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SPECIAL ISSUE ARTICLE

Leachability and basicity of Na- and K-based geopolymer powders and lattices used as biodiesel catalysts

Renata Botti[1] | **Murilo D. M. Innocentini[2]** | **Thais A. Faleiros[2]** |
Cristina F. P. R. Paschoalato[2] | **Murilo F. Mello[2]** | **Giorgia Franchin[1]** |
Paolo Colombo[1,3]

[1] Department of Industrial Engineering, University of Padova, Padova, Italy

[2] Course of Chemical Engineering, University of Ribeirão Preto, Ribeirão Preto, São Palo, Brazil

[3] Department of Materials Science and Engineering, The Pennsylvania State University, Pennsylvania

Correspondence

Renata Botti, Department of Industrial Engineering, University of Padova, via Marzolo 9, 35131 Padova, Italy
Email: renata.botti@unipd.it

Funding information

CNPq - Brazilian National Council for Scientific and Technological Development Process, Grant/Award Number: 307259/2018−8

Abstract

Geopolymer powders and 3D-printed lattices have shown promising preliminary results as heterogeneous catalysts for the transesterification of vegetable oils to produce biodiesel. However, questions about the basicity of catalytic sites and the leaching characteristics of metals (K, Na) and hydroxyl groups in the reactional mixtures remained. The leaching of alkaline ions in methanol and biodiesel for powder and printed geopolymer formulations based on K, Na, or Na+K activators and treated at 110 to 700°C was investigated, as well as the physiochemical modifications of the materials. The Hammett indicators were used to determine base strength, and both leachable and total basicities were quantified. The amount of Na and K leached into the biodiesel phase was negligible (<1% wt.%). Methanol leaching reached a maximum of 29.3%. The base strength ranged between 11.0 and 18.4. Potassium-based geopolymer lattices presented the highest basicity, followed by sodium and sodium-potassium geopolymer catalysts. The basicity of all formulations decreased gradually as the calcination temperature increased. When compared to the homogeneous catalysts NaOH and KOH, the level of biodiesel contamination with Na and K is 81–93% lower. The findings support the heterogeneous nature of geopolymers as biodiesel catalysts and further validates their use for this application.

KEYWORDS

additive manufacturing, biodiesel processing, catalysts/catalysis, chemical analysis, geopolymers

1 | INTRODUCTION

The homogeneous alkali-catalyzed transesterification of triglycerides from biological sources remains the world's leading industrial biodiesel production process.[1–3] Despite the high conversion yields achieved under moderate reaction conditions, homogeneous alkaline catalysis requires high-quality lipid feedstocks (low free-fatty acid and water contents) to avoid side-reactions and soap formation, which consumes or deactivates the catalyst and makes biodiesel purification difficult and costly.[4] Instead, the use of insoluble or heterogeneous catalysts is regarded

Honoring Dr. Mrityunjay Singh

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as an environmental friendly process that can provide a more cost-effective pathway to biodiesel production, particularly, for lower-grade and less expensive feedstocks.[5] Because of the longer catalyst lifetime, the heterogeneous catalytic process simplifies downstream purification and lowers costs. Structured porous catalysts are even more appealing because they can be used in continuous flow reactors without being separated for reuse.[6,7]

The benefits of heterogeneous catalysts can only be sustained if their performance remains stable with use and recycling. One of the primary causes of biodiesel contamination and the deactivation of solid alkaline catalysts is the leaching of alkaline ions and hydroxyl groups (OH-) into the reaction medium.[5]

We recently investigated the use of geopolymers as heterogeneous catalysts in the methanolysis of soybean oil to produce biodiesel. Geopolymers are amorphous nanostructured aluminosilicates that consolidate at near room temperature; they are synthesized by reacting aluminosilicate sources with an alkaline activator, in this case, NaOH, KOH, or a mixture of the two. Transesterification was evaluated on geopolymer powders treated to temperatures ranging from 110 to 700°C and on geopolymer-based ink-based 3D printed lattices. The catalytic activity of the geopolymer powders was compared under identical reaction conditions (70−75°C, 150% excess methanol, 4 h reaction) and with identical weight quantities (3% to oil). The Na-based geopolymers performed better, containing 85.1 and 89.9% FAME in the biodiesel phase, respectively, for samples treated at 500 and 300°C. The discrepancies in performance were related to sodium and potassium's effects on the geopolymerization process, as well as the reactants' accessibility to the catalytic sites.[10] Increased treatment temperatures resulted in a loss of specific surface area (SSA) and activity. Similarly, we examined Na, K, and Na+K 3D lattices in the previous works.[8,9] For transesterification of soybean oil, the materials yielded high FAME amounts (73.5, 85.3, and 71.3%, respectively). Despite the encouraging results, doubts remained about the catalytic character of these geopolymers: heterogeneous, because of active alkaline sites supported on the solid matrix, or homogeneous, as a result of alkalis leached from the geopolymers into the transesterification reaction media. The current work addresses this issue by examining the structure and metal leaching properties of the ground and lattice-shaped geopolymers.

