1, 2:1, 3:1).

Table 2.6 *Fixed and Total Capital Investment for Configurations I and II (FCI and TCI, respectively). Total Production Cost (TPC) is also reported (feedstocks cost included).*

Configuration I	**Ethanol rate [kt/y]**	**FCI [M€]**	**TCI [M€]**	**TPC [€/t]**	**TPC (without depreciation) [€/t]**
Instance A	200	293	343	662	413
Instance B	289	388	455	603	369
Instance C	373	463	543	569	345
Configuration II	**Ethanol rate [kt/y]**	**FCI [M€]**	**TCI [M€]**	**TPC [€/t]**	**TPC (without depreciation) [€/t]**
Instance A	200	289	339	654	407
Instance B	289	387	454	597	363
Instance C	373	462	542	563	339

2.4 Scale effects on capital costs

In the previous section, the detailed techno-economic analysis has been performed for the technologies considered in this Thesis. However, capital investment values have been reported referring to a facility of fixed capacity and scale effects need to be embedded when different plant size are taken into account. In order to determine the *TCI* for a scale of interest, the accurate estimation of size effects on the capital investments requires the usual power law (Peters *et al.*, 2003), as stated by Eq. (2.2):

$$TCI = TCI^0 \cdot \left(\frac{ER}{ER^0} \right)^r \tag{2.2}$$

where TCI^0 corresponds to the capital investment for a facility of reference scale (e.g., ethanol production rate, ER^0 is set to 110 kt/y); ER represents the nominal ethanol production rate for the facility of current scale, r the scaling exponent.

Scaling exponent values r are collected in Table 2.7 per each of the processing technologies considered for ethanol production along with the corresponding literature source.

Table 2.7 *Scaling exponent r accounting for size effects on TCI.*

technology	***r***	**reference**
DGP	0.836	Franceschin *et al.* (2008)
LCEP	0.67	Kaylen *et al.* (2000)
Hybrid	0.67	Kaylen *et al.* (2000)
Hybrid-CHP	0.67	Kaylen *et al.* (2000)
DAP	0.67	Kaylen *et al.* (2000)
SEP	0.67	Kaylen *et al.* (2000)
GBP	0.67	Kaylen *et al.* (2000)

Chapter 3

A multi-period model for hybrid bioethanol supply chain design and planning

This chapter[1] addresses the strategic design and planning of corn- and stover-based bioethanol supply chains involving first and second generation technologies as well as the possibilities of integration between them. An MILP modelling framework is proposed to optimise the SC environmental and financial performances simultaneously.

A general description of the biofuels SC design issues is first presented. Next, the mathematical formulation of the main body of the model is drawn in details. Then, the multi-objective optimisation is performed after model decomposition into sub-problems. Solutions are presented and results discussed to show the trade-offs between optimal strategic investments. A real-world case study is proposed, related to the emerging biomass-based ethanol production in Italy during the period from 2010 to 2024 so as to demonstrate the actual model capabilities in steering strategic policies according to the stakeholders' interests focus.

3.1 Motivation

The design process of a general biofuels SC involves a wide range of decisions to establish the best network configuration in order to achieve the desired performance. Future biofuels supply system investment decisions usually imply tradeoffs between conflicting purposes (e.g., environmental, economic) and this kind of problems might be properly addressed by adopting a deterministic approach based upon a multi-objective optimisation framework.

In particular, the overall SC performance is greatly affected by the technological route selection for ethanol production. If on the one side, first generation ethanol represents the most well-entrenched technology, the silver bullet to set up a sustainable bioethanol platform is claimed to be found in promoting second generation (Dwivedi *et al.*, 2009; Londo *et al.*, 2010) which is still far from commercial availability.

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[1] Portions of this chapter have been published in Giarola *et al.*, (2011a), Giarola *et al.*, (2011b), in Giarola *et al.*, (2011c), in Giarola *et al.*, (2011d) and Zamboni *et al.*, (2011b).

A smooth transition to pave the way for low-carbon second generation fuels is advocated. One challenging aspect to support ethanol market deployment might rely on the possibility of establishing future energy systems taking the best of both first and second generation ethanol. In particular, the exploitation of both starchy feedstocks (corn) and their residues (stover) for ethanol production might be a key aspect for paving the way for more sustainable ethanol production systems (e.g., favouring the revamping of already existing first generation facilities at lower costs). Corn stover abundance and composition make it a favourable feedstock in terms of supply security and oil displacement (Petrolia, 2008), although issues related to soil quality depletion due to intensive biomass removal (Andrews, 2006), and competition with other agricultural uses or with other industries (Rejinders, 2008) need to be properly addressed.

The integration between starchy and cellulosic ethanol ought to be based upon a comprehensive approach including the overall production network in order to ensure the full management and optimisation of production systems along the entire SC for supporting investment strategies.

This chapter focuses on the development of an moMILP model for bioethanol SC optimisation problems through a comprehensive approach. The purpose is to deliver an environmentally conscious decision-making tool addressing the design and planning of hybrid bioethanol production systems to assist the policy-making process on biofuels industry at a strategic and tactical level. The model is based on the approaches commonly applied to the multi-period and multi-echelon bi-objective MILP steering design and planning tasks under financial and environmental criteria (Sahinidis *et al.* 1989; Tsiakis *et al.*, 2001; Hugo and Pistikopoulos, 2005). Capacity planning of strategic fuel systems (Liu *et al.*, 2007) is dealt with within a spatially-explicit framework (Zamboni *et al.*, 2009a).

3.2 Assumptions and problem statement

This chapter discusses a modelling approach to address strategic design and planning of a general biofuel SC over a 15-years horizon. The design process is conceived as an optimisation problem in which the production system is required to comply with the dual objectives formulation: *(i)* maximisation of the financial performance of the business (NPV) and *(ii)* minimisation of the impact on global warming (in terms of overall GHG emissions) in operating the system. The problem is formulated as a spatially-explicit multi-period and multi-echelon modelling framework devised for the strategic design and investment planning of hybrid biofuels supply networks, where both corn grain and its lignocellulosic residue (i.e., corn stover) are accounted for as suitable feedstocks for ethanol production.

3.2.1 Biofuels multi-echelon supply chain

As already stated in chapter 1, SCs can be generally viewed as production networks denoted by a structure including a number of facilities (e.g., logistics nodes or echelons) involving suppliers, production sites and demand centres (Shah, 2005). In a similar context, a biofuel SC is defined as a network of integrated nodes that are mutually connected and work together in the endeavour to satisfy the customer demand of a specific fuel. As depicted in Figure 3.1, a general biofuel supply network can be divided into two main substructures: the former concerns the upstream fuel production and involves biomass cultivations, biomass delivery and fuel production sites; the latter is related to the downstream product distribution to the demand centres.

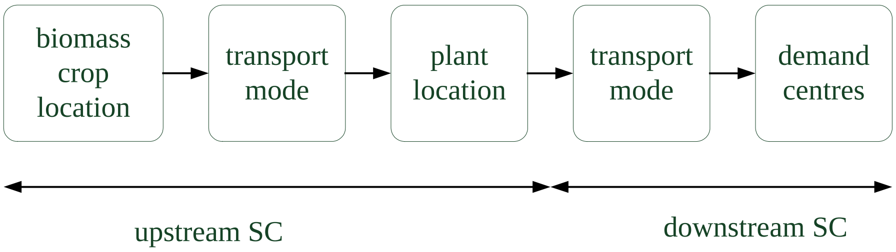

Figure 3.1 *Biofuels supply chain network.*

It is assumed that corn is grown independently of its usage for ethanol production. Thus, if corn grain is not exploited for bioenergy from a certain region, corn stover might still be available from this area.

3.2.2 Spatially-explicit framework

The problem here addressed is formulated as a spatially-explicit modelling framework, in which geographical details of the territory are embedded. Spatial features are addressed in an explicit way within the formulation, so that the locations of biomass and conversion sites as well as the logistics issues are settled within a grid resulted from the territory discretisation. The geographical context in which the system is going to be operating might indeed affect biofuels SC design outcomes to investigate opportunities for improving transportation connections. In fact, the fragmentation of cultivated land as well as the short biomass collection period and its low energy density, might result in biofuels network involving complicated logistics and a large share of transportation costs (Petrou and Pappis, 2009).

3.2.3 Environmental and economic issues integration

SCA and LCA are needed to be integrated within a unique tool to compare alternative topologies of the same production network on economic and environmental terms.

The economics of the entire network is assessed by means of SCA techniques, focusing on biomass cultivation site locations, ethanol production capacity assignment and facilities location as well as transport system optimisation.

The environmental performance of the system is evaluated in terms of GHG emissions, by adopting a life cycle assessment (ISO, 1997) limited to the WTT approach (CONCAWE, 2007) in order to consider the operating impact of the system from biomass cultivation up to fuel distribution. In particular, the set of LCA stages *s* considered in the evaluation are given by biomass production (*bp*), biomass pre-treatment (*bpt*), biomass transport (*bt*), fuel production (*fp*) and fuel distribution (*fd*); the emission credits *(ec)* in terms of GHG saving (as a result of goods or energy displacement by process by-products end-uses) are accounted for as a pseudo-life cycle stage. Accordingly:

$S = \{bp, bpt, bt, fp, fd, ec\}$.

The tank-to-wheel (TTW) contribution to the overall performance of the system, including issues such as potential differences in vehicle conversion efficiency (from fuel energy to mechanical energy), as well as vehicle technology for gasoline substitution, is not dealt with. This is supported by the fact that the new biofuel must be used in blends without needing for specific engines. Moreover, carbon dioxide emissions resulting from the combustion of biofuels are assumed to offset the ones captured during crop growth.

Finally, the set of environmental burdens contributing to the total ecological damage associated with the SC operation (Cherubini, 2010) needs to be properly identified. The GHG impact on global warming is captured by a whole set of burdens (CO_2, CH_4, N_2O). They have been grouped together in a single indicator representing the carbon dioxide equivalent emissions (CO_2-eq) as derived through the concept of 100-year global warming potentials (IPCC, 2001).

3.2.4 Model objectives

The biofuels SC design problem can be formulated as follows. Given the following inputs:

- geographical distribution of demand centres;
- fuel demand over the entire time horizon;
- biomass geographical availability;
    - geographical location of potential biomass production sites;
    - biomass production potential for each site;
    - biomass production costs as a function of geographical region;

- technical (yields) and economic (capital and operating costs) parameters as a function of biomass type, production technology and plant scale;
- environmental burdens of biomass production as a function of biomass type and geographical region;
- environmental burdens of biofuel production as a function of biomass type and production technology;
- transport logistics (modes, capacities, distances, availability, environmental burdens and costs);
- biofuel market characteristics;
- energy market prices and existing subsidies (green credits);

the objective is to determine the optimal system configuration which maximises the financial profitability while minimising the GHG emissions.

Accordingly, strategic design involves decisions dealing with the biomass typology selection, the technology definition, the by-products valorisation option and, eventually, the logistics characterisation as well as the description of each SC node location. On the other hand, SC planning decisions regard the production facilities capacity assignment along the time framework. Therefore, the key variables to be optimised are:

- geographical location of biomass production sites;
- biomass production rate and feedstock mix to the plant;
- bioethanol facilities technology selection, location and scale;
- characterisation of transport logistics;
- financial performance of the system over the time horizon;
- system impact on global warming.

Bioethanol demand is set to vary within the multi-period formulation, along the 15-year time horizon, starting from 2010 to 2024. In accordance to the EU Directive (EC, 2009), the bioethanol quota is initially set equal to 5.75% for 2010 and then from 2011 to 2024, it is gradually increased until the 2020 EU target of 10% (percentages are set on energetic basis). The overall time horizon has been divided into five time intervals (each three-years long) to achieve a computationally-tractable formulation.

3.3 Mathematical formulation

The problem has been formulated as an moMILP problem based on the modelling approaches commonly adopted in the strategic design of multi-echelon SCs (Sahinidis *et al.* 1989; Tsiakis *et al.*, 2001). It embodies features for spatially-explicit siting of supply networks nodes (Zamboni *et al.*, 2009a) as well as facility capacity planning and technology selection of strategic fuel systems (Liu *et al.*, 2007). The environmental frame as well as the MoMILP solution algorithm follow the approach proposed by Hugo and Pistikopoulos (2005).

3.3.1 Objective functions

The mathematical formulation description first deals with the definition of the objective functions to be minimised in configuring the system.

The economic objective function considered here is the *NPV* [€] of the business to be established. This imposes the maximisation of profit-related indexes, and hence the objective value (Obj_{eco}) is required to be written in its negative form:

$$Obj_{eco} = -NPV \tag{3.1}$$

The *NPV* is calculated by summing up the discounted cumulative cash flows (*CCF* [€]) minus the capital investment required to establish the biofuels production facilities (*FCC* [€]). Accordingly:

$$NPV = CCF - FCC \tag{3.2}$$

The second objective Obj_{env} is to minimise the total GHG impact (*TIOT* [kg CO_2-eq]) resulting from the operation of the biofuel SC over the 15-years horizon.

$$Obj_{env} = TIOT \tag{3.3}$$

As represented by Eq. (3.4), this is estimated by summing up the impacts TI_t [kg CO_2-eq/time period] resulting from the operation of the production chain for each time period *t*. Accordingly:

$$TIOT = \sum_t TI_t \tag{3.4}$$

All the above terms need to be expressed as explicit functions of the design variables.

3.3.2 Economics

The term *CCF* of Eq. (3.2) can be evaluated as the sum of the cash flows (CF_t [€]) for each time period *t* multiplied by the time-dependent discount factor ($dfCF_t$) specific for CF_t. Accordingly:

$$CCF = \sum_t CF_t \cdot dfCF_t \tag{3.5}$$

Still referring to Eq. (3.2), the *FCC* term represents the overall capital investment required to build up the new set of fuel conversion plants. Accordingly, no other facilities (e.g., the biomass production-related equipments or the product delivery transport means) are considered to contribute to the overall investment. The underlying assumption is that a biofuel system is not a completely *ex-novo* process but can be integrated to the existing production system. Therefore, *FCC* can be evaluated as:

$$FCC = \sum_t TCI_t \cdot dfTCI_t \tag{3.6}$$

where TCI_t [€] stands for the capital investment which occurs at the time period t and $dfTCI_t$ is the time dependent discount factor specific for TCI_t.

Both terms, CF_t and TCI_t, are discounted through factors collected in the two different arrays $dfCF_t$ and $dfTCI_t$, since capital costs are allocated at the beginning of each time period while revenues are received at the end of each year composing the time period and then discounted on a yearly base. They are defined as in Peters *et al.* (2003):

$$dfTCI_t = \frac{1}{(1+\varsigma)^{3(t-1)}} \tag{3.7}$$

$$dfCF_t = \frac{3+3\varsigma+\varsigma^2}{3\cdot(1+\varsigma)^{2t}} \tag{3.8}$$

where ζ is the future interest rate. Here ζ has been assumed to be constant (Tsang *et al.*, 2007) and equal to 10% as resulting from the application of the CAPM (Capital Asset Pricing Model) rule (Sharpe, 1964). The resulting discount factors are reported in Table 3.1.

Table 3.1 *Values of the discount factors for cash flows and total capital investment ($dfCF_t$ and $dfTCI_t$ arrays, respectively).*

period	**1**	**2**	**3**	**4**	**5**
$dfCF_t$	0.761	0.5	0.329	0.216	0.142
dfTCIt	1	0.658	0.432	0.284	0.187

3.3.2.1 Cash flow

The cash flow per each time period, CF_t, on the right hand side of Eq. (3.5), is given by the following relation:

$$CF_t = PBT_t + D_t - TAX_t, \quad \forall t \tag{3.9}$$

where PBT_t [€/time period] is the profit before taxes, D_t [€/time period] the depreciation charge and TAX_t [€/time period] the tax amount for each time period *t*.

PBT_t is defined as the business incomes (Inc_t [€/time period]) minus the overall operating costs, both fixed ($FixC_t$ [€/time period]) and variable ($VarC_t$ [€/time period]) ones, and minus the depreciation charge for each time period t. Accordingly:

$$PBT_t = Inc_t - VarC_t - FixC_t - D_t \ , \quad \forall\, t \tag{3.10}$$

TAX_t is defined as the total tax amount. A taxation charge has to be applied only when a positive annual gross profit is obtained, otherwise it must be avoided; moreover, TAX_t, being a function of PBT_t, would make Eq. (3.9) a non-linear relation. Hence, the problem is overcome through the following formulation:

$$TAX_t \geq Tr \cdot PBT_t \ , \quad \forall\, k,t \tag{3.11}$$

$$TAX_t \geq 0 \ , \quad \forall\, k,t \tag{3.12}$$

where Tr is the taxation rate (set equal to 36%, which represents a conservative approximation with respect to the current Italian taxation (IT, 2010a)).

The business incomes for each time period t (Inc_t as referred to as in Eq. (3.10)) come from the sum of the total annual revenues earned through the selling of product j (i.e. ethanol, DDGS or electricity) obtained from a conversion facility of technology k at time period t. Accordingly:

$$Inc_t = \sum_j \sum_k \sum_g P^T_{j,k,g,t} \cdot MP_j \ , \quad \forall\, t \tag{3.13}$$

where $P^T_{j,k,g,t}$ [t/time period or MWh/time period, depending on the product nature] is the production rate of product j obtained from a conversion facility of technology k in region g at time period t, and MP_j is the market price of product j [€/t or €/MWh, depending on the product nature].

The products j set includes DDGS, ethanol and electricity whose amounts and proportions are subject to yields constraints depending on the processing technology k: for instance, DDGS is sold only for a subset of conversion technologies, denoted as $tech_k$ (as shown later on in Table 3.8). Eq. (3.14) must hold:

$$P^T_{'DDGS',k,g,t} = 0 \ , \quad \forall\, g,t,k \notin tech(k) \tag{3.14}$$

Term $FixC_t$, which accounts for the facility general expenses, is derived through the application of a fixed quota ϕ, set equal to 15% (Berk and De Marzo, 2008), to the global incomes:

$$FixC_t = \phi \cdot Inc_t \ , \quad \forall\, t \tag{3.15}$$

Term $VarC_t$ of Eq. (3.10) results as the sum of the main costs involved in the operation of a conventional biofuels SC: biomass production costs (BPC_t [€/time period]), biomass transport costs (TCb_t [€/time period]), ethanol production costs (EPC_t [€/time period]) and fuel distribution costs (TCf_t [€/time period]). Accordingly:

$$VarC_t = EPC_t + BPC_t + TCb_t + TCf_t \, , \quad \forall\, t \tag{3.16}$$

BPC_t is evaluated by multiplying the total biomass i rate produced in region g at time period t, $Pb_{i,g,t}$ [t/time period], by the corresponding unit production costs, $UPC_{i,g}$ [€/t]:

$$BPC_t = \sum\nolimits_i \sum\nolimits_g Pb_{i,g,t} \cdot UPC_{i,g} \ , \quad \forall\, t \tag{3.17}$$

EPC_t is defined as the sum of two main contributions (Douglas, 1988), a linear function of the total production rate of ethanol, $P^T_{'ethanol',k,g,t}$ and a fixed quota depending on the production technology adopted:

$$EPC_t = \sum_k \left(coef_{k,'1'} \cdot \sum_g P^T_{'ethanol',k,g,t} + coef_{k,'2'} \cdot \sum_g Y_{k,g,t} \right), \quad \forall t \tag{3.18}$$

where $coef_{k,'2'}$ [€/t] and $coef_{k,'2'}$ [€/time period] are linear coefficients specific for each technology k ethanol production cost, and $Y_{k,g,t}$ is the binary variable accounting for whether a facility is operating with the conversion technology k in region g at time period t (a value of 1 is assigned when a plant is established, 0 otherwise).

With regard to transports, both the biomass delivery to conversion plants (TCb_t) and the fuel distribution to blending terminals (TCf_t) are treated as an additional service provided by actors already operating within the industrial/transport infrastructure. Accordingly:

$$TCb_t = \sum\nolimits_{i,l} UTCb_l \cdot \left(\sum\nolimits_{g,g'} Qb_{i,g,l,g',t} \cdot LD_{g,g'} \cdot \tau_{g,l,g'} \right) + \sum\nolimits_{i,g} UTCl \cdot Pb_{i,g,t} \cdot LD_{g,g} \, , \quad \forall\, t \tag{3.19}$$

$$TCf_t = \sum\nolimits_{i,l} UTCf_l \cdot \left(\sum\nolimits_{g,g'} Qf_{g,l,g',t} \cdot LD_{g,g'} \cdot \tau_{g,l,g'} \right), \quad \forall\, t \tag{3.20}$$

where $UTCb_l$ and $UTCf_l$ [€/(t·km)] are the unit transport cost for biomass i and ethanol via mode l, respectively; $Qb_{i,g,l,g',t}$ [t/time period] is the flow rate of biomass i which needs to be transferred via mode l between two elements g and g' at time period t; $Qf_{g,l,g',t}$ [t/time period] is the flow rate of bioethanol to be delivered via mode l between two elements g and g' at time period t; $UTCl$ [€/(t·km)] is the unit transport cost for biomass transfer within g; $LD_{g,g}$ [km] is the average delivery distance within each element g; $LD_{g,g'}$ [km] is the local distance, resulting from the measurement of the straight route between the centre of each network element g, and $\tau_{l,g,g'}$ is a tortuousity factor depending on the different transport mode l.

3.3.3 Costs linearisation

A purposed-devised linearisation model is used to achieve an accurate estimation of the capital expenditure and depreciation. Following the approach suggested by Liu *et al.* (2007) and the mathematical technique proposed by Williams (1978), D_t and TCI_t are linearised by introducing two sets of discrete parameters, whose values define the capital investment ($CI_{p,k}$) to establish a production plant of nominal size p and technology k, and the corresponding facility scale (ER_p). A set of linear combinations, where the positive continuous variables $\lambda^{plan}_{p,k,g,t}$ and $\lambda_{p,k,g,t}$ (ranging between 0-1) play a key role, is adopted for determining the actual capital investment, TCI_t, the depreciation, D_t and the total production capacity $P^T_{'ethanol',k,g,t}$.

The actual amount of fuel produced in each element g at period t, $P^T_{'ethanol',k,g,t}$, is evaluated through the relation:

$$P^T_{'ethanol',k,g,t} \le \sum\nolimits_p \lambda_{p,k,g,t} \cdot 3 \cdot ER_p, \quad \forall\, k,g,t \tag{3.21}$$

where $\lambda_{p,k,g,t}$ is a continuous recursive variable which has assumed a non-zero value since the moment an investment decision was taken; ER_p [t/y] is the nominal production rate of ethanol for each plant size p; and the conversion factor 3 [y/time period] accounts for the time period length.

The evaluation of TCI_t resulting from the sum of the expenditures needed to establish the set of production facilities planned at each time period t, is determined through the following relation:

$$TCI_t = \sum\nolimits_p \sum\nolimits_k \sum\nolimits_g \lambda^{plan}_{p,k,g,t} \cdot CI_{p,k}, \quad \forall\, t \tag{3.22}$$

where $\lambda^{plan}_{p,k,g,t}$ is a continuous planning variable which is assigned a non-zero value only for the time period t in which the investment decision occurs and $CI_{p,k}$ [€] is a parametric set needed to evaluate the capital investment related to the establishment of a production plant of size p and technology k.

Concerning D_t, this is usually evaluated adopting the straight line depreciation method and hence depreciating the total capital investment TCI_t through a fixed quota (dk_t, set equal to

20%). However, this approach is not sufficient in dealing with a multi-period strategy, where investment decisions may occur at each time period and therefore capital depreciations should have been evaluated since the time period in which the investment decision actually took place. Accordingly:

$$D_t = \sum_p \sum_k \sum_g \lambda_{p,k,g,t} \cdot CI_{p,k} \cdot dk_t \ , \quad \forall\, t \tag{3.23}$$

$\lambda_{p,k,g,t}$ and $\lambda^{plan}_{p,k,g,t}$ are not independent, but $\lambda_{p,k,g,t}$ is bound to $\lambda^{plan}_{p,k,g,t}$ according to the following recursive definition:

$$\lambda_{p,k,g,t} = \lambda_{p,k,g,t-1} + \lambda^{plan}_{p,k,g,t} , \quad \forall\, k,g,t \tag{3.24}$$

Moreover, the two continuous variables, $\lambda_{p,k,g,t}$ and $\lambda^{plan}_{p,k,g,t}$, should be constrained by the actual planning decision:

$$\sum_p \lambda_{p,k,g,t} = Y_{k,g,t} , \quad \forall\, k,g,t \tag{3.25}$$

$$\sum_p \lambda^{plan}_{p,k,g,t} = Y^{plan}_{k,g,t} , \quad \forall\, k,g,t \tag{3.26}$$

where $Y^{plan}_{p,k,g,t}$ is the binary variable planning the establishment of a new production facility of technology k in region g at time t (a value of 1 means that the construction of a new production plant is allowed, otherwise 0 is assigned); $Y_{k,g,t}$ is the recursive variable keeping memory of the plant establishment.

According to Liu *et al*. (2007), the following set of constraints on the key linearisation variables, $\lambda_{p,k,g,t}$ and $\lambda^{plan}_{p,k,g,t}$, must hold, too:

$$\lambda_{p,k,g,t} - y_{p+1,k,g,t} - y_{p,k,g,t} \le 0 , \quad \forall\, k,g,t,p \in sub(\,p\,) \tag{3.27}$$

$$\lambda^{plan}_{p,k,g,t} - y_{p+1,k,g,t} - y_{p,k,g,t} \le 0 , \quad \forall\, k,g,t,p \in sub(\,p\,) \tag{3.28}$$

$$y_{p,k,g,t} = 0 , \quad \forall\, k,g,t,p = 6 \tag{3.29}$$

The new set of binary variables, $y_{p,k,g,t}$ binds the selection of the continuous values of $\lambda_{p,k,g,t}$ and $\lambda^{plan}_{p,k,g,t}$ within a suitable scale range; i.e. $\lambda_{p,k,g,t}$ and $\lambda^{plan}_{p,k,g,t}$ assume non-zero values for at most two adjacent linearisation intervals p and $p+1$.

Finally, another link between the investment decisions $Y_{k,g,t}$, and the linearisation procedure must be imposed: the $y_{p,k,g,t}$ variables are subject to the planning decision variable value according to the following relation:

$$\sum_{p}^{P-1} y_{p,k,g,t} = Y_{k,g,t} \ , \quad \forall\, k,g,t \tag{3.30}$$

3.4. Logical constraints and mass balances

Logical constraints and mass balances are needed to be satisfied at each SC node.

3.4.1. Planning constraints

A rational SC planning over the time is based upon the assumption that once a production facility has been built, it will be operating for the remaining time frame. This is ensured by the following recursive definition:

$$Y_{k,g,t} = Y_{k,g,t-1} + Y_{k,g,t}^{plan} , \quad \forall\, k,g,t \tag{3.31}$$

Note that in a region g, $Y_{k,g,t}^{plan}$ and $Y_{k,g,t}$ cannot be equal to 1 simultaneously: as soon as a new plant is planned at time $t = t^*$ ($Y_{k,g,t=t^*}^{plan}$ = 1), then $Y_{k,g,t=t^*+1}^{plan}$ becomes equal to 1, too. Thus, for the successive time periods, Eq. (3.31) imposes $Y_{k,g,t>t^*}^{plan}$ = 0.
The first year configuration is set by initialising $Y_{k,g,t}$ as:

$$Y_{k,g,'1'}^{plan} = Y_{k,g}^{start} , \quad \forall\, k,g \tag{3.32}$$

where $Y_{k,g}^{start}$ is the binary decision variable that initialises the problem at the time period t = 1.
It is eventually assumed that only one conversion facility can be established within one territorial element g:

$$\sum_{k} Y_{k,g,t} \leq 1 , \quad \forall\, t,g \tag{3.33}$$

3.4.2. Production constraints

Eq. (3.21) imposes that the production rate cannot exceed the limits of a certain production facility, even if it allows for a capacity adjustment according to market demand. However, $P_{'ethanol',k,g,t}^{T}$ must be also lower-bounded to the minimum capacity of a plant: $PCap^{min}$ [t/time period] is the minimum production rates allowed according to economic and technical feasibility considerations. Thus:

$$P^T_{'ethanol',k,g,t} \geq PCap^{min} \cdot Y_{k,g,t} \,, \quad \forall\, k,g,t \tag{3.34}$$

The production rates of the other sub-products belonging to the products set J can be calculated through the following relations:

$$P^T_{'DDGS',k,g,t} = Pf_{'corn',k,g,t} \cdot \delta \,, \quad \forall\, k,g,t \tag{3.35}$$

$$P^T_{'power',k,g,t} = P^T_{'ethanol',k,g,t} \cdot \frac{\omega_k}{\rho} \,, \quad \forall\, k,g,t \tag{3.36}$$

where $P^T_{'DDGS',k,g,t}$ [t/time period] and $P^T_{'power',k,g,t}$ [MWh/time period] represent the production rates of DDGS and electricity, respectively; δ is the DDGS conversion factor (set equal to 0.954 $t_{DDGS}/t_{ethanol}$ according to Franceschin *et al.* (2008)) and ρ is a scalar representing the ethanol density (equal to 0.7891 kg/$L_{ethanol}$); whilst, ω_k [kWh/$L_{ethanol}$] is the exceeding electricity production specific for each conversion technology k.

Term $Pf_{'corn',k,g,t}$ of Eq. (3.35) represents the amount of ethanol produced converting corn as primary biomass. In fact, according to the technological options envisaged for bioethanol production, different biomass can be fed to a conversion plant (i.e. corn and corn stover). Hence, the total amount of fuel produced in each element g results from the sum of different production lines, each one corresponding to the biomass type (e.g., corn and stover):

$$P^T_{'ethanol',k,g,t} = \sum_i Pf_{i,k,g,t} \,, \quad \forall\, k,g,t \tag{3.37}$$

where $Pf_{i,k,g,t}$ [t/time period] is the specific contribution of biomass i to the global ethanol production from technology k in region g at time t. This variable depends on the nominal ratios, $\beta_{i,k}$, of bioethanol from biomass i in technology k:

$$Pf_{i,k,g,t} = P^T_{'ethanol',k,g,t} \cdot \beta_{i,k} \,, \quad \forall\, i,k,g,t \tag{3.38}$$

The local demand of biomass i, $Db^T_{i,g,t}$, necessary to supply at each time period t the production plant sited within region g depends on two contributions. The first one is the biomass (corn and/or stover) to be converted into fuel, which strictly depends on the biomass-specific ethanol production, $Pf_{i,k,g,t}$. The second one is the biomass needed to produce electricity when this is envisaged by the technology k. Accordingly:

$$Db^T_{i,g,t} = \sum_k \frac{Pf_{i,k,g,t}}{\gamma_i} \cdot (1 + burn_{i,k}) \,, \quad \forall\, i,g,t \tag{3.39}$$

where γ_i [t of ethanol/t of biomass] is the conversion factor for each biomass type *i*, and $burn_{i,k}$ represents the fraction of biomass *i* exclusively involved in electricity production for each technology *k*.

The following set of mass balances is formulated to constrain the commodity production rates. First, a global mass balance on ethanol production should be fulfilled:

$$\sum_k P^T_{'ethanol',k,g,t} = Df^T_{g,t} + \sum_l \sum_{g'} \left(Qf_{g,l.g',t} - Qf_{g',l.g,t} \right), \quad \forall\, g,t \tag{3.40}$$

where, $Df^T_{g,t}$ [t/time period] is the ethanol demand for each region g at time t.

Biomass production in each region g has to comply with the mass balance, too:

$$Pb_{i,g,t} = Db^T_{i,g,t} + \sum_l \sum_{g'} \left(Qf_{g,l.g',t} - Qf_{g',l.g,t} \right), \quad \forall\, i,g,t \tag{3.41}$$

and must be upper-bounded according to the limits imposed by the effective regional production capability:

$$Pb_{i,g,t} \le BA_{g,i}\,, \quad \forall\, i,\mathrm{g},t \tag{3.42}$$

where $BA_{g,i}$ [t/time period] is a parameter representing the biomass *i* availability for ethanol production in region *g*, which depends on agronomic-related factors such as maximum biomass cultivation fractions BCD^{max}_g of cultivated land over arable land in element *g*, and the biomass cultivation yield $BY_{i,g}$ [t/(time period·km^2)]. Additionally, geographical characteristics such as the actual surface in a region GS_g [km^2] and the related percentage of arable land AD_g contribute to define the biomass productivity. Thus, the following condition must hold:

$$BA_{g,i} = GS_g \cdot BY_{i,g} \cdot AD_g \cdot BCD^{max}_g \tag{3.43}$$

To ensure a sustainable biomass to biofuel SC, a threshold to the collection rate limiting the maximum amount of domestic biomass available for bioethanol production, is to be set: an utilisation factor q_i (set equal to 14% for corn (Zamboni *et al.*, 2009a) and 33% for stover (USDA, 2005)) is applied to the overall potential domestic biomass *i* production at time *t*, $TPot_{i,t}$ [t/time period]:

$$TPot_{i,t} \cdot q_i \ge \sum_g (\, Pb_{i,g,t} \cdot IBF_g \,), \quad \forall\, i,t \tag{3.44}$$

where:

$$TPot_{i,t} = \sum_g \left(BA_{i,g} \cdot IBF_g \right), \quad \forall\, i,t \tag{3.45}$$

with IBF_g a binary parameter establishing whether a cultivation is located on a certain region g: a value of 1 identifies a domestic cultivation regions; otherwise 0 is assigned.

3.4.3. Transport constraints

A further set of constrains is devoted to transport logistics. First of all, it must be ensured that the flow rate of a specific product i does not go through internal loop trips:

$$Qb_{i,g,l,g,t} = 0 \text{ and } Qf_{g,l,g,t} = 0 \qquad \forall\, i,g,l,g',t : g = g' \tag{3.46}$$

Finally, the representation of the logistics behaviour is completed by a transport feasibility condition (for instance, transport by barges is not allowed if a waterway is not available):

$$Qb_{i,g,l,g',t} = 0 \text{ and } Qf_{g,l,g',t} = 0 \qquad \forall\, i,g,l,g',t : (g,l,g') \neq Total_{g,t,g'} \tag{3.47}$$

where $Total_{g,t,g'}$ represents the total transport links allowed between regions g and g' via mode l.

3.4.4. Non-negativity constraints

Some last constraints impose that a number of variables should be non-negative in order to retain a physical meaning:

$$P^{T}_{'ethanol',k,g,t} \geq 0, \quad \forall\, i,k,g,t \tag{3.48}$$

$$\lambda_{p,k,g,t} \geq 0, \quad \forall\, p,k,g,t \tag{3.49}$$

$$\lambda^{plan}_{p,k,g,t} \geq 0, \quad \forall\, p,k,g,t \tag{3.50}$$

$$Pb_{i,g,t} \geq 0, \quad \forall\, i,g,t \tag{3.51}$$

$$Qb_{i,g,l,g',t} \geq 0, \quad \forall\, i,g,l,g',t \tag{3.52}$$

$$Qf_{g,l,g',t} \geq 0, \quad \forall\, \mathrm{g},l,g',t \tag{3.53}$$

3.5. Environmental issues

With reference to the total GHG impact (Eq. (3.4)), the definition of TI_t needs considering each life cycle stage s contribution as well as the effect of emission credits coming from by-products end-use. Accordingly:

$$TI_t = \sum_s Imp_{s,t} \ , \quad \forall t \tag{3.54}$$

where $Imp_{s,t}$ [kg CO_2-eq/time period] is the GHG emission rate resulting from the operation of each single stage s at time t.

The core of the environmental framework relies on the GHG emission rate evaluation, $Imp_{s,t}$, generally defined as follows:

$$Imp_{s,t} = f_s \cdot F_{s,t} \ , \quad \forall \ s,t \tag{3.55}$$

where the reference flow $F_{s,t}$ [units/time period], specific for each life cycle stage s and time t is multiplied by a global emission factor, f_s [kg CO_2-eq/unit], representing the carbon dioxide emissions equivalent at stage s per unit of reference flow.

As will be further detailed in the following, both f_s and $F_{s,t}$ are grid-, biomass- or transport-dependent according to the specific life cycle stage s they refer to.

3.5.1 Biomass production

GHG emissions resulting from the production of biomass depend on the cultivation practice adopted as well as on the geographical region in which the biomass crop has been established (Zamboni *et al.*, 2009b). In particular, the actual environmental performance is affected by fertilisers and pesticides usage, irrigation techniques and soil characteristics. The impact due to biomass production stage (Eq. 3.56) is defined by using $fbp_{i,g}$, a factor representing the carbon dioxide emissions equivalent per unit of biomass i produced in element g [kg CO_2-eq/t], which may differ strongly from one production region to another.

$$Imp_{'bp',t} = \sum_i \sum_g fbp_{i,g} \cdot Pb_{i,g,t} \ , \quad \forall \ t \tag{3.56}$$

3.5.2 Biomass pre-treatment

Pre-treatment refers to the operations connected with biomass drying. The environmental performance of this stage has no relation with the geographical location of the dedicated facilities but rather depends on the biomass i as well as on the processing technology.

Therefore, the total emission of the drying and storage of biomass is supposed to be only influenced by the amount and the type of biomass processed:

$$Imp_{'bpt',t} = \sum_i \sum_g fbpt_i \cdot Pb_{i,g,t} \ , \quad \forall\, t \tag{3.57}$$

where an average emission factor, $fbpt_i$ representing the carbon dioxide emissions equivalent per unit of biomass i treated [kg CO2-eq/t], is estimated by referring to the performance of most common practices.

3.5.3 Transport system

The global warming impact related to both biomass supply and fuel distribution depends on the use of different transport means fuelled with fossil energy (e.g., conventional oil-based fuels or electricity). The resulting GHG emissions of each transport option is modelled as to be dependent on both the distance run by the specific means and the freight load delivered. Thus, the emission factors for both biomass transport (fbt_l, $fbtl^*$) as well as fuel distribution (ffd_l) represent the total carbon dioxide emissions equivalent released by transport unit l per km driven and t carried. Accordingly:

$$Imp_{'bt',t} = \sum_{i,l} fbt_l \cdot \left(\sum_{g,g'} Qb_{i,g,l,g',t} \cdot LD_{g,g'} \cdot \tau_{g,l,g'} \right) + \sum_{i,g} fbtl^* \cdot Pb_{i,g,t} \cdot LD_{g,g} \ , \quad \forall\, t \tag{3.58}$$

$$Imp_{'ft',t} = \sum_l ffd_l \cdot \left(\sum_{g,g'} Qf_{g,l,g',t} \cdot LD_{g,g'} \cdot \tau_{g,l,g'} \right), \quad \forall\, t \tag{3.59}$$

with the reference flow $F_{s,t}$ now representing the delivery distance ($LD_{g,g'}$) and the load of goods transported ($Qb_{i,g,l,g'}$, $Qf_{g,l,g'}$ or $Pb_{i,g,t}$ if the local biomass transport is considered).

3.5.4 Fuel production

The environmental impact of the biofuel production stage is related to enzymes, chemicals and utilities required in the conversion facilities. This life cycle stage GHG emissions are assumed to be independent on location (ffp_i). Thus, fuel production impact on global warming potential is modelled as to be only proportional to the biomass-specific amount of biofuel produced, $Pf_{i,k,g,t}$:

$$Imp_{'fp',t} = \sum_i \sum_g \sum_k ffp_i \cdot Pf_{i,k,g,t} \ , \quad \forall\, t \tag{3.60}$$

3.5.5 Emission credits

The effect of by-products which might be valuable products in other markets, is essential to allocate the total impact associated with a particular production chain. Currently, there is no generally accepted approach to cope with this issue. The substitution method is here chosen following the recommendations of Rickeard *et al.* (2004). Accordingly, the credits derived by the emissions avoided due to displacements of alternative goods by the by-products are deducted from the total GHG emissions bill assigned to the primary product.

On the one hand, DDGS is the main by-product for the corn-based bioethanol system. This could be a valuable substitute for cattle feed and may also be used as a fuel for CHP generation (Zamboni *et al.*, 2009b). On the other hand, stover-based processes deliver electricity as main by-product, generated from the valorisation of stover lignin in a CHP system: this is capable of satisfying the heat and power needs of the conversion plant while providing a power excess which can be sold to the grid (USDOE, 2002). Thus, in a hybrid technology, integrating corn- and stover-based bioethanol production, two alternative options can be investigated: DDGS and power surplus may be both sold; otherwise, it is possible to fuel both DDGS and lignin to a CHP system.

The modelling framework was developed to take all these options into account. Emission credits were included in the mathematical formulation and considered as a negative contribution to the life cycle stage impact calculation. Accordingly:

$$Imp_{'ec',t} = -\sum_k \sum_g fec_k \cdot P^T_{'ethanol',k,g,t} \ , \quad \forall \, t \tag{3.61}$$

where fec_k [kg of CO_2-eq/t] represents the emission credits assigned to cattle feed and/or energy displacement per unit of ethanol rate produced through technology k.

Another important assumption is that no penalties are assigned to land usage change. The land conversion from crop-for-food to crop-for-fuel would generate a gap in the biomass market that ought to be filled by either importing or cultivating new lands. However, a proper assessment and modelling of this issue involves the evaluation of an extremely wide and complex interaction between several and different systems (Gnansounou *et al.*, 2009) and is currently beyond the scope of this analysis, since methodologies in addressing this aspect need to be substantially improved.

3.6 Case study

A real world case study is proposed to illustrate the applicability of the proposed approach in steering the strategic design and planning of hybrid first and second generation bioethanol systems. The emerging bioethanol infrastructure in Northern Italy is chosen to the scope. The region under investigation represents a self-sufficient area in terms of conventional fuel supply infrastructure. Moreover, both soil conditions and farming practices make this territory a promising area for biomass production at high yield. Additionally, the existing distribution infrastructure includes a full-scale range of transport options available for industrial purposes. According to this, each network node (i.e. SC or life cycle stage) has been characterised tailoring actual economic and environmental data to the case study under assessment. The SCA and LCA approaches proposed by Zamboni *et al*. (2009a, 2009b) have been adopted to evaluate the specific modelling parameters. The environmental assessment of the stover-to-ethanol pathway has followed the fuel-cycle model developed at Argonne National Laboratory (ANL, 2006) and the work by Luo *et al.* (2009b).

3.6.1 Spatially-explicit features

Table 3.2 *Values for the squared region surfaces (GS_g) in Northern Italy.*

g	GS_g km^2	g	GS_g km^2	g	GS_g km^2
1	1875	21	2500	41	2500
2	2500	22	2500	42	2500
3	1500	23	1250	43	1500
4	1250	24	2000	44	2500
5	1000	25	2500	45	2500
6	1250	26	2500	46	1750
7	2000	27	2500	47	2000
8	2500	28	2500	48	2500
9	2500	29	2500	49	2500
10	2500	30	2500	50	2500
11	2500	31	2500	51	2500
12	1250	32	1500	52	1000
13	2000	33	750	53	1000
14	2250	34	250	54	1500
15	2500	35	2500	55	1500
16	2000	36	2500	56	2500
17	2500	37	2500	57	2500
18	2500	38	2500	58	2500
19	2500	39	2500	59	1750
20	2500	40	2500	60	200000

Northern Italy is chosen as the territorial area of study and it is set the geographical benchmark for the model parameters. The territorial characterisation relies on a spatially-explicit modelling framework to map all the possible network configurations along with each node location description.

Northern Italy is discretised according to the grid approach described by Zamboni *et al.* (2009a): the whole region is approximated through a grid of 59 homogeneous squares of equal size (50 km of length), each one representing an element identified by g. One additional cell ($g = 60$) was added as a pseudo-region to represent the option of importing biomass from foreign suppliers. The actual land surface of each squared region (GS_g) is measured by considering the specific geographical configuration of the area, as reported in Table 3.2. Element 60 is assigned a very large value so as to represent a pseudo-region capable of a biomass production that may satisfy the domestic demand.

3.6.2 Demand centres

The core driver of the design process of a biofuel supply network can be identified in the system capabilities of satisfying the product demand imposed by markets, which is supposed to be only driven, in this study, by the European policy for biofuels promotion. In complying with EU guidelines on biofuels, the Italian energy policy set the minimum blending fraction of bioethanol within gasoline at 5.75% (on energy content) for 2010 (IT, 2007). Yet, assuming as mandatory the future EU targets on biofuels, the global share of 10% ought to be reached by 2020.

Bioethanol is assumed to be sent to blending terminals existing at given locations and the corresponding biofuel rates are determined by applying a percentage to their gasoline demand, which is supposed constant all over the time horizon. Location, number and actual gasoline delivery rate of each terminal are defined according to the secondary distribution model by Zamboni *et al*. (2009a).