Geopolymer formulations with varying amounts of NaOH and KOH activators were thermally treated from 110 to 700°C and their total and leachable basicities were quantified. The Hammett indicator method was also used to evaluate the base strength qualitatively. Metal (K and Na) leaching was assessed after mixing ground geopolymer samples with methanol or biodiesel phases.

2 | MATERIALS AND METHODS

Three formulations of geopolymers with varying contents of sodium and potassium activators were produced and converted to powder, after drying (110°C), grinding, and sieving ($d_p < 125\ \mu m$). The powders (here referred to as Na-GP, K-GP, and Na.K-GP) were then heat treated in air in a muffle at 110, 300, 500, or 700°C for 1 h at a heating rate of 10°C/min; mass losses after calcination were recorded using a digital scale. The lattices were composed of a sodium-based geopolymer matrix, rheological agent (polyethylene glycol), and filler (geopolymer powder prepared previously). Additive Manufacturing, namely Direct Ink Writing, was used to fabricate the lattices which were shaped as short cylinders with a diameter of 25 mm and a height of 9.6 mm. All powders and lattice materials were successfully tested for methanolysis of soybean oil, and the results were published in our previous articles.[8–10] Table 1 summarizes the theoretical compositions of the powder and lattice geopolymers tested. The entire processing procedure is described elsewhere.[9]

The phase assemblage of the geopolymers was examined by X-ray diffraction analysis (XRD) using an X-ray diffractometer (D8 Advance, Bruker Corporation, Karlsruhe, Germany) with Cu-Kα radiation, operated at 40 kV and 40 mA with a .05° step width, a scanning range of 10−50° and a scanning speed of 1 s/step.

SSA was determined by multipoint Brunauer, Emmett, Teller method with Quantachrome Autosorb iQ (Quantachrome Instruments, Boynton Beach, FL). The samples were previously degassed at 110°C for approximately 16 h under reduced pressure and analyzed by N_2 adsorption at liquid nitrogen temperature.

To compare the geopolymer before and after the leaching test, FTIR measurements were carried out on ATR-FTIR spectrometer (ATR Pro ONE attachment, FTIR6200, JASCO, Japan); the infrared range of the analysis was 3800 to 400 cm^{-1} with a spectral resolution of 4 cm^{-1}, recording 64 scans.

It is worth noting that evaluating the leaching of metals under actual reaction conditions would be more realistic. Nonetheless, it is well established that the transesterification of vegetable oils to biodiesel begins with two immiscible phases (oil and alcohol) that are gradually changed into two further immiscible phases (FAME and glycerol).[3,8] All of these phases have varying affinities for hydrophilic and hydrophobic components present in the catalyst, including the alkalis, which may influence their preferential leaching into one phase or the other. Due to the unpredictable and uncontrollable nature of the solubility changes during transesterification, in this work, leaching was evaluated in two distinct phases: methanol, which is polar and less viscous, and biodiesel (FAME),

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TABLE 1 Formulation of powder and lattice geopolymers (not heat treated)

Component	Content in geopolymer powder Dry basis (wt.%)			Content in geopolymer 3D lattice Dry basis (wt.%)		
	Na-GP	K-GP	Na.K-GP	Na-GP_3D	K-GP_3D	Na.K-GP_3D
Si	25.8	23.5	24.6	24.9	22.8	23.8
Al	12.4	11.3	11.8	12.0	11.0	11.5
Na	*13.9*	*.2*	*6.8*	*13.5*	*.2*	*6.6*
O	46.1	42.0	44.0	44.5	40.9	42.6
Fe	.8	.7	.7	.7	.7	.7
Ti	.5	.5	.5	.5	.5	.5
K	*.3*	*21.5*	*11.4*	*.2*	*20.9*	*11.0*
Ca	.1	.1	.1	.1	.1	.1
Mg	.1	.1	.1	.1	.1	.1
Total (matrix and filler)				96.6	97.0	97.0
PEG				3.4	3.0	3.0
Total geopolymer	100.0	100.0	100.0	100.0	100.0	100.0
Na+K	14.2	21.7	18.2	13.7	21.1	17.6

Italics components are the main components of the work.

which is nonpolar and more viscous. This experiment is more systematic since it allows for controlling the solvent-solid ratio and the contact time and temperature. The agitation process and reaction temperature were not identical to those employed in an actual transesterification because the objective was not to replicate the reaction but to compare the limits of Na and K leaching from different geopolymer systems under the same conditions. Therefore, the geopolymers with formulations listed in Table 1 were subjected to the following leaching tests: (i) powders and methanol 99.9% in a mass proportion of 3:100; (ii) powders and purified methyl soybean biodiesel in a mass proportion of 3:100; (iii) lattice components and methanol 99.9% in a mass proportion of 3:43. The solid-liquid contact took place in airtight glass tubes shaken at room temperature (30°C) for 4 h. After centrifuging the samples, the liquid phase was digested in nitric/hydrochloric acids to quantify sodium and potassium using atomic absorption spectrophotometry (AA analyst 700, Perkin Elmer, Waltham, MA).

Following this set of experiments, the leaching of Na and K was also determined for an actual transesterification reaction between refined soybean oil (Soya, Bunge, Mato Grosso, Brazil) and methanol (Applychem PanReac, Darmstadt, Germany). The reaction was carried out in a 100 mL flask with vigorous agitation and total reflux at 75°C. The reaction time was 4 h, and the molar ratio of methanol to oil used for transesterification was 7.5:1 (150% molar excess methanol) with 3% Na.K-GP 3D catalyst (w/w oil). The mixture was cooled and centrifuged after the reaction time to separate the produced phases (biodiesel and glycerol). The 3D catalyst was extracted from the reactional

flask, calcined at 550°C, and then quantified for Na and K. For comparison, an unused piece of catalyst was subjected to the same thermal treatment and alkali analyses.

Titration with benzoic acid was used to determine the quantitative basicity of powder samples.[11,12] To determine the total basicity, a solid (.3 g) suspension in a toluene solution of phenolphthalein (4 mL, .1 mg/mL) was stirred for 30 min and titrated with a toluene solution of benzoic acid (.01 M). After that, new solid suspensions (.5 g) were shaken in water (50 mL) for 1 h at room temperature. The solid catalyst was removed, and the filtrate was treated with a methanol solution of phenolphthalein (5 mL, .1 mg/mL); the resulting mixture was titrated with a methanol solution of benzoic acid (.01 M) to determine the leachable basicity. Both total and leachable basicities were expressed in mmol/g.

The base strength of a solid catalyst indicates its ability to extract H^+ ions from methanol to produce anionic intermediates (methoxide), which is the first step in the transesterification reaction.[13] Hammett indicators are widely used to assess the base strength of heterogeneous catalysts. When an electrically neutral acid indicator is adsorbed on a solid base from a nonpolar solution, the color of the acid indicator changes to that of its conjugate base, provided the solid has the necessary basic strength to impart electron pairs to the acid. As a result, the basic strength can be assessed by observing the color changes of acid indicators over a range of *pKa* values.[14] The indicators used in this work and their respective *pKa* and color changes were: bromothymol blue (*pKa* = 7.2; colorless-blue); phenolphthalein (*pKa* = 9.8; colorless-pink), alizarin yellow R (*pKa* = 11.0; yellow-red),
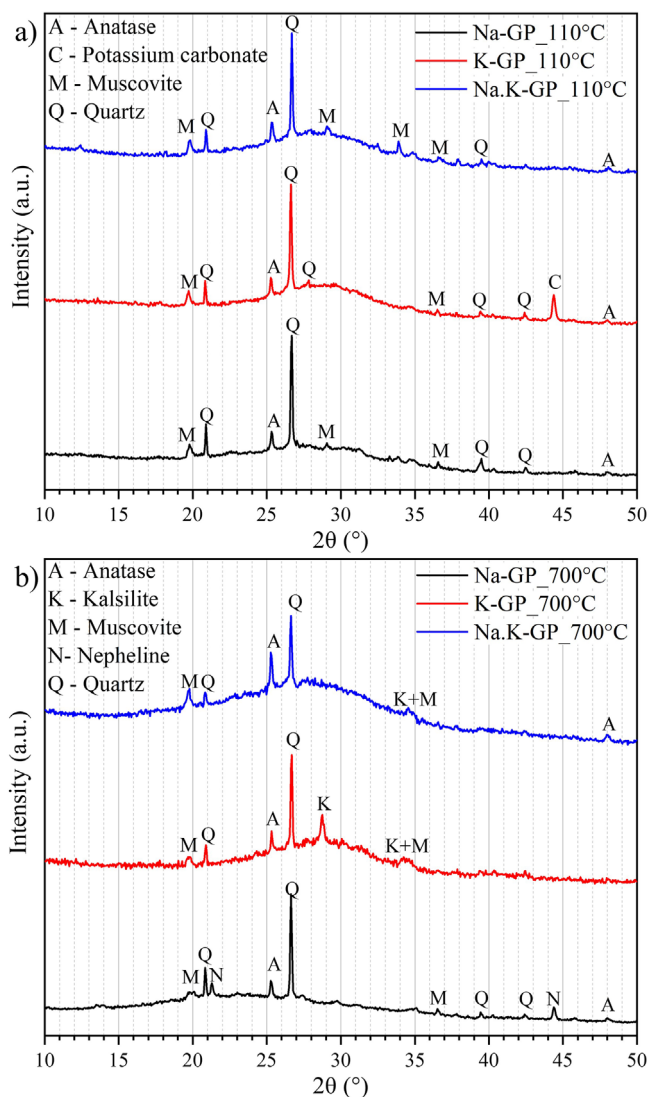
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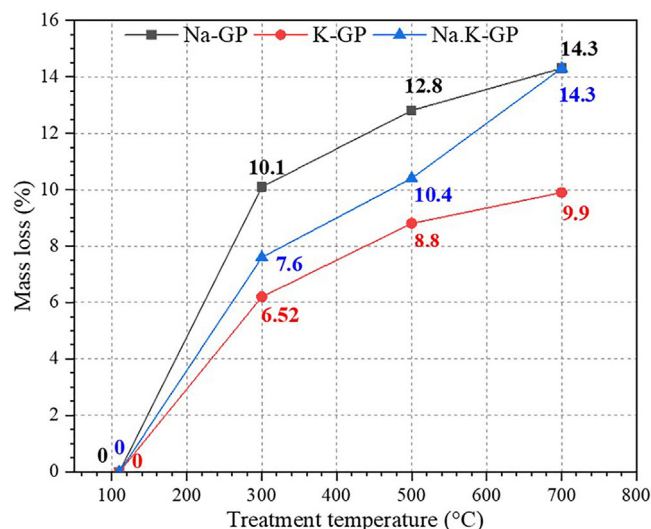**FIGURE 1** XRD patterns for powder samples treated at 110 and 700°C