Bioethanol market demand varies according to the Governmental regulation that imposes minimum blending percentages increasing every year. Table 3.3 shows the varying blending quota (represented by the $etperc_t$ parameter) for the 5 time periods. In the $etperc_t$ array, the blending percentages (on a weight basis) are averaged over the three years composing the single time period t. Bioethanol demand is set to vary along the 15-years time horizon, starting from 2010 to 2024.

Table 3.3 *The $etperc_t$ array with ethanol blending percentages on mass basis over the years.*

t	**1**	**2**	**3**	**4**	**5**
$etperc_t[\%]$	10.2	12.1	14.0	15.8	17.6

The entire set of time-dependent bioethanol demand, $Df_{g,t}^{T}$ of Eq. (3.40), for each terminal is reported in Table 3.4.

Table 3.4 *Values for the ethanol demand,* $Df_{g,t}^{T}$ *[t/time period], for each region g a time period t.*

t *g*	1	2	3	4	5
22	139332	165286	191240	215828	240416
25	207329	245949	284570	321157	357745
27	402312	477253	552194	623190	694186
32	207664	246346	285029	321675	358322
37	66125	78442	90759	102428	114097
39	206787	245306	283825	320317	356808
41	142453	168989	195524	220663	245802
46	130270	154536	178802	201791	224780
52	172082	204137	236191	266559	296926

3.6.3 Biomass production

With concerns to corn cultivation, the spatially specific data sets of Eq. (3.43) (i.e. BCD_g^{max}, AD_g, $BY_{i,g,}$) and $UPC_{i,g}$ in Eq. (3.17) were taken from Zamboni *et al.* (2009a). Stover yields ($BY_{'stover',g}$) are set equal to corn yield according to the common assumption of a fixed grain to stover ratio equal to 1:1, according to the work by Lal (1995), as already discussed in chapter 2. Stover costs ($UPC_{'stover',g}$) are derived by assuming a fixed allocation factor of about 24%.

LCA-wise, the set of emission factors from biomass cultivation, is grid-dependent and the results are reported in Table 3.5.

Data to estimate the impact on global warming from the cultivation phase (Eq. 3.56), $fbp_{'corn',g}$, of corn grain production were taken from Zamboni *et al.* (2009b). Concerning stover supply, one critical aspect in addressing the exploitation of crop residue within sustainable biofuels production networks, refers to the upper level of removal rate. Recommended residue removals need to consider soil type, climate, cropping system and management in order to protect soil quality. Irresponsible removal of crop residue might cause impacts on soil quality degradation and eventually yields reduction, requiring increased fertilisation rates to maintain soil fertility and high biomass yields (e.g., corn). Thus, as already stated, a stover collection rate upper bound (33%, (USDA, 2005)) has been set as a conservative threshold to mitigate environmental impacts associated with crop residue removal: e.g., soil erosion, degradation, moisture content stability reduction, effects on storing/recycling of nutrient and maintenance of soil organic carbon (SOC) content (Lal, 2005; Andrews, 2006). Next, following the literature (Luo *et al*., 2009b; ANL, 2006), stover-related environmental parameters, $fbp_{'stover',g}$, have been derived considering the GHG emissions as exclusively associated to the differential amount of fertilisers required to offset soil nutrients depletion (Petrolia, 2008) due to stover removal as well as to the diesel usage employed for the harvesting referring to common agricultural practices (IT, 2008).

Table 3.5 *Values for the global emission factor related to biomass cultivation, $fbp_{i,g}$ [kg CO_2-eq/t].*

g	**$fbp_{i,g}$ kg CO_2-eq/t**		**g**	**$fbp_{i,g}$ kg CO_2-eq/t**		**g**	**$fbp_{i,g}$ kg CO_2-eq/t**	
	corn	**stover**		**corn**	**stover**		**corn**	**stover**
1	356.5	31.0	21	345.5	30.0	41	346.8	30.2
2	356.5	31.0	22	347.4	30.2	42	345.7	30.1
3	356.5	31.0	23	345.8	30.1	43	345.6	30.1
4	352.0	30.6	24	354.7	30.8	44	346.5	30.1
5	347.8	30.2	25	348.3	30.3	45	353.2	30.7
6	347.0	30.2	26	345.5	30.0	46	363.5	31.6
7	347.7	30.2	27	349.7	30.4	47	348.9	30.3
8	425.1	37.0	28	360.8	31.4	48	347.5	30.2
9	394.8	34.3	29	352.1	30.6	49	346.6	30.1
10	351.7	30.6	30	345.4	30.0	50	345.4	30.0
11	347.5	30.2	31	348.6	30.3	51	346.7	30.1
12	347.5	30.2	32	345.7	30.1	52	349.1	30.4
13	363.5	31.6	33	346.9	30.2	53	747.6	65.0
14	350.4	30.5	34	346.3	30.1	54	747.6	65.0
15	345.3	30.0	35	349.9	30.4	55	363.5	31.6
16	346.0	30.1	36	346.4	30.1	56	345.9	30.1
17	371.1	32.3	37	365.4	31.8	57	345.4	30.0
18	346.3	30.1	38	345.3	30.0	58	352.9	30.7
19	388.7	33.8	39	351.3	30.5	59	352.9	30.7
20	345.4	30.0	40	349.4	30.4	60	359.9	31.3

3.6.4 Biomass pre-treatment

Biomass pre-treatment deals with the drying and storage operations after biomass harvesting and collection. With concerns to the SCA, these costs are not considered because already included in the biomass production costs.

Dealing with the LCA analysis, the environmental impact deriving from biomass (Eq. (3.57) has to be addressed separately from the production stage. On one hand, no emission factors have been assigned to stover drying, because Northern Italy is a region where field-drying is generally sufficient for a safe baling; on the other hand, the drying and storage of corn cannot be neglected: the specific emission factor was determined as in Zamboni *et al.* (2009b) and set equal to 63.34 kg CO_2-eq/t of corn.

3.6.5 Transport systems

According to current Northern Italy distribution infrastructure, the transport system here modelled includes trucks, rail, barges and ships as possible delivery means. Trans-shipping is also comprised as a viable transport option for biomass importation. The biomass transfer within each production element *g* is described assuming the employment of small road tankers. All the transport-related parameters have been defined according to Zamboni *et al.* (2009a). In particular, transport costs ($UTCb_l$ and $UTCf_l$ of Eq. (3.19-3.20), respectively) and impact factors (fbt_l and ffd_l in Eq. (3.58-3.59)) characterising the transport means are summarised in Table 3.6 and Table 3.7, respectively.

Table 3.6 *Transport costs for biomass and ethanol, $UTCb_l$ and $UTCf_l$ [€/(t·km)].*

transport mode *l*	**$UTCb_l$ [€/(t · km)]**	**$UTCf_l$ [€/(t · km)]**
small truck	0.270†	-
truck	0.540	0.500
rail	0.200	0.210
barge	0.120	0.090
ship	0.064	0.059
trans-ship	0.005	-

$^\dagger UTCl$

Table 3.7 *Global emission factors to deliver biomass and ethanol, fbt_l and ffd_l [kg CO_2-eq/(t·km)].*

transport mode *l*	**fbt_l [kg CO_2-eq/(t·km)]**	**ffd_l [kg CO_2-eq/(t·km)]**
small truck	0.591†	-
truck	0.123	0.123
rail	0.021	0.021
barge	0.009	0.009
ship	0.007	0.007
trans-ship	0.006	-

$^\dagger fbtl^*$

3.6.6 Fuel production

The modelling framework has been conceived considering both first and second generation technologies as suitable options to convert biomass into ethanol. Ten possible solutions (see Table 3.8) have been investigated. The available technical alternatives are grouped into three main processing designs, as already discussed in chapter 2: *i)* the Dry Grind Process (DGP), i.e. the standard corn-based ethanol process (Franceschin *et al.*, 2008); *ii)* the Ligno-Cellulosic Ethanol Process (LCEP), where stover only is converted into ethanol (USDOE, 2002); *iii)* the Hybrid Process (Hybrid), where both corn grain and stover are processed to obtain ethanol.

Table 3.8 *Ethanol technologies: identification and products description of each technology belonging to the set k.*

technology *k*	Process			Input		Output		
	DGP	LCEP	Hybrid	Corn	Stover	ethanol	CHP	DDGS
1	X			X		X		X
2	X			X		X	X	
3	X			X	X	X	X	X
4		X			X	X	X	
5,6,7			X	X	X	X	X	X
8,9,10			X	X	X	X	X	

With concern to DGP, three instances are analysed according to how power is supplied to the plant: either by the grid ($k = 1$) or by using DDGS ($k = 2$) or stover ($k = 3$) to fuel a CHP generation system.

LCEP is identified by $k = 4$. As usual heat and power are provided by feeding lignin to a CHP station. Also in the hybrid processes, where stover is used to produce ethanol, lignin is always exploited to provide heat and power as a process output.

As regards the processes combining first and second generation technologies (Hybrid), a purpose-designed Aspen Plus® model as discussed in chapter 2, was set up to define three instances representing specific (1:1, 1:2, 1:3) corn-to-stover ratios. The process design integrated the recovery and utilities sections to reduce capital and production costs (USDA, 2005). Two alternative DDGS end-uses are taken into account, i.e. either DDGS is sold in the animal feed market ($k = 5,6,7$, where the three indexes stand for the three decreasing corn to stover ratios) or it is fed along with lignin to the CHP station ($k = 8,9,10$).

Each technology k has been characterised from a technical and economic point of view. Considering the economics first, both capital investment, $CI_{p,k}$ of Eq. (3.22-3.23), and production costs, $PC_{p,k}$ were taken into account. $CI_{p,k}$ was defined according to the usual formulation:

$$CI_{p,k} = a_k \cdot ER_p^{r_k} \tag{3.62}$$

where the power factor, r_k, and the specific coefficient, a_k, are estimated from industrial data, financial models or the literature (according to chapter 2). Eq. (3.62) has been linearised by dividing the overall capacity range into six intervals (p, whose specific capacity is assigned through the parameter ER_p reported in Table 3.9), according to the approach proposed by Liu *et al.* (2007), so as to obtain the size-specific coefficient ($CI_{p,k}$) summarised in Table 3.10.

Table 3.9 *Production capacity: nominal values for each plant size p, ER_p.*

plant size *(p)*	**ER_p [t/y]**
1	96000
2	110000
3	150000
4	200000
5	250000
6	276000

Cost indexes are recommended to update capital investments values from a base time (t_ref) to the present time (t) of the estimate. The Marshall and Swift Equipment Cost Index (M&S) was chosen in this case (Douglas, 1988). Capital investment values ($CI_{p,k}$) are estimated for the year of interest according to the following formulation:

$$CI_{p,k} = CI_{p,k,t\_ref} \cdot \left(\frac{M\&S_t}{M\&S_{t\_ref}} \right) \tag{3.63}$$

where CI_{p,k,t_ref} is the base cost, $M\&S_t$ is the cost index for the year of interest, and $M\&S_{t\_ref}$ is the cost index for the base year.

Table 3.10 *Capital Investment: values of the linearisation parameters $CI_{p,k}$ [10^6€].*

k \ **p**	**1**	**2**	**3**	**4**	**5**	**6**
1	62	70	91	115	139	151
2	81	90	117	149	179	195
3	74	82	106	134	162	175
4	396	434	535	648	753	804
5	179	196	242	293	340	363
6	186	203	250	304	353	377
7	187	204	252	305	354	379
8	177	194	239	289	336	359
9	185	203	250	303	352	376
10	186	204	251	304	354	378

$PC_{p,k}$ [€/time period] are supposed to be a linear function of the production capacity (Douglas, 1988) and can be described as follows:

$$PC_{p,k} = coef_{k,'1'} \cdot PCap_p + coef_{k,'2'} \tag{3.64}$$

where $PCap_p$ [t of ethanol/time period] is the plant capacity over a three-years time horizon; the technology-related parameters $coef_{k,'1'}$ and $coef_{k,'2'}$ (see Table 3.11) are, respectively, the slope and the intercept of the linear equation of the operating costs obtained by the regression of production costs values related to several capacity intervals (p) per each technology k which have been used in used in Eq. (3.18).

Table3. 11 *Production costs: values of the linearisation parameters* $coef_{k,c}$.

coef / **k**	$coef_{k,'1'}$ [€/t]	$coef_{k,'2'}$ [€/time period]
1	140.83	6000000
2	17.746	10000000
3	108.92	6000000
4	202.88	30000000
5	132.54	20000000
6	140.05	20000000
7	143.36	20000000
8	126.24	20000000
9	134.18	20000000
10	137.52	20000000

Table 3.12 *Parameter* ω_k *representing the exceeding electricity production for each conversion technology k.*

technology k	ω_k [kWh/L of ethanol]
1	0
2	0.743
3	0.496
4	0.602
5	0.482
6	0.515
7	0.533
8	0.482
9	0.515
10	0.533

With concern to the technical aspects, the main modelling parameters relate to the technological features of the different conversion options. The exceeding electricity production specific for each conversion technology k, ω_k (Eq. (3.36)), and the nominal ratios, $\beta_{i,k}$ (Eq. (3.38)), of bioethanol produced from biomass i, are summarised in Table 3.12 and Table 3.13, respectively. The values of the biomass conversion factors, γ_i of Eq. (3.39), and the fraction of biomass fuelled to CHP generation, $burn_{i,k}$ in Eq. (3.39), reported in Table 3.14-3.15, respectively, are set according to the process models as developed in chapter 2.

Table 3.13 *Parameter $\beta_{i,k}$ representing the nominal ratios of bioethanol produced from biomass i over the total production rate of technology k.*

technology *k*	**$\beta_{i,k}$**	
	corn	**stover**
1	1	0
2	1	0
3	1	0
4	0	1
5	0.554	0.446
6	0.383	0.617
7	0.292	0.708
8	0.554	0.446
9	0.383	0.617
10	0.292	0.708

Table 3.14 *Parameter γ_i representing the biomass-to-ethanol conversion factors.*

biomass *i*	**γ_i [t of ethanol/t of biomass]**
corn	0.332
stover	0.267

Table 3.15 *Parameter $burn_{i,k}$ representing the biomass fraction fuelled to CHP generation, $burn_{i,k}$.*

technology *k*	**$burn_{i,k}$**	
	corn	**stover**
1	0	0
2	0	0
3	0	0
4	0	0
5	0	0.507
6	0	0.341
7	0	0.199
8	0	0.11
9	0	0.143
10	0	0.068

Market prices of Eq. (3.13) for ethanol, DDGS and power where taken from Zamboni *et al.* (2009b) and fixed equal to 710 €/t, 300 €/ and 180 €/MWh (considering current subsidies for green credits).

With regard to the environmental aspect (Eq. (3.60)), the GHG emissions from the biofuel production stage were assumed to be proportional to the total annual bioethanol produced from the facility operating through technology *k* fed with biomass *i*. The global emission factors assigned to the corn-based processes ($ffp_{'corn'}$ = 1052.2 kg CO_2-eq/t of ethanol) were calculated through a spreadsheet tool (HGCA, 2005) adapted to the specific case study (Zamboni *et al.*, 2009b). The same approach was used to calculate the emission factors for the cellulosic-based processes ($ffp_{'stover'}$ = 257.55 kg CO_2-eq/t of ethanol) after substituting the specific process inputs and including the contribution to the emissions coming from offsite enzyme production (Slade *et al.*, 2009).

3.6.7 Emission credits

The emissions credits according to the substitution approach as discussed earlier and determined according to Eq. (3.61), are assigned to both DDGS and electric energy and reflect their potential end-uses. The calculation inputs derive from the assumptions by Zamboni *et al.* (2009b). Regarding the corn-derived main by-product, the DDGS-to-soy substitution ratio (0.69 kg/kg, according to Zamboni *et al.* (2011a)) has been applied to the typical DDGS-to-ethanol ratio (0.954 kg/kg). Regarding stover-derived main by-product, the emissions discount has been determined by applying ω_k to the corresponding unitary emission for electricity generation within the general Italian context (130.05 kg CO_2-eq/GJ, according to HGCA (2005)). The resulting set of emission credits, fec_k is reported in Table 3.16.

Table 3.16 *Parameter fec_k representing the credits for avoided emission achieved by each technology k.*

technology ***k***	fec_k **kg CO_2-eq/t**
1	342.22
2	1427.38
3	1383.47
4	357.40
5	628.41
6	648.02
7	658.19
8	286.19
9	305.80
10	315.97

3.7 Results and discussion

In order to downsize the problem, a decomposition of the global framework was carried out. First the sub-problem obtained by dropping down the spatially explicit features was solved, focusing only on the selection of the most performing production technologies. Then, the second sub-problem was formulated implementing the entire model (Eq. 3.1-3.61) within the resulting new set of technological options.

3.7.1 Decomposition approach

The first sub-problem refers to a single bioethanol production plant, which is supplied with the necessary biomass (corn, stover or both) through the cultivation of a hypothetical land surface of limited, although flexible, extension. Only the upstream SC is taken into account, according to the purpose of driving decisions associated with optimal technology selection and capacity planning over the long-term. In fact, the downstream part accounting for both fuel distribution and utilisation is little sensitive to the feedstock and technological choices to be made in the upstream supply chain design (Zamboni et al. 2009b). In addition, the simplification seems quite reasonable also considering that the technology selection does not depend on the geographical location in a homogeneous context like Northern Italy territory.

The modelling framework of the sub-problem was implemented as a multi-objective mathematical pattern according to the formulation of Eq. (3.1-3.61) dropping down the grid dependence of variables and parameters, as well as neglecting the relations of the transportation system (Eq. (19-20); Eq. (58-59)). The design problem has the objective to determine the optimal system configuration referring to only one production facility, maximising the financial profitability while minimising the GHG emissions. Therefore, the key variables to be optimised are:

- bioethanol facilities capacity and technology selection;
- feedstocks mix;
- by-products end-use option;
- financial performance of the system over the long-term;
- system impact on global warming.

In order to explore a wider set of solutions to investigate the effect of public instruments for supporting renewable energies production, the optimisation sub-problem is also addressed by formulating two alternative instances assessing in terms of price for electricity (GSE, 2011):

I: MP_{power} = 67.18 €/MWh, i.e. the current electricity selling price (without subsidies)

II: MP_{power} = 180 €/MWh, i.e. the price encompassing Green Credits (GCs)

In addition, DDGS selling price is supposed to decrease over time (with MP_{DDGS} ranging between 300-100 €/t) as soon as a consolidated ethanol production is established. Uncertainty in GHG emissions estimations is also assessed by performing a sensitivity analysis on some predominant parameters.

The problem was solved through the CPLEX solver in the GAMS® modelling tool (Rosenthal, 2006). Figure 3.1 shows the resulting trade-off set of non-inferior solutions for both instances I (A-D) and II (B1-D1). As expected, trends reveal the existing conflict between environmental and economic performance.

3.7.1.1 Instance I: no subsidies

The multi-objective optimisation solutions in absence of governmental subsidies reported in Figure 3.1, belong to the Pareto optimal frontier moving from an economic (A) to an environmental optimum (D), as discussed in the following.

The economic optimum (point A in Figure 3.1) involves the selection of the standard DGP technology (k = 1) in which DDGS is sold as animal fodder. This option allows for more revenues coming from the by-product business and results in a normalised NPV of about 1.07 €/$GJ_{ethanol}$ and in a Return On Investment (ROI) index of 19% (evaluated on a medium basis over the business horizon). The environmental outcomes show an overall GHG emission of 78.03 kg CO_2-eq/$GJ_{ethanol}$ which leads to an emissions reduction of about 9% with respect to the conventional gasoline pathway. These results are not surprising and match the usual performance of first generation ethanol productions. In fact, from an economic standpoint corn-based technologies are acknowledged to perform better than lignocellulose-based ones, mainly because of less capital expenditures and production costs involved in the SC operation, particularly when economy of scale is exploited (p = 6, i.e. maximum plant capacity). On the other hand, the resulting 9% emissions savings are insufficient for eligibility for public incentives (asking for at least 35% of GHG reduction with respect to conventional fuels).

Moving down towards better performance in terms of environmental impact mitigation, a suitable technological option is represented by the Pareto non-inferior point B in Figure 3.1: this would involve the establishment of a production facility still exploiting the technology DGP (k = 2) and operating at maximum capacity (p = 6). This option takes advantage of burning DDGS in the power station: as shown in Figure 3.2.a in spite of the higher capital expenditures (1.31 €/$GJ_{ethanol}$ against the 1.01 €/$GJ_{ethanol}$ needed to establish the standard DGP facility, k = 1), this solution would lead to a global decrease in ethanol production costs due to the heavier effect of energy supply savings. The normalised NPV is now 0.61 €/$GJ_{ethanol}$ (ROI = 16%). As shown in the emissions breakdown reported in Figure 3.2.b, this process design entails substantially larger emission savings due to higher emission credits coming from the alternative use of by-products. The overall GHG emissions are about 55% lower with respect to gasoline, thus matching the EU requirements for 2017 (i.e. 50% savings).

If the 2018 emission target (i.e. 60% savings) needs to be reached, solution C (Figure 3.1) is suggested: this SC configuration may provide very positive effects on global warming mitigation leading to an overall GHG savings of about 84%. This performance is achieved by operating the hybrid technology (k = 7) at the maximum capacity (p = 6): as shown in Figure

3.2.b, although higher emissions for biomass distribution and lower credits come from the current by-product end-use, the bioethanol production determines a lower impact when stover is used. On economic terms (Figure 3.2.a), the higher investment for establishing hybrid technologies (about 2.55 €/GJ$_{\text{ethanol}}$) entails a consistent worsening on the economic performance. As a result, the solution indicates a normalised NPV of 0.39 €/GJ$_{\text{ethanol}}$ (ROI = 12%).

Eventually, the environmental optimum is reached in configuration D (Figure 3.1), which establishes a full second generation facility (technology LCEP, $k = 4$) operating at minimum capacity (p = 1) and with an impact on global warming reduced to only 1.8 kg CO$_2$-eq/GJ$_{\text{ethanol}}$ (about 97% less than gasoline). This is mainly due to the lower emissions resulting from stover production and conversion to ethanol when compared to conventional first generation biomass: as shown in Figure 3.2.b, stover cultivation results in nine-fold lower emissions than grain cropping, whereas second generation fuel production impact is four times lower than the first generation one. Although the remarkable performance in terms of global warming mitigation, this solution is not economically feasible: the normalised NPV drops down to -7.18 €/GJ$_{\text{ethanol}}$, which clearly shows the scarce competitiveness of such a business. As Figure 3.2.a reports, this is mainly due to the much higher capital costs (about 7.7 €/GJ$_{\text{ethanol}}$) needed to establish second generation technologies.

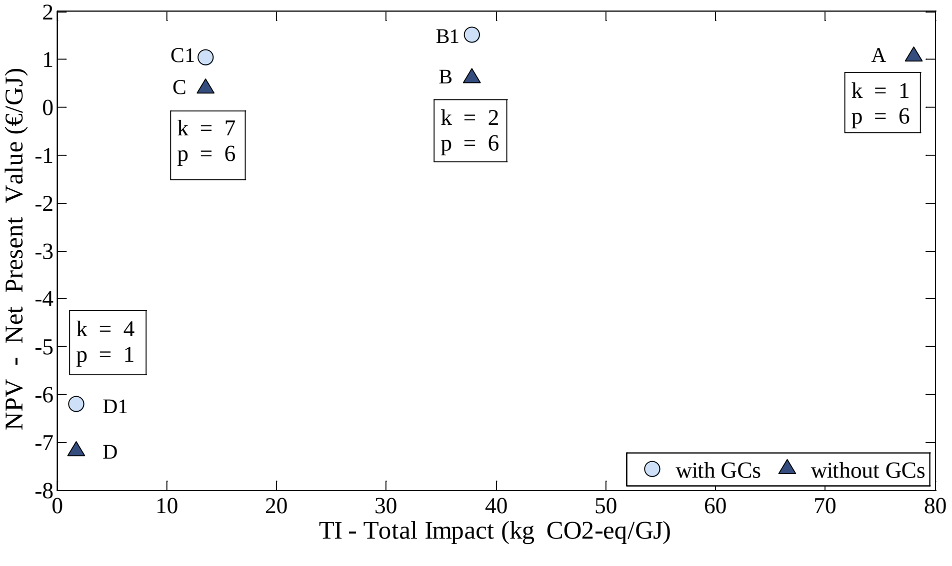

Figure 3.1 *Pareto set of non-inferior solutions: simultaneous optimisation under NPV maximisation and GHG emissions minimisation criteria (p = plant scale; k = production technology). Triangles represent points from instance I (no GCs); circles represent points from instance I (with GCs). NPV normalisation is performed by applying the factor* $\left(P^{T}_{'ethanol',k,g,t} \cdot LHV_e \cdot tf\right)^{-1}$. *$LHV_e$ is the ethanol lower heating value (26.952 GJ/t of ethanol); tf is the facility operating period (20 years).*

3.7.1.2 Instance II: effect of subsidies

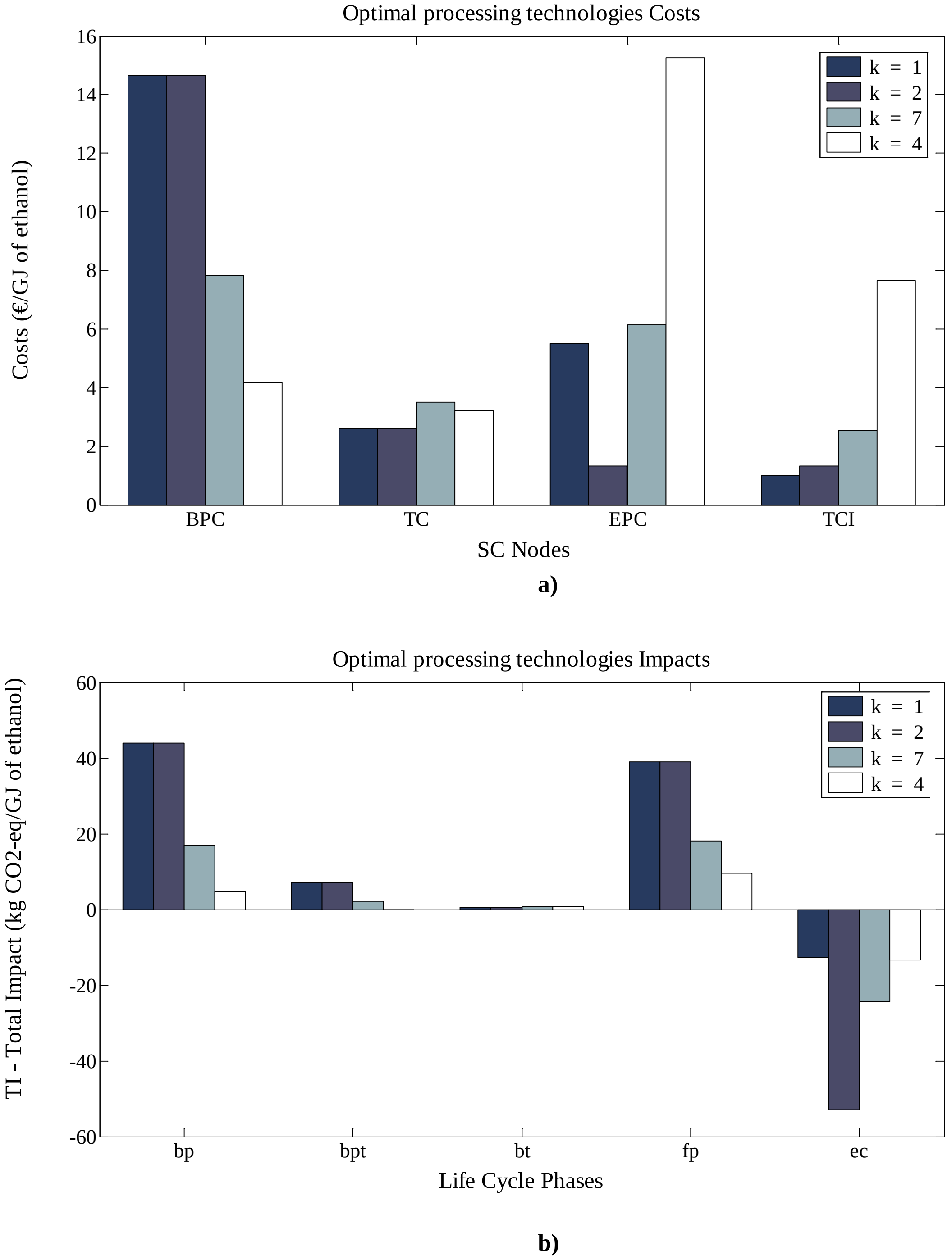

Figure 3.2 *Non-inferior Pareto solutions: (a) costs (where SC phases are: BPC - biomass production cost, TC - transport cost, EPC - ethanol production cost, TCI - total capital investment) and (b) emissions breakdown (where LCA phases are: bp – biomass production, bpt – biomass pretreatment, bt – biomass transport, fp – fuel production, ec – emissions credits). TCI is normalised by applying the factor* $\left(P^{T}_{ethanol,k,g,t} \cdot LHV_e \cdot tf\right)^{-1}$. *$LHV_e$ is the ethanol lower heating value (GJ/t); tf is the facility operating period (20 years).*

Solutions obtained from the multi-objective optimisation carried out at a higher power selling price belonging to the Pareto frontier (B1-D1 in Figure 3.1), also reveal balanced trade-offs between economic and environmental objectives, as discussed in the following.

As shown in Figure 3.1, a higher electricity price obviously allows reaching better economic performance, particularly for those technologies taking advantage of power surplus generation. Apart for the shift upwards in the NPV, the optimal planning is quite similar to the one of instance I. However, the economic optimum is not given by DGP ($k = 1$), which is not rewarded by GCs. The optimum is now represented by point B1 ($p = 6$ and DGP ($k = 2$)), taking advantage of the possibility of burning DDGS in a power station and exploiting GCs. The normalised NPV for point B1 is 1.52 €/GJ$_{ethanol}$ (almost 42% more than instance A) while the ROI index rises to 24% (matching the minimum acceptable threshold for a new product entering an established market) (Peters *et al.*, 2003).

Point C1 operating the hybrid technology ($k = 7$) at the maximum capacity ($p = 6$) reaches a NPV of 1.05€/GJ$_{ethanol}$ while the ROI index increases from 12% up to 15%. Finally, the environmental optimum, represented by point D1 ($k = 4$), is still an unprofitable option with NPV = -6.2€/GJ$_{ethanol}$, even though GCs allow increasing the income power share (from 6% to 16%).

3.7.1.3 Sensitivity analysis on emission factors

A sensitivity analysis was also carried out to assess the effect of uncertainty on the most important factors in determining the environmental sustainability. These are the biomass and fuel production emissions factors (respectively *bp* and *fp*), which are supposed to vary of ±30%. Table 3.17 summarises the results obtained for three processing technologies allowing for at least 35% GHG reduction with respect to conventional fuels ($k = 2,4,7$). Note that even a significant 30% uncertainty on the key emission factors does not change the sustainability ranking in the three conversion technologies. However, it is clear that the environmental performance of the corn-based technology is much more sensitive to uncertainty in the emission factors and is characterised by emissions savings ranging between 40% and 70% (the latter would comply with all EU emission targets).

Table 3.17 *Sensitivity on emission factors: GHG emission reduction evaluated for the optimal technologies per each instances (LCA phases considered are: bp - biomass production, fp - fuel production).*

		GHG emission reduction			
technology k	base case	bp 30% more	bp 30% less	fp 30% more	fp 30% less
2	55%	40%	71%	42%	69%
7	84%	78%	90%	77%	90%
4	97%	96%	99%	94%	>99%

3.7.2 Solutions to the spatially-explicit model

The first sub-problem solutions has led to reduce the dimension of the set of biomass conversion technologies: in particular, only four options (k = 1,2,4 and 7, referring to Table 3.8) were identified as efficient alternatives to produce ethanol. Accordingly, the second sub-problem was formulated implementing the entire model (Eq. (3.1-3.61)) within a reduced space involving a new set of technological option *K'* defined as:

$K' \subset K = \{1,2,4,7\}$.

3.7.2.1 Strategic policy

The Pareto set of optimal solutions (see Figure 3.3) resulting from the bi-objective problem solution can be used to steer strategic policies on biofuels infrastructures within a geographical framework. The results trend reveals the Pareto frontier showing the conflict between environmental and economic performance in dealing with biofuels productions. In the following, the discussion will be only focussed on the solutions of Figure 3.3, named as A, B, C, D, E, representing SC configurations involving a technological shift in bioethanol production, whose detailed economic and emissions breakdown is provided in appendix B (despite the similar names, these solutions are not directly related to the ones of the first subproblem). The remaining points of Figure 3.3, representing investment strategies in biofuels industry, are neglected in this discussion, since they only reveal variations of facilities capacities.

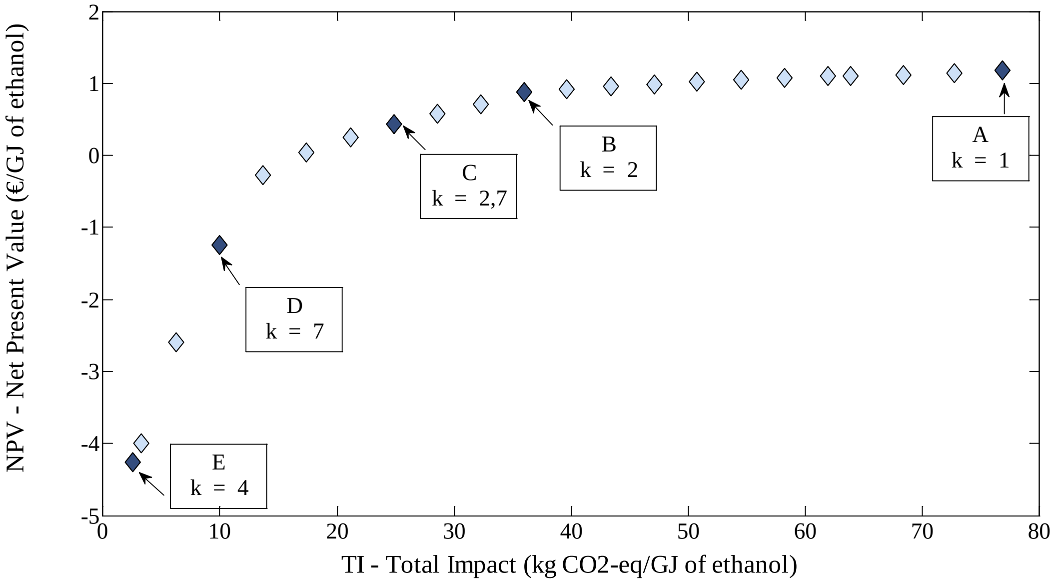

Figure 3.3 *Pareto set of optimal solutions: simultaneous optimisation under NPV maximisation and GHG emissions minimisation criteria (k = production technology). NPV normalisation is performed by applying the factor* $\left(P^{T}_{ethanol,k,g,t} \cdot LHV_e \cdot tf\right)^{-1}$. *$LHV_e$ is the ethanol lower heating value (GJ/t); tf is the facility operating period (15 years).*

The optimal configuration in terms of economic performance (case A as reported in Figure 3.3) entails a marginal NPV of 1.18 €/GJ$_{\text{ethanol}}$ against a global environmental impact of 76.9 kg CO_2-eq/GJ$_{\text{ethanol}}$ corresponding to a GHG reduction of about 10% compared to gasoline (the GHG emissions factor for gasoline was assumed equal to 85.8 kg CO_2-eq/GJ, according to HGCA (2005)). The system design would involve the establishment of standard DGP production plants ($k = 1$) and biomass (corn) importation from Eastern European countries. As a consequence, corn is directly shipped to the production plants whose location is mainly set within industrial areas very close to the main sea ports. At the end of time period 5, the amount of corn utilised for ethanol production is about 2 900 000 t/y (70% imported), which corresponds to about 29% of the current corn annual production in Northern Italy. This configuration allows for the best economic performance in terms of both biomass supply costs, due to the lower price of the imported corn, and of global revenues, positively affected by the great incomes coming from the DDGS side business. However, in terms of impact on global warming, the 10% of GHG emissions reduction is not enough to meet the latest EU standards which require biofuels to have a minimum of 35% of GHG emissions savings. This is mainly due to the adoption of first generation technologies, which are less efficient in terms of GHG reduction, as well as to the increase in the transport systems emissions due to biomass importation.

Great improvements on the environmental performance can be obtained through the conversion of the DGP ethanol conversion facilities by simply changing the DDGS end-use: if this by-product is fuelled to a CHP station ($k = 2$), higher GHG emission savings would be achieved due to the emissions credits coming from the exceeding power production. As the case B (whose SC topology is quite similar to the one of case A in terms of plant location) of Figure 3.3 shows, the marginal impact goes down to 36.0 kg CO_2-eq/GJ$_{\text{ethanol}}$ still maintaining a good economic performance which involve a marginal NPV of 0.88 €/GJ$_{\text{ethanol}}$. The impact mitigation potential, now accounting for about 58% of GHG reduction, would be sufficient to meet both the 2010 and the 2017 targets (set to 35% and 50%, respectively). This threshold can be met by introducing hybrid technologies within the production systems: as shown in Figure 3.3, all the solution points placed between case B and case C ensure the satisfaction of the EU emission targets and feasible economic performance. For instance, case C configuration envisages the establishment of ethanol production system involving both first ($k = 2$) and hybrid generation ($k = 7$) conversion facilities: this allows reaching excellent performance in terms of GHG emissions (24.9 kg CO_2-eq/GJ$_{\text{ethanol}}$, corresponding to about 71% of emissions savings) against reasonable revenues (the marginal NPV is about 0.43 €/GJ$_{\text{ethanol}}$).

If the global warming mitigation potential needs augmenting, second and hybrid generation technologies ($k = 4$ and 7) should be introduced in the fuel system configuration. However, these technologies do not appear to be sufficiently mature to compete with other fuel productions: the high capital costs involved in the establishment of second generation facilities make the economic performance of such a business drop down to unsustainable levels. Case D in Figure 3.3, for example, involves a system configuration envisaging the construction of hybrid corn- and stover-based conversion plants ($k = 7$), reaching remarkable performance in terms of GHG reduction (beyond 84%, corresponding to a marginal emission of 13.7 kg CO_2-eq/$GJ_{ethanol}$): this is due to the low emission attributable to stover production[2] and pre-treatment as well as to fuel production (stover by-product valorisation as fuel for CHP allows for a good performance in terms of both energy savings and emissions credits). However, the operation of such a system would be feasible only under a strong support policy: to lift the business up to the feasibility region, the governmental subsidy to bioethanol production should account for about 0.27 €/$GJ_{ethanol}$ (corresponding to about 85 M€ parcelled out over the 15 years horizon).

Finally, when the establishment of a sole stover-based technology ($k = 4$) is envisaged (case E of Figure 3.3), the best environmental performance are achieved, with a global warming mitigation potential of about 97% of GHG reduction. However, the amount of subsidies should be higher, too: the economic gap now results conspicuous (4.26 €/$GJ_{ethanol}$, corresponding to about 1.3 billion over 15 years).

3.7.2.2 Strategic design and planning

In this section the design and planning capabilities of the model are illustrated by taking case C of Pareto frontier shown in Figure 3.3 as a demonstrative example. Figure 3.4 illustrates the planning strategy while the detailed transport system at the final period of the time horizon, is drawn in Figure 3.5, where railway represents the preferred transport mode. At $t = 1$ (Figure 3.4.a), we have the construction of three production plants. The biggest one (size $p = 6$, corresponding to a nominal production capacity of about 280 kt/y) is a hybrid process ($k = 7$) and is located in the industrial area of Venice ($g = 32$). Stover is produced locally, whereas corn is shipped from abroad. The second plant, too, avails of imported corn (with DGP technology, $k = 2$) and is located in the industrial area close to the port of Genoa ($g = 46$). This is assigned a medium size ($p = 3/4$) corresponding to a production capacity of about 180 kt/y. Another small plant is needed to meet the bioethanol demand needs of Northern Italy in the first time period. This should be set within the industrial area of Milan ($g = 27$) and assigned a small production capacity (size $p = 1/2$, corresponding to a nominal production capacity of about 100 kt/y).

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[2] Fertilisers usage is the major source of emissions associated with corn-farming operations and residues removal requires additional quantities of soil amendments to supplement stover nutrients value for the next corn crop. As a consequence of the substitution method (ANL, 2006; Luo *et al.*, 2009b), the stover-based pathway is only chargeable of the additional soil conditioners demand leading to a lower global emission factor for the biomass production stage.

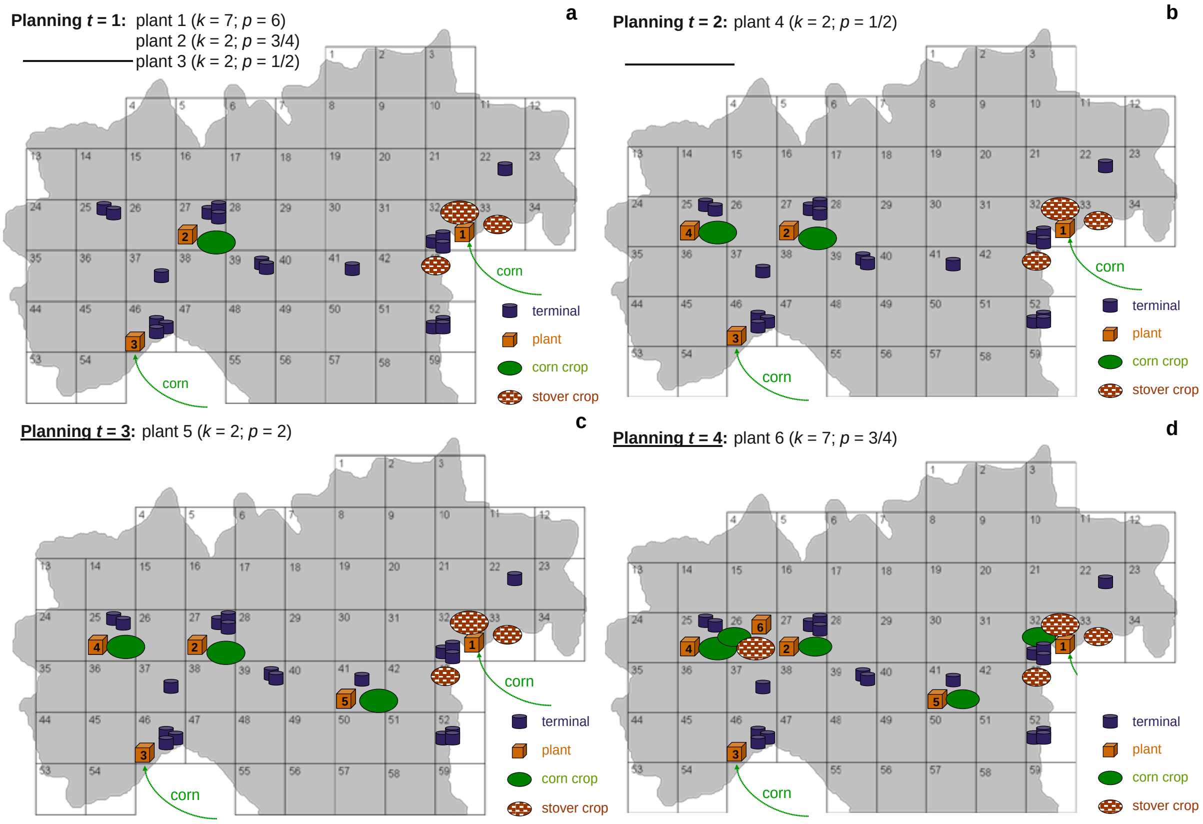

Figure 3.4 *Design and planning strategy along the entire time horizon: case C (k represents the technology, p the size of ethanol production facility).*

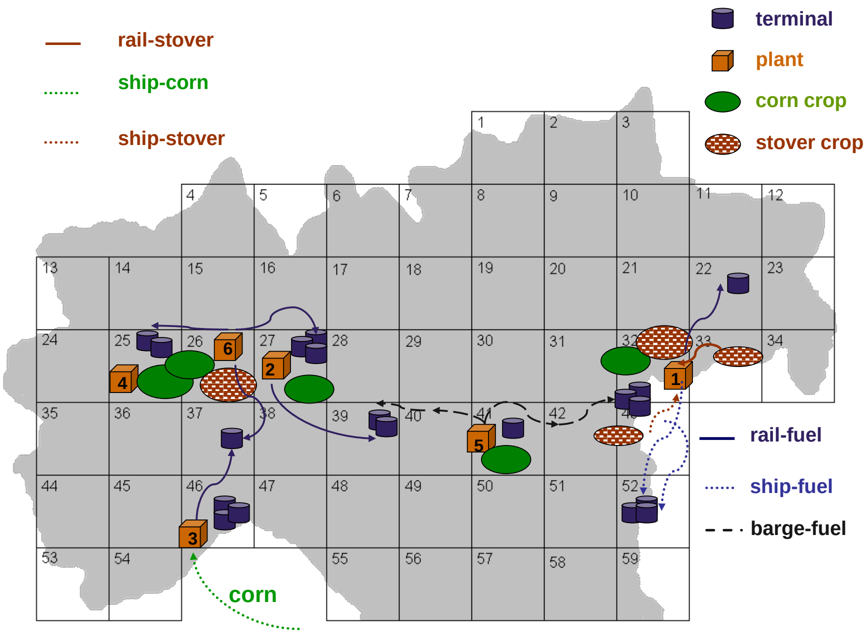

Figure 3.5 *Transport system for the final configuration of the ethanol SC: case C.*

A standard DGP technology ($k = 2$) is established, thus availing of the local corn stocks. This last planning decision is quite similar to the ones envisaged to meet the fuels demand increment for $t = 2$ and $t = 3$ (Figure 3.4.b and 3.4.c). Standard DGP plants of small size ($k = 2$, $p = 1/2$) would be established close to Turin ($g = 25$) and Mantua ($g = 41$), both of them supplied with local biomass (corn).