FIGURE 2 Mass loss profiles for geopolymer powders prepared with different contents of Na- and K-based activators

of geopolymers, with a hump centered at approximately 27°; few peaks are present in all spectra and relate to the impurities of the metakaolin raw material, that is, quartz, anatase, and muscovite. K-GP treated at 110°C also shows a peak at approximately 44° which was attributed to potassium carbonate (it can be formed by the reaction of excess K_2O with atmospheric CO_2). Samples treated at 700°C remained mainly amorphous; however, the onset of crystallization could be detected for Na-GP (nepheline) as well as K-GP and Na.K-GP (kalsilite).

Table 2 reports the values of SSA of the geopolymer powders treated at the different temperatures. Values for Na-GP and K-GP are reported from Reference [10] and compared with those of Na.K-GP. Consistently with the previous results, the SSA decreases with increasing treatment temperature also for Na.K-GP; this can be attributed to the reduction of the fraction of mesopores during the densification of the amorphous matrix, caused by thermal shrinkage. Surprisingly, the mixed cation composition shows much lower SSA values compared to Na-GP and K-GP; this could be caused by some antagonistic effect of the two cations in the activating solution, which have different kinetics of dissolution of the metakaolin (faster for K than for Na) that could lead to the formation of a less homogeneous network with a lower amount of micro- and mesopores.[15,16]

The mass losses in geopolymer powders treated at temperatures ranging from 110 to 700°C are shown in Figure 2. Similar profiles (losses ranging from 6 to 15%) for various geopolymer systems have been reported in the literature.[17] Mass loss is caused by the elimination of adsorbed water and the decomposition of K and Na hydrates up to 300°C, and from 300 to 600°C it is attributed to the loss of water

4-nitroaniline (*pKa* = 18.4 yellow-orange), and benzidine (*pKa* = 22.4; colorless-purple). In each case, about 2 mL of Hammett indicator solution in benzene was added to 200 mg of catalyst, shaken in glass tubes, allowed to settle, and observed for color change. If the solution changes color after the procedure, this indicates that the catalyst's base strength is greater than the indicator's, and vice-versa.

3 | RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern for powdered geopolymers heat treated at 110 and 700°C. Patterns for samples treated at 300 at 500°C are omitted as they showed no difference with the ones treated at 110°C.[10] The samples treated at the lowest temperature show the amorphous structure typical

TABLE 2 Specific surface area of powder samples. (*data from Ref. 10)

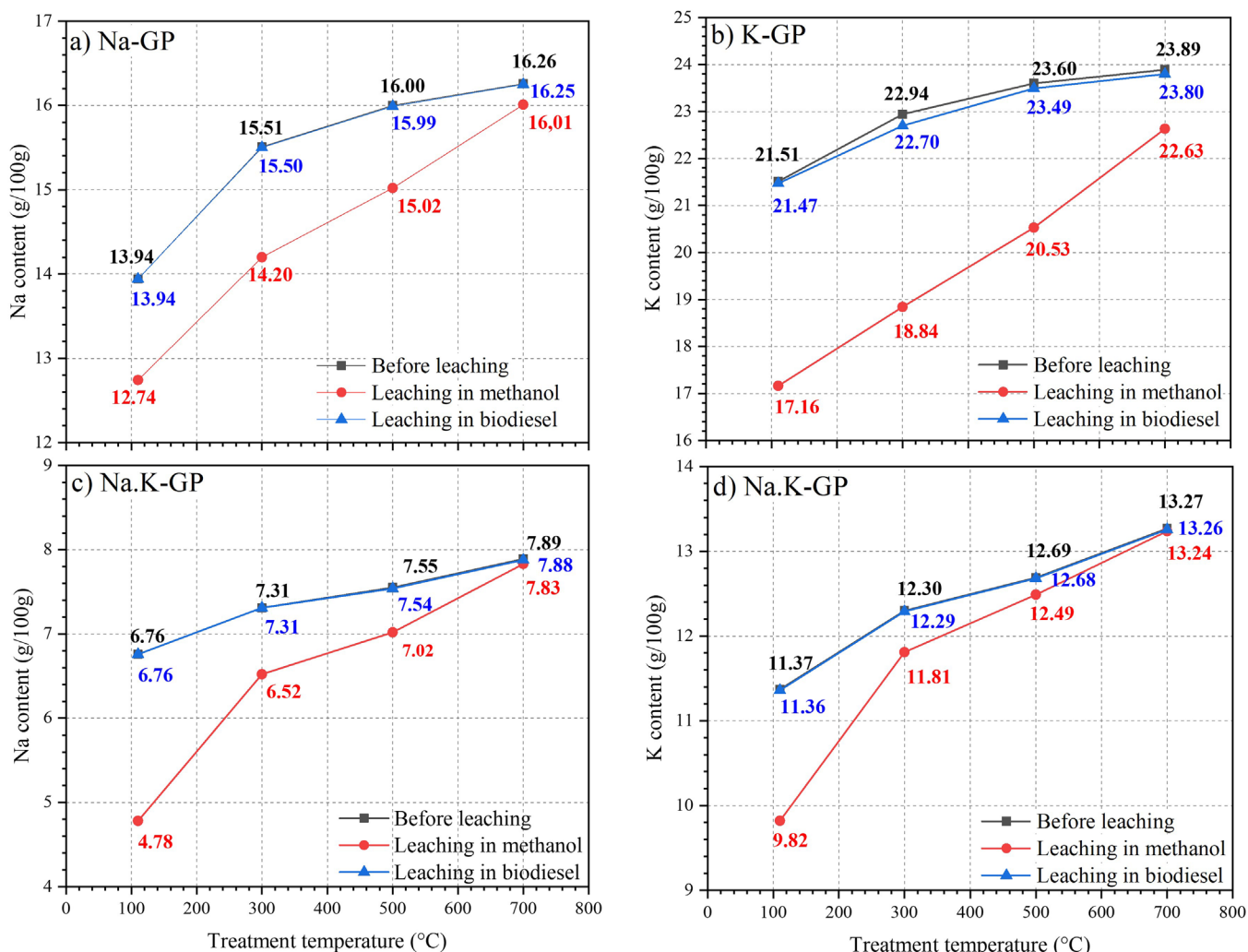| Sample	*SSA (m²/g)	Sample	*SSA (m²/g)	Sample	SSA (m²/g)
Na-GP_110°C	32.6	K-GP_110°C	63.5	Na.K-GP_110°C	9.2
Na-GP_300°C	31.4	K-GP_300°C	42.2	Na.K-GP_300°C	6.2
Na-GP_500°C	27.4	K-GP_500°C	29.9	Na.K-GP_500°C	5.6
Na-GP_700°C	6.3	K-GP_700°C	28.6	Na.K-GP_700°C	3.3

FIGURE 3 Leaching of sodium and potassium ions from geopolymer powders after contact with methanol or biodiesel

formed by condensation/polymerization of Si–OH and Al–OH groups. The primary cause of weight change above 600°C is the decomposition of carbonate species, formed by the reaction of the alkaline ions and CO_2 from the environment.[18]

The leaching behavior of geopolymer powders in methanol and soybean biodiesel as a function of the thermal treatment temperature is shown in Figure 3. Because Na and K are both nonvolatile, their content in the powders prior to leaching (green curves) increased proportionally to the mass loss at each treatment temperature. Na and