With concerns to the planning strategy at $t = 4$ (Figure 3.4.d), the establishment of a medium-sized second generation plant ($k = 7$ and size $p = 3/4$, corresponding to a production capacity of about 190 kt/y) is involved. This is necessary to meet the fuel needs for both $t = 4$ and $t = 5$. The hybrid production plant is located close to Milan ($g = 26$, which is one of the most fuel-demanding areas) and would avail of locally produced biomass (both corn and stover).

Still referring to case C of Figure 3.3, let us assess the financial issues related to the specific planning strategy. Figure 3.6 captures the cumulative and discounted cash position along the entire time frame. The discontinuities denote the investments into new plants which follow the planning strategy reported in the previous section. It also shows that the NPV reaches 134 M€ and the overall investment is paid back in about ten years. Note that the last planning decision (occurring in 2019) is paid back in about two years. It is also worth pointing out that the ROI (Return On Investment) index, evaluated on a medium basis over the business horizon, is about 16%, lower than the minimum acceptable threshold for a new product entering an established market (usually set at 24% (Peters *et al.*, 2003)). To meet the minimum standards imposed through the ROI index, case B is the first acceptable solution of Figure 3.3.

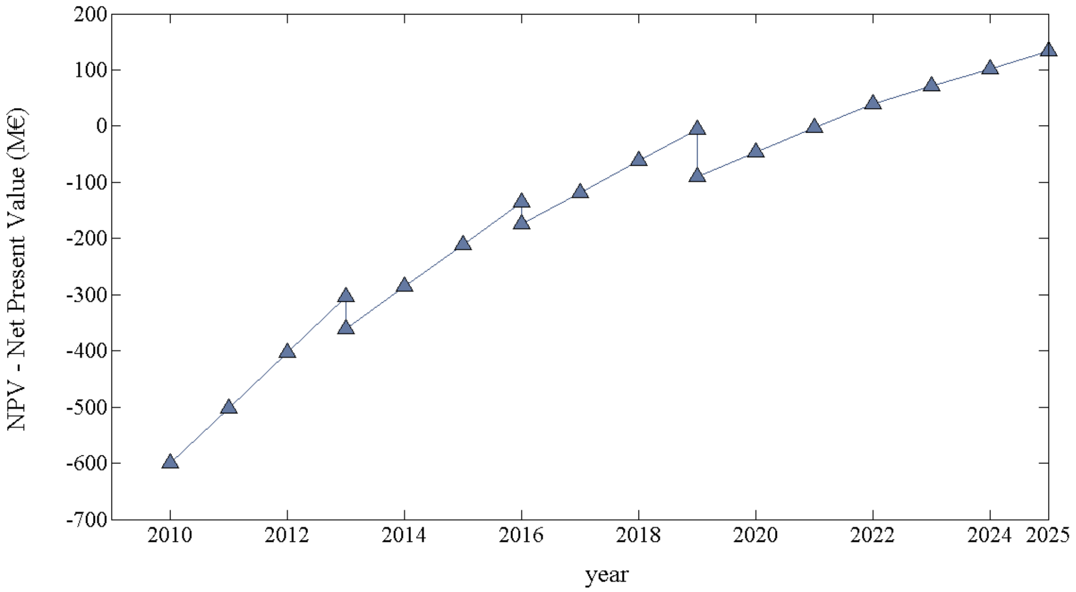

Figure 3.6 *Cumulative and discounted cash position: case C.*

3.8 Final remarks

A critical issue for decision makers in the renewable energy sector is to be provided with quantitative assessment tools to evaluate how different policies and investment strategies may affect either the system profitability or its environmental impact. In this chapter a spatially-explicit and multi-period moMILP modelling framework for the design and planning of multi-echelon biofuels SCs has been presented and discussed. First generation corn grain- and second generation stover-based supply chains for bioethanol production in Italy have been analysed and optimised in terms of profitability and environmental impact.

From a strategic policy standpoint, the modelling outcomes suggest that the only way to match the EU targets on global warming mitigation is to produce ethanol adopting second generation technologies or, at least, hybrid infrastructures. In fact, first generation technologies, although more economically competitive, are not a sustainable answer to the energy supply question, particularly if the latest EU legislation is taken into account. On the other hand, second generation technologies alone are not viable on economical terms. However, integrated corn grain and stover technologies allow for a significant reduction of GHG emission (abiding by the EU emission limits), while retaining a good profitability, being capable of ensuring a viable trade-off between economic and environmental performance.

Chapter 4

Carbon trading mechanisms effects on biofuels supply chain design

Two main topics are dealt with in this chapter[1]. Flexible market mechanisms are embedded within the process of ethanol supply chain design: a value is assigned to the CO_2-equivalent emissions and mechanisms for the trade of allowances to emit are set up. A stochastic MILP modelling framework is presented to address uncertainties in biofuels supply chain management arising from carbon and feedstocks costs variability.

After presenting the main hypotheses about the general behaviour of the ethanol SC considered, the mathematical framework, embedding features for carbon trading schemes mechanisms within a stochastic framework, is dealt with. The economic optimisation is then carried out. Results show the effects on strategic investment decisions in the bioenergy markets due to the regulation on GHG emissions and trading of permits to emit. Two instances are studied accounting for uncertainties on soil capacity of storing carbon and the way they affect total SC emissions bill. A case study is then presented, addressing the emerging biomass (first and second generation)-to-ethanol SC development in Northern Italy.

4.1 Motivation

In the previous chapter, a thorough investigation of a possibility of paving the way for more sustainable biofuels systems was performed referring to the mutual integration of first (from corn grain) and second generation (from corn stover) technologies within well-advised hybrid infrastructures. It has been shown that this would have the advantage of reducing both capital and operating costs as well as simplifying the logistics and allow for balancing stricter emissions limits with greater profitability.

Chapter 4 addresses the prospective of promotion of second generation technologies boosted by a market where flexible mechanisms are introduced. The potential of a carbon trading scheme as a cost-effective tool to promote low carbon fuels production technologies for transportation are studied. In fact, extensive market-based tools, such as emissions trading integrated with regulation targets, might play a key role for managing costs related to the

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[1] Part of this chapter has been published in the work by Giarola *et al.* (2011e).

transition to biofuels (Turk *et al.*, 2008) and delivering a sustainable transport systems at lower costs (Skinner *et al.*, 2010). Even if the road transport sector is currently excluded from the EU Emissions Trading System (EU ETS), several institutions have adopted market-based tools addressing the issue of biofuels sustainability to help accelerating the implementation of new technologies. The Californian ‘Low Carbon Fuel standard’ (ARB, 2011) set a target on GHG emissions over biofuels life cycle, representing the baseline with respect to which tradable credits may be generated.

In addition, sustainability of future biofuels production systems needs to be properly addressed considering the ever-changing energy markets; uncertainty, in particular, has been recognised as one of the most challenging aspect for modern enterprises development (Guillén-Gosàlbez and Grossmann, 2009). Raw materials prices volatility needs to be carefully addressed to perform a financial evaluation of bioenergy systems: as it is shown in the sensitivity analysis performed in appendix C, feedstocks costs variability might greatly affect strategic decisions.

Thus, the decisions-making process on ethanol investments should be supported by quantitative design tools assessing both financial and environmental performance of biofuels production in a holistic approach along the entire SC over the long-term. MILP represents an effective tool in steering decision making about completely undetermined infrastructures particularly when complex optimisation tasks involve uncertainty of exogenous factors.

In this chapter, a model to assist decisions on optimal multi-period and multi-echelon upstream bioethanol SC design and planning under market uncertainty is proposed to assess the effect of CO_2-equivalent emissions allowances trading and its inherent volatility level (Chevallier, 2011) to boost investments on sustainable ethanol production. A stochastic modelling framework adopting a scenario-based approach is proposed to address feedstocks and carbon costs uncertainty. The problem is addressed through a MILP model for SC optimisation selecting among several technological options (including both first and second generation production) and feedstocks. The framework deals with the analysis and optimisation of one production facility and its upstream supply chain. In order to achieve a computationally feasible problem, with respect to the previous chapter, the geographical context has been dropped down and the transport system simplified, too.

4.2 Problem definition

The long-term strategic design and planning of a bioethanol SC is addressed through a general modelling framework aiming at the maximisation of the financial performance of the business (expected Net Present Value, eNPV) and complying with environmental sustainability criteria (minimum GHG emissions savings). Differently from the previous chapter, the upstream supply chain is only taken into account in this modelling framework. In fact, the downstream part accounting for both fuel distribution and utilisation is little sensitive to the feedstock and technological choices to be made in the upstream supply chain design. Considerations of a carbon trading scheme and temporal distribution of environmental interventions are included according to the approach by Bojarski *et al.* (2009). Uncertainty on carbon and biomass cost is dealt with to capture the high market volatility over a 20-year time horizon. SCA and LCA are integrated in a unique framework to compare alternative network configurations on economic and environmental terms.

The methodology proposed to assess the impact over the biofuel life cycle of the ethanol production, evaluated on energy basis, refers to the standard LCA approach as laid out by the ISO (2006) guidelines series. The system boundaries have been set according to the WTT approach (CONCAWE, 2007). The TTW contribution is neglected. In fact fuel usage effect to the overall environmental performance of the system (including issues such as potential differences in vehicle conversion efficiency) is not very significant since the new biofuel is going to be used in blends not requiring for specific engines. In addition, carbon dioxide emissions resulting from the combustion of biofuels can be assumed to offset the carbon dioxide captured during crop growth (Zamboni *et al.*, 2009b). Thus, the set of LCA stages s considered in the evaluation is given by biomass production (*bp*), biomass pre-treatment (*bpt*), biomass transport (*bt*) and fuel production *(fp*); the emission credits (*ec*) in terms of GHG savings (as a result of goods or energy displacement by process side products end-use) are accounted for as a pseudo-life cycle stage. Accordingly:

$s \in S \equiv \{bp, bpt, bt, fp, ec\}$.

The GHG contribution to global warming is captured by inventorying CO_2, CH_4, N_2O emissions, grouped together in a single indicator expressed as carbon dioxide equivalent emissions (CO_2-eq), according to the concept of 100 year global warming potentials as specified by IPCC (2007).

The design problem can be formulated as follows. Given are the following inputs:

- technical (yields) and economic (capital and operating costs) parameters as a function of biomass type and production technologies;
- biofuel and energy market characteristics;
- transport costs and emissions;
- environmental burdens of each LCA stage as a function of biomass type and ethanol technology;
- biomass and carbon market uncertainty.

The objective is to determine the optimal system configuration which maximises the expected financial profitability assessing the influence of feedstock and carbon costs volatility within an emissions allowances trading scheme. Therefore, the key variables to be optimised are:

- bioethanol facilities capacity, technology and biomass selection;
- financial performance of the system over the long-term;

- system impact on global warming.

The problem refers to a single bioethanol production plant, which is supplied with the necessary biomass (corn, poplar, willow, miscanthus, stover, barley straw, wheat straw, switchgrass) through cultivating a hypothetical land surface of limited extension. Dry Grind Process (DGP) with two different end uses of the main by-product (i.e. DDGS) is accounted for starchy biomass-based ethanol. Several technological options are considered for cellulosic biomass: Dilute Acid Hydrolysis (DAP), Steam Explosion (SEP) and Gasification Biosynthesis (GBP) processes. Considering the high level of uncertainty surrounding the technical performance of the GBP production technologies, here two scenarios are accounted for considering different stage of technological development (e.g., GBP_{high}, GBP_{ave}) according to the description provided in chapter 2.

The financial optimisation carried out along with setting minimum stricter thresholds of GHG emissions reductions as the baseline of a carbon trading scheme, is focused on providing the best decisions in terms of biomass and technology for ethanol production in using a certain land available. The economics of the upstream production network will be assessed by means of SCA techniques, focusing on biomass cultivation type, ethanol production capacity and technology assignment, and integrated with a LCA methodology to consider the impact of the system on global warming including also considerations about Soil Organic Carbon (SOC) effects. The emerging bioethanol production in Italy from 2010 to 2029 will be assessed as a case study.

4.3 Mathematical formulation

The mathematical framework has been formulated as a multi-period MILP problem based on the modelling approaches commonly adopted in the strategic design of multi-echelon SCs (Sahinidis *et al.*,1989; Tsiakis *et al.*, 2001). It also embodies features addressing capacity planning and technology selection (Hugo and Pistikopoulos, 2005; Liu *et al.*, 2007) of fuel systems design. A two-stage stochastic programming based on a scenario planning approach is used to capture uncertainty on biomass and carbon costs (You *et al.*, 2009). Feedstock cost and carbon cost parameters are assumed to obey a discrete probability distribution so as to represent uncertainty via several possible realisations (scenarios). Although other sources of uncertainty (e.g., the ethanol selling price or oil and natural gas prices) may also affect the optimisation results, the above two parameters are those impacting more on the technological choices in terms of their relative profitability and have therefore been considered in this study. In particular, it is widely known that biomass cost represents the most important contribution to operating costs sharing about 40-80% of the total (Petrou and Pappis, 2009). A scenario is described by the value of the uncertain parameter with the associated probability. The uncertain parameters values have been represented by randomly sampled scenarios *sc* ranging between 1-*NS*, where *NS* = 35, per each time interval *t*, determined using pseudorandom number generation; they are assigned an equiprobability value $\pi_{sc} = 1/NS$.

The model is structured as follows. First the model objective function (i.e. the expected Net Present Value) is introduced by discussing the modelling assumptions with concern to the representation of cash flows and capital investment. Then, the stochastic framework is dealt with according to a two-stage approach splitting 'here-and-now' decisions from 'wait-and-see' ones. Later, the effect on the system profitability of GHG emissions according to a CO_2 trading scheme is incorporated in the model. The implementation of some logical constraints to ensure sensible solutions is finally presented.

4.3.1. Definition of the economic objective function

The objective function to be maximised in configuring the system, Obj_{eco}, is the *eNPV* [€]:

$$Obj_{eco} = eNPV = \sum_{sc} \pi_{sc} \cdot NPV_{sc} \tag{4.1}$$

where NPV_{sc} [€] is the Net Present Value per each scenario *sc* and is defined according to:

$$NPV_{sc} = \sum_{i,k,t} \left(CF_{i,k,sc,t} \cdot df_t \right) - \sum_{i,k} TCI_{i,k}, \quad \forall sc \tag{4.2}$$

$CF_{i,k,sc,t}$ [€/y] represents the annual cash flow at market scenario *sc* and $TCI_{i,k}$ [€] stands for the capital investment related to the establishment of a production facility treating biomass *i* with technology *k*. The parameter df_t is the discount factor related to each year *t* (Table 4.1) and stated by Eq. (4.3) according to Douglas (1988).

$$df_t = \left(\frac{1}{1+\zeta} \right)^t, \quad \forall t \tag{4.3}$$

where ζ is the interest rate (equal to 10%, according to Sharpe (1964), as already discussed in chapter 3).

Numerical details concerning the specific linearisation routine adopted for dealing with the nonlinearity issues for the accurate estimation accounting for scale effects of $TCI_{i,k}$, will be addressed in §4.3.3.

The annual cash flow $CF_{i,k,sc,t}$ of Eq. (4.2) is given by summing up the profit before taxes $PBT_{i,k,sc,t}$ [€/y] and the depreciation charge $D_{i,k,t}$ [€/y], and by deducting the taxes $TAX_{i,k,sc,t}$ [€/y]:

$$CF_{i,k,sc,t} = PBT_{i,k,sc,t} - TAX_{i,k,sc,t} + D_{i,k,t}, \quad \forall i,k,sc,t \tag{4.4}$$

A linear approach is used to evaluate $D_{i,k,t}$ and hence a fixed quota, dk_t, is applied to depreciate the total capital investment $TCI_{i,k}$, as shown by:

$$D_{i,k,t} = TCI_{i,k} \cdot dk_t\,, \quad \forall i,k,t \tag{4.5}$$

A depreciation plan covering 7 years of the plant lifetime has been set and dk_t value has been set according to the conventional procedure for chemical industry (portaleaziende, 2011) (see Table 4.1).

Table 4.1 *Yearly discount factor df_t for the cash flows; yearly depreciation quota dk_t; unitary selling price $MP_{j,t}$ for product j = DDGS at time t.*

t [year]	**df_t**	**dk_t**	**$MP_{'DDGS'}$[€/t]**
1	0.91	0.0875	300
2	0.83	0.175	300
3	0.75	0.175	300
4	0.68	0.175	300
5	0.62	0.175	300
6	0.56	0.175	300
7	0.51	0.0375	200
8	0.47	0	200
9	0.42	0	200
10	0.39	0	200
11	0.35	0	200
12	0.32	0	200
13	0.29	0	200
14	0.26	0	100
15	0.24	0	100
16	0.22	0	100
17	0.20	0	100
18	0.18	0	100
19	0.16	0	100
20	0.15	0	100

The gross profit, $PBT_{i,k,sc,t}$, is defined as the difference between the revenues, $Inc_{i,k,sc,t}$ [€/y], and the cost terms accounting for depreciation, $D_{i,k,t}$, and the operating costs $VarC_{i,k,sc,t}$ [€/y]:

$$PBT_{i,k,sc,t} = Inc_{i,k,sc,t} - VarC_{i,k,sc,t} - D_{i,k,t}\,, \quad \forall i,k,sc,t \tag{4.6}$$

The term $Inc_{i,k,sc,t}$ is derived summing up the total annual revenues obtained both from selling the products j, and from emissions allowances trading:

$$Inc_{i,k,sc,t} = \sum_j P^T_{i,j,k,sc,t} \cdot MP_{j,t} + MP\_All_{sc,t} \cdot \left(S\_All_{i,k,sc,t} - P\_All_{i,k,sc,t}\right), \quad \forall i,k,sc,t \quad (4.7)$$

where the product selling price $MP_{j,t}$ [€/t or €/MWh], applied to the corresponding rate of product *j* ($P^T_{i,j,k,sc,t}$, [t/y] or [MWh/y]), is kept constant for ethanol and power (set equal to 710 €/t and 67.18 €/MWh, respectively, according to Zamboni *et al.* (2009a)), while a gradual depreciation is considered for DDGS between 300 €/t to 100 €/t according to the assumptions by Dal-Mas *et al.* (2011) (see Table 4.1). The net amount of permits to emit (i.e., the difference between sold and purchased allowances, $S\_All_{i,k,sc,t}$ and $P\_All_{i,k,sc,t}$, [kg CO_2-eq/y]) gives a contribution to the business revenues and is multiplied by the allowances price $MP\_All_{sc,t}$ [€/kg CO_2-eq] for scenario *sc* and time *t*. The stochastic parameter $MP\_All_{sc,t}$ is defined through randomly sampled scenarios *sc* of carbon cost per each time period *t*. It is also assumed that the carbon costs maximum and minimum bounds may grow linearly, thus assuming that uncertainty increases with time. The maximum possible values increase from 0.025 in the first year up to 0.1 €/kg CO_2-eq at the end of the time horizon, while minimum ones change from 0.015 up to 0.03 €/kg CO_2-eq.

$VarC_{i,k,sc,t}$ involves biomass purchase costs ($BPC_{i,k,sc,t}$ [€/y]), biomass transport costs ($TC_{i,k,sc,t}$ [€/y]) and ethanol production costs ($EPC_{i,k,sc,t}$ [€/y]). Accordingly:

$$VarC_{i,k,sc,t} = BPC_{i,k,sc,t} + TC_{i,k,sc,t} + EPC_{i,k,sc,t}, \quad \forall i,k,sc,t \quad (4.8)$$

$BPC_{i,k,sc,t}$ and $TC_{i,k,sc,t}$ are estimated by multiplying the biomass rate entering the conversion plant, $Cap_{i,k,sc,t}$ [t/y], by the unit purchase and transport cost, $UPC_{i,sc,t}$ [€/t] and $UTC_{i,}$ [€/t] respectively. A stochastic approach is also used to handle volatility on raw materials costs $UPC_{i,k,sc,t}$: pseudo-random scenarios per each time period have been generated within cost bounds proposed in the literature (see Table 4.2). Accordingly:

$$BPC_{i,k,sc,t} = Cap_{i,k,sc,t} \cdot UPC_{i,sc,t}, \quad \forall i,k,sc,t \quad (4.9)$$

$$TC_{i,k,sc,t} = Cap_{i,k,sc,t} \cdot UTC_i, \quad \forall i,k,sc,t \quad (4.10)$$

$EPC_{i,k,sc,t}$ is defined as a linear function of the total production rate of ethanol, as it has already been discussed in chapter 3, $P^T_{i,'ethanol,k,sc,t}$ [t/y]:

$$EPC_{i,k,sc,t} = coef_{'1',i,k} \cdot P^T_{i,'ethanol',k,sc,t} + coef_{'2',i,k} \cdot Y_{i,k}, \quad \forall i,k,sc,t \quad (4.11)$$

$Y_{i,k}$ is the binary variable accounting for whether a facility comprises the conversion technology *k* for biomass *i* or not.

The product *j* includes ethanol, DDGS and electricity whose production rate $P^{T}_{i,'ethanol,k,sc,t}$ are subject to yields constraints depending on the processing technology *k* and the starting biomass *i*:

$$P^{T}_{i,j,k,sc,t} = Cap_{i,k,sc,t} \cdot \gamma_{i,j,k}\,, \quad \forall i,k,sc,t;\; j = ethanol,DDGS \tag{4.12}$$

$$P^{T}_{i,j,k,sc,t} = \frac{P^{T}_{i,'ethanol',k,sc,t} \cdot \gamma_{i,j,k}}{\rho}\,, \quad \forall i,k,sc,t;\; j = power \tag{4.13}$$

where $\gamma_{i,j,k}$ represents the yield of product *j* from technology *k* using biomass *i* (ρ is the ethanol density, 0.7891 kg/$L_{ethanol}$).

The mathematical routine to determine an accurate estimation of the taxation applied is reported in §4.3.4.

Table 4.2 *Biomass cost assumptions for random sampling in the stochastic analysis.*

biomass	corn	poplar	willow	miscanthus
$UPC_{min,i}$ $UPC_{max,i}$[€/t]	127-221 (Dal-Mas *et al.*, 2011)	44.1-63.7 (agriforenergy, 2011)	44.1-63.7 (agriforenergy, 2011)	37.57-59.35 (Schade and Wiesenthal, 2011)
biomass	**corn stover**	**wheat straw**	**barley straw†**	**switchgrass**
$UPC_{min,i}$ $UPC_{max,i}$[€/t]	20.31-32.07 (Schade and Wiesenthal, 2011)	25-110 (IT, 2010b)	20.31-32.07	28.73-45.39 (Schade and Wiesenthal, 2011)

† Values extended from wheat straw

4.3.2 Planning model

In the two-stage stochastic framework, the problem is decomposed into first stage-decisions not dependent on future scenarios, according to a non-anticipativity constraint, and two-stage decisions whose equations include uncertain parameters and variables. When dealing with a design problem in presence of uncertainty, plant capacity and technology options may be treated as 'here-and-now' decisions, taken at the first time period (t = 1), before resolution of uncertainty in the future scenarios *sc*. On the other side, the successive decisions ($t \geq 2$) about limited capacity adjustments are possible according to a 'wait-and-see' approach after the uncertainties are revealed. Accordingly, the related equations and variables are dependent on the scenario *sc*.

The key variable of the optimisation framework is the amount of feedstock *i* converted to ethanol via facility *k* at time t = 1, $In\_Cap_{i,k}$ [t/y]. As previously explained, the first stage planning decisions (capacity and technology selection as well as capital expenditures $TCI_{i,k}$) are taken before resolution of the uncertainty:

$$In\_Cap_{i,k} = \sum_p \lambda_{i,k,p} \cdot BN_{i,k,p}, \quad \forall i,k \tag{4.14}$$

$$TCI_{i,k} = \sum_p \lambda_{i,k,p} \cdot CI_{i,k,p}, \quad \forall i,k \tag{4.15}$$

where $BN_{i,k,p}$ [t/y] is the nominal feedstock rate for each plant size p and $CI_{i,k,p}$ [€] is a parametric set needed to evaluate the capital investment related to the establishment of a production plant of size p and technology k. A purposed-devised linearisation model, whose modelling core is centred on the use of continuous positive variables $\lambda_{i,k,p}$ ranging between 0-1, has been integrated within the stochastic formulation to achieve an accurate estimation of the capital expenditure. The complete linearisation framework will be detailed explained in §4.3.3.

Moving to the second stage decision, the amount $Cap_{i,k,sc,t}$ [t/y] of feedstock i converted to ethanol via facility k depending on biomass and carbon cost scenario sc at time $t \geq 2$ is taken as optimisation variable. In this second stage, decisions about capacity expansion ($I\_Cap_{i,k,sc,t}$, [t/y]) or reduction ($D\_Cap_{i,k,sc,t}$, [t/y]) can be taken:

$$Cap_{i,k,sc,t} = Cap_{i,k,sc,t-1} + I\_Cap_{i,k,sc,t} - D\_Cap_{i,k,sc,t}, \quad \forall i,k,sc;\ t \geq 2 \tag{4.16}$$

Note that for $t = 1$, the first stage decision variable does not depend on the scenarios and thus it holds:

$$Cap_{i,k,sc,t} = In\_Cap_{i,k}, \quad \forall i,k,sc;\ t = 1 \tag{4.17}$$

$I\_Cap_{i,k,sc,t}$, and $D\_Cap_{i,k,sc,t}$, are constrained as follows:

$$\gamma_{i,j,k} \cdot I\_Cap_{i,k,sc,t} \leq Z_{i,k,sc,t} \cdot UpperLimit, \quad \forall i,k,sc;\ t \geq 2 \tag{4.18}$$

$$\gamma_{i,j,k} \cdot D\_Cap_{i,k,sc,t} \leq \left(1 - Z_{i,k,sc,t}\right) \cdot UpperLimit, \quad \forall i,k,sc;\ t \geq 2 \tag{4.19}$$

$$\gamma_{i,j,k} \cdot \sum_t I\_Cap_{i,k,sc,t} \leq UpperLimit, \quad \forall i,k,sc,t \tag{4.20}$$

$$\gamma_{i,j,k} \cdot \sum_t D\_Cap_{i,k,sc,t} \leq UpperLimit, \quad \forall i,k,sc,t \tag{4.21}$$

$$I\_Cap_{i,k,sc,t}, D\_Cap_{i,k,sc,t} = 0, \quad \forall i,k,sc;\ t = 1 \tag{4.22}$$

$Z_{i,k,sc,t}$ is the binary variable setting whether an already established capacity is increased ($Z_{i,k,sc,t} = 1$) at time $t \geq 2$. *UpperLimit* is intended as a maximum and reasonable allowable size change (20000 t/y of ethanol). Note that it is not possible to have a simultaneous capacity expansion and reduction (Eq. (4.18-4.19)); Eq. (4.22) states that capacity adjustment cannot occur at time $t = 1$.

$Cap_{i,k,sc,t}$ is lower- and upper-bounded according to the minimum and maximum capacities allowed for conversion technology k per each biomass i: $CapMin_{i,k}$ and $CapMax_{i,k}$ [t/y] (reported in Table 4.3) represent, respectively, the annual minimum and maximum rates of biomass i allowed for a plant of technology k. Accordingly:

$$Cap_{i,k,sc,t} \le Y_{i,k} \cdot CapMax_{i,k}, \quad \forall i,k,sc,t \tag{4.23}$$

$$Cap_{i,k,sc,t} \ge Y_{i,k} \cdot CapMin_{i,k}, \quad \forall i,k,sc,t \tag{4.24}$$

Table 4.3 *Minimum and maximum biomass rate allowed to the plant (CapMin and CapMax [t/y]).*

CapMin$_{i,k}$						
biomass	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
corn	234568	234568				
poplar	-	-	489691	470297	499015	699172
willow	-	-	512129	490639	506329	708955
miscanthus	-	-	324370	312886	369830	518064
corn stover	-	-	393987	370010	542083	543634
wheat straw	-	-	416667	388151	523056	529617
barley straw	-	-	413493	385591	537102	543634
switchgrass	-	-	435530	406200	470880	567164
CapMax$_{i,k}$						
biomass	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
corn	913580	913580				
poplar	-	-	1907216	1831683	1943533	2723091
willow	-	-	1994609	1910910	1972019	2761194
miscanthus	-	-	1263338	1218608	1440389	2017723
corn stover	-	-	1534474	1441091	2111270	2117310
wheat straw	-	-	1622807	1511747	2037164	2062718
barley straw	-	-	1610446	1501776	2091873	2117310
switchgrass	-	-	1696275	1582042	1833953	2208955

The overall biomass entering the conversion plant, is bounded according to

$$Cap_{i,k,sc,t} \le BA_{i,t}, \quad \forall i,k,sc,t \tag{4.25}$$

where

$$BA_{i,t} = LA \cdot BY_{i,t} \cdot q_i, \quad \forall i,t \tag{4.26}$$

BA_i [t/y] represents the biomass availability and depends on agronomic-related factors (i.e. cultivation yields, $BY_{i,t}$ [t/ha]), on the maximum biomass utilisation quota for biofuel production q_i, and the available land for cropping LA (set equal to 1310000 ha).

4.3.3 Linearisation model

Capital costs $TCI_{i,k}$ follow the usual power formulation for scale effect on the business economics:

$$TCI_{i,k} = a_{i,k} \cdot In\_Cap_{i,k}^{r_k}, \quad \forall i,k \tag{4.27}$$

where $In\_Cap_{i,k}$ represents the biomass i entering the conversion plant k; the power factor, r_k, is dependent on the technology, while $a_{i,k}$, is specific per each technology k and biomass i.
Following the approach suggested by Liu *et al.* (2007), $TCI_{i,k}$ was linearised by introducing two sets of discrete parameters (Eq. (4.28-4.29), recalling Eq. (4.14-4.15)), $BN_{i,k,p}$ and $CI_{i,k,p}$, which represent the biomass need and the capital investment for a production plant of size p, technology k and biomass i, respectively. A set of linear combinations, where $\lambda_{i,k,p}$, as already stated, is a positive continuous variable ranging in 0-1, is adopted for determining the actual capital investment, $TCI_{i,k}$:

$$In\_Cap_{i,k} = \sum\nolimits_p \lambda_{i,k,p} \cdot BN_{i,k,p}, \quad \forall i,k \tag{4.28}$$

$$TCI_{i,k} = \sum\nolimits_p \lambda_{i,k,p} \cdot CI_{i,k,p}, \quad \forall i,k \tag{4.29}$$

$BN_{i,k,p}$ and $CI_{i,k,p}$ are related according to:

$$CI_{i,k,p} = a_{i,k} \cdot BN_{i,k,p}^{r_k}, \quad \forall i,k,p \tag{4.30}$$

The power relation of Eq. (4.27) is linearised by dividing the overall capacity range into several intervals p (specific capacity is assigned through the parameter $BN_{i,k,p}$ as reported in Table 4.4, so as to obtain the size-specific capital investment cost coefficient ($CI_{i,k,p}$).
The following logical conditions for $\lambda_{i,k,p}$ must hold (Liu *et al.*, 2007):

$$\lambda_{i,k,p} \geq 0, \quad \forall i,k,p \tag{4.31}$$

$$\lambda_{i,k,p} - y_{i,k,p} - y_{i,k,p-1} \leq 0, \quad \forall i,k,p \tag{4.32}$$

$$y_{i,k,p} = 0, \quad \forall i,k; \; p = 6 \tag{4.33}$$

$$\sum\nolimits_p y_{i,k,p} = Y_{i,k}, \quad \forall i,k;\ p \in sub_p \tag{4.34}$$

This introduces a new set of binary variables, $y_{i,k,p}$ which helps bounding the continuous value of $\lambda_{i,k,p}$ within the pertinent range. Besides, $\lambda_{i,k,p}$ must be constrained by the actual planning decision:

$$\sum\nolimits_p \lambda_{i,k,p} = Y_{i,k}, \quad \forall i,k \tag{4.35}$$

When technology k is chosen, $Y_{i,k}$ is set equal to 1 and then the sum of $\lambda_{i,k,p}$ must be 1.

Table 4.4 *Parameter $BN_{i,p,k}$ representing the biomass i need [t/y] to the conversion facility of technology k and plant scale p.*

k \ p	**1**	**2**	**3**	**4**	**5**	**6**
corn						
DGP	296296	339506	462963	617284	771605	851852
DGP-CHP	296296	339506	462963	617284	771605	851852
poplar						
DAP	618557	708763	966495	1288660	1610825	1778351
SEP	594059	680693	928218	1237624	1547030	1707921
GBP_{high}	630335	722259	984898	1313198	1641497	1812213
GBP_{ave}	883165	1011960	1379945	1839926	2299908	2539098
willow						
DAP	646900	741240	1010782	1347709	1684636	1859838
SEP	619755	710136	968367	1291156	1613944	1781795
GBP_{high}	639574	732845	999334	1332445	1665556	1838774
GBP_{ave}	895522	1026119	1399254	1865672	2332090	2574627
miscanthus						
DAP	409731	469484	640205	853606	1067008	1177977
SEP	395224	452861	617538	823384	1029230	1136270
GBP_{high}	467153	535280	729927	973236	1216545	1343066
GBP_{ave}	654397	749830	1022495	1363327	1704158	1881391
corn stover						
DAP	497667	570244	777605	1036807	1296008	1430793
SEP	467381	535540	730282	973710	1217137	1343720
GBP_{high}	684736	784593	1069900	1426534	1783167	1968616
GBP_{ave}	686695	786838	1072961	1430615	1788269	1974249
wheat straw						
DAP	526316	603070	822368	1096491	1370614	1513158
SEP	490296	561798	766088	1021450	1276813	1409602
GBP_{high}	660702	757054	1032347	1376462	1720578	1899518
GBP_{ave}	668990	766551	1045296	1393728	1742160	1923345
barley straw						
DAP	522307	598477	816104	1088139	1360174	1501632
SEP	487062	558092	761035	1014713	1268392	1400304
GBP_{high}	678445	777385	1060071	1413428	1766784	1950530
GBP_{ave}	686695	786838	1072961	1430615	1788269	1974249
switchgrass						
DAP	550143	630372	859599	1146132	1432665	1581662
SEP	513095	587921	801710	1068947	1336184	1475147
GBP_{high}	594796	681537	929368	1239157	1548947	1710037
GBP_{ave}	716418	820896	1119403	1492537	1865672	2059701

4.3.4 Taxation model

The taxation charge is applied only when a positive annual gross profit is obtained; moreover, $TAX_{i,k,sc,t}$, being a function of $PBT_{i,k,sc,t}$, would make Eq. (4.4) a non-linear relation. Hence, the problem is overcome through the introduction of an indicator variable, $V_{i,k,sc,t}$, so that if $PBT_{i,k,sc,t}$ results positive $V_{i,k,sc,t}$ takes a value of 0, otherwise 1 is assigned.
The taxation is set therefore according to the following routine:

$$TAX_{i,k,sc,t} \geq Tr \cdot PBT_{i,k,sc,t} - V_{i,k,sc,t} \cdot M, \quad \forall i,k,sc,t \tag{4.36}$$

$$M \cdot \left(1 - V_{i,k,sc,t}\right) \geq PBT_{i,k,sc,t}, \quad \forall i,k,sc,t \tag{4.37}$$

$$-M \cdot V_{i,k,sc,t} \leq PBT_{i,k,sc,t}, \quad \forall i,k,sc,t \tag{4.38}$$

$$TAX_{i,k,sc,t} \geq 0, \quad \forall i,k,sc,t \tag{4.39}$$

where Tr is the taxation rate (set equal to 36%, which represents a conservative approximation with respect to the current Italian taxation) and M is a constant (set equal to 1000 M€) representing the hypothetical upper bound for $PBT_{i,k,sc,t}$. If $PBT_{i,ksc,t}$ is positive, Eq. (4.37) imposes $V_{i,k,sc,t}$ equal to 0, and thus, as Eq. (4.36) holds, $TAX_{i,ksc,t}$ is applied; conversely, if $PBT_{i,k,sc,t}$ is negative, $V_{i,k,sc,t}$ is set equal to 1 by Eq. (4.38), and, according to Eq. (4.36) and (4.39), $TAX_{i,k,sc,t}$ is set equal to 0.

4.3.5 Environmental model

CO_2 emission trading is modelled according to the approach by Bojarski *et al.* (2009) and referring to the Californian ‘Low Carbon Fuel standard’ (ARB, 2011):

$$TI_{i,k,sc,t} \leq MaxCO2_{i,k,sc,t} + P\_All_{i,k,sc,t} - S\_All_{i,k,sc,t}, \quad \forall i,k,sc,t \tag{4.40}$$

Eq. (4.40) states that $TI_{i,k,sc,t}$ [kg CO_2-eq/y], the total equivalent CO_2 emissions occurring in the SC in period t must be equal to the cap $MaxCO2_{i,k,sc,t}$ [kg CO_2-eq/y] plus the extra credits bought to emit $P\_All_{i,k,sc,t}$, and minus the sold credits $S\_All_{i,k,sc,t}$. The cap $MaxCO2_{i,k,sc,t}$ has been defined as a regulation-based limit on the total emissions from fuel SC, by taking as a reference the EU policy framework (EC, 2009). Accordingly:

$$MaxCO2_{i,k,sc,t} = TI^{*}_{i,k,sc,t} \cdot \left(1 - GHG_{red}\right), \quad \forall i,k,sc,t \tag{4.41}$$

where $TI^{*}_{i,k,sc,t}$ [kg CO_2-eq/y] is the GHG emitted from production and utilisation of the same amount of conventional fuel (i.e., GJ of gasoline), while GHG_{red} represents the GHG emissions savings required to biofuels for eligibility for public support. GHG_{red} is set equal to 35%, 50% and 60% according to EU regulation (EC, 2009). Eq. (4.40) and (4.41) are stated according to the following hypotheses (Bojarski *et al.*, 2009): i) any quota of permits can be sold or obtained in the emission market; ii) the emission trading occurs yearly and each emission allowance transaction takes place only at the end of each period; iii) the emission trading scheme is evaluated on the total equivalent CO_2 emission occurring in the SC.

The total GHG impact, $TI_{i,k,sc,t}$, must consider the contribution of each life cycle stage s as well as the effect of emission credits coming from by-products end-use. Accordingly:

$$TI_{i,k,sc,t} = \sum_{s} Imp_{i,k,s,sc,t}, \quad \forall i,k,sc,t \tag{4.42}$$

where $Imp_{i,k,s,sc,t}$ [kg CO_2-eq/y] is the GHG emission rate resulting from the operation of each single stage s at time t and scenario sc when a technology k using biomass i is chosen. The GHG emission rate is provided by:

$$Imp_{i,k,s,sc,t} = f_{i,k,s,t} \cdot F_{i,k,s,sc,t}, \quad \forall i,k,s,sc,t \tag{4.43}$$

which is the core of the environmental framework, where each LCA stage impact is evaluated by multiplying the corresponding emission factor $f_{i,k,s,t}$ [kg CO_2-eq/unit] by the specific reference flow $F_{i,k,s,sc,t}$ [units/y]. In particular, $F_{i,k,s,sc,t}$ is represented by the feedstock rate, $Cap_{i,k,sc,t}$ for $s = \{bp,bt,bpt\}$, while is defined equal to the main product rate $P^{T}_{i,j,k,sc,t}$ for $s = \{fp,ec\}$.

The effect of by-product allocation on emissions discount, is addressed according to the so-called substitution procedure, e.g. by incorporating the effects of by-products final destination (CONCAWE, 2007), as already performed in chapter 3. According to this, the emission credits derived from the displacement of alternative goods with by-products are subtracted from the primary product (ethanol) total GHG emissions. For instance, in the corn-based bioethanol system, DDGS could be used either as a substitute for cattle feed or as a fuel for CHP generation (or, although not considered here, in wet form as a feedstock for anaerobic digestion). On the other hand, in cellulose-based processes, lignin is exploited to produce electricity and a power excess can be sold to the national grid, as already discussed in chapter 2 and 3.

4.3.4. Logical constraints

Non-negativity constraints are set for key design variables:

$$Cap_{i,k,sc,t}, I\_Cap_{i,k,sc,t}, D\_Cap_{i,k,sc,t}, P\_All_{i,k,sc,t}, S\_All_{i,k,sc,t} \geq 0, \quad \forall i,k,sc,t \qquad (4.44)$$

The two decision variables $Z_{i,k,sc,t}$ and $Y_{i,k}$, are not independent, as capacity adjustments can happen only after its facility establishment, therefore:

$$Z_{i,k,sc,t} - Y_{i,k} \leq 0, \quad \forall i,k,sc,t \qquad (4.45)$$

Each technology *k* can convert only one type *i* of biomass and therefore the sum of the decision variable $Y_{i,k}$ over the sets *(i,k)* must be equal to 1:

$$\sum_{i,k} Y_{i,k} = 1, \quad \forall i,k \qquad (4.46)$$

The decision variable $Y_{i,k}$ is set to 0 for the couples (*i,k*) not included in the subset of the allowed combinations. In this way the optimiser cannot allocate a first generation feedstock to a second generation technology and vice versa.

4.4 Case study

A real world case study has been formulated to illustrate the applicability of the proposed approach in steering the strategic design and planning of first and second generation bioethanol systems. The emerging bioethanol infrastructure in Northern Italy was chosen to the scope. Towards reaching the goal of diversifying the feedstocks portfolio and supporting energy security, several starting raw materials all widely available in Northern Italy are investigated (i.e. corn, poplar, willow, miscanthus, corn stover, wheat and barley straw, switchgrass).

The biofuels SC has been modelled according to the approach by Zamboni *et al.* (2009a).

The environmental frame proposed by Zamboni *et al.* (2009b) has been adopted to evaluate the specific corn-based modelling parameters. The environmental assessment of the biomass-to-ethanol pathway has followed the fuel-cycle model developed by ANL (2006) and Luo *et al.* (2009b).

The potential effect on the carbon stock variation coming from biomass production has been addressed, too. While annual and intensive crops are considered to reduce the amount of organic carbon stored in the soil (SOC), perennial crops can promote carbon sequestration. Although this issue is still intensely debated (Stephenson *et al.*, 2010), it may play a critical role in an emissions trading scheme. Therefore, two cases have been tackled to assess this effect: instance I does not encompass any SOC-related effect; instance II includes carbon sequestration effects.

4.4.1 Biomass production

In relation to cultivation of the feedstocks, specific yield values ($BY_{i,t}$) (Eq. (4.26)), are retrieved from the literature and reported in Table 4.5. Perennial crops are assumed to exhibit biomass yield dependence with time; here it is assumed that their first year growth rate is only 64% of the steady state value (Singh *et al.*, 2010). To avoid potential risk of local conflict between 'biomass for food' and 'biomass for fuel', the possibility of devoting completely the destination of first generation crops to bioenergy is prevented. A maximum limit on the availability of corn for biofuels generation has been defined, $q_{i,}$ in Eq. (4.26), equal to 14.3% for corn (Zamboni *et al.*, 2009a). Lignocellulosic biomass availability levels for bioethanol production has been set, too, according to sustainability levels: 33% for residues, to preserve soli nutrients level (extending the assumptions of chapter 3 referring to corn stover), 50% for SRF (Short Rotation Forestry) with 2-years-cycle of growth, and 100% for the remaining energy crops. Estimation of impacts in biomass production relies on time dependent emissions factors ($f_{i,k,'bp',t}$, in Eq. (4.43)), as needed to handle agricultural activities over time (e.g., for cultivating energy crops). SOC effect has been also embedded in the $f_{i,k,'bp',t}$ to determine the influences on the total organic carbon stored in the soil due to cultivation practices (see Table 4.6).

Table 4.5 *Biomass agricultural yields $BY_{i,t}$ at the steady state ($t \geq 2$) and feedstocks composition.*

Biomass	**$BY_{i,t}$ ($t \geq 2$) [t/ha]**	**Feedstock composition**
corn	9 (see chapter 3)	Zamboni *et al.* (2009a)
poplar	18.49 (Facciotto *et al.*, 2006)	USDOE (1999)
willow	19.35 (Facciotto *et al.*, 2006)	Sassner *et al.* (2008)
miscanthus	18.632 (Monti *et al.*, 2009)	Collura *et al.* (2006)
corn stover	9 (see chapter 3)	USDOE (2002)
wheat straw	5.844 (ISTAT, 2011; Kim and Dale, 2004)	Linde *et al.* (2007)
barley straw	4.90 (ISTAT, 2011)	Viola *et al.* (2008)
switchgrass	14.4 (Monti *et al.*, 2009)	Laser *et al.* (2009)

In this framework, corn stover, barley and wheat straw are given a residual value, thus, it is assumed that they are available independently of the main crop destination to bioethanol production.

4.4.2. Biomass pre-treatment and transport

Biomass pre-treatment deals with the drying and storage operations after biomass harvesting and collection. Even if such costs are already included in the biomass production costs ($UPC_{i,sc,t}$ in Eq. (4.9)), the related environmental impact ($Imp_{i,k,'bpt',sc,t}$, Eq. 4.42-4.43) needs to be addressed separately from the production stage by defining specific emissions factors ($f_{i,k,'bpt',t}$ in Eq. (4.43)).

Table 4.6 *Assumptions and data for the biomass cultivation phase.*

biomass	**corn**	**poplar**	**willow**	**miscanthus**
SOC	Brandão *et al.*, 2011[a]	Sartori *et al.*, 2006	Sartori *et al.*, 2006	Andreson-Teixeira *et al.*, 2009
seed	Zamboni *et al.*, 2009b	-	-	-
rhizomes	-	-	-	Monti *et al.*, 2009, Smeets *et al.*, 2009
fertiliser	Zamboni *et al.*, 2009b	Manzone *et al.*, 2009, Zamboni *et al.*, 2009b, IEA, 2004	Manzone *et al.*, 2009, Zamboni *et al.*, 2009b	Monti *et al.*, 2009, Zamboni *et al.*, 2009b
pesticide	Zamboni *et al.*, 2009b	-	-	-
herbicide	-	Manzone *et al.*, 2009, Smeets *et al.*, 2009	Manzone *et al.*, 2009, Smeets *et al.*, 2009	Monti *et al.*, 2009, Smeets *et al.*, 2009
leaf senescence	-	Heller *et al.*, 2003[b], Zamboni *et al.*, 2009b	Heller *et al.*, 2003[b], Zamboni *et al.*, 2009b	-
fuel	Zamboni *et al.*, 2009b	Bidini *et al.*, 2006, Zamboni *et al.*, 2009b	Bidini *et al.*, 2006, Zamboni *et al.*, 2009b	Monti *et al.*, 2009, Zamboni *et al.*, 2009b
$f_{i,k,'bp't}$ [kgCO$_2$-eq/t]	489.61	establishment: 1.13 harvest year: -58.97. after harvest: -25.86 last year: -44.67	establishment: 10.85 harvest year: -52.75 after harvest: -19.64 last year: -19.33	establishment: -228.86 from II year: -135.37
Biomass	**Corn Stover**	**Wheat Straw**	**Barley Straw**[c]	**Switchgrass**
SOC	Cherubini and Ulgiati, 2010	Cherubini and Ulgiati, 2010	Cherubini and Ulgiati, 2010	Sartori *et al.*, 2006
seed	-	-	-	Monti *et al.*, 2009, Smeets *et al.*, 2009
rhizomes	-	-	-	-
fertiliser	ANL, 2006, Zamboni *et al.*, 2009b	Cherubini and Ulgiati, 2010, Zamboni *et al.*, 2009b	Cherubini and Ulgiati, 2010, Zamboni *et al.*, 2009b	Monti *et al.*, 2009, Zamboni *et al.*, 2009b
pesticide	-	-	-	-
herbicide	-	-	-	Monti *et al.*, 2009, Zamboni *et al.*, 2009b
leaf senescence	-	-	-	-
fuel	IT, 2010b, Zamboni *et al.*, 2009b	IT, 2010b, Zamboni *et al.*, 2009b	IT, 2010b, Zamboni *et al.*, 2009b	Monti *et al.*, 2009, Zamboni *et al.*, 2009b
$f_{i,k,'bp't}$ [kgCO$_2$-eq/t]	196.50	249.22	248.86	establishment: -371.94, from II year: -208.83

[a] Assumed equal to oilseed rape.

[b] Leaf senescence assume equal for both willow and poplar.

[c] Values derived from wheat straw and scaled on yield basis.

No emission factors have been assigned to cellulosic biomass drying, assuming general conditions for field-drying in Northern Italy. Conversely, the drying and storage of corn cannot be neglected: the specific emission factor was determined as in Zamboni *et al.* (2009b) and $f_{'corn',k,'bpt',t}$ is equal to 63.34 kg CO_2-eq/t of corn. In order to reduce the computational burden, the impact of the transport system has been addressed in a simplified way, averaging economic and environmental performance of several transport means. In particular, unitary transport cost (UTC_i in Eq. (4.10)) and emissions factor ($f_{i,k,'bt',t}$ in Eq. (4.43)) are respectively set equal to 23.2 €/t and 5.38 kg CO_2-eq/t of biomass (Zamboni *et al.*, 2009b).

4.4.3 Fuel production

The modelling framework has been conceived considering both first and second generation technologies as suitable options to convert biomass into ethanol. Among the available technical alternatives, four main processing designs can be identified: i) the Dry Grind Process (DGP), i.e. the standard corn-based ethanol process (Zamboni *et al.*, 2009a); ii*)* the Dilute Acid Process (DAP), where cellulosic feedstock is hydrolysed with dilute sulphuric acid (USDOE, 1999); iii) the Steam Explosion Process (SEP), where the cellulosic biomass is pre-treated with high pressure steam before being converted into ethanol (Sassner *et al.*, 2008); iv) the Gasification Biosynthesis Process (GBP), where biomass-based syngas is fermented to ethanol (Wei *et al.*, 2009). As already stated, a sensitivity analysis has been carried out on the GBP process yields and two instances corresponding to different levels of technology development have been analysed, here called as GBP_{high} and GBP_{ave}.

With concern to DGP, two instances are analysed according to how power is supplied to the plant: either by the grid (k = DGP) or by using DDGS (k = DGP-CHP) to fuel a combined heat and power (CHP) generation system. Both technical and economic characterisation relates to the work by Zamboni *et al.* (2009a). With concern to second generation technologies (i.e. DAP, SEP, GBP), the black-box system model illustrated in chapter 2, was the platform for analysing the mass balance of converting biomass into ethanol to determine biomass yields into products ($\gamma_{i,j,k}$ in Eq. (4.12-4.13)). With concern to the gasification-based technologies, the GBP_{high} option has been modelled using as modelling parameters the work by Carpenter *et al.* (2010) for the syngas composition and the approach by Wei *et al.* (2009). A more cautionary technical performance (GBP_{ave}) has been evaluated according to the work by Piccolo and Bezzo (2009) to address uncertainties in yields estimation.

The economic assessment of each cellulose-based ethanol technologies (e.g., the capital investment estimation, $CI_{i,k,p}$, as used in the linearisation model, and production processes operating costs) has been dealt with according to the approach described in chapter 2.

Table 4.7 *Technical yields, capital investment and environmental impacts/credits from the production processes considered.*

corn	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
ethanol yield	0.324	0.324	-	-	-	-
DDGS yield[a]	0.309	0	-	-	-	-
power yield[a]	0	0.743	-	-	-	-
$CI^0_{i,k}$ [b]	$70 \cdot 10^6$	$90 \cdot 10^6$	-	-	-	-
$f_{i,k,'fp't}$ [c]	1052.23	1052.23	-	-	-	-
$f_{i,k,'ec't}$ [c]	298.35	1427.38	-	-	-	-
poplar	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
ethanol yield[a]	-	-	0.2296	0.2390	0.2252	0.1608
power yield[a]	-	-	0.4619	0.3556	1.2706	1.0636
$CI^0_{i,k}$ [b]	-	-	$361 \cdot 10^6$	$327 \cdot 10^6$	$366 \cdot 10^6$	$394 \cdot 10^6$
$f_{i,k,'fp't}$ [c]	-	-	340.77	274.50	79.02	110.70
$f_{i,k,'ec't}$ [c]	-	-	274.04	210.97	753.85	631.02
willow	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
ethanol yield[a]	-	-	0.2226	0.2323	0.2252	0.1608
power yield[a]	-	-	0.4605	0.3537	1.2706	1.0636
$CI^0_{i,k}$ [b]	-	-	$364 \cdot 10^6$	$330 \cdot 10^6$	$366 \cdot 10^6$	$394 \cdot 10^6$
$f_{i,k,'fp't}$ [c]	-	-	352.71	281.72	79.34	111.15
$f_{i,k,'ec't}$ [c]	-	-	273.23	209.84	753.85	631.02
miscanthus	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
ethanol yield[a]	-	-	0.2568	0.2662	0.2252	0.1608
power yield[a]	-	-	0.4648	0.3607	1.2706	1.0636
$CI^0_{i,k}$ [b]	-	-	$329 \cdot 10^6$	$299 \cdot 10^6$	$366 \cdot 10^6$	$393 \cdot 10^6$
$f_{i,k,'fp't}$ [c]	-	-	280.42	262.59	73.17	102.51
$f_{i,k,'ec't}$ [c]	-	-	275.77	213.98	753.85	631.02
corn stover	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
ethanol yield[a]	-	-	0.2219	0.2363	0.1613	0.1608
power yield[a]	-	-	0.4666	0.3523	1.4830	1.0636
$CI^0_{i,k}$ [b]	-	-	$344 \cdot 10^6$	$308 \cdot 10^6$	$382 \cdot 10^6$	$393 \cdot 10^6$
$f_{i,k,'fp't}$ [c]	-	-	294.18	266.84	103.32	103.66
$f_{i,k,'ec't}$ [c]	-	-	276.84	209.04	879.87	631.02
wheat straw	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
ethanol yield[a]	-	-	0.2043	0.2192	0.1627	0.1608
power yield[a]	-	-	0.4652	0.3485	1.6397	1.0636
$CI^0_{i,k}$ [b]	-	-	$368 \cdot 10^6$	$328 \cdot 10^6$	$390 \cdot 10^6$	$393 \cdot 10^6$
$f_{i,k,'fp't}$ [c]	-	-	305.80	275.62	101.78	103.02
$f_{i,k,'ec't}$ [c]	-	-	276.00	206.75	972.85	631.02
barley straw	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
ethanol yield[a]	-	-	0.2113	0.2266	0.1627	0.1608
power yield[a]	-	-	0.4682	0.3512	1.6397	1.0636
$CI^0_{i,k}$ [b]	-	-	$359 \cdot 10^6$	$320 \cdot 10^6$	$390 \cdot 10^6$	$393 \cdot 10^6$
$f_{i,k,'fp't}$ [c]	-	-	293.34	250.80	102.41	103.66
$f_{i,k,'ec't}$ [c]	-	-	277.78	208.34	972.85	631.02
switchgrass	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
ethanol yield[a]	-	-	0.2094	0.2246	0.1937	0.1608
power yield[a]	-	-	0.4678	0.3503	1.2151	1.0636
$CI^0_{i,k}$ [b]	-	-	$366 \cdot 10^6$	$326 \cdot 10^6$	$364 \cdot 10^6$	$393 \cdot 10^6$
$f_{i,k,'fp't}$ [c]	-	-	301.92	253.05	86.93	104.73
$f_{i,k,'ec't}$ [c]	-	-	277.56	207.86	720.91	631.02

[a] Ethanol and DDGS yields are expressed as [t of product/t of corn] for first generation. Biofuel yields are defined as [t of ethanol/t of dry biomass]. Power excess yield is expressed as [kWh/L of ethanol]. All the values are determined according to chapter 2.

[b] $CI^{0}_{i,k}$ represents $CI_{i,k,'2'}$ (Capital Investment, €), used in (Eq. (4.28-4.30)) is evaluated for a facility of medium capacity [p = 2, corresponding to 100000 t of ethanol/y] using biomass i and technology k. Capital expenditures at different scale are evaluated as in chapter 2.

[e] $f_{i,k,'fp't}$ [kg CO_2-eq/t of ethanol], $f_{i,k,'ec't}$ [kg CO_2-eq/t of ethanol].

Table 4.8 *Coefficients for operating costs of Eq. (4.11) ($coef_{'1',i,k}$,[€/t] and $coef_{'2',i,k}$,[€/y]) for the production processes considered.*

corn	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
$coef_{'1',i,k}$	140.83	17.746	-	-	-	-
$coef_{'2',i,k}$	$2 \cdot 10^6$	$5 \cdot 10^6$	-	-	-	-
poplar	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
$coef_{'1',i,k}$	-	-	119.87	186.68	92.744	98.898
$coef_{'2',i,k}$	-	-	$7 \cdot 10^6$	$6 \cdot 10^6$	$7 \cdot 10^6$	$7 \cdot 10^6$
willow	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
$coef_{'1',i,k}$	-	-	122.11	190.26	92.746	98.902
$coef_{'2',i,k}$	-	-	$7 \cdot 10^6$	$6 \cdot 10^6$	$7 \cdot 10^6$	$7 \cdot 10^6$
miscanthus	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
$coef_{'1',i,k}$	-	-	101.58	170.36	92.695	98.837
$coef_{'2',i,k}$	-	-	$6 \cdot 10^6$	$6 \cdot 10^6$	$7 \cdot 10^6$	$7 \cdot 10^6$
corn stover	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
$coef_{'1',i,k}$	-	-	109.56	184.39	100.22	98.846
$coef_{'2',i,k}$	-	-	$7 \cdot 10^6$	$6 \cdot 10^6$	$7 \cdot 10^6$	$7 \cdot 10^6$
wheat straw	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
$coef_{'1',i,k}$	-	-	115.58	196.75	101.63	98.841
$coef_{'2',i,k}$	-	-	$7 \cdot 10^6$	$6 \cdot 10^6$	$7 \cdot 10^6$	$7 \cdot 10^6$
barley straw	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
$coef_{'1',i,k}$	-	-	113.74	191.41	101.63	98.846
$coef_{'2',i,k}$	-	-	$7 \cdot 10^6$	$6 \cdot 10^6$	$7 \cdot 10^6$	$7 \cdot 10^6$
switchgrass	**DGP**	**DGP-CHP**	**DAP**	**SEP**	**GBP$_{high}$**	**GBP$_{ave}$**
$coef_{'1',i,k}$	-	-	116.65	193.53	94.321	98.854
$coef_{'2',i,k}$	-	-	$7 \cdot 10^6$	$6 \cdot 10^6$	$7 \cdot 10^6$	$7 \cdot 10^6$

With regard to the environmental aspect, the GHG emissions from the biofuel production stage ($f_{i,k,'fp',t}$ in Eq. (4.43)) depend on the amount of chemicals, nutrients, utilities, enzymes and waste disposal required in operating the conversion facility. The global emission factors estimation relies on each term impact on global warming and they are based on the literature (Zamboni *et al.*, 2009b; Slade *et al.*, 2009; Stephenson *et al.*, 2010) and on industrial data (EUNOMIA, 2010). Emissions discounts factors ($f_{i,k,'ec',t}$ in Eq. (4.43)) are determined according to the approach by Zamboni *et al.* (2009b) for the replacement of conventional products with biomass-derived ones (e.g., DDGS can be sold as a soy-meal substitute in the animal feed market or can be used for heat and power generation replacing a certain amount of energy otherwise produced from fossil fuels). Technical, economic and environmental characterisation of all the technologies for ethanol generation is reported in Table 4.7 and 4.8.

4.5 Results and discussion

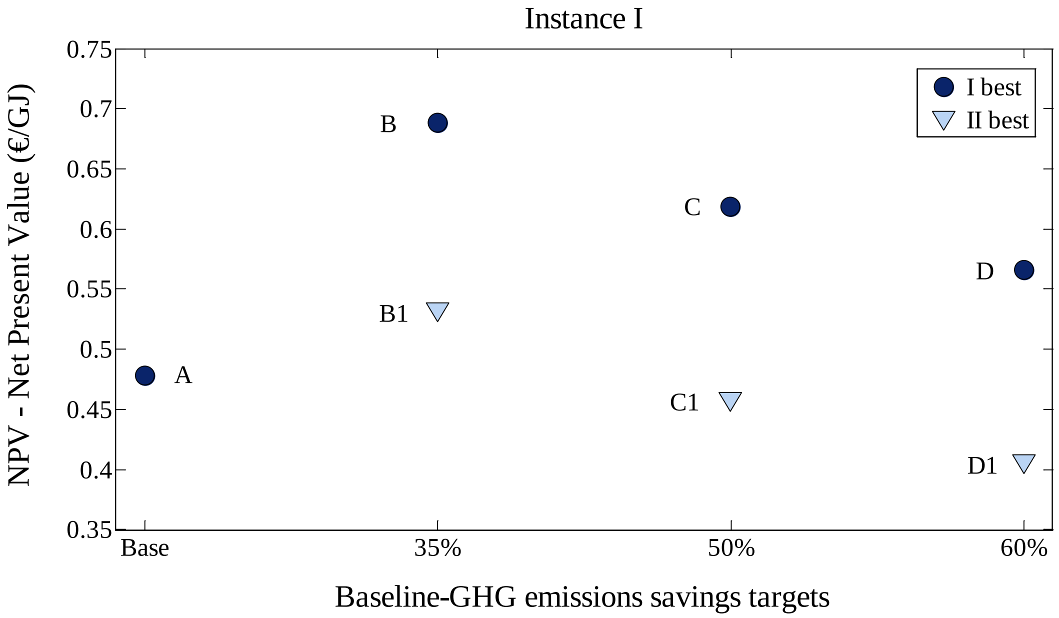
Design variables were optimised by means of the CPLEX solver in the GAMS® modelling tool (Rosenthal, 2006). In the following, the classification of optimal configurations of ethanol SC in terms of technological options and capacity planning will be shown, within a carbon trading scheme where the GHG emissions baseline is set according to the EU threshold levels (EC, 2009). For each instance (I or II), the following strategies will be taken into account: A) no carbon trading; B) carbon trading and 35% GHG emission reduction constraint; C) carbon trading and 50% GHG emission reduction constraint; D) carbon trading and 60% GHG emission reduction constraint.

4.5.1 Instance I: SOC neglected

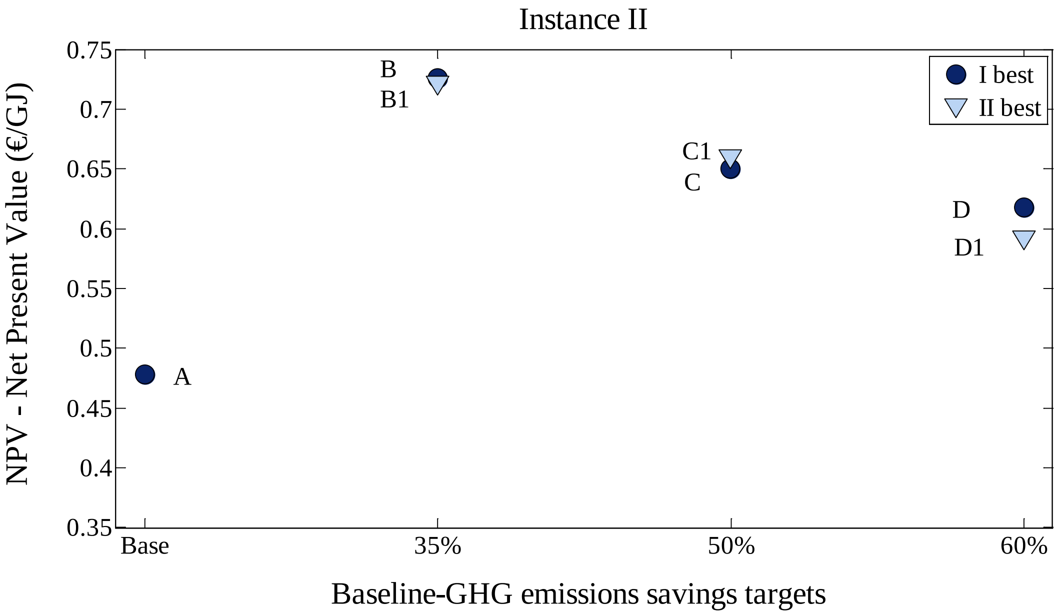
The economic optimum in absence of carbon trading and constraints on CO_2-eq emissions, (point A in Figure 4.1.a) involves the selection of a facility of large scale (286 kt/y of ethanol) operating with the standard corn-based DGP technology in which DDGS is sold as fodder. This option allows for more revenues coming from the by-product business and results in a normalised eNPV of about 0.48 €/$GJ_{ethanol}$. No GHG emissions savings threshold is set and this configuration leads to about 80.7 kg CO_2-eq/$GJ_{ethanol}$, which results in low GHG emissions savings with respect to the gasoline pathway.

The reason for this might be found in the significant impact associated with the agricultural phase; this exceeds the impact related to ethanol production (Figure 4.2.a). The technology environmental performance is reduced thanks to the credits from side-product end-use, since DDGS may partly replace soy meal (0.69 kg of soy/kg of DDGS on an energetic content, according to Zamboni *et al.*, 2011a).

If the emissions trading scheme is allowed, (following the different strategies indicated by points B to D, Figure 4.1.a), the establishment of an ethanol facility of large scale (about 290 kt/y) operating with technology DAP on corn stover, is suggested. The configurations lead to an eNPV ranging between 0.69 and 0.57 €/GJ respectively for GHG_{red} moving between 35% and 60% with respect to gasoline. Interestingly, these solutions now appear to be more profitable than first generation bioethanol. This is partly due to the lower cost related to lignocellulosic residues than corn, which is subject to a considerable price volatility (Figure 4.2.b). The share of the revenues from traded emissions (ranging from about 2% to about 3.5%) on the average annual income demonstrates that the emissions trading scheme may promote the establishment of more sustainable technologies in a cost-effective way. The overall GHG emissions are estimated at about 12 kg CO_2-eq/$GJ_{ethanol}$, thus abiding by the 2017 EU regulations on minimum GHG emissions savings. This favourable result depends on the low environmental impact of biomass production, pre-treatment and conversion steps, and on the credits for power displacement (Figure 4.2.a).



(a)



(b)

Figure 4.1 *Best technological options for instance I not including SOC (a) and instance II comprising SOC (b). Points represent different strategies: no carbon trading (A); carbon trading and 35% GHG emission reduction constraint (B and B1); carbon trading and 50% GHG emission reduction constraint (C and C1); carbon trading and 60% GHG emission reduction constraint (D and D1). NPV normalisation is performed by applying the factor* $\left(P^{T}_{ethanol,k,g,t}\cdot LHV_e\cdot tf\right)^{-1}$. *$LHV_e$ is the ethanol lower heating value (GJ/t); tf is the facility operating period (20 years).*

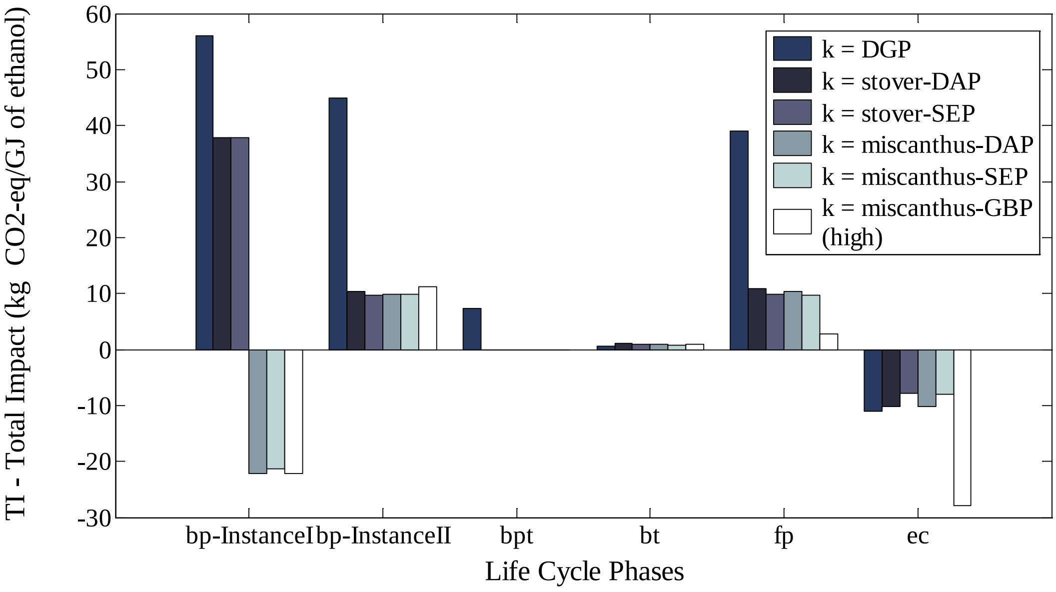
The second best technological options for GHG_{red} =35%, 50% and 60% (B1, C1 and D1 in Figure 4.1.a) are given by miscanthus-based GBP_{high} plant operating at about 290 kt/y of ethanol (the eNPV is between 0.53 and 0.41 €/$\text{GJ}_{\text{ethanol}}$, only 15% less than DGP). The environmental performance seems extremely promising and results in a negative emissions output (-13 kg CO_2-eq/ $\text{GJ}_{\text{ethanol}}$) thanks to the low impacts of the biofuel production process and to the large amount of credits from power displaced (Figure 4.2.a). The share of the incomes from trading of permits to emit (between 5.3% and 3.9%) plays an important role in determining the profitability of a business characterised by high capital investments (Figure 4.2.b). However, since in the literature there is a lot of uncertainty surrounding this technology, a more cautionary technical performance (taken from Piccolo and Bezzo, 2009) has been considered (here named GBP_{ave}), too. In such a case, GBP would not be selected anymore and the optimal configuration would be represented by a stover-based SEP with a plant of the largest allowable size (about 296 kt/y of ethanol). In this case, the expected profitability decreases, moving from 0.5 (strategy B) down to 0.28 €/$\text{GJ}_{\text{ethanol}}$ (strategy D). The impact on global warming is about 12.9 kg CO_2-eq/$\text{GJ}_{\text{ethanol}}$.

4.5.2 Instance II: SOC included

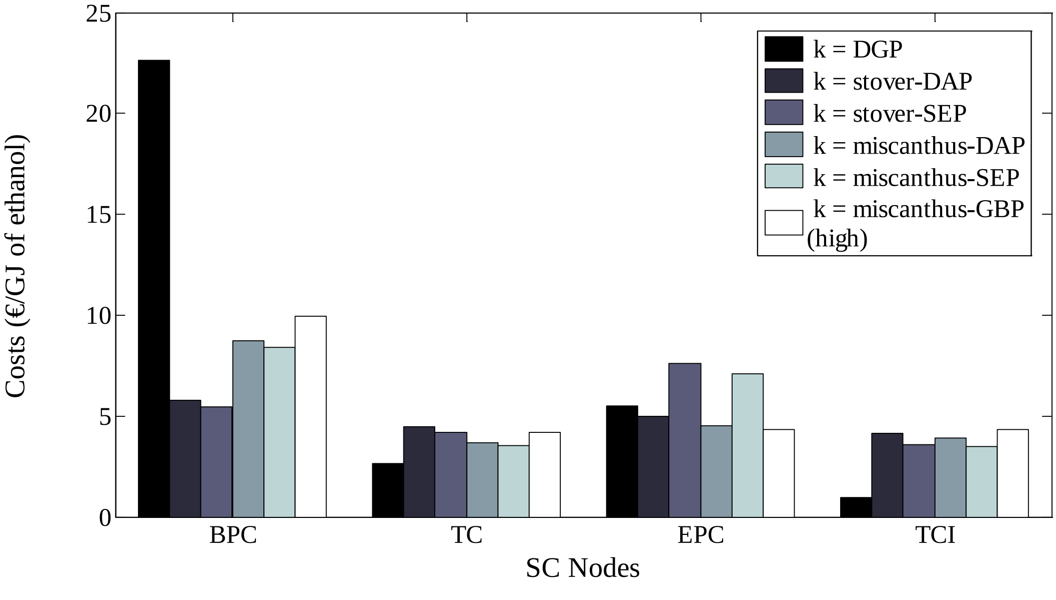
In the following section, optimisation tasks will be performed including the effect of potentials carbon sequestration in the soil.

Figure 4.1.b overviews the strategic technological options. The general trend retains some similarities with instance I. The optimum in absence of an emissions trading scheme (point A) is still given by a DGP plant. The economic performance does not change. However, the impact on global warming from the agricultural phase is 25% higher than in absence of consideration on SOC, because of high carbon emissions from intensive crop practices, as is likely with annual crops.

If the emissions trading scheme is assumed to be operating, the first best technological option (B and C, Figure 4.1.b) is represented by miscanthus-based DAP plants (about 290 kt/y of ethanol) if GHG_{red} is constrained to 35% and 50%. Although the configurations are characterised by high capital costs (Figure 4.2.b), the solution appears profitable with an eNPV ranging between 0.73 and 0.65 €/$\text{GJ}_{\text{ethanol}}$ and a share of emissions from carbon trading moving from 7.6% to 6.9%. The considerable amount of tradable emissions permits is obtained thanks to a negative impact on global warming (about -21.1 kg CO_2-eq/$\text{GJ}_{\text{ethanol}}$) related to the high carbon sequestration during cultivation of perennial crops (Figure 4.2.a).



(a)



(b)

Figure 4.2 *a) Impacts breakdown of the LC phases (biomass production bp, biomass pre-treatment bpt, biomass transport bt, fuel production fp, and emission credits ec); b) costs breakdown along the SC nodes (biomass purchase costs BPC, transport costs TC, fuel production costs EPC, and capital costs TCI) for the selected technologies. TCI is normalised by applying the factor* $\left(P^{T}_{'ethanol',k,g,t} \cdot LHV_e \cdot tf\right)^{-1}$. *LHV*$_e$ *is the ethanol lower heating value (GJ/t); tf is the facility operating period (20 years).*

A large GBP_{high}-based plant (operating at about 286 kt/y of ethanol) is selected as first best when the baseline is set to 60% of emissions savings (point D, Figure 4.1.b). The profitability of the business is good (eNPV is about 0.62 €/$GJ_{ethanol}$) and the revenues from permits trade are at 6% over the whole incomes. This configuration appears attractive for the very low impacts, that results negative (-49.5 kg CO_2-eq/$GJ_{ethanol}$) because of both high organic carbon sequestration rate and credits amount for power displacement (Figure 4.2.a).

Second best technological options (B1, C1, D1 of Figure 4.1.b) present several similarities with the previous solutions: strategies B and C are matched through miscanthus-based GBP_{high} plants, while strategy D requires a miscanthus-based DAP process. In this case, if a less performing GBP technology is assumed (GBP_{ave}), miscanthus-based SEP or DAP technologies are chosen instead of GBP.

Miscanthus appears to be the most suitable biomass when the effects on carbon sequestered due to cropping management are taken into account. Corn residues, which may be interesting due to the current low prices, is not encouraged because the effect on SOC related to their removal rate might endanger the overall carbon balance.

4.5.3 Final remarks

In this chapter a carbon trading scheme has been incorporated in a multi-period stochastic MILP modelling framework for the design and planning of feasible and sustainable multi-echelon ethanol SCs. The proposed framework can be exploited to assess the effect of a carbon-trading scheme (according to the approach proposed by Bojarski *et al.* (2009)) to steer innovation and promote more sustainable technologies for biofuels production with respect to GHG emissions. The model has been tailored to the upstream ethanol supply chain, but the approach is quite general and may be adapted to other production systems in the energy sector. From a strategic design standpoint, the modelling outcomes suggest that a carbon emissions scheme implemented for transport sector may represent a cost-effective way to help reaching significant reduction of GHG emissions through the promotion of competitive cellulosic bioethanol generation technologies. Carbon trading may have a key role at promoting more sustainable second generation technologies: dilute acid or gasification biosynthesis processes may be the winning choices. In general, stricter limits on GHG emissions would make the business more advantageous with respect to either fossil fuels (i.e. gasoline) or first generation ethanol technologies (i.e., corn-based ethanol).

The suggested framework may be helpful in assessing the effect of strategic decision policy on biofuels production system. However, in a context of uncertainty, it is of great importance to evaluate risk on strategic investments in biofuels systems in a comprehensive way. In particular, investors’ decisions may be greatly affected by the amount of risk they are willing to accept.

In the next chapter, a modelling framework based on mathematical programming will be provided to help investors in addressing risk management in the bioenergy systems, in order to support their decisions on strategic planning and design for future bioethanol infrastructures.

Chapter 5

A comprehensive approach to risk mitigation in the biofuels supply chain design

The main purpose of this chapter[1] is to deal with financial risk mitigation in the design of bioethanol supply chains. The stochastic MILP modelling framework presented in chapter 4 addressing uncertainties in biofuels supply chain management, is here extended to approach financial risk mitigation when investing in the bioenergy systems. A risk-constrained multi-objective formulation is presented where financial risk measures have been modelled to account for different investment strategies according to stakeholders' interests. In addition, features related to technological learning are addressed, too, in order to give a more sensible representation of future bioethanol networks development.

The chapter is organised as follows. First, the multi-objective risk-constrained modelling framework is described, including issues referring to emissions allowances trading schemes mechanisms, experience curves, as well as carbon and feedstocks cost uncertainty. The multi-objective (e.g., economic and environmental) optimisation is then carried out. Results show the effects of the investors' attitude towards financial risk (e.g., risk-aversion, risk-propensity) on the strategic planning of bioethanol supply chains. The modelling framework is tailored to a case study, addressing the emerging biomass (first and second generation)-to-ethanol SC development in Northern Italy, to assess the capabilities of the modelling approach in steering decisions about future bioenergy infrastructures.

5.1 Motivation

Biofuels technologies should be promoted by properly devised policy instruments at different levels according to their costs of production and the benefits they may provide (e.g., net carbon reduction). This could be the rationale for developing a transport-sector wide cap and trade on GHG emissions, since it would be able to systematically incentivise low carbon fuels (Creutzig *et al.*, 2011) leading to a cost effective transition towards more sustainable biofuels-

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[1] Part of this chapter has been presented in the work by Giarola *et al.* (2011f).

based system. The potentials of policy in steering more sustainable technologies for biofuels production was addressed in chapter 4, where a flexible market mechanism was studied (i.e., emissions allowances trading) in steering investment decisions for sustainable biofuels supply chains. Results have shown that a carbon trading scheme can be implemented in a biofuels market as a cost-effective tool to promote low-carbon fuels production technologies (e.g., second generation biofuels). However, some topics need to be further discussed to have a more comprehensive view about the potentials of sustainable biofuels production development. One critical issue in dealing with market uncertainty, refers to investors' attitude towards financial risk, which might greatly affect decisions on investments. Even if process systems engineering researchers have considered the management of financial risk within the general context of process industry (Liu and Sahinidis, 1996; Sahinidis, 2004; You *et al.*, 2009; Khor *et al.* 2011) relatively few studies have been able to address uncertainty related to biofuels SCs (Kostin *et al.*, 2011; Dal-Mas *et al.*, 2011). In fact, the biofuels industry is more vulnerable to risk than many other industries because of feedstocks cost and competition with the established petroleum-based fuels (An *et al.*, 2011). Since the early nature of the market, the high level of uncertainty still makes ethanol production quite a risky business, particularly if obtained from second generation technologies.

In addition, another issue to be discussed refers to the technological breakthroughs accounting for costs reduction over time due to accumulated experience of production, which might be capable of modifying bioethanol market development trends (Hamelinck *et al.*, 2005). Technological learning in ethanol production needs being integrated in the long-term assessment of biofuels market development and its capabilities of developing more sustainable technologies addressed.

In this chapter, the main purpose is to cover the gap of the previous formulation. A general MILP modelling framework supporting strategic design and planning decisions for multi-period and multi-echelon ethanol supply chains is developed and implemented. A multicriteria decision making tool is proposed to support strategic design and planning on ethanol fuel SC under market uncertainty. Uncertainty arising from feedstocks and carbon cost within an emission allowances trading scheme (Chevallier, 2011) is addressed through a multi-scenario two-stage stochastic model (Liu and Sahinidis, 1996). Moreover, in studying the integrated long-term vision for biofuels and their market diffusion, the crucial role of technological learning in determining costs reduction, has been implemented (de Wit *et al.*, 2010) through the experience curve approach (Hettinga *et al.*, 2009) so as to link changes in production costs with cumulative production. The SC is described through a MILP model selecting among several technological options (including both first and second generation production) and feedstocks, as well. The economics of the entire network will be assessed by means of SC analysis techniques, focusing on biomass cultivation type, ethanol production capacity and technology assignment, and integrated with a LCA methodology to consider the impact of the system on global warming. The solution strategies have been provided according to decision makers' risk preferences through the implementation of several risk metrics: eDR as defined by Eppen *et al.* (1989), and VaR (Guldimann, 2000).

A demonstrative case study is proposed involving the potential future Italian biomass-based ethanol production. Results show the effectiveness of the modelling framework as a decision making-tool to steer decisions and investments in the long-term horizon among different ethanol fuel configurations.

This chapter is organised as follows. After introducing SCA and LCA issues referring to the biofuels network under assessment, the mathematical formulation follows. A case study concerning the potential ethanol fuel production in Northern Italy is described, and results are presented and discussed. Some final remarks conclude the chapter.

5.2 Problem statement

This section aims at developing a multicriteria decision analysis tool to steer investments on biofuels SCs at a strategic level. A general moMILP modelling framework is proposed to promote a sustainable long-term design and planning of ethanol fuel SC, where business profitability is supported by environmental consciousness and investment decisions are influenced by investors' willingness to take financial risk. The upstream substructure of typical biofuels SCs is addressed: biomass cultivation, biomass pre-treatment, biomass delivery as well as fuel production are the SC nodes. In order to keep feasible the computational burden, bioethanol capacity planning under uncertainty is investigated over a 18-years horizon, gathered into 6 time periods of 3 years each.

The methodology proposed to assess the environmental impact over the biofuel life cycle is based on the standard LCA approach as laid out by the ISO (2006) guidelines series. The SC impact on global warming is evaluated on energy basis, as approached in chapter 4. The WTT approach (CONCAWE, 2007) is used to define the set of LCA stages s considered in the evaluation: biomass production (*bp*), biomass pre-treatment (*bpt*), biomass transport (*bt*) and fuel production *(fp*) are evaluated. In addition, the emission credits (*ec*) in terms of GHG savings (as a result of goods or energy displacement by process side products end-use) are accounted for as a pseudo-life cycle stage. Accordingly:

$s \in S \equiv \{bp, bpt, bt, fp, ec\}$.

CO_2, CH_4, N_2O emissions are accounted for to capture SC impact on global warming, and grouped together in a single indicator expressed as carbon dioxide equivalent emissions (CO_2-eq), according to the concept of 100 year global warming potentials (IPCC, 2007).

The problem considers the following inputs to the optimisation model:

- technical (yields) and economic (capital and operating costs) characterisation of production processes;

- biofuel and energy market characteristics;
- carbon and biomass market stochastic behaviours;
- transport costs;
- environmental burdens of each stage as a function of biomass type and ethanol technology.

The objective is to provide decision-makers with a set of optimal SC configurations among which they might select the investment strategy according to their preferences in balancing the expected financial profitability of the business, GHG emissions savings potentials as well as risk-mitigation opportunities. The ethanol supply chain is optimised according to a comprehensive mathematical framework where multiple decision criteria are simultaneously considered in an uncertain market scenario. The source of uncertainty arises from raw materials and emissions allowances cost volatility and is addressed through a scenario-based two-stage stochastic approach. The economic and environmental performances are both optimised also considering the decision makers' risk mitigation preferences. Crop management and technology learning issues are encompassed, too. The different attitudes towards financial risk may be expressed through risk-indices (eDR and VaR) providing the decision-makers with criteria to control and manage the SC risk on investment and allowing them to choose the strategy which better fits their risk-preferences. Moreover, as a result of the spread of future ethanol business (Hettinga *et al.*, 2009), technological improvements due to accumulated experience of production, are modelled in terms of production costs reduction through a learning curve approach.

Therefore, the key variables to be optimised are:

- ethanol fuel facilities number, capacity and technology selection;
- biomass type and amount shipped;
- financial performance of the system over the long-term;
- system impact on global warming;
- SC planning strategies at the desired level of financial risk.

A land surface of limited extension (LA = 2000000 ha) is assumed to provide ethanol production plants with the suitable feedstocks (corn, poplar, willow, miscanthus, stover, barley straw, wheat straw, and switchgrass are considered). It is assumed that corn is grown independently of its usage for ethanol production. Thus, even if corn grain is not exploited to produce ethanol, corn stover is still available and the same approach is used to consider wheat straw and barley straw.

Strategic decisions on bioethanol SC design involve capacity planning (e.g., establishment or closure as well as operating level changes) of production facilities. Several technological options are accounted for as the ethanol conversion process from biomass. Dry Grind Process (DGP) with two different end uses of the main by-product (i.e. DDGS, Distiller's Dried Grains with Solubles) is considered for starchy biomass-based ethanol. Among the cellulose-based processes, Dilute Acid Hydrolysis (DAP), Steam Explosion (SEP) and Gasification Biosynthesis (GBP) are taken into account. In particular, the uncertainties surrounding the gasification-based ethanol are addressed considering the most cautionary technical performance as assumed in instance GBP_{low} (chapter 2) to assess risk mitigation opportunities.

5.3 Mathematical formulation

The model aims at providing a general purpose approach applicable to a wide variety of strategic decisions to be taken under risk as it is likely for future ethanol fuel SC development. In doing this, a multi-objective risk-constrained formulation is proposed to determine an efficient frontier of tradeoffs complying with both environmental, economic performance and financial risk-mitigation preference according to decision-makers' risk-acceptance levels.

The modelling framework has been formulated as a multi-period MILP problem according to the common approaches adopted in the strategic design of multi-echelon SCs (Sahinidis *et al.*, 1989; Tsiakis *et al.*, 2001). It is focused on capacity planning and technology selection issues (Hugo and Pistikopoulos, 2005; Liu *et al.*, 2007) for ethanol fuel production in the presence of market uncertainty (Liu and Sahinidis, 1996). Some features concerning SC capacity planning are here modelled embedding also the possibility of establishing new facilities or closing down previous plants over time, in this differing from the framework provided in chapter 4.

According to the modelling procedure discussed in chapter 4, the uncertainty arising from biomass and carbon costs is handled by adopting a scenario planning approach, where uncertain parameters distribution is modelled by adopting randomly sampled distinct and mutually exclusive scenarios. Each scenario *sc* ranging between 1-*NS*, representing a particular occurrence for the values of uncertain parameters, is determined using pseudorandom number generation and given an equiprobability value $\pi_{sc} = 1/NS$ per each time interval *t*. Differently from the previous chapter, however, the number of studied scenarios has been increased ($NS = 100$) to have a sensible representation of the system variability and, at the same time, keep the problem computationally feasible.

Uncertainty is addressed through a two-step decomposition approach, according to a non-anticipativity constraint. In fact, in the presence of uncertainty, some decisions need to be made 'here-and-now' before the resolution of uncertainty and independently of the future scenarios *sc* (first stage), while other ones should be made subsequently in a 'wait-and-see' mode after the uncertainties are revealed so that the related equations are dependent on the scenario *sc* (second stage). In this modelling framework, the stochastic programming approach has been implemented considering capital investment and technology selection as decisions to be taken at the first stage of the planning process, while operating levels, purchases and sales are determined at the second stage (Liu and Sahinidis, 1996).

First the multi-objective formulation is dealt with (i.e., expected Net Present Value, expected Total Impact over time). The stochastic formulation is carried out along with investment planning decisions and technological learning considerations. Then the constraints on the level of risk acceptance are explained. Finally, some logical constraints are needed to achieve sensible results.