K leaching in biodiesel was negligible for all geopolymer samples (≤1 wt.%), confirming their low solubility in nonpolar liquids. The leaching in methanol, on the other hand, was more pronounced due to the higher polarity of this solvent. The maximum leaching occurred for samples dried at 110°C; the sodium content decreased 8.6% for Na-GP (from 13.94 to 12.74 g/100 g), and 29.3% for Na.K-GP (from 6.76 to 4.78 g/100 g). Similarly, the potassium content was reduced 20.2% for K-GP (from 21.51 to 17.16 g/100 g) and 13.6% for Na.K-GP (from 11.37 to 9.82 g/100 g). The gradual decrease in leaching with increasing heat treatment
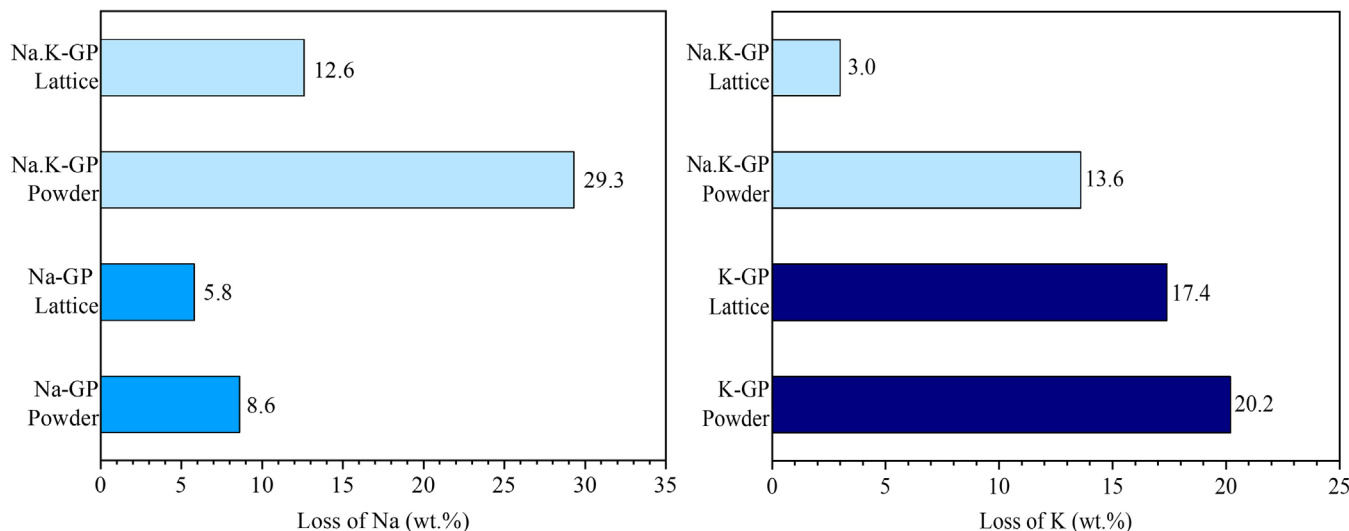
FIGURE 4 Percentage loss of sodium and potassium ions from geopolymer 3D printed lattices and powders heat treated at 110°C, after contact with methanol

temperature was most likely caused by a decrease in the SSA[10] and solvent accessibility within the solid particles.

It is worth noting that Na-GP and K-GP powders treated at temperatures ranging from 110 to 700°C were recently tested for methanolysis of soybean oil using a ratio of 3 g of geopolymer to 100 g of oil and a 150% methanol excess for a 4-h reaction at 75°C.[10] In that study, all powders tested yielded some biodiesel, even those treated at 700°C (51.4% for Na-GP and 16.7% for K-GP). Therefore, based on the data in Figure 3, it is possible to predict that for the above reaction conditions, there would be a maximum solubilization of 39 mg Na per 100 g oil or 131 mg K per 100 g oil into the reaction medium. In comparison, the Na and K solubilized during homogeneous methanolysis using 1% NaOH or KOH are 575 mg Na per 100 g oil and 696 mg K per 100 g oil, respectively. The level of metal contamination is, therefore, 93% lower for Na-GP and 81% lower for K-GP when compared to the use of NaOH and KOH, respectively. To confirm these predictions, a transesterification test was performed with the 3D printed mixed formulation lattice (Na.K_GP) under similar reactional conditions used in our previous work.[10] The loss of Na and K was 5.01 and 4.10% in mass, respectively, corresponding to the solubilization of 17 mg Na per 100 g oil and 23 mg K per 100 g oil into the reaction medium. These values are lower than those predicted for pure methanol solubilization and confirm that leaching is even less pronounced under reactional conditions where phase polarities change over time.