5.3.1 Risk-constrained multi-objective formulation

The multi-objective decision-making framework addresses two objective functions (i.e., economic, environmental) to be solved simultaneously:

$$Obj_{eco} = eNPV \tag{5.1}$$

$$Obj_{env} = eTIOT \tag{5.2}$$

The economic objective function to be minimised in configuring the system, Obj_{eco} (Eq.(5.1)), includes the profit expectation from the business to be established, *eNPV* [€], as discussed in Eq. (4.1) of chapter 4, which relies on the $NPV_{i,k,sc}$ definition:

$$NPV_{i,k,sc} = \sum_t \left(CF_{i,k,sc,t} \cdot dfCF_t - TCI_{i,k,t} \cdot dfTCI_t \right), \quad \forall i,k,sc \tag{5.3}$$

$CF_{i,k,sc,t}$ [€/time period] represents the cash flow at market scenario *sc*, and $TCI_{i,k,t}$ [€] stands for the capital investment related to the establishment of a production facility treating biomass *i* with technology *k* at period *t*. The dependence of the capital investment term on time gives evidence of the possibility for new facilities to be established over time. Both terms are applied to the corresponding period-based discount factors which are needed to be evaluated over three-year long periods, $dfCF_{,t}$ and $dfTCI_{,t}$ (Douglas, 1988):

$$dfCF_t = \frac{1}{(1+\zeta)^{3(t-1)}}, \quad \forall t \tag{5.4}$$

$$dfTCI_t = \frac{3+3\zeta+\zeta^2}{3\cdot(1+\zeta)^{2t}}, \quad \forall t \tag{5.5}$$

where ζ is the future interest rate, set equal to 10% (Sharpe, 1964). The resulting discount factors are reported in Table 5.1.

A linearisation approach to account for scaling effects for the accurate estimation of $TCI_{i,k,t}$ is discussed in §5.3.2.2.

The total impact on global warming over time (*eTIOT*, [kg CO_2-eq], Eq. (5.2)) due to the SC operation, is expressed as expectation of the overall GHG emissions bill. Accordingly:

$$eTIOT = \sum_{sc} \pi_{sc} \cdot \sum_{i,k,t} TI_{i,k,sc,t} \tag{5.6}$$

where $TI_{i,k,sc,t}$ [kg CO_2-eq/time period], is defined as the total equivalent CO_2 emissions occurring in the SC in period *t*. The environmental model will be discussed later on in §5.3.3.

Table 5.1 *Discount factors for cash flows ($dfCF_t$) and capital investment ($dfTCI_t$); unitary selling price $MP_{j,t}$ per each product j = {ethanol; power; DDGS}; GHG emissions savings ($GHG_{red,t}$) at each time period t.*

t	$dfCF_{,t}$	$dfTCI_{,t}$	$MP_{'ethanol',t}$ [€/t]	$MP_{'power',t}$ [€/MWh]	$MP_{'DDGS',t}$ [€/t]	$GHG_{red,t}$
1	0.829	1	710	67.18	300	0.35
2	0.623	0.751	710	67.18	300	0.5
3	0.468	0.564	710	67.18	200	0.6
4	0.352	0.424	710	67.18	200	0.6
5	0.264	0.319	710	67.18	100	0.6
6	0.198	0.239	710	67.18	100	0.6

The core of the risk mitigation model is expressed in terms of setting an upper limit on the expected downside risk (*eDR*, [€]), according to the approach proposed by Eppen *et al.* (1989):

$$eDR \le \mu \cdot eDR_{max} \tag{5.7}$$

μ ranges between 0-1, and represents the decision-makers' attitude towards financial risk. Risk-taking investors might be willing to accept the highest risk-level for the investment, corresponding to the maximum expected downside risk (eDR_{max}, [€]), when μ approaches 1. Risk-averse investors, instead, have a low propensity for risk; this is modelled setting *eDR* lower than the maximum risk level and having μ approaching 0. eDR_{max} is given by the configuration of the biofuel SC only maximising the economic performance without any constraint on risk.

5.3.2 Economic model

The term $CF_{i,k,sc,t}$ of Eq. (5.3) is given by summing up the profit before taxes $PBT_{i,k,sc,t}$ [€/time period] and the depreciation charge $D_{i,k}$ [€/time period] as well as deducting the tax amount $TAX_{i,k,sc,t}$ [€/time period]:

$$CF_{i,k,sc,t} = PBT_{i,k,sc,t} - TAX_{i,k,sc,t} + D_{i,k}, \quad \forall i,k,sc,t \tag{5.8}$$

$D_{i,k}$ is determined through a linear approach and hence a fixed quota, dk, is applied to depreciate the discounted total capital investment $TCI_{i,k,t}$, as stated by:

$$D_{i,k} = \left(\sum_t TCI_{i,k,t} \cdot dfTCI_t\right) \cdot dk, \quad \forall i,k \tag{5.9}$$

The depreciation plan has been set according to the conventional procedure for the chemical industry (portaleaziende, 2011), by using dk equal to 0.175.

The gross profit of Eq. (5.8), $PBT_{i,k,sc,t}$, accounts for the total revenues from the products sold and the revenues from traded emissions, $Inc_{i,k,sc,t}$ [€/time period], the cost terms including depreciation $D_{i,k}$, and operating costs $VarC_{i,k,sc,t}$ [€/time period]:

$$PBT_{i,k,sc,t} = Inc_{i,k,sc,t} - VarC_{i,k,sc,t} - D_{i,k}, \quad \forall i,k,sc,t \tag{5.10}$$

$Inc_{i,k,sc,t}$ is derived from summing up revenues obtained from selling the products and from traded emissions. The former term is determined by applying the product selling price $MP_{j,t}$ [€/t or €/MWh] to the corresponding rate of product j ($P^T_{i,j,k,sc,t}$ [t/time period] or [MWh/y] depending on the nature of the product). The second term depends on the net amount of permits to emit (the difference between sold and purchased allowances, $S\_All_{i,k,sc,t}$ and $P\_All_{i,k,sc,t}$, [kg CO_2-eq/time period]), which is applied to the allowances price $MP\_All_{sc,t}$ [€/kg CO_2-eq] of scenario sc and time t. Accordingly:

$$Inc_{i,k,sc,t} = \sum_j P^T_{i,j,k,sc,t} \cdot MP_{j,t} + MP\_All_{sc,t} \cdot \left(S\_All_{i,k,sc,t} - P\_All_{i,k,sc,t}\right), \quad \forall i,k,sc,t \tag{5.11}$$

$MP_{j,t}$ is kept constant for ethanol and power, while a gradual depreciation is considered for DDGS between 300 €/t to 100 €/t (see Table 5.1). The stochastic parameter, $MP\_All_{sc,t}$, is defined through randomly sampled scenarios sc of carbon cost per each time period t, between cost bounds increasing with time, according to the approach already outlined in chapter 4.

$VarC_{i,k,sc,t}$ accounts for biomass purchase costs $BPC_{i,k,sc,t}$ [€/time period], biomass transport costs $TC_{i,k,sc,t}$ [€/time period] and ethanol production costs $EPC_{i,k,sc,t}$ [€/time period]. Accordingly:

$$VarC_{i,k,sc,t} = BPC_{i,k,sc,t} + TC_{i,k,sc,t} + EPC_{i,k,sc,t}, \quad \forall i,k,sc,t \tag{5.12}$$

$BPC_{i,k,sc,t}$ and $TC_{i,k,sc,t}$ are estimated by multiplying the biomass rate used in the conversion plant $E\_Cap_{i,k,sc,t}$ [t/time period] by the corresponding unit purchase and transport cost $UPC_{i,sc,t}$ [€/t] and $UTC_{i,}$ [€/t], respectively:

$$BPC_{i,k,sc,t} = E\_Cap_{i,k,sc,t} \cdot UPC_{i,sc,t}, \quad \forall i,k,sc,t \tag{5.13}$$

$$TC_{i,k,sc,t} = E\_Cap_{i,k,sc,t} \cdot UTC_{i}, \quad \forall i,k,sc,t \tag{5.14}$$

The stochastic method proposed to handle volatility on raw materials costs ($UPC_{i,k,sc,t}$) is based on a multiscenario approach. As earlier discussed in chapter 4, pseudorandom number generation is adopted to sample unitary product costs probability distribution per each feedstock *i* (assumed to be uncorrelated) and time period *t*.

$EPC_{i,k,sc,t}$ estimation has been implemented embedding learning curves-based approach for costs reduction due to experience over time and is discussed in §5.3.2.3.

The approach to determine an accurate estimation of the taxation reported in chapter 4, Eq. (4.36-4.39) has been here adapted, to determine, the amount of taxes applied $TAX_{i,k,sc,t}$ not referring to a yearly basis but to a 3-year long period.

5.3.2.1 Economic model: capacity planning

The products *j* rate $P^{T}_{i,j,k,sc,t}$ (i.e., ethanol, DDGS, electricity) is modelled in terms of the actual facility operating level, $E\_Cap_{i,k,sc,t}$ [t/time period] through yield constraints depending on the processing technology *k* and the starting biomass *i*:

$$P^{T}_{i,j,k,sc,t} = E\_Cap_{i,k,sc,t} \cdot \gamma_{i,j,k}, \quad \forall i,k,sc,t;\ j = ethanol, DDGS \tag{5.15}$$

$$P^{T}_{i,j,k,sc,t} = \frac{P^{T}_{i,'ethanol',k,sc,t} \cdot \gamma_{i,j,k}}{\rho}, \quad \forall i,k,sc,t;\ j = power \tag{5.16}$$

where $\gamma_{i,j,k}$ represents the yield of product *j* from technology *k* using biomass *i* while ρ is the ethanol density (0.7891 kg/L).

$E\_Cap_{i,k,sc,t}$ represents the actual biomass rate used in the conversion facility. It is modelled as a second-stage decision made after resolution of market uncertainties and allowing for some flexibility of production rate with respect to the first-stage representing the nominal capacity (i.e., $Cap_{i,k,t}$ [t/time period]). $E\_Cap_{i,k,sc,t}$ needs properly being bounded within suitable ranges:

$$\theta \cdot Cap_{i,k,t} \le E\_Cap_{i,k,sc,t} \le Cap_{i,k,t}, \quad \forall i,k,t \tag{5.17}$$

where θ is the plant flexibility, set to 75% of the nominal capacity.

The term $Cap_{i,k,t}$ represents the key variable of the optimisation, being the nominal rate of feedstock i to the facility operating with technology k at time t, which is determined by the accumulated capacity expansion ($I\_Cap_{i,k,t}$, t/time period). However, the installed capacity may be modified also through decisions of capacity reduction ($D\_Cap_{i,k,t}$, t/time period) over time:

$$Cap_{i,k,t} = Cap_{i,k,t-1} + I\_Cap_{i,k,t} - D\_Cap_{i,k,t}, \quad \forall i,k,t \tag{5.18}$$

Decisions about capacity expansion, $I\_Cap_{i,k,t}$, or reduction, $D\_Cap_{i,k,t}$, are limited within a reasonable range (*UpperLimit* and *LowerLimit*, respectively 888 and 288 kt/time period of ethanol, i.e. 276 kt/year and 96 kt/year). They cannot occur at the same time period t and are determined by a Boolean variable, $Z_{i,k,t}$, assuming a value of 1 if a facility is to be enlarged and 0, if the scale is kept equal to that of the previous period or undergoes a size decrease. Accordingly:

$$I\_Cap_{i,k,t} \cdot \gamma_{i,'ethanol',k} \le Z_{i,k,t} \cdot UpperLimit, \quad \forall i,k,t \tag{5.19}$$

$$I\_Cap_{i,k,t} \cdot \gamma_{i,'ethanol',k} \ge Z_{i,k,t} \cdot LowerLimit, \quad \forall i,k,t \tag{5.20}$$

$$D\_Cap_{i,k,t} \cdot \gamma_{i,'ethanol',k} \le \left(1 - Z_{i,k,t}\right) \cdot UpperLimit, \quad \forall i,k,t \tag{5.21}$$

$$D\_Cap_{i,k,t} \ge 0, \quad \forall i,k,t \tag{5.22}$$

where $\gamma_{i,'ethanol',k}$ represents the biomass-to-ethanol yield (t of ethanol/t of biomass).

The number of expansions might be limited according to the specific requirements depending on the study under assessment by including the following constraints

$$L \le \sum_t Z_{i,k,t} \le U \tag{5.23}$$

where L and U represent the lower- and upper-bounds over the time horizon, respectively. It is assumed that no more than four expansions may take place so as to account for the time needed for capital depreciation ($U = 4$).

$Cap_{i,k,t}$ cannot exceed the sustainability limits imposed by the availability of biomass for fuel production $BA_{i,k,t}$ [t/time period]:

$$Cap_{i,k,t} \le BA_{i,k,t}, \quad \forall i,k,t \tag{5.24}$$

$BA_{i,k,t}$ accounts for agronomic factors (biomass yield, BY_i, [t/ha]), sustainability issues (maximum collection rate, q_i), and crop sharing (actual area devoted to crop i at time t, $LA\_crop_{i,k,t}$, [ha]).

$$BA_{i,k,t} = LA\_crop_{i,k,t} \cdot BY_i \cdot q_i, \quad \forall i,k,t \tag{5.25}$$

Finally, the land devoted to supplying each plant site has to be physically limited by the total available land (LA):

$$\sum_{i,k} LA\_crop_{i,k,t} \leq LA, \quad \forall t \tag{5.26}$$

5.3.2.2 Economic model: capital investment linearisation

In order to have an accurate estimation of the total capital investment, $TCI_{i,k,t}$ in Eq. (5.3) and (5.9), is modelled according to a linearisation routine where new continuous ($I\_BN_{i,k,p,t}$ and $I\_BNexp_{i,k,t}$, [t/time period]) and binary variables ($Y_{i,k,p,t}$) are encompassed (Hugo and Pistikopoulos, 2005). The parameters supporting the linearisation approach (i.e., $BN_{i,k,p}$ and $BNexp_{i,k,p}$) are collected in Table 5.2 and 5.3.

The facility capacity increase is obtained by summing up a scale-dependent variable, $I\_BN_{i,k,p,t}$, which is used to determine the effective facility size (Eq. (5.27)). $I\_BN_{i,k,p,t}$, is bounded between reasonable ranges ($BN_{i,k,p-1}$, $BN_{i,k,p+1}$, [t/time period]) by applying the binary variable, $Y_{i,k,p,t}$, accounting for whether a facility using biomass i, technology k, size p at time t is established, or not (Eq. (5.28)).

$$I\_Cap_{i,k,t} = \sum_p I\_BN_{i,k,p,t}, \quad \forall i,k,t \tag{5.27}$$

$$Y_{i,k,p,t} \cdot BN_{i,k,p-1} \leq I\_BN_{i,k,p,t} \leq Y_{i,k,p,t} \cdot BN_{i,k,p+1}, \quad \forall i,k,t \tag{5.28}$$

Total capital investment $TCI_{i,k,t}$ is estimated through Eq. (5.29), where $CI^0_{i,k}$ [€] corresponds to the capital investment for a facility of reference scale. $BN\,exp^0_{i,k}$ is the parameter for the biomass needs of reference scale raised to the power of the scaling exponent r_k. (Eq. (5.30)). $M\&S_t$ is the Marshall and Swift Index accounting for inflation effects (a yearly 2% increase is assumed).

$$TCI_{i,k,t} = \frac{CI^0_{i,k} \cdot M\&S_t \cdot I\_BNexp_{i,k,t}}{M\&S_{t=1} \cdot BNexp^0_{i,k}}, \quad \forall i,k,t \tag{5.29}$$

$$BN\,exp_{i,k,p} = \left(BN_{i,k,p}\right)^{r_k}, \quad \forall i,k,p \tag{5.30}$$

Table 5.2 *Parameters $BN_{i,k,p}$ representing the need of biomass i [t of biomass/time period] for technology k and plant scale p as used for the linearisation step.*

p	**1**	**2**	**3**	**4**	**5**	**6**
corn						
DGP	888888	1018518	1388889	1851852	2314815	2555556
DGP-CHP	888888	1018518	1388889	1851852	2314815	2555556
poplar						
DAP	1872561	2145645	2925879	3901170	4876464	5383614
SEP	1997226	2288487	3120666	4160889	5201109	5742024
GBP_{low}	2820764	3232125	4407444	5876592	7345739	8109696
willow						
DAP	1965870	2252559	3071673	4095564	5119455	5651877
SEP	2097597	2403495	3277494	4369992	5462490	6030591
GBP_{low}	2862823	3280318	4473161	5964215	7455268	8230616
miscanthus						
DAP	1232349	1412067	1925547	2567394	3209244	3543003
SEP	1312074	1503417	2050113	2733486	3416856	3772209
GBP_{low}	2089985	2394775	3265602	4354136	5442671	6008708
corn stover						
DAP	1490682	1708074	2329194	3105591	3881988	4285713
SEP	1529475	1752522	2389803	3186405	3983007	4397238
GBP_{low}	2239502	2566096	3499222	4665630	5832037	6438569
wheat straw						
DAP	1581549	1812192	2471169	3294894	4118616	4546953
SEP	1612542	1847703	2519598	3359463	4199328	4636059
GBP_{low}	2239502	2566096	3499222	4665630	5832037	6438569
barley straw						
DAP	1559286	1786680	2436384	3248511	4060638	4482945
SEP	1580682	1811196	2469813	3293085	4116357	4544457
GBP_{low}	2300319	2635783	3594249	4792332	5990415	6613419
switchgrass						
DAP	1643835	1883562	2568492	3424659	4280823	4726026
SEP	1667631	1910829	2605674	3474234	4342791	4794441
GBP_{low}	2487047	2849741	3886010	5181347	6476684	7150259

The variable $I\_BNexp_{i,k,t}$ is an approximation of the facility capacity actually installed determined according to the linear approach proposed in Eq. (5.31):

$$I\_BN\,exp_{i,k,t} = \sum\nolimits_p \left(BN\,exp_{i,k,p-1} \cdot Y_{i,k,p,t} + \left(I\_BN_{i,k,p,t} - BN_{i,k,p-1} \cdot Y_{i,k,p,t} \right) \cdot Q \right), \quad \forall i,k,t \tag{5.31}$$

where

$$Q = \frac{BN\,exp_{i,k,p} - BN\,exp_{i,k,p-1}}{\left(BN_{i,k,p} - BN_{i,k,p-1} \right)} \tag{5.32}$$

$Y_{i,k,p,t}$ and $Z_{i,k,t}$ are not independent, but the linearisation routine is started only when a production facility is established or enlarged (i.e., $Z_{i,k,t} = 1$).

$$\sum_p Y_{i,k,p,t} = Z_{i,k,t}, \quad \forall i,k,t \tag{5.33}$$

Table 5.3 *Parameters $BNexp_{i,k,p}$ representing the need of biomass i [t of biomass/ time period] (raised to the power of the scaling factor) for technology k and plant scale p as used in the linearisation step.*

p	1	2	3	4	5	6
corn						
DGP	94023	105357	136543	173668	209284	227331
DGP-CHP	94023	105357	136543	173668	209284	227331
poplar						
DAP	15942	17464	21498	26068	30271	32346
SEP	16645	18235	22446	27218	31607	33773
GBP_{low}	20977	22980	28288	34302	39833	42563
willow						
DAP	16470	18042	22210	26931	31274	33417
SEP	17201	18844	23196	28127	32663	34901
GBP_{low}	21186	23209	28570	34643	40230	42987
miscanthus						
DAP	12045	13195	16242	19695	22871	24439
SEP	12561	13761	16939	20540	23852	25487
GBP_{low}	17159	18798	23140	28058	32583	34816
stover						
DAP	13683	14989	18451	22374	25982	27762
SEP	13920	15249	18772	22762	26433	28244
GBP_{low}	17972	19689	24236	29388	34127	36466
wheat straw						
DAP	14236	15595	19197	23278	27032	28885
SEP	14422	15800	19449	23583	27386	29263
GBP_{low}	17972	19689	24236	29388	34127	36466
barley straw						
DAP	14101	15448	19016	23058	26777	28612
SEP	14231	15590	19190	23270	27022	28874
GBP_{low}	18298	20045	24675	29920	34745	37127
switchgrass						
DAP	14609	16004	19701	23889	27741	29642
SEP	14751	16159	19891	24120	28009	29929
GBP_{low}	19280	21121	26000	31527	36611	39120

5.3.2.3 Economic model: learning curves

The approach here described, ensures the estimation of operating costs encompassing the learning curves effect since the time at which the facility was established, and takes into account decisions about varying the plant operating level.

Ethanol production costs, $EPC_{i,k,sc,t}$ have been implemented through piecewise linear functions where the effects of technological breakthrough are taken into account through unitary cost reduction ($UEPC_{i,k,p,t}$, [€/t]). A learning curve approach has been adopted to quantify technological development over time representing potentials for future costs reduction.

The learning curve describes the changing cost of a given technology according to a factor which represents its cumulative production, i.e. the acquired experience (Hettinga *et al.*, 2009). Accordingly, cost of production over time, is defined recursively

$$UEPC_{i,k,p,t} = UEPC_{i,k,p,t=1} \cdot \left(\sum\nolimits_{t' \le t} P^{T}_{i,'ethanol',k,sc,t}\right)^{b}, \quad \forall i,k,p,t \tag{5.34}$$

$P^{T}_{i,'ethanol',k,sc,t}$ [t/time period] is the production of ethanol at time period t; $UEPC_{i,k,p,t}$ [€/t] is the current marginal production cost at time t and b represents the experience index, which is determined empirically through regression of production costs over cumulative production. One common approach sees industrial processing costs decline by a fixed percentage over each doubling in cumulative production, and provides the progress ratio (*PR*) whose definition is given in Eq. (5.35):

$$PR = 2^{b} \tag{5.35}$$

The accurate description of technological learning is based on a linearisation approach of the current facility operating level, $E\_Cap_{i,k,sc,t}$, through new binary ($W_{i,k,p,sc,t}$) and continuous variables (the effective biomass rate used in the facility, $EBR_{i,k,p,sc,t}$ [t/time period] and the total ethanol production cost, $EPC_{i,k,sc,t}$ [€/time period]).

From the actual facility operating level $E\_Cap_{i,k,sc,t}$ of the production facility, the continuous size-dependent variable $EBR_{i,k,p,sc,t}$, is derived by Eq. (5.36). $EBR_{i,k,p,sc,t}$ is also bounded between reasonable ranges ($BN_{i,k,p-1}$, $BN_{i,k,p+1}$), according to Eq. (5.37) where the binary $W_{i,k,p,sc,t}$, assumes value 1 when a conversion facility of biomass i, technology k at scenario sc and time t works at p operating level (Eq. (5.37)).

$$E\_Cap_{i,k,sc,t} = \sum\nolimits_{p} EBR_{i,k,p,sc,t}, \quad \forall i,k,sc,t \tag{5.36}$$

$$W_{i,k,p,sc,t} \cdot BN_{i,k,p-1} \le EBR_{i,k,p,sc,t} \le W_{i,k,p,sc,t} \cdot BN_{i,k,p+1}, \quad \forall i,k,p,sc,t \tag{5.37}$$

$$\sum\nolimits_{p} W_{i,k,p,sc,t} \le 1, \quad \forall i,k,sc,t \tag{5.38}$$

The linearisation approach is based on the introduction of a new set of parameters $E\_EPC_{i,k,p,t}$ [€/time period], representing the period-based operating costs for a facility of size $BN_{i,k,p}$. The total ethanol production cost for biomass i, technology k scenario sc and time t, $EPC_{i,k,sc,t}$ is determined in Eq. (5.39) through a linear relation between the operating costs at the lower and upper sizes (parameters $E\_EPC_{i,k,p-1,t}$ and $E\_EPC_{i,k,p+1,t}$) and the actual biomass rate entering the plant, $EBR_{i,k,p,sc,t}$.

$$EPC_{i,k,sc,t} = \sum_p \left(E\_EPC_{i,k,p-1,t} \cdot W_{i,k,p,sc,t} + \left(EBR_{i,k,p,sc,t} - BN_{i,k,p-1} \cdot W_{i,k,p,sc,t} \right) \cdot P \right), \quad \forall i,k,sc,t \tag{5.39}$$

where:

$$P = \frac{E\_EPC_{i,k,p,t} - E\_EPC_{i,k,p-1,t}}{\left(BN_{i,k,p} - BN_{i,k,p-1} \right)} \tag{5.40}$$

The learning effect is represented by Eq. (5.41). The total ethanol production cost for biomass i technology k at time t, $E\_EPC_{i,k,p,t}$, is calculated from the corresponding unitary ethanol production cost, $UEPC_{i,k,p,t=1}$ [€/t] (Table 5.4) which is applied to the period-based rate of product ($BN_{i,k,p} \cdot \gamma_{i,'ethanol',k}$) and the time-dependent cost reduction factor $CR_{k,t}$. The reduction of the production costs embodied in the $CR_{k,t}$ reported in Table 5.5, is calculated according the experience curve approach expressed in Eq. (5.42),where PR_k is determined according to the literature. In particular, Hettinga *et al.* (2009) suggest a value for *PR* equal to 0.87 for first generation technologies, based on data regression of U.S. ethanol processing costs between 1980 and 2005. If, on the one side, the wide availability of historic data has led to the determination of the progress ratio for first generation ethanol, second generation ethanol suffers from the lack of processing costs data since only experimental-scale and pilot plants have been available so far. De Wit *et al.* (2010) suggest an approach combining engineering insights regarding scale effects with a scale-independent learning over time and *PR* is set equal to 0.99. Here, a more conservative approach is followed for first generation technologies and PR_k is set equal to 0.96 (k = DGP, DGP-CHP), closer to the value (PR_k = 0.99) suggested for second generation technologies (k =DAP, SEP, GBP_{low}) (De Wit *et al.*, 2010).

$$E\_EPC_{i,k,p,t} = UEPC_{i,k,p,t=1} \cdot BN_{i,k,p} \cdot \gamma_{i,'ethanol',k} \cdot CR_{k,t}, \quad \forall i,k,p,t \tag{5.41}$$

$$CR_{k,t} = t^{\log_2 PR_k}, \quad \forall i,t \tag{5.42}$$

Table 5.4 *Parameters* $UEPC_{i,k,p,t=1}$ *representing unit ethanol conversion cost for biomass i, technology k, size p and at time t = 1.*

p	**1**	**2**	**3**	**4**	**5**	**6**
corn						
DGP	161.66	159.4	154.4	151	149	148.08
DGP-CHP	69.83	60	49	41	37.75	35.86
poplar						
DAP	192.79	181.37	167.11	155.06	147.08	145.23
SEP	249.18	243.71	230.47	219.28	211.91	208.42
GBP$_{low}$	173.54	167.15	151.74	138.71	130.05	125.98
willow						
DAP	195.03	184	169.66	157.52	149.5	147.47
SEP	252.76	247.58	234.28	223.03	215.63	212
GBP$_{low}$	173.54	167.15	151.74	138.72	130.05	125.98
miscanthus						
DAP	164.08	158.82	145.54	134.3	126.91	123.32
SEP	232.86	223.63	211.26	200.78	193.94	192.1
GBP$_{low}$	173.47	167.04	151.64	138.62	129.96	125.91
stover						
DAP	182.48	168.8	155.06	143.44	135.77	134.92
SEP	246.89	238.78	226.15	215.46	208.46	206.13
GBP$_{low}$	171.65	163.95	148.84	136.07	127.59	124.1
wheat straw						
DAP	188.5	177.99	163.52	151.29	143.19	140.94
SEP	259.25	253.87	240.62	229.4	222.03	218.49
GBP$_{low}$	173.95	167.54	152.14	139.11	130.45	126.39
barley straw						
DAP	186.66	174.96	160.77	148.77	140.83	139.1
SEP	253.91	247.47	234.46	223.45	216.22	213.15
GBP$_{low}$	173.95	167.55	152.15	139.12	130.46	126.39
switchgrass						
DAP	189.57	178.79	164.38	152.2	144.14	142.01
SEP	256.03	250.38	237.18	226.02	218.68	215.27
GBP$_{low}$	173.37	166.38	151.11	138.2	129.61	125.81

Table 5.5 *Parameters* $CR_{k,t}$. *representing operating cost reduction for technology k and time t.*

t	1	2	3	4	5	6
DGP	1	0.937347	0.899853	0.87862	0.863859	0.852581
DGP-CHP	1	0.937347	0.899853	0.87862	0.863859	0.852581
DAP	1	0.984197	0.974355	0.968643	0.964611	0.961495
SEP	1	0.984197	0.974355	0.968643	0.964611	0.961495
GBP$_{low}$	1	0.984197	0.974355	0.968643	0.964611	0.961495

5.3.3 Environmental model

The environmental model concerns the impacts on global warming due to the whole SC operations. The environmental performance of the system is evaluated in terms of GHG emissions as expressed by the CO_2 equivalent emitted by each stage of the production network. The potential of a carbon trading scheme is also quantified in steering more sustainable technologies. The emissions allowances trading scheme refers to the Californian ‘Low Carbon Fuel standard’: a baseline is set for the overall SC GHG equivalent emissions representing a sustainability requirement for biofuels settled by the legislation, with respect to which tradable permits might be generated (ARB, 2011). The carbon trading modelling framework is based on the approach by Bojarski *et al.* (2009). It is supposed that any amount of rights can be sold or obtained in the emissions market. Each emission allowance transaction may take place only at the end of each period and it is evaluated on the total equivalent CO_2 emission occurring in the SC. Thus, the following relationship holds:

$$TI_{i,k,sc,t} \leq MaxCO2_{i,k,sc,t} + P\_All_{i,k,sc,t} - S\_All_{i,k,sc,t}, \quad \forall i,k,sc,t \tag{5.43}$$

where $TI_{i,k,sc,t}$ [kg CO_2-eq/time period] represents the SC total impact, [kg CO_2-eq/time period] the cap on the emissions; $P\_All_{i,k,sc,t}$ and $S\_All_{i,k,sc,t}$ [kg CO_2-eq/time period] are respectively the purchased and sold emissions allowances. According to Eq. (5.43), the total amount of GHG emissions produced by the SC is bounded from above by the cap $MaxCO2_{i,k,sc,t}$, also representing the free amount of allowances for the system. However, if a trading market of permits to emit is running, the ethanol SC might reach the goal by buying more allowances ($P\_All_{i,k,sc,t}$) if the cap is exceeded, otherwise the surplus credits might be sold ($S\_All_{i,k,sc,t}$). $MaxCO2_{i,k,sc,t}$ has been defined taking as reference the EU policy framework (EC, 2009) as a regulation-based limit on the total emissions from fuel SC. Accordingly:

$$MaxCO2_{i,k,sc,t} = TI^{*}_{i,k,sc,t} \cdot \left(1 - GHG_{red,t}\right), \quad \forall i,k,sc,t \tag{5.44}$$

where $TI^{*}_{i,k,sc,t}$ [kg CO_2-eq/time period] is the GHG emitted from production and utilisation of the same amount of conventional fuel (i.e., GJ of gasoline) while $GHG_{red,t}$ represents the GHG emissions savings required from biofuels for eligibility for public support at time period t. $GHG_{red,t}$ is set equal to 35%, 50% and 60% according to EU regulations (Table 5.1).

The total GHG impact $TI_{i,k,sc,t}$ (Eq. (5.45)) must consider the contribution of each life cycle stage s as well as the effect of emission credits arising from by-products end-use:

$$TI_{i,k,sc,t} = \sum_{s} Imp_{i,k,s,sc,t}, \quad \forall i,k,sc,t \tag{5.45}$$

where $Imp_{i,k,s,sc,t}$ [kg CO_2-eq/time period] is the GHG emission rate resulting from the operation of each single stage s at time t and scenario sc when a technology k using biomass i is chosen, and is provided by:

$$Imp_{i,k,s,sc,t} = f_{i,k,s,t} \cdot F_{i,k,s,sc,t}, \quad \forall i,k,s,sc,t \tag{5.46}$$

Each LCA stage impact $Imp_{i,k,s,sc,t}$ is evaluated by multiplying the corresponding emission factor $f_{i,k,s,t}$ [kg CO_2-eq/unit] by the specific reference flow $F_{i,k,s,sc,t}$ [units/time period]. In particular, $F_{i,k,s,sc,t}$ is represented by the actual feedstock rate $E\_Cap_{i,k,sc,t}$ for $s = \{bp, bt, bpt\}$, it is equal to the ethanol rate $P^{T}_{i,'ethanol',k,sc,t}$ for $s = \{fp, ec\}$.

In dealing with by-products effects, the so-called ‘substitution method’ (CONCAWE, 2007) is implemented, as already discussed in the previous chapters. The emission credits derived from the displacement of alternative goods with by-products are detracted from the primary product (ethanol) total GHG emissions (e.g., in the corn-based ethanol system, the main by-product, DDGS, can be used either as a substitute for cattle feed or as a fuel for CHP generation; in cellulose-based processes, an excess amount of power is usually produced and may be sold to the national grid).

5.3.4 Risk mitigation

According to the approach suggested by Eppen *et al.* (1989), the risk associated *eDR* (Eq. (5.7)) with capacity planning decisions might be conveniently defined as the expectation of not meeting a certain profit, which decision makers consider the desired level of profitability for the business. Thus, it holds:

$$eDR = \sum_{i,k} \sum_{sc} \pi_{sc} \cdot dev_{i,k,sc} \tag{5.47}$$

where $dev_{i,k,sc}$, [€] is a positive variable representing the deviation from the desired target profit Ω, [€] when a facility working with biomass i, technology k under scenario sc is established. This is stated by the following relations:

$$dev_{i,k,sc} \geq \Omega \cdot \delta_{i,k,sc} - NPV_{i,k,sc} \cdot \delta_{i,k,sc}, \quad \forall i,k,sc \tag{5.48}$$

$$dev_{i,k,sc} \geq 0, \quad \forall i,k,sc \tag{5.49}$$

being $\delta_{i,k,sc}$ a binary variables accounting for whether a facility production is established ($\delta_{i,k,sc} = 1$) or not ($\delta_{i,k,sc} = 0$). Eq. (5.48) needs linearising for being modelled, as discussed later on.

5.3.4.1 Risk mitigation: a linerisation model

To avoid non-linearity issues, Eq. (5.48) is substituted by the following one:

$$dev_{i,k,sc} \geq \Omega \cdot \delta_{i,k,sc} - q_{i,k,sc}, \quad \forall i,k,sc \tag{5.50}$$

The term $(NPV_{i,k,sc} \cdot \delta_{i,k,sc})$ is linearised by adopting the variable $q_{i,k,sc}$ [€] adding a set of constraints as suggested by Williams (1978):

$$q_{i,k,sc} - N \cdot \delta_{i,k,sc} \leq 0, \quad \forall i,k,sc \tag{5.51}$$

$$-NPV_{i,k,sc}+q_{i,k,sc}\le 0,\quad \forall i,k,sc \tag{5.52}$$

$$NPV_{i,k,sc}-q_{i,k,sc}+N\cdot\delta_{i,k,sc}\le N,\quad \forall i,k,sc \tag{5.53}$$

Using N as a reasonable upper limit for the $NPV_{i,k,sc}$, the binary variable $\delta_{i,k,sc}$ indicates whether a business is established or not and its value is determined by $NPV_{i,k,sc}$. When $NPV_{i,k,sc}$ is equal to 0, no business is established: $\delta_{i,k,sc}$ becomes 0 and thus $q_{i,k,sc}$, too. Otherwise, if a business is established, $NPV_{i,k,sc}$ might be lower or higher than 0, making the indicator variable assuming the value 1 and $q_{i,k,sc}$ equal to $NPV_{i,k,sc}$, thus allowing the accurate estimate of *eDR*.

In order to ensure, $\delta_{i,k,sc}$ equal to 1 both when $NPV_{i,k,sc}$ is lower and greater than 0, a set of constraints is needed, where n is a suitable lower limit for $NPV_{i,k,sc}$, ε represents a proper tolerance level, $\delta 1_{i,k,sc}$ and $\delta 2_{i,k,sc}$ are binary variables to help bounding $\delta_{i,k,sc}$ properly. This is stated by the following set of relations:

$$NPV_{i,k,sc}+N\cdot\left(1-\delta_{i,k,sc}\right)\le N,\quad \forall i,k,sc \tag{5.54}$$

$$NPV_{i,k,sc}+n\cdot\left(1-\delta_{i,k,sc}\right)\ge n,\quad \forall i,k,sc \tag{5.55}$$

$$NPV_{i,k,sc}-\left(n-\varepsilon\right)\cdot\delta 1_{i,k,sc}\ge\varepsilon,\quad \forall i,k,sc \tag{5.56}$$

$$NPV_{i,k,sc}-\left(N+\varepsilon\right)\cdot\delta 2_{i,k,sc}\le-\varepsilon,\quad \forall i,k,sc \tag{5.57}$$

$$\delta 1_{i,k,sc}+\delta 2_{i,k,sc}-\delta_{i,k,sc}\le 1,\quad \forall i,k,sc \tag{5.58}$$

$$-\delta 1_{i,k,sc}+\delta_{i,k,sc}\le 0,\quad \forall i,k,sc \tag{5.59}$$

$$-\delta 2_{i,k,sc}+\delta_{i,k,sc}\le 0,\quad \forall i,k,sc \tag{5.60}$$

5.3.5 Logical constraints

Non-negativity constraints are set for key design variables in order to achieve sensible results:

$$Cap_{i,k,sc,t},P\_All_{i,k,sc,t},S\_All_{i,k,sc,t}\ge 0,\quad \forall i,k,sc,t \tag{5.61}$$

$$LA\_crop_{i,k,t}\ge 0,\quad \forall i,k,t \tag{5.62}$$

5.4 Case study

The emerging ethanol fuel SC in Northern Italy has been chosen as a case study to show the model capabilities in steering the strategic design of biofuels systems. According to this, each SC and LC node has been tailored for representing actual economic and environmental data. The SCA and LCA approaches proposed in chapter 4 have been adopted to evaluate the specific modelling parameters. A wide variety of technological options (detailed in the following) has been taken into account and broadly available feedstocks in Northern Italy are investigated for ethanol production, encompassing annual, perennial and residues feedstocks (i.e., corn, poplar, willow, miscanthus, corn stover, wheat and barley straw and switchgrass).

5.4.1 Biomass production

Actual data regarding the cultivation practices for each specific crop have been retrieved either from the literature or from institutional databases. The steady-state crop yields, (BY_i, in Eq.(5.25)) determined according to chapter 4 (Table 4.5) have been used. In particular, crop yields, mineral and organic fertiliser requirements, seeds usage, pesticides and herbicides amounts, leaf senescence and diesel fuel for irrigation represent the main contributions to both the economic profitability and the environmental sustainability of the biofuel SC.

Biomass availability for ethanol fuel production is limited according to sustainability levels (q_i) of Eq. (5.25): 14.3% for corn and 33% for residues (extending the assumptions made for stover in chapter 3), 50% for SRF (Short Rotation Forestry) with 2-years-cycle of growth, and 100% for the remaining energy crops. The agricultural management activities require specific time-dependent emissions factors reported in Table 5.6 on annual basis. Effects on carbon storage (SOC, soil organic carbon) in soil due to agricultural management are here neglected.

5.4.2 Biomass pre-treatment and transport

After harvesting and collection, biomass needs pre-treatment in terms of drying and storage operations. It is important to consider these activities as an independent network node since the related environmental impact has to be addressed separately. As previously discussed in chapter 4, field-drying is assumed for cellulosic biomass, and thus no emissions factors have been assigned. However, the drying and storage of corn cannot be neglected and the specific emission factor $f_{'corn',k,\ 'bpt',t}$ (Eq. (5.46)) is equal to 63.34 kgCO_2-eq/t of corn (Zamboni *et al.*, 2009b).

The transport network stage has been addressed by averaging the economic UTC_i (Eq. (5.14)) and environmental $f_{i,k,'bt',t}$ (Eq. (5.46)) performance of several transport means, that are respectively set equal to 23.2 €/t and 5.38 kg CO_2-eq/t of biomass (Zamboni *et al.*, 2009a; Zamboni *et al.*, 2009b).

Table 5.6 *Input, assumptions and literature data sources for the cultivation phase, referring to corn, poplar, willow and miscanthus, corn stover, wheat straw, barley straw and switchgrass. SOC effects are neglected. Values on a yearly basis.*

Biomass	**Corn**	**Poplar**	**Willow**	**Miscanthus**[b]
seed	Zamboni *et al.*, 2009b	-	-	-
rhizomes	-	-	-	Monti *et al.*, 2009; Smeets *et al.*, 2009
fertiliser	Zamboni *et al.*, 2009b	Manzone *et al.*, 2009; Zamboni *et al.*, 2009b, IEA, 2004	Manzone *et al.*, 2009; Zamboni *et al.*, 2009b	Monti *et al.*, 2009; Zamboni *et al.*, 2009b
pesticide	Zamboni *et al.*, 2009b	-	-	-
herbicide	-	Manzone *et al.*, 2009; Smeets *et al.*, 2009	Manzone *et al.*, 2009; Smeets *et al.*, 2009	Monti *et al.*, 2009; Smeets *et al.*, 2009
leaf senescence	-	Heller *et al.*, 2003[b]; Zamboni *et al.*, 2009b	Heller *et al.*, 2003[b]; Zamboni *et al.*, 2009b	-
fuel	Zamboni *et al.*, 2009b	Bidini *et al.*, 2006; Zamboni *et al.*, 2009b	Bidini *et al.*, 2006; Zamboni *et al.*, 2009b	Monti *et al.*, 2009; Zamboni *et al.*, 2009b
$f_{i,k,'bp't}$ [kg CO$_2$-eq/t]	391.83	establishment: 249.05 harvest year: 99.69 after harvest: 132.81 last year: 114	establishment: 247.72 harvest year: 98.84 after harvest: 131.96 last year: 132.26	establishment: 78.63 from II year: 61.42
Biomass	**Corn Stover**	**Wheat Straw**	**Barley Straw**[c]	**Switchgrass**[b]
seed	-	-	-	Monti *et al.*, 2009; Smeets *et al.*, 2009
rhizomes	-	-	-	-
fertiliser	ANL, 2006; Zamboni *et al.*, 2009b	Cherubini and Ulgiati, 2010; Zamboni *et al.*, 2009b	Cherubini and Ulgiati, 2010; Zamboni *et al.*, 2009b	Monti *et al.*, 2009; Zamboni *et al.*, 2009b
pesticide	-	-	-	-
herbicide	-	-	-	Monti *et al.*, 2009; Zamboni *et al.*, 2009b
leaf senescence	-	-	-	-
fuel	IT, 2010b; Zamboni *et al.*, 2009b	IT; 2010b; Zamboni *et al.*, 2009b	IT, 2010b; Zamboni *et al.*, 2009b	Monti *et al.*, 2009; Zamboni *et al.*, 2009b
$f_{i,k,'bp't}$ [kg CO$_2$-eq/t]	53.91	79.82	79.45	establishment: 65.7 from II year: 71.26

[a] Assumed equal to oilseed rape

[b] Leaf senescence assumed equal for poplar and willow.

[c] Values derived from wheat straw and scaled on yield basis.

5.4.3 Fuel production

Four main processing technologies have been studied encompassing both first generation from starchy feedstock and second generation from cellulosic ones: *i)* the Dry Grind Process (DGP); ii*)* the Dilute Acid Process (DAP), where cellulosic feedstock is hydrolysed with dilute sulphuric acid (USDOE, 1999); *iii)* the Steam Explosion Process (SEP), where the cellulosic biomass is pre-treated with high pressure steam before conversion into ethanol

(Sassner *et al.*, 2008); *iv)* the Gasification Biosynthesis Process (GBP), where biomass-based syngas is fermented to ethanol (Wei *et al.*, 2009). In particular, the GBP process has been dealt with according to the instance called GBP_{low} as detailed in chapter 2, in order to represent the more cautionary scenario of technological progress.

DGP is the standard corn-based ethanol process and is dealt with according to Zamboni *et al.* (2009a). It is assumed that either DDGS is sold in the cattle feed market (k = DGP) thus substituting soy or it is burnt to fuel a combined heat and power (CHP) generation system (k = DGP-CHP).

The black-box system detailed in chapter 2 and set up according to Wei *et al.* (2009), was used to quantify biomass yields ($\gamma_{i,j,k}$ in Eq. (5.15-5.16)) into products per each of the second generation technology considered (i.e. DAP, SEP, GBP). Although GBP seems a very promising technology from the environmental standpoint (EUNOMIA, 2010), the business is surrounded by a high level of uncertainty on both technical and economic feasibility. Here, in determining GBP ethanol yield, syngas composition has been related to that from a typical downdraft oxygen-blown gasifier (Bridgwater, 1995) in order to achieve about 45% of CO and 35% of H_2 on a volumetric base. Concerning the syngas conversion into ethanol, the values from the work by NREL (2002), which represents one of the most complete works on this topic so far, have been assumed. The resulting instance of technology has been indicated as GBP_{low}, representing the most cautionary technical performance for this technology.

The economic characterisation of each second generation technology is approached according to the method described in chapter 2.

LCA-wise, the environmental framework for GHG emissions evaluation referring to the biofuel production stage assumed according to the approach described in chapter 4. The amounts of chemicals, nutrients, utilities, enzymes and waste disposal required in operating the conversion facility have been accounted for. The global emission factors assess the individual impact on global warming coming from every input entering the plant; each of these has been determined from the literature (Zamboni *et al.*, 2009b; Slade *et al.*, 2009; Stephenson *et al.*, 2010) and, for the GBP process in particular, on industrial data (EUNOMIA, 2010). Emissions discounts are assigned when conventional products are replaced with biomass-derived by-products, according to the approach by Zamboni *et al.* (2009b). In corn-based processes, the DDGS by-product can be sold as a soy-meal substitute in the animal feed market or can be used for heat and power generation replacing a certain amount of energy, which would be otherwise produced from fossil fuels. Cellulose-based ethanol facilities provide for their own energy input by burning lignin. A power surplus is obtained and may be exported to the grid, thus displacing an equivalent amount of fossil fuels. Economic and environmental characterisation refers to values of Table 4.7, for first and second generation technologies (i.e., DAP, SEP). In Table 5.7, product yields, capital costs, emission factors and credits are reported for the bioprocessing technology (instance GBP_{low}).

Table 5.7 *Economics and environmental performance of the bioprocessing instance technology for ethanol production from biomass (GBP$_{low}$).*

poplar		
ethanol yield	0.1510	t of ethanol/t of dry biomass
power yield	1.1800	kWh/L of ethanol
$CI^0_{i,k}$	$399 \cdot 10^{6\dagger}$	€
$f_{i,k,'fp't}$	117.87	kg CO_2-eq/t of ethanol
$f_{i,k,'ec't}$	700.11	kg CO_2-eq/t of ethanol
willow		
ethanol yield	0.1510	t of ethanol/t of dry biomass
power yield	1.1800	kWh/L of ethanol
$CI^0_{i,k}$	$399 \cdot 10^{6\dagger}$	€
$f_{i,k,'fp't}$	118.35	kg CO_2-eq/t of ethanol
$f_{i,k,'ec't}$	700.11	kg CO_2-eq/t of ethanol
miscanthus		
ethanol yield	0.1510	t of ethanol/t of dry biomass
power yield	1.1800	kWh/L of ethanol
$CI^0_{i,k}$	$398 \cdot 10^{6\dagger}$	€
$f_{i,k,'fp't}$	117.87	kg CO_2-eq/t of ethanol
$f_{i,k,'ec't}$	700.11	kg CO_2-eq/t of ethanol
corn stover		
ethanol yield	0.1479	t of ethanol/t of dry biomass
power yield	1.0066	kWh/L of ethanol
$CI^0_{i,k}$	$389 \cdot 10^{6\dagger}$	€
$f_{i,k,'fp't}$	119.60	kg CO_2-eq/t of ethanol
$f_{i,k,'ec't}$	597.22	kg CO_2-eq/t of ethanol
wheat straw		
ethanol yield	0.1440	t of ethanol/t of dry biomass
power yield	1.1534	kWh/L of ethanol
$CI^0_{i,k}$	$399 \cdot 10^{6\dagger}$	€
$f_{i,k,'fp't}$	121.93	kg CO_2-eq/t of ethanol
$f_{i,k,'ec't}$	684.31	kg CO_2-eq/t of ethanol
barley straw		
ethanol yield	0.1440	t of ethanol/t of dry biomass
power yield	1.1534	kWh/L of ethanol
$CI^0_{i,k}$	$399 \cdot 10^{6\dagger}$	€
$f_{i,k,'fp't}$	121.93	kg CO_2-eq/t of ethanol
$f_{i,k,'ec't}$	684.31	kg CO_2-eq/t of ethanol
switchgrass		
ethanol yield	0.1389	t of ethanol/t of dry biomass
power yield	1.0547	kWh/L of ethanol
$CI^0_{i,k}$	$394 \cdot 10^{6\dagger}$	€
$f_{i,k,'fp't}$	125.18	kg CO_2-eq/t of ethanol
$f_{i,k,'ec't}$	625.77	kg CO_2-eq/t of ethanol

[†] $CI^0_{i,k}$ (Capital Investment, €), used in (Eq. (5.29)) is evaluated for a facility of medium capacity [corresponding to 100000 t of ethanol/y] using biomass *i* and technology *k*. Capital expenditures at different scale is evaluated as in chapter 2.

The operating costs for the ethanol production processes considered are approached as in §5.3.2.3.

5.5 Results and discussion

Design variables were optimised by means of the CPLEX solver in the GAMS® modelling tool (Rosenthal, 2006). In the following discussion, a preliminary part is devoted to presenting the strategic investment decisions according to the simultaneous optimisation framework of GHG emissions savings and economic profitability. In the second part, an investor's attitude to risk is described by means of risk metrics, eDR and VaR. Several solution strategies in terms of capacity planning and technology selection are presented in order to manage financial risk matching decision makers' preferences.

5.5.1 Simultaneous environmental and economic optimisation

Figure 5.1 represents the optimal biofuel capacity planning and design resulting from the multiobjective formulation involving GHG emissions savings and the eNPV index as optimisation drivers, while in Table 5.8 more technical details are provided. The Pareto curve represents the trade-off between the conflicting objectives considered, namely environmental impact minimisation and economic performance maximisation. The horizontal line in the diagram shows the limit to the profitability of the business, which is required to be non negative; the vertical line represents the goal for the biofuels GHG emissions (60% of emissions saving with respect to gasoline according to the EU Directive, 2009).

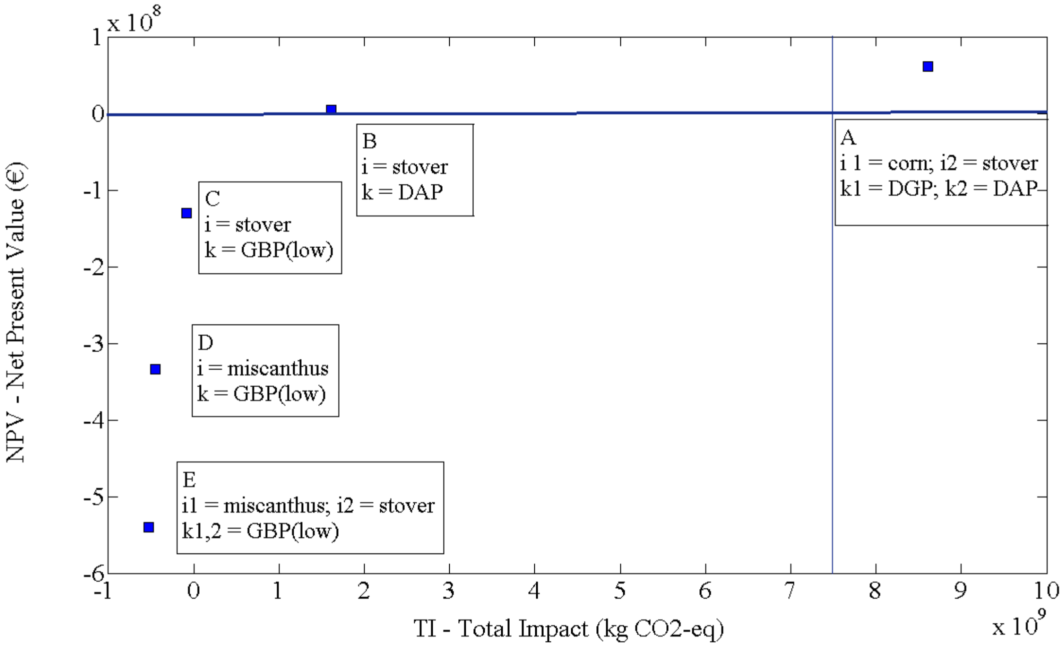

Figure 5.1 *Pareto curve. Simultaneous optimisation under expected profitability and GHG emissions minimisation criteria: i and k denote the selected feedstock and technology for the processing facilities.*

The economic optimum (point A in Figure 5.1) is represented by two equally-sized plants: a corn-based DGP and a stover-based DAP conversion facility. This system configuration reaches the economic optimum of about 0.23 €/GJ, thanks to a well-established and mature first generation technology. However, the solution is not capable to comply with the best GHG reduction targets, as provided by the legislation, requiring at least 60% of emissions reduction with respect to gasoline from 2017 onwards. The DGP facility is shut down after the fourth period of business when the carbon cost becomes too high for the process to be profitable (about 60 €/t on average). This does not occur with the facility operating with DAP technology, which allows for a reduction of about 77% in GHG emissions with respect to the DGP plant.

Moving down along the Pareto curve, (point B in Figure 5.1) better environmental performance is guaranteed by a stover-based ethanol production facility operating with DAP technology. The profitability decreases considerably, about 13% less than solution A (see Table 5.8), but still retains a positive value.

Moving towards the environmental optimum, gasification-based processes are selected (points C, D and E in Figure 5.1), showing their excellent performance in global warming mitigation. In particular, the environmental optimum (point E in Figure 5.1) providing the establishment of two cellulosic ethanol plants of equal and maximum size (276 kt/y of ethanol) operating with miscanthus- and stover-based gasification conversion process (GBP_{low}) represents the best design in terms of global warming (-2 kg CO_2-eq/GJ). However, the negative value of the eNPV (about -2 €/GJ) shows the lack of profitability for the business and indicates the need for some sort of policy support for this technology.

Table 5.8 *Pareto curve: expected profitability eNPV, impacts on global warming eTIOT and annual ethanol production rate* $P_{ethanol}$.

solution	eNPV [€/GJ]	TIOT [kg CO_2-eq/GJ]	$P_{ethanol}$ [t/y]
A	0.2318	32.6089	543935
B	0.0291	12.0297	276000
C	-0.9766	-0.6151	276000
D	-2.4976	-3.3592	276000
E	-2.0165	-1.9871	552000

5.5.2 Risk mitigation for the optimal economic solution

The optimal economic solution represented by point A in Figure 5.1, is the strategic solution in the case of a risk neutral investor. This means that he/she is willing to accept the maximum financial risk, leading to the highest profitability (the so-called unconstrained solution strategy). In the following, after having chosen a target profit ($\Omega = 3 \cdot 10^7$€), the constraint set by Eq. (5.7) is progressively tightened in order to decrease the financial risk on investment by reducing the risk-attitude parameter μ. Figure 5.2 shows the eDR and the corresponding VaR (represented as expected loss at 95% confidence level[2]) for the solution strategies obtained at different risk levels.

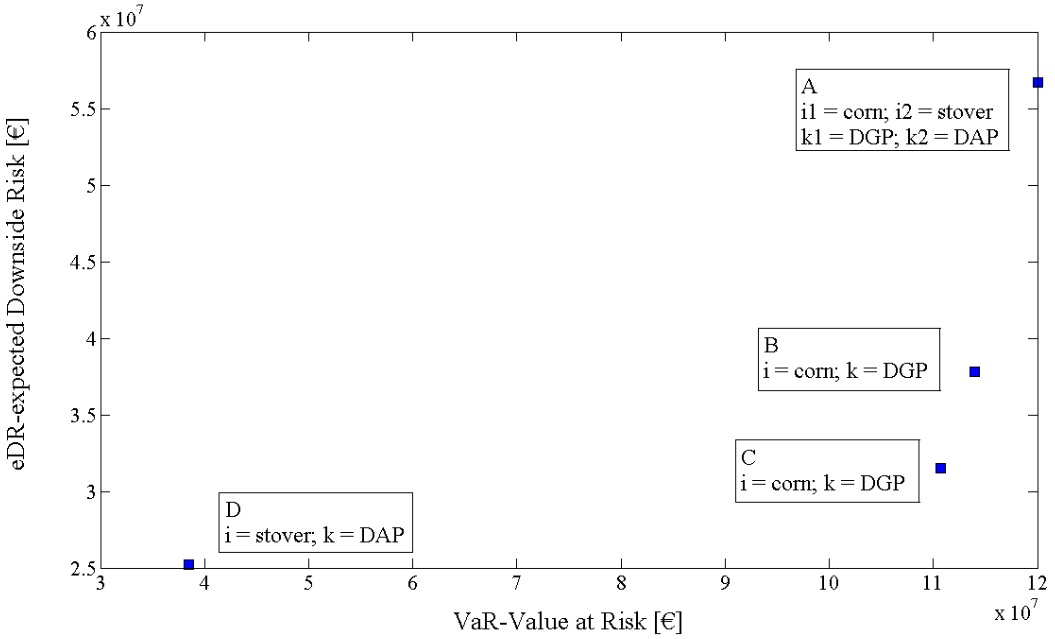

Figure 5.2 *Risk-constrained eNPV optimisation: expected downside risk (eDR) vs. potential loss (VaR). i and k denote the selected feedstock and technology for the processing facilities.*

The risk-unconstrained solution (point A of Figure 5.2) implies a very risk-oriented solution strategy, corresponding to the economic optimum in Figure 5.1, which involves the establishment of two facilities for ethanol production, belonging to first and second generation conversion processes. Thus, in order to achieve the best eNPV, the maximum risk-level should be taken.

Moving down towards less risky solutions (points B, C in Figure 5.2; $0.6 \leq \mu \leq 0.5$) biofuels SCs involve only one conversion facility operating with a corn-based DGP plant with a reduced capacity (from about 268 to 258 kt/y of ethanol).

A cellulose-based ethanol fuel SC represents the solution preferred by risk-averse investors (point D in Figure 5.2; μ = 0.4). The configuration involves one stover-based DAP process operating at the maximum available size (about 275 kt/y of ethanol). Such low propensity to risk, leads to a big drop in the eNPV: from 0.2318 €/GJ of the unconstrained solution down to only 0.0229 €/GJ.

Figure 5.3 and 5.4 represent the effective risk mitigation achieved in moving from the unconstrained to the risk-limited configurations. The strategic decision at low propensity for risk (μ = 0.4) implies a more centrally distributed NPV distribution: if, on the one hand the

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[2] Note that since here VaR is always negative, in Figures 5.2 and 5.5 it is represented as a potential absolute loss and accordingly is given a positive value.

probability of incurring into losses is now limited, on the other had the business has a lower probability of achieving large profits and the expected investment profitability is diminished.

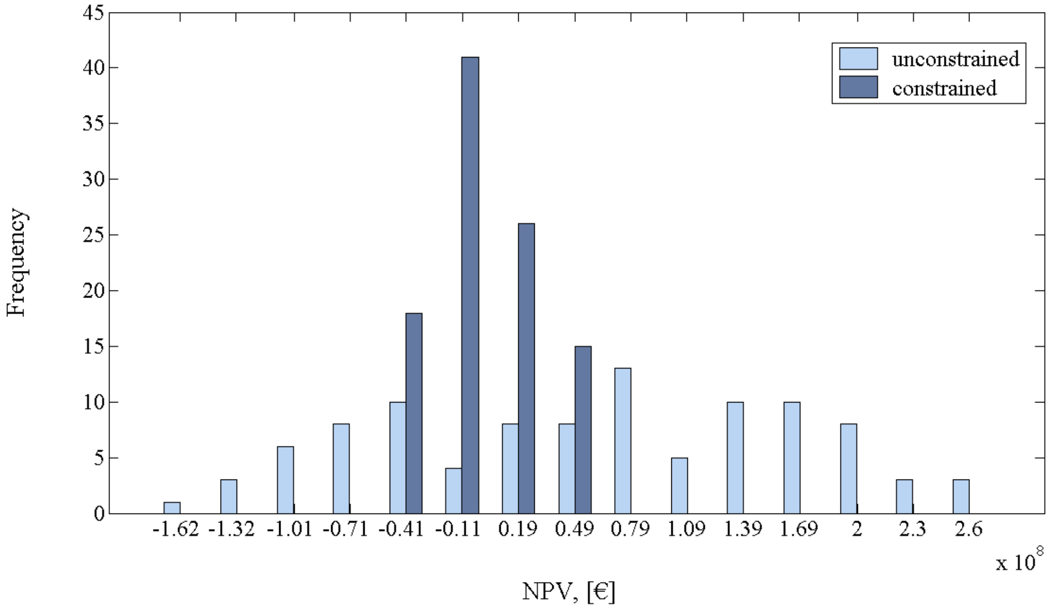


Figure 5.3 *Comparison in terms of NPV distribution between the unconstrained and risk-constrained optimisation.*

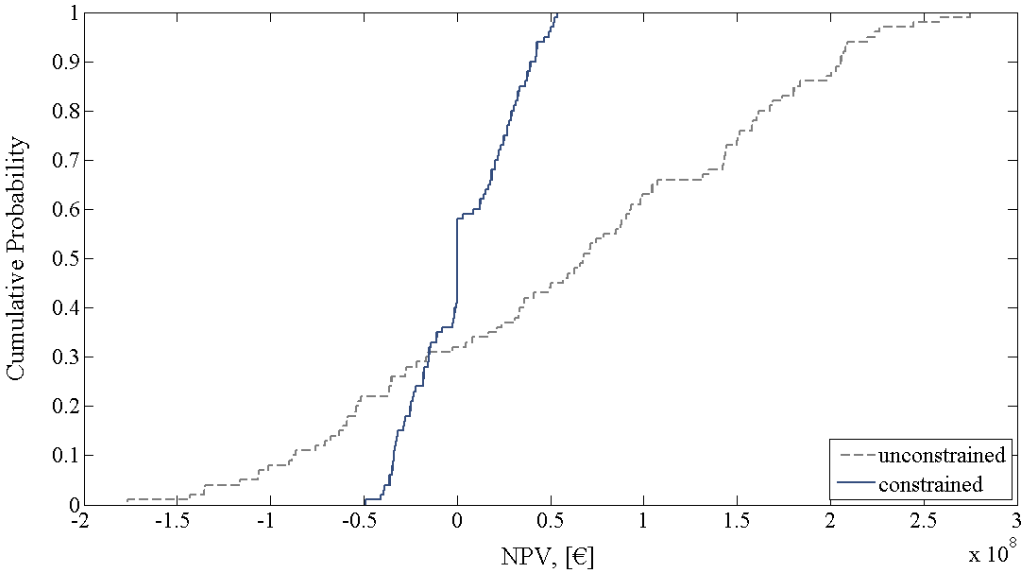


Figure 5.4 *Comparison in terms of cumulative probability NPV distribution between the unconstrained and risk-constrained optimisation.*

Risk aversion strategies seem to be driven towards the reduction of variable costs uncertainties. Thus, solutions using high-value commodities, as corn-based technologies, which suffer from a great variability in the raw materials market (whose cost can amount to about 70% of the total variable costs), are not pursued. On the contrary, low-value feedstocks (e.g., residues) are usually preferred, even if this may lead to lower profitability (e.g., stover-based technologies).

5.5.3 Risk mitigation for the optimal environmental solution

Point E in Figure 5.1 is the strategic solution for the best environmental performance in the case of a risk neutral investor. If a target profit ($\Omega = 3\cdot 10^7$ €) is set and the risk-attitude parameter μ is progressively tightened, new investment strategies are obtained representing different risk levels. Solution points are illustrated in Figure 5.5.

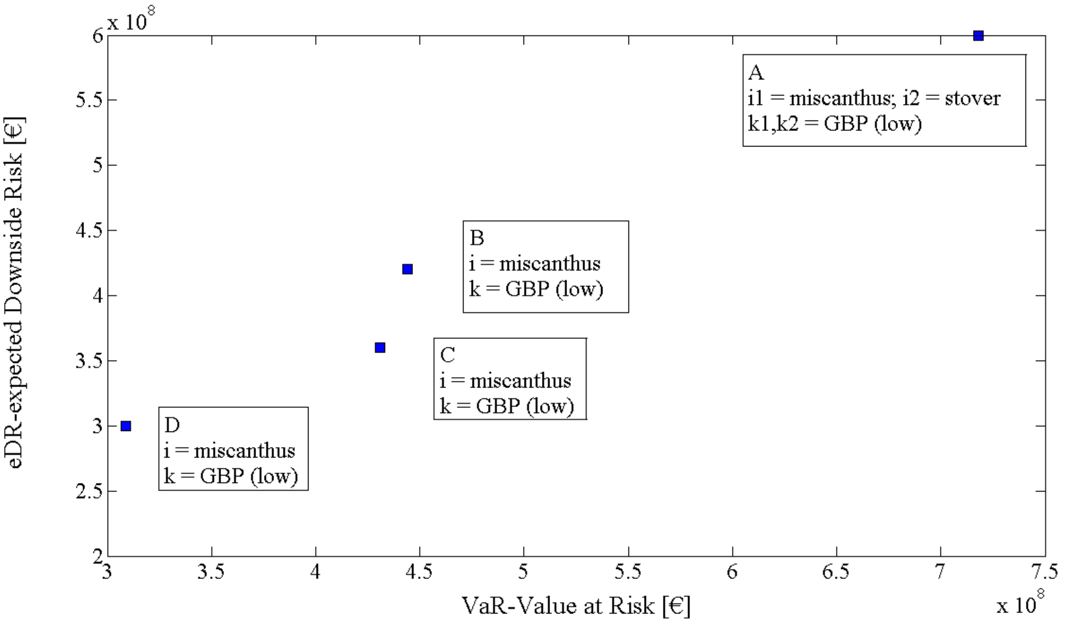


Figure 5.5 *Risk-constrained environmental optimisation: expected downside risk (eDR) vs. potential loss (VaR). i and k denote the selected feedstock and technology for the processing facilities.*

The unconstrained strategic solution of Figure 5.5 (point A), involving two GBP process-based facilities, is characterised by the maximum GHG emission savings. However, this configuration leads to a negative expected profit ($-5.4\cdot 10^8$ €, from a global ethanol production of 552 kt/y), which represents the highest potential economic loss.

Moving down towards less risky investment decisions (points B, C, D of Figure 5; μ ranging between 0.8-0.5) the optimal design is given by only one processing facility (a miscanthus-based GBP plant) operating at decreasing capacities from 276 down to 224 kt/y of ethanol. The eNPV distribution is shifted towards higher profits. Plant establishment is postponed to the third time period taking advantage of the higher value of the carbon allowances, whose revenues represent about 6% of the incomes. However, the high capital cost still hinders the profitability of the business. In this case, risk-averse decisions imply a reduction in the probability of incurring financial losses by establishing facilities of smaller capacities; therefore, the final eNPV, although still negative, is significantly improved ($-2.7 \cdot 10^8$ €).

5.6 Concluding remarks

Investments should be driven by purposed-devised quantitative multicriteria assessment tools to evaluate investment strategies in terms of business profitability, environmental impact and exposure to financial risk. To this purpose, a risk-constrained multiobjective stochastic MILP modelling framework for the design and planning of multi-echelon biofuels SCs has been proposed. The effect of carbon trading and technology learning has been assessed in an uncertain market scenario by considering first and second generation ethanol production technologies. Ethanol production in Italy has been analysed and optimised in terms of profitability and environmental impact. Results show that the strategic decisions do not only rely on the trade-off between environmental and economic performance, but are also strictly connected to the investor’s attitude towards risk.

Chapter 6

Conclusions and Future Perspectives

In acknowledging the importance and the urgency of a paradigm shift in the transportation sector, biofuels promotion represents a challenging task for future society development. Not only the settlement of a new energy provision system is advocated, but policy acts are required to be embedded within a comprehensive framework capable of addressing both pros and cons related to biofuels production.

As presented in previous chapters, biofuels systems design has been arising several and multi-faceted issues (e.g., economic profitability and environmental sustainability) and needs to be addressed through a comprehensive methodology embedding the overall steps of the production chain (supply chain, SC), from biomass cultivation up to fuel distribution, according to the principles of Supply Chain Management (SCM). Future biofuels production systems investments should be driven by purpose-devised decision-making tools based on multi-criteria analysis through Mathematical Programming and, particularly, MILP (Mixed Integer Linear Programming) modelling frameworks.

6.1 Overview of the main achievements

The main purpose of the Thesis was developed according to two general lines. First, the objective of the project was to develop a decision-making tool to support strategic policies on biofuels (bioethanol) production systems, embedding and integrating the principles of SCM with LCA (Life Cycle Assessment) within a comprehensive MILP modelling framework. Secondly, the research topic was focused on the exploration of a wider range of promising technologies with respect to the current bioethanol market, which is currently driven by first generation technologies (e.g., based on corn). The work has meant to highlight possible pathways for paving the way for most suitable technologies, showing trade-offs between environmental and financial sustainability. The model capabilities were illustrated outlining the optimal configuration of a bioethanol supply chain for transportation purposes in Northern Italy.

This Thesis has shown the effectiveness and the relevance of addressing real-world investment strategies through a comprehensive modelling approach based on the integrated analysis of a wide set of features and mutually exclusive configurations. In general, the MILP models developed represent decisions-supporting tools to industrial strategies and are often formulated as multi-criteria analyses to show trade-offs among conflicting targets (e.g., multi-objective optimisation). This is a challenging task for industrial investments planning: an investor needs to identify the best solutions of investments (e.g., capable of balancing, on the one side, business profitability, and, on the other side, environmental responsibility, with particular regard to legislation requirements). In addition, stochastic mathematical modelling frameworks have been implemented, being one of the most convenient options to address investments strategies in uncertain markets. By embedding probabilities distribution scenarios within a comprehensive framework, these models become a decision supporting tool of invaluable importance, allowing for strategic optimisation within contexts affected by uncertain exogenous factors. In this context, the investors' attitude towards financial risk has been implemented, too, to get sensible results addressing a real economic and financial context where industry is ever more exposed to changes of market conditions (e.g., feedstocks costs variability) and uncertainty may greatly affect profit expectations.

With regards to bioenergy promotion, this Thesis has addressed SCM as one of the most suitable techniques to study the multi-faceted and complex issues related to sustainability and competitiveness of biofuels generation. Biofuels sustainability is to be guaranteed on environmental terms, but they also need to be competitive with respect to the well-entrenched fossil infrastructures. Thus, the establishment of a new energy system for transportation needs considering and optimising all the steps of the production systems, according to the concept of supply chain management principles.

In the context of biofuels production promotion, the main achievements of this research project can be summarised as follows.

(i) The exploration of a wide range of production technologies and alternative by-products end-use options to steer the development of sustainable transportation systems represents one of the achievements obtained in this research.

In order to guarantee a smooth transition towards more sustainable technologies and to improve the dry-grind process environmental performance, potentials of alternative usage of first generation by-products (i.e., DDGS) or residue (i.e., stover) have been assessed. In addition, a novel contribution of the research work comes from the assessment of the possibilities of integrating first and second generation production systems within hybrid infrastructures as an economically sustainable alternative to pave the way for developing less-emitting ethanol production technologies. Optimisation results show the relevant role of hybrid ethanol generation in balancing better environmental performance than first generation at more acceptable costs than cellulosic technologies. Thus, this option appears as a promising technological alternative to help establishing advanced ethanol production processes.

Finally, several second generation technologies have been analysed to evaluate the potential pathway to the development of more sustainable biofuels. Technologies based upon dilute acid hydrolysis, representing the short-term performance of ethanol production, have been analysed along with developing processes, which may available in the mid- or long-term (steam explosion and gasification biosynthesis). In this context, the main contribution of the work was to embed environmental and economic issues in a unique stochastic moMILP formulation along with decision makers' risk mitigation preferences in facing uncertainty of feedstocks costs. Thus, business profitability is supported by environmentally-consciousness, but investment decisions are also influenced by investors' willingness to take financial risk. The different attitudes towards financial risk may be expressed through risk-indices providing the decision-makers with criteria to control and manage the SC risk on investment and allowing them to choose the strategy which better fits their risk-preferences. In addition, considerations of technological improvements due to accumulated experience of production and crop management issues, are key issues addressed in the formulation. The optimisation results show that in order to balance, economic profitability and environmental performance, DAP technologies can be considered a good option in the long-term. Planning strategies vary in terms of technology selection, number and size of the processing facilities according to the investors' attitude towards risk. Results also highlight the uncertainty surrounding GBP process, which represents a promising alternative but it is still unsustainable on economic and financial terms asking for more R&D endeavours on a microscopic and laboratory level.

(ii) Carbon trading scheme evaluated as a potential means to promote advanced biofuels production technologies represents another key aspect of this work.

The major barrier hindering the establishment of cellulosic ethanol is represented by elevated capital and operating costs with respect to the well-entrenched first generation production systems. One possibility to overcome such issues is represented by the introduction of economic subsidies as well as stricter limits on GHG emissions. It appears, however, that the promotion of biofuels in order to be effective in boosting innovative and more sustainable technologies, needs supporting them according to the technologies performance and efficacy in substituting fossil energies and reducing GHG emissions. Thus, a novel and thorough analysis has been performed implementing market-extensive mechanisms, such as carbon trading scheme where emissions allowances are traded at an uncertain price/cost depending on the technology potential on emission savings. A processing technology may have the possibility of selling or the need to buy permits to emit (according to its capability of reducing emissions with respect to fossil fuels). Thus, more sustainable technologies (i.e., second generation ones) are awarded with greater profits coming from the selling of permits and can compete with starch-based production systems. An innovative approach to bioethanol SC design has been implemented, where considerations about Soil Organic Carbon (SOC) effects, too, have been evaluated to explore its influence on carbon trading mechanisms. Results show the relevance of a carbon trading scheme in steering technological innovation in the transportation sector, promoting more sustainable processes ethanol generation at lower costs. According to this framework, dilute acid or gasification biosynthesis processes may be the winning choices, notwithstanding the uncertainties on some technological issues. In general, it appears that stricter limits on GHG emissions would reduce the process profitability, but make it more advantageous with respect to fossil fuels (i.e. gasoline).

6.2 Future perspective

Some considerations about future research directions are in order at this point.

6.2.1 Carbon trading modelling advancements

One possible advancement of the work refers to a more comprehensive analysis of international policy framework and regulation scheme capabilities in promoting biofuels, with particular regard to carbon trading scheme.

The proposed framework exploited to assess the effect of a carbon trading scheme (according to the approach proposed by Bojarski *et al.* (2009)) to steer innovation and promote more sustainable technologies for biofuels production with respect to GHG emissions, has been tailored to the upstream ethanol supply chain. The suggested framework may be helpful in assessing the effect of strategic decision policy on biofuels production system, but it is necessary to highlight its limitations and field of applicability. The work has dealt with how the profitability of a ‘closed system’ may be affected by carbon trading and how the selection of the production technology may depend on carbon cost. One basic assumption is that the product demand is fixed and the required biomass always available. This is quite a simplification, but it represents the first modelling step towards more complex frameworks, which may result computationally prohibitive if a preliminary more detailed analysis has not been carried out. This is a sensible approach is to build up ever more comprehensive models according to a bottom-up approach.

The first extension is to move the model within a spatially explicit framework (e.g., as in Zamboni *et al.* (2009a)) to account for territorial specificity in terms of biomass productivity, crop rotation, product demand, transport availability and plant location. In this context, one possibility is also to take into account product price uncertainty (e.g., Dal-Mas *et al.*, 2011).

The successive step might include the fuel production system within a comprehensive system approach where more players and consumers' attitude should be taken into account. Game's theory and non-equilibrium assumptions may be advocated (von Neumann and Morgenstern (1944); Shah *et al.* (2001)). In this context, the best solution is usually to refer to partial equilibrium models or even general equilibrium models such as the Global Trade Analysis Project (GTAP, 2011) in order to assess a global effect on the fuel market and related emissions, which would be affected by global oil prices, biofuel price and capacity in tropical countries, international trading regulation, government subsidies as well as environmental legislation.

6.2.2 Transportation sector sustainability

With concerns to bioethanol production, a more comprehensive view of a sustainable development on a large scale is advocated, taking into account other effects on environment than the sole GHG emissions.

One urgent topic in the deployment of future biofuels infrastructures refers to water consumption (the so-called water footprint) (Hoekstra, 2003; The Royal Society, 2008; Hoekstra *et al.*, 2011), which has been up to now devoted to the sole process optimisation (Ahmetović *et al.*, 2010; Grossmann and Martìn, 2010). However, biofuels SCs design and planning have to take into account the impact on water resource depletion and this advocates the need for evaluating environmental impacts in an integrated and comprehensive manner within a SCM framework. Possibly trade-offs between climate change mitigation and water stress might be generated and need to be properly addressed (Gheewala *et al.*, 2011). In appendix D, a preliminary framework for studying the impact on water resource, which was initiated during this research project, is briefly outlined. Results show the implications of technology selection for ethanol production on water usage and the urgency of identifying a standard methodology accounting for water stress (e.g., allocation method; direct and indirect impacts). A more sustainable usage of water resource might be ensured through the promotion of low-water requirements feedstocks (i.e., cellulose-based technologies), being the agricultural phase the main contributor to the resource consumption. In order to avoid episodes of water scarcity due to bioenergy deployment, however, the local level of water availability needs to be taken into account and this clearly advocates for the need to extend the mathematical modelling to a spatially-explicit approach, providing evidence of the local amount of the resource available.

Another challenging issue to support decisions on investments in biofuels deployment refers to the implementation of iLUC (indirect Land Use Change) effects. In particular, large-scale expansion of biofuels could cause the release of GHG emissions to the atmosphere through land-use change as new regions might be used to meet increased crop demand to supply food and feedstock for biofuels (Delucchi, 2006). The main issue concerning iLUC effects assessment regards the identification of the amount of land needed to be replaced to keep satisfying both bioenergy and food increasing needs. This involves a wide range of decisions and might require partial or general equilibrium models to achieve an accurate analysis (GTAP, 2011) and to capture the worldwide interactions between different markets and countries.

Finally, future development of electric mobility might represent a promising alternative for passengers' transport in its capabilities of reducing oil dependence and GHG emissions (Lucas *et al.*, 2011). This involves, in particular, strategic decisions related to power generation infrastructures establishment and technology selection which might be properly driven through adopting a comprehensive approach embedding all the SC phases according to SCM techniques.

6.2.3 Economic assessment: real option analysis

In order to address uncertainty and the impact of rising volatility in market prices, a real options analysis of entry–exit decisions for ethanol plants might also be carried out and being incorporated within the modelling framework. This study may be particularly valid in an immature industry subject to abrupt price fluctuation or for which the underlying market conditions have shifted dramatically due to market structural changes (Schmit *et al.*, 2009).

Growth in the variability of ethanol margins, due to market uncertainty, might be addressed through introducing possibilities of delays in new plant investments, as well as exits of currently operating facilities. In fact, the introduction of this kind of flexibility option within the model, would make these renewable technologies more viable. The approach of real option analysis extends financial option theory to physical assets; e.g., entry and exits by firms might be modelled as call and put options. When considering uncertainty, a company may be reluctant to make an investment because not making that investment preserves the opportunity of making a better investment later. Once the investment is made, however, a firm may be reluctant to exit the industry because it holds the option of keeping the operation going until market conditions improve.

Appendix A

This appendix addresses the procedure used to model hybrid processes for ethanol generation using both starchy (e.g., corn grain) and cellulosic (e.g., corn stover) feedstocks.

First a rigorous approach based on process simulation to the characterisation of the hybrid technology is discussed. Then capital (*FCI*, *TCI*) as well as operating costs (*TPC*) are estimated.

A.1 Hybrid process simulation

According to 2005 USDA report (USDA, 2005), the technical solution chosen to combine corn grain and lignocellulosic biomass processes at the minimum production cost, consists in integrating the ethanol rectification sections and utility generation systems (Figure 2.3).

Process configuration is modelled in Aspen Plus® and studied with three instances by varying the specific stover to grain ratios: 1:1 (Instance A), 2:1 (Instance B) and 3:1 (Instance C), respectively producing 24500 kg/h, 35400 kg/h, 45700 kg/h of ethanol.

A.1.1 Raw materials

Feed specifications are:

- Corn grains: rate = 40934 (kept constant for each instance); T = 25 °C; P = 1 atm
- corn stover: flow-rate = 40940; 81880; 122820 kg/h; T = 45 °C; P = 1 atm.

Corn grain and stover can vary in composition and moisture content due to variety, region, weather, soil type, harvesting and storage practices, but these effects have not been taken into consideration. The feedstocks compositions used in the work are reported in Table A.1 and A.2.

Table A.1 *Corn grain composition at 15% of moisture content (Franceschin et al., 2008).*

component	composition [%w/w] on dry basis
xylose	7.29
xylane	15.42
cellulose	6.73
starch	70.00
lignin	0.56

Table A.2 *Corn stover composition at 15% of moisture content (USDOE, 2002).*

component	**composition [%w/w] on dry basis**	
cellulose	37.4	
galactan	2.0	hemicellulose 27.6
mannan	1.6	
xylan	21.1	
arabinan	2.9	
acetate	2.9	
lignin	18.0	
ash	5.2	
protein	4.2	
extractives	4.7	

A.1.2 Components and properties

The combined starch and cellulose-derived ethanol process involves the presence of insoluble and soluble solids. Their physical-chemical property data are not available in the standard Aspen Plus® property databases and they have been retrieved from the literature (NREL, 1996; Franceschin *et al.*, 2008). Table A.3 shows the component list with their common, database and the abbreviate names adopted in the simulations.

Component properties are characterised in the model according to the approach by NREL (1996). Moreover:

1. ashes, which are supposed to have negligible effects upon liquid-vapour equilibria (NREL, 1996) are modelled by referring their properties to those of biomass, i.e., cell mass solids. It would be reasonably expected that this approximation does not cause any considerable changes on the equilibria, but it actually modifies the final solid amount with respect to completely neglecting the ashes existence in the feedstock.
2. supposing negligible effects upon the liquid-vapour equilibria, starch hydrolysis enzymes and fermentation yeasts are given the same property parameter data as those used for cellulosic simultaneous saccharification and co-fermentation (NREL, 1996).

A.1.3 Thermodynamic model

The thermodynamic model has to portray the distillation of ethanol and the handling of dissolved gases, thus the standard NRTL model (Renon and Prausnitz, 1968) is used along with the Henry's law for CO_2 (Franceschin *et al.*, 2008).

Table A.3 *Component list.*

component name	**database name**	**component ID**	**type**	**formula**
OXYGEN	OXYGEN	OXYGEN	CONVENTIONAL	O2
CARBON DIOXIDE	CARBON-DIOXIDE	CO2	CONVENTIONAL	CO2
ETHANOL	ETHANOL	ETHANOL	CONVENTIONAL	C2H6O-2
WATER	WATER	WATER	CONVENTIONAL	H2O
ACETIC-A	ACETIC-ACID	ACETIC-A	CONVENTIONAL	C2H4O2-1
GLYCEROL	GLYCEROL	GLYCEROL	CONVENTIONAL	C3H8O3
LACTIC ACID	LACTIC-ACID	LACTIC-A	CONVENTIONAL	C3H6O3-D1
SUCCINIC ACID	SUCCINIC-ACID	SUCCINIC	CONVENTIONAL	C4H6O4-2
SULFURIC ACID	SULFURIC-ACID	SULFURIC	CONVENTIONAL	H2SO4
XYLANE	GLUTARIC-ACID	XYLANE	SOLID	C5H8O4
XYLOSE		XYLOSE	CONVENTIONAL	C5H10O5
GLUCOSE	DEXTROSE	GLUCOSE	CONVENTIONAL	C6H12O6
CELLULOS	DILACTIC-ACID	CELLULOS	SOLID	C6H10O5
STARCH	DILACTIC-ACID	STARCH	SOLID	C6H10O5
LIGNIN		LIGNIN	SOLID	
BIOMASS		BIOMASS	SOLID	
SOLUBLE SOLIDS		SOLSLD	CONVENTIONAL	
LIME	CALCIUM-HYDROXIDE	LIME	CONVENTIONAL	CA(OH)2
GYPSUM	CALCIUM-SULFATE-DIHYDRATE-GYPSUM	CASO4	SOLID	CASO4*2H2O
CELLULASE		CELLULAS	SOLID	
ZYMO MOBILIS		ZYMO	SOLID	
CELLOBIOSE	SUCROSE	C12H2201	CONVENTIONAL	C12H22O11
FURFURAL	FURFURAL	FURFU-01	CONVENTIONAL	C5H4O2

A.1.4 Process flow-sheet

Corn stover is processed with dilute acid hydrolysis, enzymatic saccharification and co-fermentation. Corn grain biomass is treated with the dry-grind process as well as simultaneous saccharification and fermentation reactions. The integration between the two processes has been carried out according to 2005 USDA report.

In the following, the process steps modelled (e.g., pretreatment, reaction, recovery, evaporation) are presented.

A.1.5 Pretreatment and reaction

A.1.5.1 Corn stover: pretreatment

Washed and shredded corn stover is fed to the pretreatment. The main purpose of this section is to convert by hydrolysis reactions, most of the hemicelluloses to soluble sugars (primarily xylose, mannose, arabinose and galactose) exposing the cellulose for the subsequent enzymatic hydrolysis. A small portion of cellulose is converted to glucose, little part of the lignin in the feedstock is solubilised and acetic acid is liberated.

The pretreatment section is modelled with a first presteamer unit, where the feed is mixed with low-pressure steam, in order to remove non-condensable gases and later treated with dilute sulphuric acid (1.64%w/w inside the reactor) and high pressure steam (P = 13 atm) for short time (2 minutes). Then, pretreatment reactions take place at T = 190 °C, P = 12.1 atm. Reactions involved in the biomass pre-treatment are listed in Table A.4. Lignin solubilisation, as well as oligomers production, (e.g., unknown final decomposition products, TAR, and hydroxymethyl furfural, HMF) are neglected. Reactions conversion has been normalised in order to obtain the same global cellulose and xylan conversion values as literature (NREL, 2008).

Table A.4 *Corn stover pre-treatment reactions and conversions (NREL, 2008).*

reaction	reactant	fraction converted to product
$(\text{cellulose})_n + n\,\text{H}_2\text{O} \rightarrow n\,\text{glucose}$	cellulose	0.105
$(\text{xylan})_n + n\,\text{H}_2\text{O} \rightarrow n\,\text{xylose}$	xylan	0.89
$(\text{xylan})_n + n\,\text{H}_2\text{O} \rightarrow n\,\text{xylose}$	xylan	0.06
$(\text{acetate})_n \rightarrow \text{acetic acid}$	acetate	1.0

During the acid hydrolysis phase, several compounds capable of inhibiting microbial growth and fermentation are produced (e.g., furans, soluble phenolic compounds as well as acetic and other aliphatic acids) (Martinez *et al.*, 2001). Thus the hydrolysate needs of further treatments before being fermented (e.g., conditioning): it is cooled through an atmospheric flash (15 minutes), vaporising a large amount of water and most of the toxic compounds (USDOE, 2002). The hydrolysate is cooled down to 50 °C before solids are separated from liquids, through a centrifuge. Liquid portion of the hydrolysate is then conditioned, to reduce toxic content before biological reactions.

The most widely method for hydrolysate conditioning, because of its low cost and relative efficiency, is the treatment with lime (Mohagheghi *et al.*, 2006), the so-called overliming. This process can take place in a wide variety of conditions and Millati *et al.* (2002) studied the influence of detoxification pH, temperature and time: the greater pH, residence time and temperature, the better the conditioning (without drastic effects of temperature); however sugar losses are increased. So, while reducing hydrolysate toxicity (e.g., furans and phenolic compounds reduction), conditioning causes sugars reduction. The reaction is modelled as follows:

$$\mathrm{Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O}$$

The overliming step is modelled by using Mohagheghi *et al.* (2006) best performance conditions with respect to the ethanol yield. The reaction takes place at T = 50 °C, P = 1 atm, *residence time* = 30 minutes and it is supposed to have a complete conversion of sulphuric acid. Sugar losses, of about 13% of xylose and 12% of glucose (Mohagheghi *et al.*, 2006) are envisaged.

A next reacidification step is needed for keeping yeasts and bacteria in a favourable environment for growth and fermentation. This phase consists in liquor re-acidification close to neutral pH (Mohagheghi *et al.*, 2006) by adding up a stoichiometric sulphuric acid rate (USDOE, 2002). The neutralisation reaction is:

$$\mathrm{Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O}$$

that is supposed to operate at P = 1 atm and T = 53 °C and with a complete lime conversion.

The gypsum from the liquid phase is separated in two steps: the former after overliming, the latter after re-acidification through hydrocyclones and rotary drum filters. It has been supposed a complete separation of gypsum only, even though some water and soluble components might be actually carried out with the solid (Mohagheghi *et al.*, 2006). Because of the lack of information, potential effects on the downstream reactions (Mohagheghi *et al.*, 2006), due to the great amounts of soluble calcium sulphate (30%) which may remain in the conditioned hydrolysate have been neglected.

A.1.5.2 Corn stover: reaction section

After gypsum removal by two filtration steps, the conditioned liquor and solids are mixed together and pumped to the saccharification unit.