Figure 4 shows the leaching profiles of geopolymer 3D printed lattices heat treated at 110°C and exposed to contact with methanol. For comparison, the loss of metal from GP powders under the same conditions is included. Since there is a constant decrease in SSA with temperature for all

TABLE 3 Specific surface area of lattices samples before and after leaching process

Sample	SSA (m^2/g)
Na-GP-3D_before leaching	8.3 ± 2.8
Na-GP-3D_after leaching	12.0 ± 2.4
K-GP-3D_before leaching	11.7 ± .6
K-GP-3D_after leaching	19.2 ± .3
Na.K-GP-3D_before leaching	6.4 ± .3
Na.K-GP-3D_after leaching	12.2 ± .1

the tested compositions, the 3D printed lattices were only treated at the lowest temperature.

The leaching of Na and K was lower in the lattice components than in the powders in all cases. This behavior is expected due to the addition of PEG to the printing inks, which gives the struts more stability and reduces the ability of solvents to leach the metals, as well as because of the reduced geometric surface area of the 3D printed component with respect to powders (reported in Table 3).

At room temperature, the theoretical solubility of NaOH and KOH in methanol is 238 and 55 g/L, respectively. These values are significantly higher than the total amount of Na and K present in the samples during the methanol leaching tests. Thus, the differences in metal losses shown in Figure 4 are unrelated to solvent saturation. Instead, it could be related to the strength of Na and K bonds formed during the geopolymerization process[19–21] or to the solvent accessibility to the porous network to leach out the cations. Nevertheless, such losses do not seem to have significantly affected the transesterification performance, as reported in our previous work.[10]
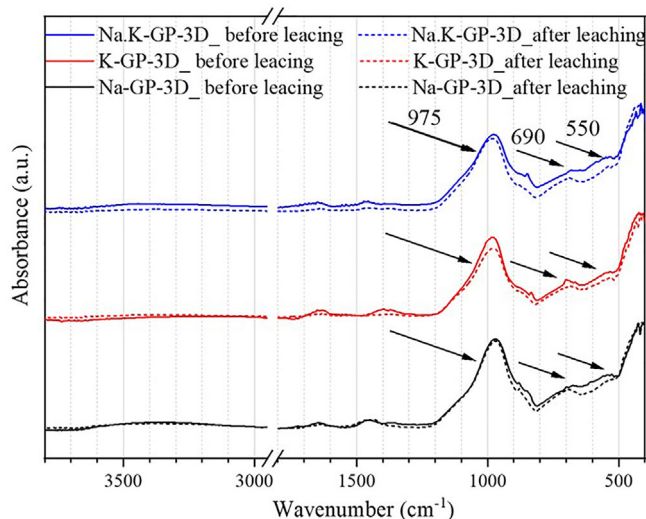
FIGURE 5 FTIR analysis of Na-GP_3D sample before and after leaching process

The SSA of the 3D printed lattices was measured again after leaching in methanol (Table 3). All samples show a slight increase in SSA after the leaching test; such increase can be attributed both to the PEG being washed away from the structures, as well as to the substitution of Na^+ and K^+ in the geopolymer network with H^+ or H_3O^+ resulting in a less stable network prone to depolymerization of the Si-O bonds (similar to what reported for silica soda-lime glass).[22]

Figure 5 shows the FTIR pattern of the lattices printed with the three compositions, before and after the leaching tests in methanol. All patterns show a characteristic peak centered at approximately 975 cm^{-1}, corresponding to the asymmetric stretching vibrations of Si-O-Si and Si-O-Al in an aluminosilicate gel. The patterns do not show significant changes before and after leaching, apart from a slight decrease in the bands centered at approximately 690 and 550 cm^{-1}.[23] These bands are associated with the tetrahedral vibrations formed by secondary building units in the aluminosilicate system and are characteristic of the double or single rings formed by SiO_4 and AlO_4 tetrahedra.[24] Their decrease could be associated with the destabilization of AlO_4 tetrahedra resulting from the leaching and substitution of Na^+ and K^+ ions in the network, consistently with what was postulated for the SSA increase.

Sodium and potassium cations are not the actual catalysts for homogeneous transesterification, but they can be good indicators of the presence of active hydroxides (OH^-) or alkoxide (OR^-) groups.[25] In heterogeneous transesterification, on the other hand, the solid structure must provide sufficient adsorptive sites for methanol, in which the O–H bonds break into methoxide anions and hydrogen cations.

TABLE 4 Base strength of geopolymer powder catalysts

Catalyst	Heat treatment temperature (°C)	Base strength
Na-GP	110	11.0-18.4
	700	<7.2
K-GP	110	11.0-18.4
	700	11.0-18.4
Na.K-GP	110	11.0-18.4
	700	11.0 - 18.4

Methoxide anions then react with triglyceride molecules to form corresponding fatty acid methyl esters.[26] The base strength and the basicity of the sites are, thus, more reliable indicators of their ability to form methoxide ions, the first step for biodiesel conversion.