The section for corn stover is modelled according to the literature (USDOE, 2002), but seed fermentation as well as bacteria metabolism and growth are neglected. SSCF, which consists in the simultaneous saccharification and co-fermentation of C_5 and C_6 compounds, has been split up into two trains of vessels. In the former, hydrolysis (or saccharification) occurs separately from the fermentation to promote *cellulase* enzyme activity with temperature. In the latter, both reactions (e.g., saccharification and co-fermentation) take place simultaneously because of the presence of both *cellulase* enzymes and *Z. mobilis* bacteria. Thus, both kinetics may be improved by the different temperatures the reactors work at. The saccharification unit works at: T = 65 °C; P = 1 atm; *residence time* = 7 days; with *cellulase* rates determined from the literature (USDOE, 2002).

Table A.5 summarises the employed reactions and conversions used.

Table A.5 *Hydrolysis reactions and conversions (USDOE, 2002) (decomposition to oligomers neglected).*

reaction	reactant	fraction converted to product
$(\text{cellulose})_n + \frac{1}{2n}\,\text{H}_2\text{O} \rightarrow \frac{1}{2n}\,\text{cellobiose}$	cellulose	0.013
$(\text{cellulose})_n + n\,\text{H}_2\text{O} \rightarrow n\,\text{glucose}$	cellulose	0.939
$\text{cellobiose} + \text{H}_2\text{O} \rightarrow 2\,\text{glucose}$	cellobiose	1

Saccharification and co-fermentation of C_5 and C_6 take place in the presence of *cellulase* enzyme and *Zymomonas mobilis* bacteria, a recombinant glucose/xylose-fermenting micro-organism. The reactor operates at: T = 37 °C (Mohagheghi *et al.*, 2004); P = 1 atm; residence time = 7 days (USDOE, 2002).

Table A.6 *Corn stover saccharification and co-fermentation reactions conversions (USDOE, 2002).*

reaction	reactant	fraction converted to product
$\text{glucose} \rightarrow 2\,\text{ethanol} + 2\,\text{CO}_2$	glucose	0.969
$\text{glucose} + 2\,\text{H}_2\text{O} \rightarrow 2\,\text{glycerol} + \text{O}_2$	glucose	0.004
$\text{glucose} + 2\,\text{CO}_2 \rightarrow 2\,\text{succinic acid} + \text{O}_2$	glucose	0.006
$\text{glucose} \rightarrow 3\,\text{acetic acid} + \text{O}_2$	glucose	0.015
$\text{glucose} \rightarrow 2\,\text{lactic acid}$	glucose	0.002
$3\,\text{xylose} \rightarrow 5\,\text{ethanol} + 2\,\text{CO}_2$	xylose	0.913
$3\,\text{xylose} + 5\,\text{H}_2\text{O} \rightarrow 5\,\text{glycerol} + 2.5\,\text{O}_2$	xylose	0.003
$3\,\text{xylose} + 5\,\text{CO}_2 \rightarrow 5\,\text{succinic acid} + 2.5\,\text{O}_2$	xylose	0.01
$2\,\text{xylose} \rightarrow 5\,\text{acetic acid}$	xylose	0.015
$3\,\text{xylose} \rightarrow 5\,\text{lactic acid}$	xylose	0.002

Table A.6 summarises the conversion values used in the model as retrieved from the literature for reactions taking place at T = 41 °C (USDOE, 2002). The 4 °C-temperature difference between the literature and the model is neglected according to Mohagheghi *et al.* (2004). Biomass growth and xylitol production are not modelled, thus, the remaining conversion values have been adapted to keep the overall glucose and xylose conversions unchanged with regard to the literature.

A.1.5.3 Corn grain pretreatment section

After being received, the corn grain feedstock is stored, cleaned and milled. Pretreatment consists of three main steps (Franceschin *et al.*, 2008): mashing, liquefaction and cooking.

1. Corn is mixed with process water to obtain the so-called mash, which is a slurry whose viscosity is lowered through the *α-amylase* enzyme. Acid and basic compounds are added up in order to regulate mash pH, but their flows are not modelled.
2. The mash undergoes liquefaction (T = 85-90 °C, P = 1 atm, *residence time* = 60 minutes (Kwiatkowski *et al.*, 2006): starch is gelatinised through reaction with direct steam injection and hydrolysed with *α-amylase* into oligosaccharides.
3. Starch is finally cooked with low pressure steam (P = 4.42 atm).

According to industrial data, the *α-amylase* flow-rate for the three instances (A, B, C) is set equal to 0.02 $t \cdot h^{-1}$.

A.1.5.4 Corn grain reaction section

The corn grain section process involves the SSF reactions, the simultaneous saccharification and fermentation: starch is first converted to simple sugars (glucose and maltose) that are finally fermented to ethanol. *Gluco-amylase* enzymes and yeasts (typically *Saccharomyces cerevisiae*) are both introduced into the reactor. Biomass growth and maltose production are neglected. The reactor operates at T = 35° C, P = 1 atm (Franceschin *et al.*, 2008). Enzymes rates are estimated according to available industrial data. The extents of the reactions taking place in the SSF reactor are collected in Table A.7.

Table A.7 *Corn SSF reactions and conversions (Franceschin et al., 2008).*

reaction	reactant	fraction converted to product
$(\text{starch})_n + n\,\text{H}_2\text{O} \rightarrow n\,\text{glucose}$	starch	0.99
$\text{glucose} \rightarrow 2\,\text{ethanol} + 2\,\text{CO}_2$	glucose	0.955
$2\ \text{glucose} + \text{H}_2O \rightarrow \text{ethanol} + 2\,\text{glycerol} + \text{acetic acid} + 2\,\text{CO}_2$	glucose	1

A.1.6 Purification

In order to remove non-condensable components (particularly O_2 and CO_2), streams coming from reaction sections are separately conveyed to two beer wells modelled as atmospheric flash: the one of the lignocellulosic plant operating at T = 37 °C and the one of the corn plant working at T = 35 °C (Franceschin *et al.*, 2008; USDOE, 2002).

The vapour streams exiting the beer wells are sent to a unique scrubber while the bottoms are conveyed to the recovery section: one beer column per each liquid beer well-exit stream and a unique rectification tower. The integration of the purification section, proposed according to

USDA (2005), is shown in Figure A.1. The vapour leaving the top of the starch-side beer column is added to the side product stream from the stover beer column and sent to the rectifier. The bottoms of the starch beer column, leading to DDGS production, (stream A in Figure A.1), are not affected by the combined purification but is conveyed to the evaporation section. The residual lignin stream mainly obtained from stover pretreatment is burned along with an excess of stover, in the CHP system to provide steam and electricity to the overall integrated process (i.e., the natural gas boiler in the corn starch ethanol plant is discarded).

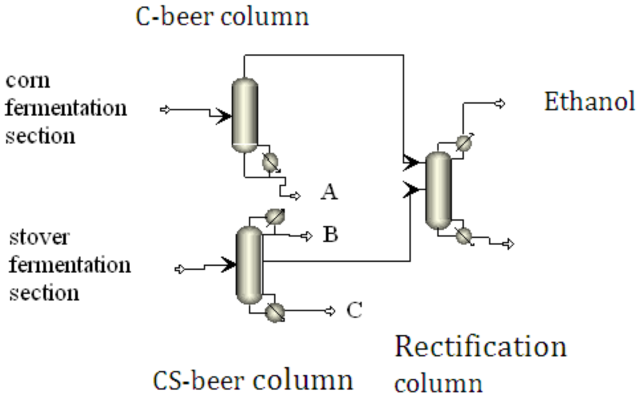


Figure A.1 *Combined purification train columns (C-beer and CS-beer columns are the columns for corn- and stover-based beers; A is the stream entering the corn evaporation section; B is the stream entering the stover scrubber; C is the stream entering the stover evaporation section).*

The corn stover beer column operates at a pressure of 3 atm. The configuration of this tower is justified by the need to remove most of the CO_2 and as little ethanol as possible overhead; about 90% of the water is recovered at the bottom. In particular, from this tower the following streams are obtained (USDOE, 2002):

- at the top a vapour stream rich of non-condensable components, also conveyed to the scrubber,
- a liquid bottom phase, where acids and soluble solids are abundant, sent to the evaporation section
- a side product rich in ethanol (about 27% (w/w)).

Corn beer column works at 2 atm and a vapour ethanol-rich stream (almost 37% (w/w)) is obtained overhead. The bottoms contain soluble and insoluble solids which are sent to the evaporation section.

The scrubber is a packed column working at P = 1 atm. This column is used for ethanol recovery from vapours of beer columns and beer wells. Vapour flows counter-current to a water stream fed at: T = 25-26 °C; P = 1 atm. The bottoms are completely recycled to the corn and stover pretreatment and beer wells.

The vapour side draw coming from the corn stover beer column and the distillate from the corn beer one are both conveyed to the rectification column operating at P = 2 atm. The rectification distillate is an ethanol-rich stream (92.5% (w/w)), that is sent to dehydration section. The bottoms are conveyed to water recycle.

The dehydration section which consists of two molecular sieve towers working alternatively, enables to obtain ethanol at 99.9% (w/w).

A.1.7 Downstream column section

Beer columns bottom solid-rich streams are sent to a set of counter-current evaporators.

The corn stover evaporator sector encompasses a first steam-fed evaporator followed by a centrifuge, from which a stillage (a stream with low solid amount, at about 5%) as well as a cake (a stream rich in solids, at about of 40%), are obtained. The stillage is partly recycled to reaction (25% (w/w)) and the remaining goes into the subsequent counter-current evaporator, each one fed by vapours coming from the previous unit, to save on the steam plant needs. A number of effects are present in the evaporation section in order to separate a syrup concentrated in solids (about 40%(w/w)), then fed to the combustor, from the evaporated condensates which are recycled to the process. The burner of the CHP station is also supplied by an excess amount of corn stover as well as the output streams of the waste water treatment section (e.g., sludge and biogas).

With concern to the corn treatment section, the beer column bottoms are sent to a centrifuge. A solid-poor stream (a stillage at about 12% of solid content) and a cake rich in solids (about 30% of solid content) are obtained. About 10% (w/w) (Franceschin *et al.*, 2008) of the stillage is recycled to fermenter and the remaining is sent to the counter-current evaporators. The syrup concentrated by evaporators is mixed with the cake from the centrifuge, and finally dehydrated to DDGS which is generally sold as fodder (an alternative use of DDGS is discussed in section A.4).

A.1.8 Wastewater treatment section

Wastewater streams (e.g., from pretreatment and separation systems) are sent to the corresponding treatment section (wastewater treatment, WWT), where feed goes through anaerobic and aerobic digestion, producing biogas and sludge, both sent to a combustor. WWT mass and energy balances, although not modelled in the Aspen Plus® simulator, are based on a spreadsheet tool devised according to the approach and assumptions by the USDOE (2002).

Biogas rate is estimated considering that:

- the total chemical oxygen demand (COD) for the stream entering the anaerobic digestion is approximately 16 g/L;
- within anaerobic digestion, 90% of each organic component is converted to methane and carbon dioxide (at the ratio 3:1); methane maximum yield of production is 0.229 kg/kg of COD at 25°C.

The sludge is constituted by cell mass (30%) and water. Biomass first grows in the anaerobic digestor (30 g per kg of COD removed) and then in the aerobic lagoons (30% of the soluble solids of the feeding stream, 0.1% (w/w), is converted to cell mass).

A.1.9 Combustion and Turbogeneration

Steam and electricity for the hybrid process are provided by a CHP station. The CHP system feed comprises:

- the lignin as well as the cellulose and hemicellulose unconverted;
- a syrup (high in soluble solids) obtained from the concentration of the stillage by corn stover evaporation section;
- biogas;
- waste biomass (sludge) produced by the aerobic digestion.

If an additional amount of corn stover is added to feed the CHP station it is possible to make the plant self-sufficient in terms of steam and electricity.

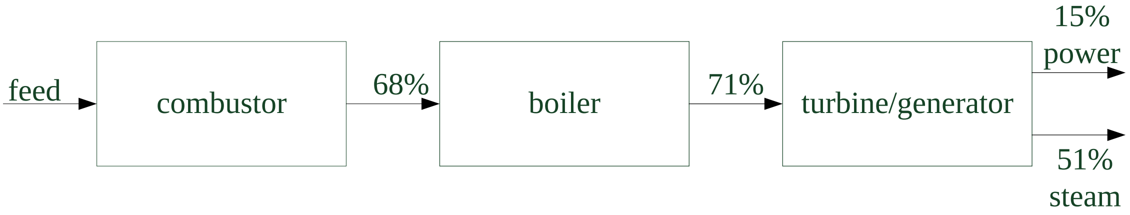


Figure A.2 *Combustor and turbogenerator energy balance: all the energy flows are fractions of the energy content of the feed to the combustor (USDOE, 2002).*

The scheme of Figure A.2 portrays the details about the combustor-boiler-turbogenerator subsystem.

The main technical devices of the CHP station are reported in the following.

- The combustor is supposed to be a Circulating Fluidised Bed operating with air supply determined according to the literature (USDOE, 2002). Feed moisture might reduce

CHP energy efficiency. A minimum threshold for the moisture content of the feedstock should be lower than 70% on a wet basis (Wang *et al.*, 2009).

- Treated water enters the heat exchanger circuit in the combustor and is evaporated and superheated to T = 510 °C and P = 86 atm producing steam. Boiler efficiency, defined as the percentage of the feed heat that is converted to steam heat, is 68%.
- A multistage turbine and generator, to which enters the 71% of the energetic content of the combustor inlet, are used to generate electricity. Steam is extracted from the turbine at two different conditions for injection into the pre-treatment reactor (P = 13 atm) and heat exchangers in distillation and evaporation (P = 4.42 atm).

A.1.10 Hybrid process technical performance

Table A.8 collects the overall technical characterisation of the hybrid process of ethanol production, including product and electricity generation yields. Power and steam requirements are determined according to literature (NREL, 2000; USDOE, 2002). The stover excess for the CHP station represents the amount of stover, which is required in addition to that used for ethanol production, in order to make the plant self-sufficient in terms of energy balance.

Table A.8 *Main technical characterisation of the hybrid plant.*

mass balance	
corn-based ethanol	0.332 kg of ethanol/kg of corn
stover-based ethanol	0.267 kg of ethanol/kg of stover
DDGS yield	0.954 kg of DDGS/kg of ethanol
additional stover feedstock for CHP station over total biomass supply (wet basis)	
stover excess - Instance A	35.4%
stover excess - Instance B	27.9%
stover excess - Instance C	19.5%
fresh well water (USDOE, 2002)	
Instance A	186370 kg/h
Instance B	268969 kg/h
Instance C	347036 kg/h
excess power generation [kWh/L of ethanol]	
Instance A	0.482
Instance B	0.515
Instance C	0.533

A.2 Hybrid process cost estimation

This section deals with the combined plant cost evaluation; the final objective is the fixed and total capital investment (*FCI* and *TCI*, [€]) assessment, performed according to the literature (Peters *et al.*, 2003). Each piece of equipment purchased cost is determined through Peters' generalised diagrams and correlations (Peters *et al.*, 2003). Costs are then updated accounting for inflation effects through Marshall & Swift equipment cost index of the process industry. Finally, a factored estimate approach (Peters *et al.*, 2003) is performed, where *FCI* and *TCI* are determined as percentages related to the purchased equipment cost.

Table A.9 provides an overview of the approach used in the cost estimation procedure per each piece of equipment modelled. Most of the results are collected and reported at the end of this appendix.

Table A.9 *Overview of the cost assessments methods.*

piece of equipment	cost method	reference	2002$ costs results
pumps	generalised diagrams for centrifugal pumps	Peters *et al.*, 2003	Tables A.15, A.16, A.17
heat exchanger	floating-head heat exchanger scaling method†	Peters *et al.*, 2003	Tables A.18, A.19, A.20
tanks and reactors	vessel cost†† generalised diagram for agitator cost	Peters *et al.*, 2003	Tables A.21, A.22, A.23
recovery system	columns, scrubber, auxiliaries	Guarise, 2000 Peters *et al.*, 2003	Tables A.24, A.25, A.26, A.27
solid-liquid separation	hydrocyclones, centrifuge	USDOE, 2002 Peters *et al.*, 2003	Table A.28
evaporation	vertical tube generalised diagram, scaling method	Peters *et al.*, 2003	Tables A.29

† $cost\,of\,equipment\,a = (cost\,of\,equipment\,b) \cdot X^{scaling\ factor}$ is the scaling rule used to determine the costs for the pieces of equipment, where X is the ratio between the reference scaling properties.

†† $vessel\ purchsed\ cost = price_{SS} \cdot (W_v)^{0.66}$ where W_v is the weight of the vessel and $price_{SS}$ represents the unitary cost of stainless steel.

A.2.1 Fixed and Total Capital Investment

In Table A.10 costs estimations are presented and grouped by process sections: feed handling, pretreatment, reaction, separation, WWT, storage, combustion as well as air pretreatment and cooling towers (CTS).

The method used for estimating the fixed and the total capital investment requires the determination of the delivered-equipment cost. For predesign estimates, a delivery margin is almost 10% of the purchased-equipment cost (Peters *et al.*, 2003). The remaining items included in the fixed and the total capital investment are then estimated as percentages of the delivered-equipment cost. The *FCI* and *TCI* are estimated assuming a standard approach, even though relevant uncertainties may be related to land cost. Table A.11 collects *FCI* and *TCI* for the Instances A, B, C.

Table A.10 *Plant sections costs (2008$) and corresponding estimation method for Instances A, B, C.*

section	**cost estimation method**	**purchased cost (A) [$,2008]**	**purchased cost (B) [$,2008]**	**purchased cost for (C) [$,2008]**
feed handling	scaling method	4840224	6554065	8008951
pre-treatment	modelled	11296404	16607851	21075150
reaction	modelled	11974025	14856507	17992845
separation	modelled	24934361	24537021	34387774
WWT	scaling method	1089351	1914299	2236926
storage	scaling method	4051704	2178850	5066776
combustion	scaling method	25200473	43945605	43334344
air pre-treatment&CTS	scaling method	3710665	4926346	5658630
total purchased cost		87097206	115520546	137761394

Table A.11 *FCI and TCI estimations for the Instances A, B, C: a) refers to total direct costs, b) to total indirect costs.*

components	**fraction of the delivered equipment**	**estimated cost (A) [$]**	**estimated cost (B) [$]**	**estimated cost (C) [$]**
purchased equipment (delivered)	1	95806926	127072600	151537534
purchased equipment installation	0.39	37364701	49558314	59099638
instrumentation and control (installed)	0.26	24909801	33038876	39399759
piping (installed)	0.31	29700147	39392506	46976635
electrical systems (installed)	0.1	9580693	12707260	15153753
buildings (including services)	0.29	27784009	36851054	43945885
yard improvements	0.12	11496831	15248712	18184504
service facilities (installed)	0.55	52693809	69889930	83345644
land	0.072	6967776	9241644	11020912
TOTAL DIRECT COST		296304693	393000897	468664263

a) Total direct costs

components	fraction of the delivered equipment	estimated cost (A) [$]	estimated cost (B) [$]	estimated cost (C) [$]
engineering and supervision	0.32	30658216	40663232	48492011
construction expenses	0.34	32574355	43204684	51522761
legal expenses	0.04	3832277	5082904	6061501
contractor's fee	0.19	18203316	24143794	28792131
contingency	0.37	35448563	47016862	56068887
TOTAL INDIRECT COST		120716727	160111476	190937292
FCI [$]		417021420	553112373	659601556
FCI [€]		292749037	388284886	463040292
working capital	0.75	71855195	95304450	113653150
TCI [$]		488876615	648416823	773254706
TCI [€]		343191384	455188610	542824804

b) Total direct costs

A.2.2 Total product cost

The Total Product Cost (*TPC*, [€/t]) is the cost of manufacturing and selling a unity of product. It is obtained by summing up manufacturing costs (combining information about mass balance and costs for raw materials and chemicals) and general expenses. (Peters *et al.*, 2003).

Table A.12 *Operating costs: a) shows the assumptions about fixed costs calculation; b) shows the total product cost for Instances A, B, C.*

Data	Value (Peters *et al.*, 2003)
labour	generalised diagram
maintenance and repair	4%FCI
assistance	15%labour
operating supplies	15% maintenance and repair
laboratory charges	10%labour
depreciation charge	7 years
administration	2% profits

a) Main hypotheses about production cost assessment

	Instance A	Instance B	Instance C
Ethanol rate [kt/y]	200	289	373
	without depreciation		
TPC[€/L]	0.326	0.291	0.272
TPC [€/t]	413	369	345
	with depreciation		
TPC[€/L]	0.523	0.476	0.449
TPC [€/t]	662	603	569

b) Total product cost (TPC), including raw materials.

As illustrated in Figure A.3, operating costs breakdown shows that raw material costs represents the largest share of the overall costs.

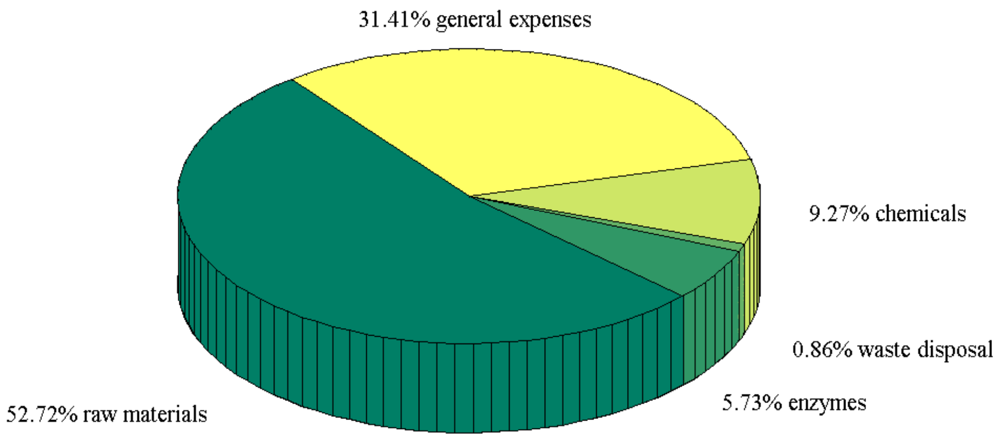


Figure A.3 *Hybrid process operating costs breakdown (without depreciation).*

A.2.3 Hybrid process: alternative use of DDGS

In this section, an alternative configuration for the hybrid process is presented for Instances A, B, C, where DDGS is burned in a CHP station to deliver steam and electricity to the process, reducing the stover excess (Table A.13). In fact, assuming that the same electricity generation is maintained (with reference to the case where only stover is fed to the CHP station), the amount of stover fed to the power station is diminished accordingly. Table A.13 summarises the amount of stover, which is required in addition to that used for ethanol production. Cost assessment is presented in Table A.13.

Table A.13 *Additional amount of stover fed to burner with respect to the total biomass supply.*

Additional stover feedstock for CHP (%wet basis)	
stover excess -Instance A	10%
stover excess -Instance B	12.5%
stover excess -Instance C	6.5%

Table A.14 *Fixed and Total Capital Investment (FCI and TCI, respectively)* .

	FCI [€]	**TCI [€]**	**TPC [€/t]**	**TPC (without depreciation) [€/t]**
Instance A	289206285	339038195	654	407
Instance B	387180485	453893914	597	363
Instance C	461939703	541534577	563	339

The alternative use of DDGS as a fuel in a CHP systems causes a decrease in both capital investments and production costs (see Tables A.11 and A.14).

A.2.4 Capital cost breakdown

In the following, Tables A.15-A.29 collect further details of the process model concerning the hybrid ethanol generation technology.

Table A.15 *Pump purchased cost values for the Instance A.*

plant section	**capacity [m^3/s]**	**discharge pressure [kPa]**	**purchased cost [$]**
corn stover pre-treatment	1.29E-02	455.96	8400
	1.97E-02	1327.36	20160
	6.92E-04	344.51	3096
corn pre-treatment	2.85E-02	405.30	11280
corn stover syrup evaporation	3.12E-02	303.98	11760
	9.76E-04	101.33	3360
	9.77E-04	101.33	3360
	1.11E-03	101.33	3480
corn syrup evaporation	2.74E-02	202.65	11040
	2.41E-03	101.33	4080
	2.50E-03	101.33	4320
	6.16E-04	101.33	3000
	1.78E-03	101.33	3840
	6.42E-03	111.46	6480

Table A.16 *Pump purchased cost values for the Instance B.*

plant section	capacity [m³/s]	discharge pressure [kPa]	purchased cost [$]
corn stover pre-treatment	4.64E-01	455.96	30000
	3.22E-02	1327.36	24696
	1.26E-03	344.51	4080
corn pre-treatment	3.08E-02	405.3	4680
corn stover ethanol recovery	6.85E-02	303.98	6720
corn ethanol recovery	2.97E-02	202.65	4560
corn stover syrup evaporation	3.63E-03	101.33	4800
	1.46E-02	101.33	8160
	3.02E-03	101.33	4560
	2.91E-03	101.33	4536
corn syrup evaporation	3.94E-03	101.33	2592
	3.91E-03	101.33	2520
	9.97E-04	101.33	2760

Table A.17 *Pump purchased cost values for the Instance C.*

plant section	capacity [m³/s]	discharge pressure [kPa]	purchased cost [$]
corn stover pre-treatment	4.32E-02	455.96	13200
	6.19E-02	1327.36	31248
	2.11E-03	344.51	3840
corn pre-treatment	2.73E-02	405.30	11040
corn stover syrup evaporation	8.46E-02	303.98	16800
	3.82E-03	101.33	5040
	4.02E-03	101.33	5280
	1.27E-02	101.33	8400
corn syrup evaporation	2.60E-02	202.65	10800
	5.22E-03	101.33	5760
	2.17E-03	101.33	3840
	2.17E-03	101.33	3840
	5.90E-03	111.46	6240

Table A.18 *Heat exchanger purchased costs for Instance A.*

plant section	duty [kW]	ΔTml [°C]	U*	fluids **	area [m^2]	material ***	pressure [kPa]	cost [$]
corn stover pre-treatment	-10848	93	850	w.-c.l.o.v.	138	cs-ss	101.33	27200
	-3855	39	420	w.-h.o.l.	235	cs-ss	101.33	37400
corn pre-treatment	2241.6	14	660	l.o.l.-l.o.l.	248	ss	405	69000
	-896.3	50	975	w.-c.l.o.v.	210	cs-ss	101	35700
corn stover ethanol reaction	534.31	16	170	h.o.l.-h.o.l.	193	cs-ss	405	32300
	-2106	16	420	w.-h.o.l.	320	cs-ss	101.33	47600
corn stover ethanol reaction	-3759	18	700	w.-m.o.l.	293	cs-ss	101.33	45900
corn stover ethanol recovery	5908.4	24	450	w.v.-h.o.l.	555	ss	304	132000
	1888.5	14	485	m.o.l.-l.o.l.	280	ss	304	75000
	-23670	36	850	w.-c.m.o.v.	779	cs-ss	304	95200
	46453	19	2000	s.-w.	1238	ss-cs	304	135242
	274.54	41	660	l.o.l.-l.o.l.	10.2	ss	203	12300
	-81293	61	1100	w.-c.l.o.v.	1208	ss-cs	203	133263
	48740	35	2000	s.-w.	688	ss-cs	203	95200
corn ethanol recovery	3699.8	43	700	w.-m.o.l.	124	ss	203	45000
	416.61	10	660	l.o.l.-l.o.l.	62.5	ss	203	27000
	22217	35	2000	s.-w.	318	cs-ss	203	49300
corn stover syrup evaporation	-2556	11	850	w.-c.l.o.v.	264	cs-ss	10.1	40800
corn syrup evaporation	-1696	30	850	w.-l.o.l.	67.5	cs-ss	20.3	16320
	-4011	29	850	w.-c.l.o.v.	161	cs-ss	20.3	28900
	-330.1	65	850	w.-l.o.l.	5.94	cs-ss	101.33	4972

*U is defined as [W/m^2s]

**Fluids:

- s. = steam
- w. = water
- w.v. = vapour water
- c.l.o.v. = condensing light organic vapour
- c.m.o.v. = condensing medium organic vapour
- l.o.l. = light organic liquid
- m.o.l. = medium organic liquid
- h.o.l. = heavy organic liquid

***Materials:

- CS=carbon steel
- SS=stainless steel

Table A.19 *Heat exchanger purchased costs for Instance B.*

plant section	duty [kW]	ΔTml [°C]	U*	fluids **	area [m^2]	material ***	Pressure [kPa]	cost [$]
corn stover pre-treatment	-4172.96	94	560	w.-m.o.l.	79.3	cs-ss	101.33	18700
	-7189.03	421	420	w.-m.o.l.	405.3	cs-ss	101.33	56100
corn pre-treatment	845.3	13	660	l.o.l.-l.o.l.	102.6	ss	405.3	39300
	-374.9	48	975	w.-c.l.o.v.	8.1	cs-ss	101.33	6800
corn stover ethanol reaction	-455.57	31	560	w.-m.o.l.	27	cs-ss	101.33	9860
	-4443.05	16	420	w.-m.o.l.	676	cs-ss	101.33	85000
corn ethanol reaction	-5617	23	700	w.-l.o.l.	347	cs-ss	101.33	50150
corn stover ethanol recovery	13547.14	19	420	w.-h.o.l.	1745.9	ss	304	293378
	-35385.85	36	850	w.-c.l.o.v.	1153.6	cs-ss	304	129654
	84955.68	19	2000	s.-w.	2247.5	ss-cs	304	193450
	-80019.23	61	975	w.-c.l.o.v.	1340.3	ss-cs	202.7	141860
	29372	35	2000	s.-w.	416.1	ss-cs	202.7	11900
corn ethanol recovery	2047.4	5	660	l.o.l.-l.o.l.	194.79	ss	304	57000
	24598.9	35	2000	s.-w.	356.79	cs-ss	202.7	52700
corn stover syrup evaporation	-7001.15	20	850	w.-c.l.o.v.	412.61	cs-ss	30.4	51850
	-6206.9	64	975	w.-c.l.o.v.	113.62	cs-ss	101.33	22100
corn syrup evaporation	-8659.47	40	850	w.-c.l.o.v.	257.75	cs-ss	30.40	40800

*U is defined as [W/m^2s]

**Fluids:

- s. = steam
- w. = water
- w.v. = vapour water
- c.l.o.v. = condensing light organic vapour
- c.m.o.v. = condensing medium organic vapour
- l.o.l. = light organic liquid
- m.o.l. = medium organic liquid
- h.o.l. = heavy organic liquid

***Materials:

- CS=carbon steel
- SS=stainless steel

Table A.20 *Heat exchanger purchased costs for Instance C.*

plant section	duty [kW]	ΔTml [°C]	U*	fluids **	area [m^2]	material ***	pressure [kPa]	cost [$]
corn stover pre-treatment	-12047.02	39	560	w.-m.o.l.	553.01	cs-ss	101.33	76500
corn pre-treatment	578.73	13	660	l.o.l.-l.o.l.	69.90	ss	405.30	30000
	-513.86	52	975	w.-c.l.o.v.	10.16	cs-ss	101.33	6970
corn stover ethanol reaction	2055.84	24	660	l.o.l.-l.o.l.	129.89	cs-ss	405.3	27200
	-6358.93	16	420	w.-h.o.l.	966.76	cs-ss	101.33	110500
corn ethanol reaction	-3467.39	18	700	w.-l.o.l.	274.66	cs-ss	101.33	44200
corn stover ethanol recovery	15196.95	26	420	w.-h.o.l	1413.99	ss	303.975	258516
	1420.02	33	660	l.o.l.-l.o.l	64.42	ss	303.975	30000
	-130.13	33	850	w.-c.l.o.v.	4.67	cs-ss	303.975	4306
	70934.89	18	2000	s.-w.	1978.13	cs-ss	303.975	179184
	-103035.78	61	1100	w.-c.l.o.v.	1529.49	cs-ss	202.65	153559
	38810.99	35	2000	s.-w.	548.97	cs-ss	202.65	73100
corn ethanol recovery	1573.68	9	700	w.-l.o.l.	244.01	ss	303.98	72000
	21292.74	34	2000	s.-w.	309.13	cs-ss	202.65	45900
corn stover syrup evaporation	-8791.82	38	975	w.-c.l.o.v.	236.31	cs-ss	31.41	39100
	-18719.16	34	975	w.-c.l.o.v.	572.15	cs-ss	101.33	81600
corn syrup evaporation	-6659.51	69	1550	w.-w.	62.19	cs-ss	96.26	15470
	-4816.59	39	850	w.-l.o.l.	146.88	cs-ss	30.40	29750
	-869.49	34	700	w.-l.o.l.	36.23	cs-ss	30.40	11050

*U is defined as [W/m^{2}s]

**Fluids:

- s. = steam
- w. = water
- w.v. = vapour water
- c.l.o.v. = condensing light organic vapour
- c.m.o.v. = condensing medium organic vapour
- l.o.l. = light organic liquid
- m.o.l. = medium organic liquid
- h.o.l. = heavy organic liquid

***Materials:

- CS=carbon steel
- SS=stainless steel

Table A.21 *Tank purchased costs for Instance A.*

item	**P‡ [kPa]**	**t‡‡ [m]**	**shell weight [kg]**	**head weight [kg]**	**total weight [kg]**	**stirring power [kW]**	**agitator cost [$]**	**total purchase cost [$]**
corn stover plant section								
overliming tank	77200	0.0059	2272	1957	5075	4	16000	57011
neutralising tank	77200	0.00938	13064	11118	29018	31	56000	185621
slurrying tank	77200	0.00583	1677	1264	3529	10	27000	59270
blowdown tank	75800	0.00556	1539	753	2750	0	0	31282
saccharification reactor	77200	0.01788	112593	88219	230934	104	116294	3129409
SSCF reactor	77200	0.01788	100720	254406	408394	101	114407	4283964
beer well	77200	0.01093	19002	16625	42752	29	54000	245312
corn plant section								
daily bin	77200	0.00706	2826	1332	4782	0	0	39434
mashing tank	77200	0.00675	1958	1408	3871	34	58000	184595
liquefaction tank	72400	0.00872	5171	2889	9268	96	111407	172435
cooking tank	72400	0.0108	1012	563	1811	5	17000	113328
fermenter	77200	0.01479	43197	32789	87383	83	103310	1114903
beer well	77200	0.01479	56343	32789	106959	0	0	306619

‡Vessel pressure
‡‡Vessel thickness

Table A.22 *Tank purchased costs for Instance B.*

item	**P‡ [kPa]**	**t‡‡ [m]**	**shell weight [kg]**	**head weight [kg]**	**total weight [kg]**	**stirring power [kW]**	**agitator cost [$]**	**total purchase cost [$]**
corn stover plant section								
overliming tank	77200	0.0032	2316	1545	4633	8	12500	51119
neutralising tank	77200	0.0032	9319	6179	18598	64	90757	187400
slurrying tank	77200	0.0058	3145	1957	6122	21	42000	88416
blowdown tank	75800	0.0056	2440	1972	5295	0	0	48203
saccharification reactor	77200	0.0179	223352	157021	437429	216	168865	4728389
SSCF reactor	77200	0.0179	216318	157021	429340	210	166131	4667163
beer well	77200	0.0109	35279	23663	70730	57	85290	352005

‡Vessel pressure
‡‡Vessel thickness

Table A.23 *Tank purchased costs for Instance C.*

item	P‡ [kPa]	t‡‡ [m]	shell weight [kg]	head weight [kg]	total weight [kg]	stirring power [kW]	agitator cost [$]	total purchased cost [$]
corn stover plant section								
overliming tank	77200	0.0032	3530	1545	6090	12	12500	58754
neutralising tank	77200	0.0032	12498	8071	24683	98	112840	229333
slurrying tank	77200	0.00583	4134	1957	7309	28	42000	94175
blowdown tank	75800	0.00556	4519	1972	7790	0	0	62190
saccharification reactor	77200	0.01788	316018	218464	614654	313	203951	5881401
SSCF reactor	77200	0.01788	306011	218464	603146	303	200631	5804535
beer well	77200	0.01093	44817	23663	82176	72	96361	390831

‡Vessel pressure

‡‡Vessel thickness

Table A.24 *Recovery equipment purchased costs for the Instances A, B, C.*

item	purchased cost [$]
corn stover beer column	288000 544000 480000
corn beer column	130000 140000 130000
rectification column	4080000 4080000 4679656
scrubber	128203 170012 210930
molsieve column	2751809 3570485 4257857

Table A.25 *Recovery system auxiliaries purchased costs for the Instance A.*

item	inlet flow-rate [L/min]	residence time [min]	P‡ [kPa]	t‡‡ [m]	shell weight [kg]	head weight [kg]	total weight [kg]	total purchased cost [$]
corn stover beer column								
accumulator	3106	3.5	72400	0.0077	1450	978	2914	28437
reflux drum	1637	10	72400	0.0082	2093	1285	4054	35359
corn beer column								
accumulator	2062	3.5	72400	0.0057	856	503	1631	19392
rectification column								
reflux drum	7425	10	72400	0.0085	6170.2	3421.7	11510	70410

‡Tower pressure

‡‡Tower thickness

Table A.26 *Recovery system auxiliaries purchased costs for the Instance B.*

item	inlet flow-rate [L/min]	residence time [min]	P‡ [kPa]	t‡‡ [m]	shell weight [kg]	head weight [kg]	total weight [kg]	total purchased cost [$]
corn stover beer column								
accumulator	4993	3.5	72400	0.0082	2234	1285	4223	36329
reflux drum	2916	10	72400	0.0091	3485	2076	6673	49132
corn beer column								
accumulator	1778	3.5	72400	0.0055	426	1432	17794	768
rectification column								
reflux drum	7209	10	72400	0.0081	6141	2890	10838	67667

‡Tower pressure

‡‡Tower thickness

Table A.27 *Recovery system auxiliaries purchased costs for Instance C.*

item	inlet flow-rate [L/min]	residence time [min]	P‡ [kPa]	t‡‡ [m]	shell weight [kg]	head weight [kg]	total weight [kg]	total purchased cost [$]
corn stover beer column								
accumulator	5915	3.5	72400	0.0084	2598	1460	4869	39906
reflux drum	1190	10	72400	0.0079	1554	1125	3214	30337
corn beer column								
accumulator	1561	3.5	72400	0.00551	674	426	1320	16859
rectification column								
reflux drum	9327	10	72400	0.00897	7500	4332	14198	80871

‡Tower pressure; ‡‡Tower thickness

Table A.28 *Solid-liquid separation systems purchased costs for Instances A, B, C.*

item	scaling property	scaling exponent *exp*	installation factor[a]	purchased cost (A) [$]	purchased cost (B) [$]	purchased cost (C) [$]
			corn stover treatment section			
hydrolysate centrifuge	solid outlet flow-rate [kg/h]	0.6	1.05	2819388	4273392	5450389
1st gypsum hydrocyclone and filter	inlet flow-rate [kg/h]	0.39	1.4	115681	153362	180512
2nd gypsum hydrocyclone and filter	inlet flow-rate [kg/h]	0.39	1.4	115752	153183	180579
lignin centrifuge	solid outlet flow-rate [kg/h]	0.6	1.05	2909279	4659504	5889221
item	**scaling property**	**scaling exponent *exp***	**installation factor[b]**	**purchased cost (A) [$]**	**purchased cost (B) [$]**	**purchased cost (C) [$]**
			corn plant section			
DGS centrifuge	solid outlet flow-rate [kg/h]	0.6	0.4	125382	125382	125124
DDGS rotary dryer	-	0.4	1.6	304973	304973	304973

[a] The estimation is performed according to USDOE (2002).

[b] Values are retrieved from Peters *et al.* (2003)..

Table A.29 *Evaporator purchased costs for Instances A, B, C.*

corn stover process								
plant section	**duty [kW]**	**ΔTml [°C]**	**U***	**fluids†**	**area [m^2]**	**material‡**	**Pressure [kPa]**	**cost [$]**
Instance A								
I effect	1199	53	610	s.-m.o.l.	37	SS	447.86	273000
II effect	1325	12	500	s.-m.o.l.	216	SS	101.33	630000
III effect	1326	29	450	s.-h.o.l.	101	SS	101.33	420000
IV effect	2143	21	400	s.-h.o.l.	250	SS	30.40	672000
V effect	2144	21	350	s.-h.o.l.	286	SS	30.40	714000
Instance B								
I effect	4797	53	610	s.-m.o.l.	149	SS	447.86	525000
II effect	357	61	600	s.-m.o.l	10	SS	447.86	126000
III effect	5310	16	450	s.-h.o.l.	759	SS	60.80	1260000
IV effect[a]	6378	7	400	s.-h.o.l.	2175	SS	20.27	2493495
Instance C								
I effect	10229	47	935	s.-l.o.l.	131	SS	447.86	483000
II effect[a]	4283	11	935	s.l.o.l.	3361	SS	141.86	3351952
III effect[a]	4509	25	400	s.-h.o.l.	1474	SS	96.26	1913472

corn process								
plant section	**duty [kW]**	**ΔTml [°C]**	**U***	**fluids†**	**area [m^2]**	**material**	**pressure [kPa]**	**cost [$]**
Instance A								
I effect	4197	45	935	s.-l.o.l.	99	SS	447.86	420000
II effect	4643	11	935	s.-l.o.l.	456	SS	141.86	94500
III effect	4980	29	610	s.m.o.l.	284	SS	96.26	69300
IV effect[a]	3937	4	400	s.-h.o.l.	2634	SS	30.40	2839860
Instance B								
I effect	7195	45	935	s.-l.o.l.	170	SS	447.86	588000
II effect	7763	11	935	s.-l.o.l.	767	SS	141.86	1260000
III effect	8151	24	400	s.-h.o.l.	863	SS	96.26	1323000
Instance C								
I effect	10229	47	935	s.-l.o.l.	233	SS	447.86	399000
II effect	4283	11	935	s.-l.o.l.	431	SS	141.86	546000
III effect	4509	25	400	s.-h.o.l.	457	SS	96.26	945000

*= U is defined as [W/m^{2}s]

†s. = steam; w. = water; w.v. = vapour water; c.l.o.v. = condensing light organic vapour; c.m.o.v. = condensing medium organic vapour; l.o.l. = light organic liquid; m.o.l. = medium organic liquid; h.o.l. = heavy organic liquid

‡SS = stainless steel

Appendix B

A more exhaustive account of the results from the spatially-explicit multi-objective optimisation performed in chapter 3 related to a bioethanol supply chain design in Northern Italy, is here offered. A breakdown of both economic and environmental assessment of the Pareto optimal solutions (A, B, C, D, E of Figure 3.3) is presented.

Table B.1 *Results of the multiobjective optimisation problem at the final time period: solution A in Figure 3.3.*

Pareto optimum A			
SC	**[€/month]**	**LCA phase**	**kg CO_2-eq/GJ**
biomass purchase cost	28851417	**biomass purchase**	39.857
biomass transport cost	3010047	**biomass pretreatment**	7.079
ethanol production cost	12321364	**biomass transport**	3.326
ethanol distribution cost	696662	**fuel production**	39.04
variable costs	44879489	**fuel distribution**	0.032
fixed costs	11992100	**emissions credits**	-12.697
incomes	79947333	**total**	76.64

Table B.2 *Results of the multiobjective optimisation problem at the final time period: solution B in Figure 3.3.*

Pareto optimum B			
SC	**[€/month]**	**LCA phase**	**kg CO_2-eq/GJ**
biomass purchase cost	29913639	**biomass purchase**	39,446
biomass transport cost	2587051	**biomass pretreatment**	7,079
ethanol production cost	3366783	**biomass transport**	2,567
ethanol distribution cost	691444	**fuel production**	39,04
variable costs	36558918	**fuel distribution**	0,032
fixed costs	10587092	**emissions credits**	-52.96
incomes	70580611	**total**	35.20

Table B.3 *Results of the multiobjective optimisation problem at the final time period: solution C in Figure 3.3.*

Pareto optimum C			
SC	**[€/month]**	**LCA phase**	**kg CO_2-eq/GJ**
biomass purchase cost	24044903	**biomass purchase**	27.387
biomass transport cost	2396090	**biomass pretreatment**	4.649
ethanol production cost	8880978	**biomass transport**	2.208
ethanol distribution cost	596571	**fuel production**	28.918
variable costs	35918541	**fuel distribution**	0.028
fixed costs	10795278	**emissions credits**	-39.122
incomes	71968528	**total**	24.07

Table B.4 *Results of the multiobjective optimisation problem at the final time period: solution D in Figure 3.3.*

Pareto optimum D			
SC	**[€/month]**	**LCA phase**	**kg CO_2-eq/GJ**
biomass purchase cost	16715553	**biomass purchase**	14.961
biomass transport cost	3093750	**biomass pretreatment**	2.067
ethanol production cost	14041986	**biomass transport**	2.661
ethanol distribution cost	461961	**fuel production**	18.165
variable costs	34313249	**fuel distribution**	0.021
fixed costs	11016456	**emissions credits**	-24.421
incomes	73443028	**total**	13.45

Table B.5 *Results of the multiobjective optimisation problem at the final time period: solution E in Figure 3.3.*

Pareto optimum E			
SC	**[€/month]**	**LCA phase**	**kg CO_2-eq/GJ**
biomass purchase cost	9045692	**biomass purchase**	4.195
biomass transport cost	3063872	**biomass pretreatment**	
ethanol production cost	20740358	**biomass transport**	2.089
ethanol distribution cost	602864	**fuel production**	9.556
variable costs	33452786	**fuel distribution**	0.028
fixed costs	10199917	**emissions credits**	-13.261
incomes	67999444	**total**	2.61

Appendix C

The MILP problem proposed in chapter 4 has been here simplified by dropping down the stochastic formulation and the environmental framework to study just the influence of feedstocks cost on the overall SC design. The main purpose is to propose a multi-parametric sensitivity analysis to evaluate the effects of feedstocks cost variability on investments strategies in bioenergy. Results are presented and discussed in order to evaluate the need for a more sophisticated investigations on market costs variability (e.g., stochastic modelling framework).

C.1 Sensitivity analysis on feedstocks cost

The problem statement refers to chapter 4, where LCA issues are neglected and the sole economic analysis is carried out. The approaches proposed in chapter 4 have been adopted to evaluate the modelling parameters related to the corn- and cellulose-based SC issues.

The mathematical formulation refers to the economic MILP modelling framework proposed in chapter 4, Eq. (4.1-4.39), where the stochastic approach is dropped down. The economic objective function is represented by the NPV index (Eq. (4.2)), being neglected the design variables dependence on the scenario *sc*.

The main purpose is to perform a preliminary analysis of feedstocks cost variability effects on capacity planning decisions, to evaluate if a more complex and rigorous approach based on a stochastic approach is advocated by the extents of the effects on the economics of bioethanol SC design at a strategic and tactical levels.

In order to explore a wider set of solutions to investigate the effect of public instruments for supporting renewable energies production, the optimisation problem is also addressed by formulating two alternative instances assessing in terms of price for electricity (GSE, 2011):

I: MP_{power} = 67.18 €/MWh, i.e. the current electricity selling price (without subsidies)

II: MP_{power} = 180 €/MWh, i.e. the price encompassing Green Credits (GCs)

Per each instance, a sensitivity analysis is performed addressing several occurrences of costs UPC_i ([€/t]), for every biomass *i* according to the following hypotheses:

- corn cost (UPC_{corn}) values have been varied assuming a reasonable costs range determined according to the literature (Dal-Mas *et al.*, 2011). In particular, the optimisation problem has been carried out setting UPC_{corn} equal to: 130, 150 and 200 €/t.
- cellulosic biomass cost has been varied establishing a percentage of variations (increase/decrease) with respect to base case values retrieved from the literature (see

Table C.1). In particular, biomass costs values used in the sensitivity analysis have been determined by varying the base case values of ±20%; ±40%.

Table C.1 *Base case unitary production costs for cellulosic biomass i, UPC_i.*

biomass costs	UPC_i [€/t]	reference
poplar	67	agriforenergy (2011)
salix	83.97	agriforenergy (2011)
miscanthus	46.37	agriforenergy (2011)
corn stover	30	Schade and Wiesenthal (2011)
wheat straw	62.5	IT (2010b)
barley straw	30	Schade and Wiesenthal (2011)
switchgrass	35.46	Schade and Wiesenthal (2011)

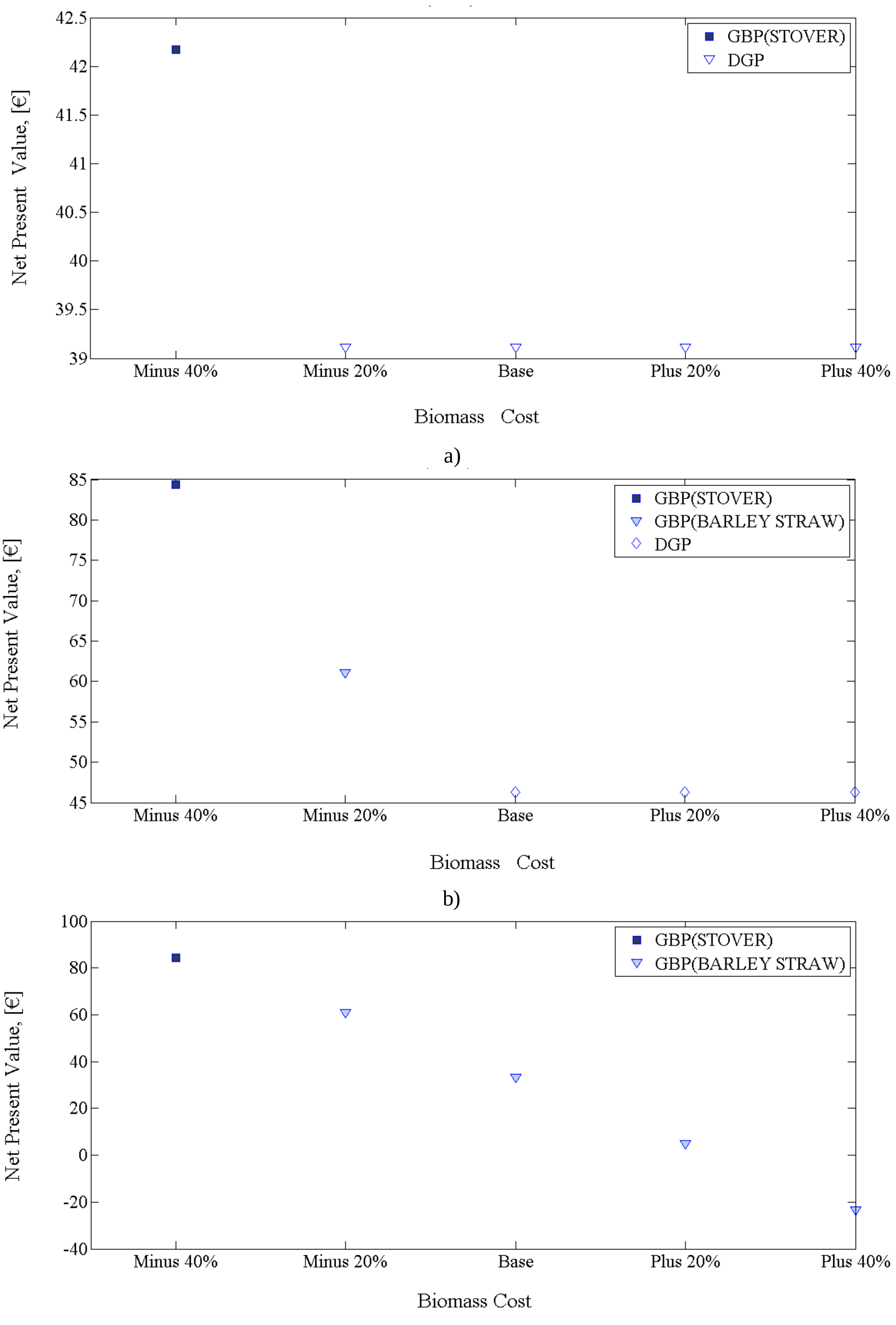
C.2 Results

According to Instance I, the optimal technological options are selected in absence of an incentive on power selling price at three increasing corn cost (e.g., 130, 150, 200 €/t). In this condition, first generation technologies (i.e., DGP) always represents the preferred choice. However, NPV changes considerably, moving from 39 down to -35 €/t, showing the lack of profitability of the business at high corn cost.

According to the above, the optimisation is carried out in Instance II considers the effects of government subsidies at three increasing corn cost (see Figure C.1). As it appears from Figure C.1, when corn cost is considerably low (UPC_{corn} = 130, 150 €/t), DGP is the most preferred processing alternative chosen for ethanol production if biomass price is assumed equal to the base case or augmented. At the highest corn cost value, however, only gasification-based processes are always selected, even including a considerable increase of biomass cost. NPV shows the profitability of the business and becomes negative only if biomass cost is expected to grow up to 40% more with respect to the base case.

These results show that bioethanol processing technologies choice varies considerably according to the feedstocks cost. In particular, first generation appears to be even more affected from feedstocks market costs variability than second generation. This strong dependence on feedstocks cost values might change significantly the profitability of the business even resulting in negative NPV for both of them.

Two main conclusions may be drawn.



a)

b)

c)

Figure C.1 *Sensitivity analysis according to Instance II (green credits effect) at three corn cost:* UPC_{corn} *= 130 €/t (a);* UPC_{corn} *= 150 €/t (b);* UPC_{corn} *= 200 €/t (c).*

First, large effects on bioethanol SC design due to feedstocks costs variability (for both first and second generation production) give reason for a more rigorous and sophisticated investigation by adopting a stochastic formulation to optimisation. In these cases, the stochastic approach to planning represents one of the best modelling solutions. In fact, the representation of costs as stochastic parameters, assumed to obey discrete probability distributions represented by a number of potential cost realisations (the so-called scenarios) gives a more accurate approach in dealing with uncertainty.

Secondly, advanced cellulose-based technologies profitability is also greatly affected by the introduction of governmental subsidies. Economic support seem dramatically important to allow for the spread of these technologies. One possibility is represented by the adoption of more extensive market mechanisms (e.g., carbon trading) capable of promoting cellulose-based processes for ethanol production according to their effective environmental benefits.

The outlined issues (i.e., stochastic approach, carbon trading) are dealt with in chapter 4 and 5.

Appendix D

In this appendix, a framework for assessing the water usage along the biofuels SC (the so-called, water footprint) is proposed. The moMILP formulation of chapter 3 is here extended to approach a more comprehensive view of biofuels environmental sustainability and support strategic investments on bioethanol infrastructures, embedding features addressing impact on global warming and on water resource depletion along with business economic profitability.
In the following, a literature survey is proposed and results are discussed.

D.1 Literature survey

As the production of biofuel continues to expand, their environmental and social implications have come under scrutiny, especially their life cycle GHG emissions. However, a paradigm shift towards sustainable transport systems needs to account for other urgent issues. In particular, water consumption has become a major concern: its demand is expected to grow significantly, and recent occurrences of local scarcity have showed its supply vulnerability (EC, 2011). Even though total global withdrawals are thought to be within the proposed safe operating limit (Ridoutt and Pfister 2010), the most critical issue refers to the regional nature of freshwater scarcity, revealed from local episodes of water stress. Being current freshwater usage skewed towards highly stressed water basins, Ridoutt and Pfister suggested humanity's water footprint to be globally reduced by 48.6% in order to achieve the stabilisation target. In particular, growing concerns about water resource depletion are surrounding the promotion of bioenergy: according to a 2006 USDOE report, an increase in water demand might proceed at an alarming speed due to biofuel production. The Water Footprint (WF) concept, introduced by Hoekstra (2003), is an indicator to express the water use in the production chain of commodities and it is defined as the total volume of freshwater consumed or polluted during the whole production process. Earlier WF estimation were related to agricultural commodities (Hoekstra and Hung, 2002), whose production is in charge of about 70% of freshwater withdrawals from lakes, rivers, basins and aquifers (UNESCO, 2009). A first methodology was set up in dealing impacts on water stress by distinguishing between water consumption, referred to crop water consumption during the growing period, and water pollution, mainly related to the leaching of fertilisers and pesticides applied to the field (Hoekstra and Chapagain, 2008). Accordingly, the WF assessment embeds three main contributions: the green, the blue and the grey WF. The green WF refers to rainwater that evaporated during production, mainly during crop growth. The blue WF refers to surface and groundwater for irrigation evaporated during crop growth. The grey WF is the volume of water which becomes polluted during production, defined as the amount of water needed to dilute pollutants, to reach established levels of water quality.

Subsequent studies were performed to analyse WF for specific products, e.g. for cotton (Chapagain *et al.*, 2006), for coffee and tea (Chapagain and Hoekstra, 2007) providing more details on specific WFs of crops and crop products. WF was assessed for bioenergy only later (Gerbens-Leenes *et al.*, 2009a).

Only a few works have addressed WF assessment in the context of biofuels. Varghese (2007) discussed the water requirement for corn-based ethanol in the U.S. and sugarcane-based ethanol in Brazil. The potential nexus between water and energy due to transportation was later addressed in the work by King and Webber (2008). They examined the amount of water taken from a surface (e.g., water or groundwater source water) either returned to that source after usage (known as water withdrawal) or not (known as water consumption) for a wide variety of transportation fuels (e.g., gasoline, diesel, biofuels) as well as for electric vehicles. In terms of stress on water resources, biofuels for transport appear to be less efficient than biomass for heat and power production since usually only a fraction of the crop (its sugar, starch or oil-content) is used (Gerbens-Leenes *et al.*, 2009a; Gerbens-Leenes *et al.*, 2009b). After comparing their blue, green and grey WFs, some ethanol production technologies (e.g., derived from sugar cane, sugar beet and corn grain) have been recognised as water intensive processes, but results are strictly connected to the geographical context (Gerbens-Leenes and Hoekstra, 2009). According to Chiu *et al.* (2009), water embodied in corn-based bioethanol produced in several regions of the U.S.A., showed a large variability, ranging between 5 and 2138 L/L of ethanol depending on irrigation practices.

Water consumption assessment has been evaluated accounting for all life cycle stages of corn- and cellulose-based ethanol, as well as of conventional crude oil-based gasoline in the work by Wu *et al.* (2009). After highlighting a high variability due to geographical context for first generation ethanol (ranging between 10 and 324 L/L of ethanol from corn), they showed that the largest share comes from irrigation water. Cellulosic ethanol appears to perform better, particularly if drought-resistant crops are exploited. With an overall water consumption between 1.9 and 9.8 L/L of ethanol from switchgrass, such a biofuel chain is comparable with the conventional gasoline pathway (3.4-6.6 L of water/L of gasoline).

Harto *et al.* (2010) carried out a water consumption assessment for internal combustion engines biofuels, through a life cycle approach, including water embedded for crop production, farm inputs, ethanol plant construction, as well as biofuel production, distribution and marketing. Irrigated crop-based biofuels were found again to have significant impact on water resources when scaled up to macroscopic production levels. Fingerman *et al.* (2010) developed a quantitative framework based on a county-level approach to capture spatial heterogeneity of water consumption due to bioenergy development in California. They used the Penman-Monteith model to determine crop evapotranspiration water losses, accounting for both irrigation and rainfalls, and considering geographical plant physiology and climate variability. It emerges the need to implement a general water accounting system, since no standard method is present for embedding indirect effects as well as by-products allocation. Recently, Singh and Kumar (2011) developed a total water consumption assessment for corn wheat and switchgrass by adopting a life cycle approach, also including indirect impacts and avoiding allocation procedures.

It becomes clear from the above that in accomplishing with biofuels mandates, ethanol expansion development in some regions might have large impacts on vulnerable fossil aquifers. Investments strategies should be driven by a comprehensive analysis and boosted in the states with lower irrigation rates. In addition, the endeavours of assessing the stress on water resources due to bioenergy have shown some methodological and theoretical gaps. Recently, the work by Hoekstra *et al.* (2011) aimed at defining a standard methodology for water footprint assessment.

The evaluation of effects of anthropogenic activities over water resources based on the WF approach, however, has been criticised by a part of the literature, advocating the need for a more comprehensive modelling of water stress into the common LCA impact categories. In fact, freshwater consumption is recognised as a phenomenon than can create impacts in human health, ecosystems and resources depletion. Accordingly, the ISO is considering the development of a new standard to solve the abovementioned inconsistencies and controversies (Berger and Finkbeiner, 2010). The need for a comprehensive approach is mainly related to the allocation procedure to account for by-products effects (e.g., either on economic or on energy- or price- based allocation; expansion method) and for including considerations of water embedded as indirect effects.

In view of the above, WF, as well as carbon footprint, assessment is claimed to account for the water consumed along the entire SC, and, varying considerably with crop type and geographical region, needs integrating in a comprehensive financial and environmental framework. Mathematical programming techniques can provide decision makers with the necessary quantitative tools to optimise the overall water requirement guaranteeing an efficient use of the resource. Environmental aspects (carbon and water footprint) should be coupled with economic ones within a Multi-Objective Mathematical Programming framework involving the overall SC, to offer an effective approach exploring trade-offs between conflicting objectives. In the context of water usage optimisation in biofuels production systems, mathematical programming has dealt with the sole process (Ahmetović *et al.*, 2010; Grossmann and Martìn, 2010; You *et al.*, 2011). So, there is the need to cover the gap of the literature by addressing biofuels SCs design and planning according to a comprehensive approach, taking into account the impact on water resource depletion in an integrated manner within a SCM framework. Possibly trade-offs between climate change mitigation and water stress might be generated and need to be properly addressed (Gheewala *et al.*, 2011), as well as simultaneously analysed through a moMILP approach.

Here, a moMILP modelling framework is proposed extending the formulation proposed in chapter 3, addressing sustainable design of long-term ethanol SCs, involving first (from corn), second (from stover) and hybrid (from corn grain and stover) generation technologies.

D.2 Problem definition

The environmental performance in terms of stress on water resources is evaluated according to the WF assessment methodology. The operating impact of the system is evaluated from biomass cultivation up to fuel production. In particular, the same set of LCA stages *s* used for determining the impact on global warming, has been considered in the WF evaluation are given by biomass production (*bp*), biomass pre-treatment (*bpt*), biomass transport (*bt*) and fuel production (*fp*). Accordingly:

$S = \{bp, bpt, bt, fp\}$.

In the absence of a universally recognised method to cope with the effect of by-products end-use on the overall impact, three approaches have been assessed: a substitution method as well as a price- and energy-based allocation procedures. The substitution method, in particular, involves credits derived from the displacement of alternative goods with by-products determining GHG emissions savings, which are subtracted from the primary product (ethanol) overall impact. Credits and the subsequent emissions discount is a result of goods or energy displacement by process by-products end-uses: DDGS could be used either as a substitute for cattle feed or as a fuel for CHP generation; in cellulose-based processes, lignin is exploited to produce electricity and a power excess can be sold to the national grid. In case of allocation, the overall SC impact (i.e., GHG emissions, WF) is divided among the products according to their corresponding sharing quota determined either on price or energy content.

In accounting for the impact of the biofuels SC on water resources, indirect effects due to farm and process inputs are encompassed, according to a LCA approach to WF assessment.

The biofuels SC design problem can be formulated as follows. Given the following inputs:

- technical (yields) and economic (capital and operating costs) parameters as a function of biomass type, production technology and plant scale;
- environmental burdens (water consumption, GHG emissions) of biomass production as a function of biomass type and geographical region;
- environmental burdens (water consumption, GHG emissions) of biomass transport as a function of distance length;
- environmental burdens (water consumption, GHG emissions) of biofuel production as a function of biomass type and production technology;
- biofuel market characteristics;

- energy market prices and existing subsidies (green credits).

The objective is to determine the optimal system configuration which maximises the financial profitability while minimising the GHG emissions.

Accordingly, strategic design involves decisions dealing with the biomass typology selection, the technology definition, the by-products valorisation option and, eventually, the logistics characterisation as well as the description of each SC node location. On the other hand, SC planning decisions regard the production facilities capacity assignment along the time framework. Therefore, the key variables to be optimised are:

- feedstock mix to the plant;
- bioethanol facilities technology selection;
- financial performance of the system over the time horizon;
- system impact on global warming;
- system impact on water resources.

D.3 Mathematical features

The model extends the moMILP formulation of chapter 3 dealing with environmentally-conscious design of biofuels multi-echelon SCs embedding also features to address the production network impact on water resource. In the following, only objective functions and the main differences with respect to the previous formulation will be outlined. In fact, the economic and environmental objective are defined as a function of the design variables, whose definition follows the mathematical formulation detailed in chapter 3 Eq. (3.5-3.61), after dropping down the grid-dependency of the equations and simplifying transport equations.

The economic objective function (Obj_{eco} [€]), is estimated in terms of the Net Present Value (NPV) of the system and needs being maximised in configuring the production network to optimise business profitability. It is calculated by summing up the discounted annual cash flows ($CF_{k,t}$ [€/y]) for each technology k and time period t minus the capital investment (TCI_k [€]) when a production facility of technology k is established. Accordingly:

$$Obj_{eco} = NPV = \sum_k \left(\sum_t \left(CF_{k,t} \cdot df_t \right) - TCI_k \right) \tag{D.1}$$

where df_t is the discount factor related to the year t of production considered.

Two environmental objective functions are embedded within the formulation. The former concerns minimisation of the impact on global warming, estimated in terms of the total GHG emissions due to SC operation during time, (Obj_{env} [kg CO_2-eq]), $TIOT^{GHG}$. This is estimated by summing up the annual impact related to technology k, $TI_{k,t}^{GHG}$ [kg CO_2-eq/y] over time:

$$Obj_{env} = TIOT^{GHG} = \sum_t TI_{k,t}^{GHG} \tag{D.2}$$

The second environmental objective function ($Obj_{env,2}$, $\mathrm{m}^3_{\mathrm{H_2O}}$) refers to the minimisation of the overall water footprint due to SC operation over time ($TIOT^{WF}$) and determined by summing up the annual impact on water resource $TI_{k,t}^{WF}$ [$\mathrm{m}^3_{\mathrm{H_2O}}$/y] of technology k for ethanol production:

$$Obj_{WF} = TIOT^{WF} = \sum_t TI_{k,t}^{WF} \tag{D.3}$$

Environmental impacts on a yearly basis might be expressed in general terms as $TI_{k,t}^{\sigma}$ (Eq. (D.4)) ($\sigma \in \{GHG,WF\}$), needs considering the SC operation effect on carbon and water footprint per each LCA stage s, $Imp_{k,s,t}^{\sigma}$, [kg CO_2-eq/y or $\mathrm{m}^3_{\mathrm{H_2O}}$/y].

$$TI_{k,t}^{\sigma} = \sum_{k,s,t} Imp_{k,s,t}^{\sigma} \tag{D.4}$$

D.4 Case study

The emerging ethanol production system in Northern Italy was chosen as a case study. The problem refers to a single bioethanol production plant of fixed scale (160 kt/y of ethanol) which is supplied with the necessary biomass (corn, stover or both) cultivating a hypothetical land surface of limited extension. Only the upstream SC is analysed, according to the hypotheses discussed in §3.7.1.

The SCA and LCA issues referring respectively to business profitability and impact on global warming are approached in the way discussed in chapter 3.

The impact in terms of water resource consumption has been defined in terms of blue WF according to the methodology proposed by Hoekstra *et al.* (2011) and encompassing also the indirect effects due to farm (e.g., fertilisers) and processing inputs (e.g., chemicals, enzymes) (Harto *et al.*, 2010).

The optimisation problem has been addressed by formulating three instances, according to the way by-products end-use effects on the overall LCA impact has been approached: substitution method (instance 1); economic allocation (instance 2); energy-based allocation (instance 3).

The modelling parameters reveal the current level of technology development (base case). In addition, three scenarios have been analysed involving improved efficiency of agricultural irrigation (scenario A), process water consumption reduction (scenario B) and both of them (scenario C).

In the following, the main hypotheses regarding WF assessment will be discussed per each of the LCA stage considered, according to current level of technology and considering first the substitution method for approaching by-products effects. Then, the main differences will be outlined for scenarios embedding technological advancements and for different allocation procedures.

D.4.1 Biomass production

The characterisation of biomass production blue WF implies the account for all direct and indirect impacts causing the consumption of the resource for crop cultivation.

The direct contribution accounts for the amount of irrigation water lost by evapotranspiration due to the presence of crop (i.e., corn) (Hoekstra *et al.*, 2011) and it is here approximated by the overall irrigation requirement diminished by the rate recharging ground and surface water (about 30% of the irrigation rate, according to Wu *et al.*, 2009). Crop water requirements represent the largest contribution to the overall impact, even though strictly dependent on the geographical context and the climate conditions in which the SC is going to be operating. In order to have an accurate description of the effective water flows involved in corn cropping, an average of the irrigation values among the regions of Northern Italy, between the period 1995-2002, has been used (100 L/kg of corn, Mekonnen and Hoekstra, 2010).

The indirect contribution of biomass production on water consumption is sometimes neglected, depending on the purpose of the analysis (Gerbens-Leenes *et al.*, 2009b; Chiu *et al.*, 2009). Since our main objective is to give a comprehensive account of bioethanol blue WF, indirect effects of biomass production have been included, even though they play a minor role with respect to irrigation use. Indirect effects depend on the production of farm inputs, whose amounts are determined as in chapter 3), concerning fertilisers and pesticides (Singh *et al.*, 2011; Harto *et al.*, 2010) as well as diesel usages for corn and stover collection (Sheehan *et al.*, 1998; King and Webber, 2008). The impact on water resources due to biomass production step result to be: 77.4 (direct effect) and 1.56 (indirect effect) m^3/t of corn; 0 (direct effect) and 0.45 (indirect effect) m^3/t of stover. In fact, the possibility of using stover for ethanol production, according to the substitution method approach to WF assessment, is studied giving this feedstock a residual value; thus, no crop irrigation requirement is attributed to the cellulosic biomass.

D.4.2 Biomass pre-treatment

Biomass pretreatment usually involves feedstocks drying operations. Water embedded within the biomass is lost due to either natural or mechanical evapotranspiration. This amount of (direct) water consumption, however, has been already accounted for within crop irrigation water rates. Here, the amount of indirect water consumption due to corn drying has been neglected, according to the literature (Harto *et al.*, 2010).

D.4.3 Biomass transport

After being harvested, biomass needs being collected to the facility site. Even though transportation description has been here simplified and the mathematical formulation does not encompass a georeferentiation-based approach to biofuels SC design, as implemented in chapter 3, the impact on water resources due to the collection phase has been assessed to evaluate its order of magnitude. In fact, transportation impact on water resources is often neglected in the literature.

Infrastructures development impact on water stress has been neglected according to King and Webber (2008). Assuming a reasonable distance for biomass collection (100 km, as suggested by Sheehan *et al.*, 1998) and an average diesel consumption for the current trucks fleet (King and Webber, 2008), transportation impact on water usage only depends on the indirect effects due to fuel production (Sheehan *et al.*, 1998). The overall impact on water resources due to transportation, results equal to $8.62 \cdot 10^{-4}$ m^3/t of corn and to $5.92 \cdot 10^{-3}$ m^3/t of stover.

D.4.4 Ethanol production

The ten production technologies considered in Table 3.8, technically, economically and environmentally (GHG emissions) characterised according to the approach detailed in chapter 3, have been studied in terms of water consumption, too. Water consumption has been evaluated as a consequence of facility being brought into operation, neglecting the manufacture of physical capital (King and Webber, 2008). The amount of water directly consumed by a biomass-to-ethanol facility, given by the process and cooling towers makeup, has been determined according to industrial data for DGP-based technologies (6 m^3/t of ethanol) (Franceschin *et al.*, 2008) and from the literature for LCEP technologies (7.37 m^3/t of ethanol) (USDOE, 2002). As regards the processes combining first and second generation technologies (Hybrid and Hybrid-CHP), their water consumption rates have been analysed through composing make-up rates of a cellulose- and ethanol-based processes considered as working independently.

The indirect stress on water resources due to biofuel production step is mainly due to the production of the chemical reagents, enzymes and energy (e.g., natural gas, electricity) required for their realisation. This contribution has been determined equal to 1.78 and 0.68 m^3/t of ethanol obtained from corn and stover respectively (King and Webber, 2008; Singh *et al.*, 2009; Torcellini *et al.*, 2003).

Thus, the overall impact in terms of water consumption is 7.78 and 8.05 m^3/t of ethanol respectively produced from corn and stover.

D.4.5 By-products end-use effect

The credits on the overall impact are set up according to the substitution approach as discussed earlier and assigned to both DDGS and electric energy reflecting their potential end-uses.

The calculation inputs derived for DDGS and electricity credits are accomplished according to chapter 3. From the assumptions by Zamboni *et al.* (2011a), it is generally assumed a DDGS-to-soy substitution ratio equal to 0.69, and a DDGS-to-ethanol ratio of 0.954. Then, irrigation requirements for soy cropping (173 L/kg of soy) have been determined as an average value for Northern Italy regions between 1995-2002 (Mekonnen and Hoekstra, 2010). As regards electricity-derived credits, power generation yields per each of the technology considered have been applied (see chapter 3) to the water requirements determined for power generation technologies currently used in Italy (Torcellini *et al.*, 2003).

In addition, two allocation methods have been implemented to account for by-products end-use effect on the overall WF. The allocation factors have been determined according to energy or price values.

D.4.6 Technological improvements for irrigation and process water usage

Three scenarios of technological advancements have been considered for improving water consumption with respect to the base case earlier discussed.

Scenario A accounts for a better water management in the agricultural phase replacing sprinkler with drop irrigation. Taking as reference a corn crop in Italy, water consumption might drop down to 33% less with respect to the base case (Mercurio, 2008). Assuming the same performance improvements for soy irrigation, final direct WF results to be 52 and 116 L/kg, of corn and soy, respectively.

Scenario B is modelled accounting for process water consumption reduction though energy and water flows optimisation. According to the literature, water consumption reduction has been determined. Direct water requirements for the process might drop down to 1.17 L/L of ethanol for corn-based DGP (Ahmetović *et al.*, 2010) and to 2.7 L/L of ethanol for second generation facilities (considering a 53% of water usage reduction with respect to the base case, according to a 3% of water usage reduction (Martìn *et al.*, 2011).

In addition, scenario C has been included within the formulation considering water requirements reduction taking place both in the process and in the agricultural phase.

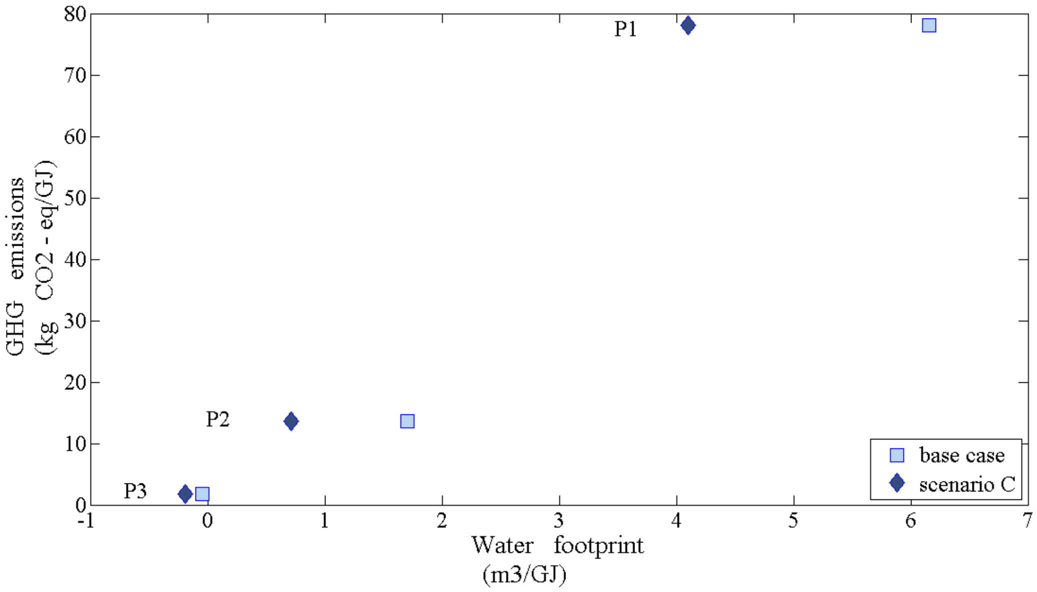
D.5 Results

The three-objective optimisation problem (economic, impact on global warming and on water resources) was solved with the CPLEX solver of the GAMS® modelling tool. The resulting set of Pareto optimal solutions (P1, P2, P3) obtained with the substitution method (instance 1) is shown for the base case and scenario C: Figure 1.a presents the trade-off between WF and the GHG emissions; Figure 1.b illustrates the trade-off between WF and economic profitability. In the following, the base case results is first discussed, then the effects of increased efficiency in water consumption outlined. Finally a discussion is provided about the allocation procedure consequences on the optimisation results.

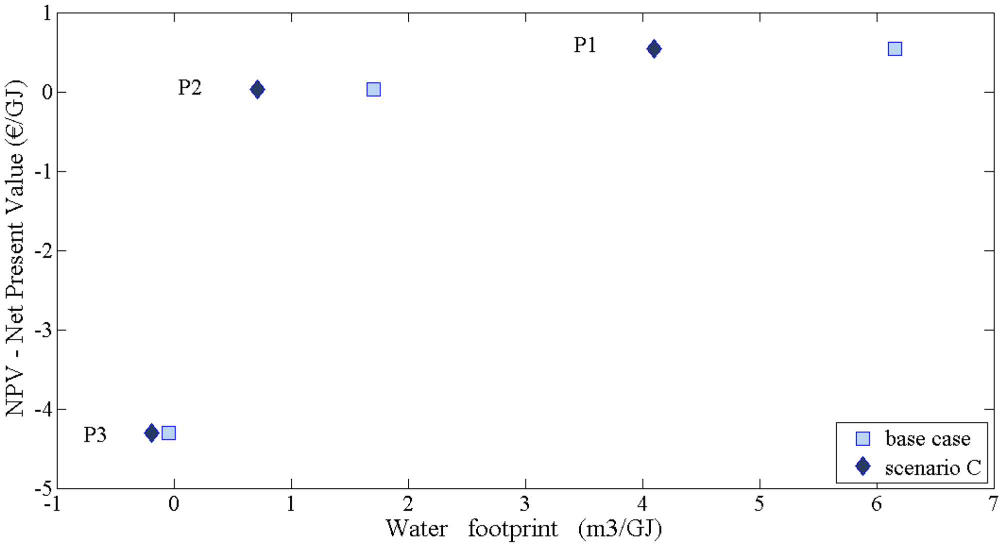
The economic optimum (point P1 in Figure 1.b) involves the establishment of the standard DGP process with DDGS sold as animal fodder. This option allows for more revenues coming from the by-product selling and results in a normalised NPV of 0.54 €/GJ. The environmental outcomes show a high impact on global warming (78.03 kg CO_2/GJ, Figure 1.b) as well as on WF (about 6.16 m^3/GJ). Moving down towards a better environmental performance, (point P2 in Figure 1) the strategic investment involves the establishment of a hybrid technology with a corn/stover ratio of 1/3, where DDGS is sold as animal fodder. This solution has a lower profitability (NPV equal to 0.03 €/GJ, Figure 1.b), but leads to great improvements in the environmental performance (e.g., WF is about 1.71 m^3/GJ and GHG emissions drop down to 13.59 kg CO_2-eq/GJ).

The environmental optimum (point P3 in Figure 1) involves the establishment of a standard DAP process. The negative value for the WF (-0.046 m^3/GJ) is due to the amount of credits from electricity displacement which exceeds the water consumed along the entire SC. The carbon footprint is reduced down to 1.8 kg CO_2-eq/GJ (Figure 1.b). This is mainly due to the lower emissions resulting from stover production and conversion to ethanol when compared to conventional first generation biomass. However, this solution is not economically sustainable: the normalised NPV drops down to -4.31 €/GJ (Figure 1.a), which clearly shows the scarce competitiveness of the business due to the consistent capital costs.

The improvement of water efficiency in scenarios A, B and C does not change the optimal solutions, in terms of technology selection for the business to be established. WF changes considerably, however, dropping down to 4.1 and 0.72 m^3/GJ for solutions P1 and P2 of scenario C (with about 33% and 58% of reduction with respect to the base case). A complete cellulose-based facility (P3) will lead to a negative WF (-0.19 m^3/GJ, Figure 1), thus providing water use savings up to four times greater than the base case. The water use decrease characterising scenario C, is mainly due to improvements of irrigation efficiency for solutions P1 and P2, accounting for about 31% and 49% of WF reduction (scenario A). Being corn stover a residual feedstock, according to the substitution method, which attributes the overall water consumption to the main crop, a complete stover-based WF, solution P3 (Figure 1), is not affected by increasing efficiency of irrigation, but from process water usage optimisation, only (scenario B).



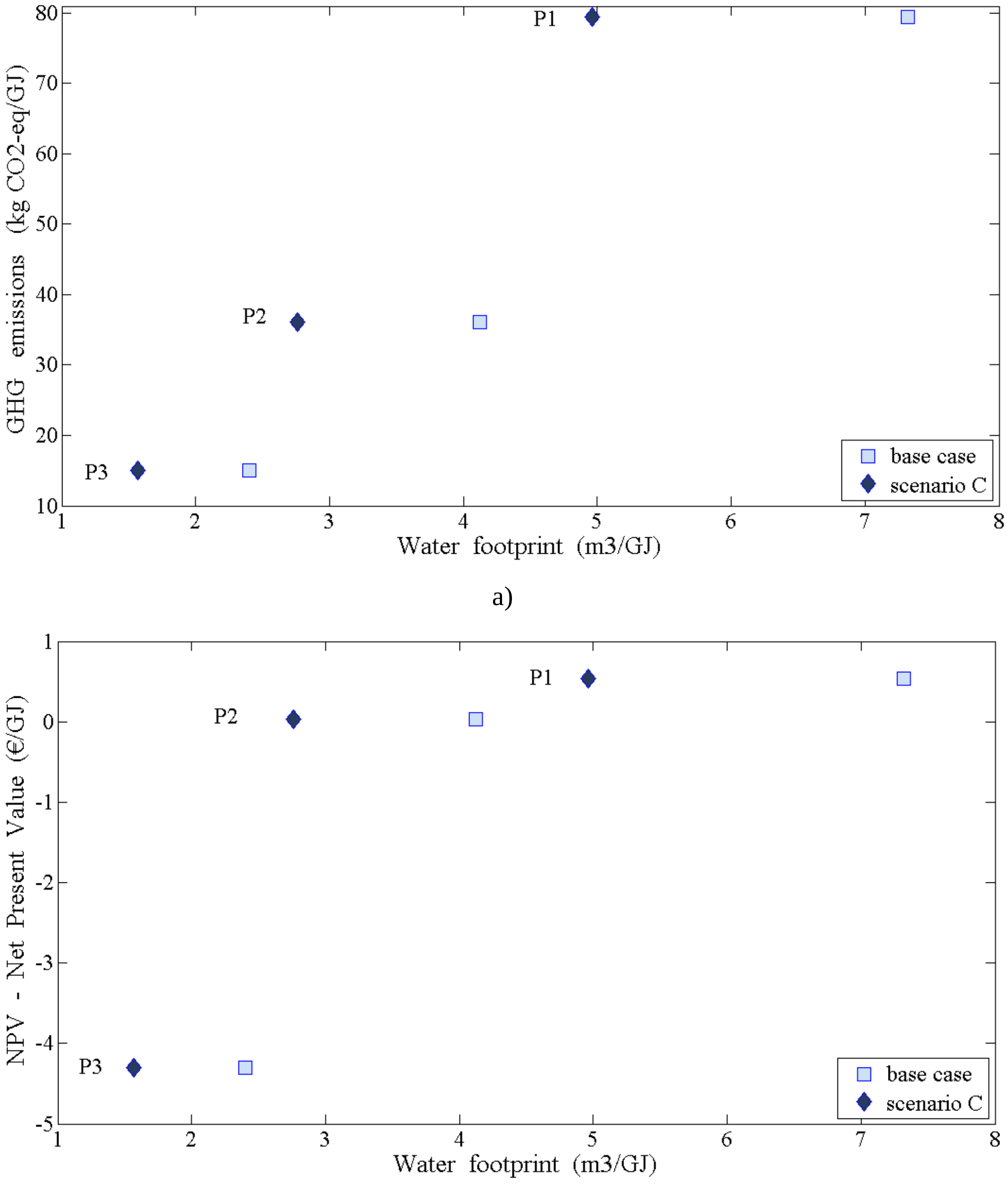
a)



b)

Figure D.1 *Pareto curve according to substitution method (instance 1): water footprint vs. GHG emissions (a); water footprint vs. profitability (b).*

Two allocation methods have also been considered to estimate the impacts in terms of WF and GHG emissions. According to instance 2, price allocation (Figure D.2) is used, giving the same trade-off between environmental and economic purposes as those obtained with the expansion method in terms of technological selection (i.e., P1 corresponds to a DGP technology; P2 represents a Hybrid process; P3 involves a LCEP technology). In case 2.C, effects of water usage improvement is more evident because of a greater contribution from the irrigation phase, with a 28% of reduction with respect to the base case.

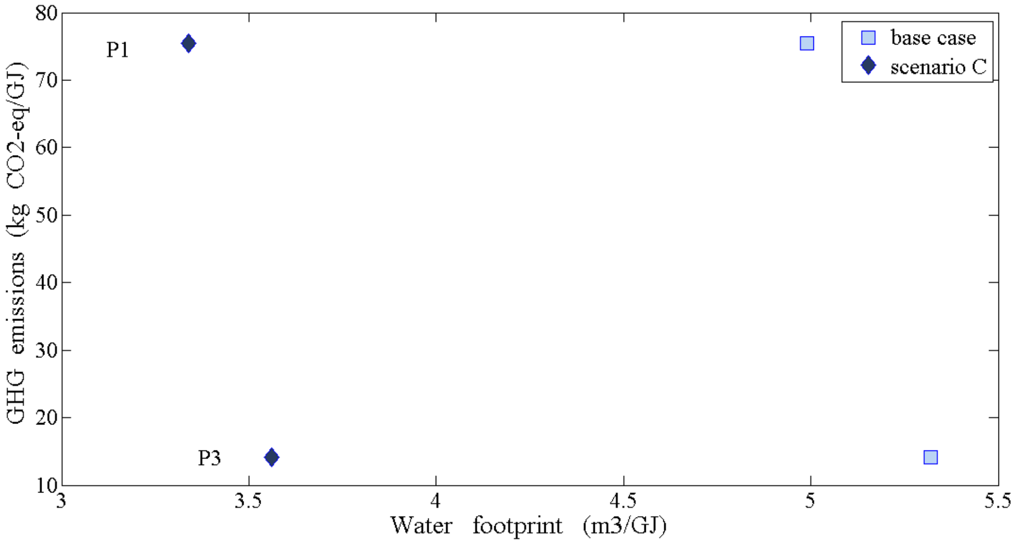


a)

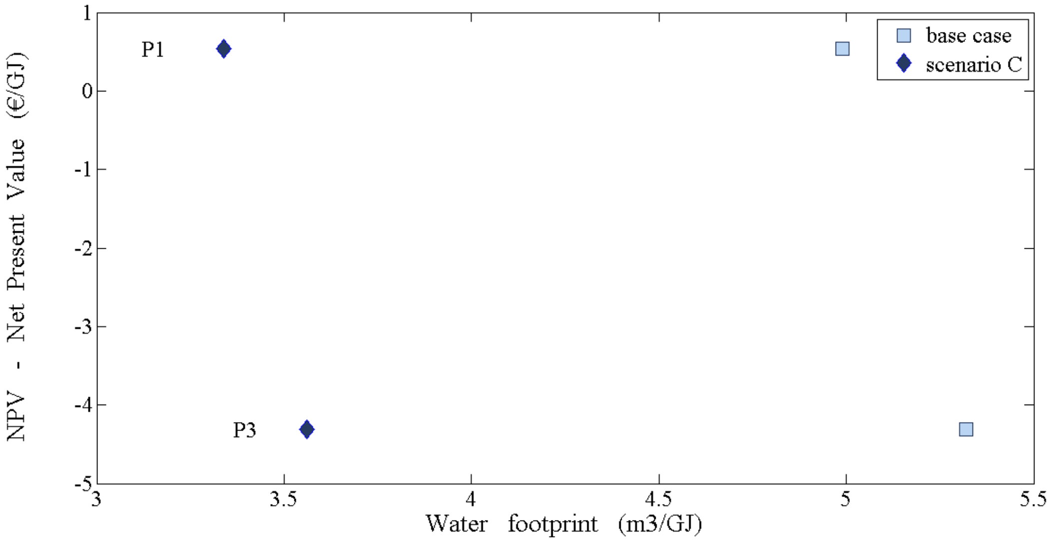
b)

Figure D.2 *Pareto curve according to price allocation (instance 2): water footprint vs. GHG emissions (a); water footprint vs. profitability (b).*

According to an energy allocation method (instance 3), only the DGP (P1) and the LCEP (P3) processes are selected (Figure D.3). The lignocellulosic process, while minimising the GHG emissions, produces a greater WF than first generation, which becomes the most suitable solution not only on economic terms but also when considering water use impact.



a)



b)

Figure D.3 *Pareto curve according to energy allocation (instance 3): water footprint vs. GHG emissions (a); water footprint vs. profitability (b).*

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