As shown in Table 4, the base strength of geopolymer powders assessed by the Hammett indicator method ranged between 11.0 (color change to pink with phenolphthalein) and 18.4 (no color change with 4-nitroaniline). The results were unaffected by increasing the thermal treatment temperature from 110 to 700°C. The results are consistent with those reported by Thangaraj et al. for a list of solid base catalysts with strength greater than 11 and conversion greater than 92% for biodiesel conversion.[27] The only exception observed here was the Na-GP sample heat treated at 700°C, which had a base strength of less than 7.2, probably due to the very low SSA of this sample (6.2 m^2/g).

The total and leachable basicity of the geopolymer samples are shown in Figure 6. Except the sample treated at 110°C, potassium-based geopolymers had the highest basicity level, followed by sodium and then sodium-potassium lattices. Temperature caused a gradual decrease in basicity. These trends are consistent with the SSA data reported in our previous work, which ranged from 32.72 to 6.34 m^2/g, and 62.54 to 28.64 m^2/g, for Na-GP and K-GP, respectively.[10] Xie et al. reported similar basicity levels for Mg-Al solid catalysts tested for the methanolysis of soybean oil.[28] Conversion reached 67% under much harsher conditions than those used with our geopolymer catalysts, with a molar ratio of soybean oil to methanol of 15:1, a reaction time of 9 h, and a catalyst amount of 7.5%. Fraile et al. investigated the basicity of mixed oxide catalysts for biodiesel transesterification. They discovered similar orders of magnitude for total and leachable basicity, but with no direct correlation, demonstrating the different nature of the sites involved.[29] Manríquez-Ramírez et al. reported that potassium-based catalysts had a higher base strength and biodiesel conversion than sodium-based catalysts,[13] which is consistent with the trends shown in Figure 6.
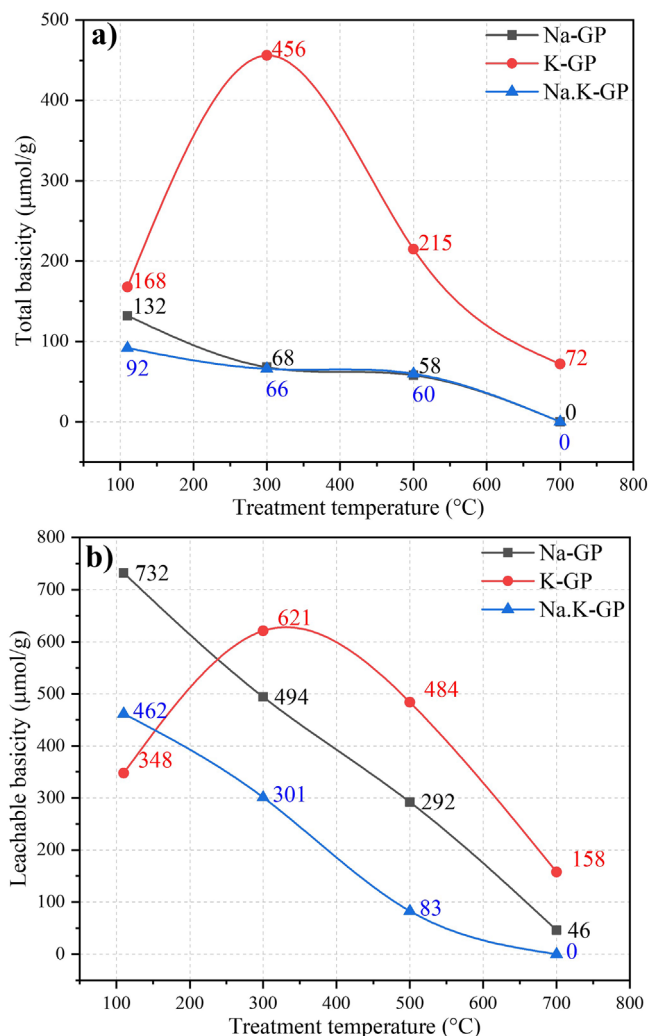
FIGURE 6 Basicity of Na-, K-, and Na.K-based geopolymer powders heat treated at different temperatures: (A) total basicity; (B) leachable basicity

4 | CONCLUSIONS

The data collected in this study confirm that Na- and K-based geopolymers primarily act as heterogeneous catalysts in the biodiesel synthesis reaction, as the amount of alkaline ions dissolved in the reaction is significantly lower than in conventional homogeneous transesterification with NaOH or KOH. When compared to other heterogeneous catalytic systems, the studied geopolymers demonstrated promising FAME content for soybean oil transesterification, especially given the mild temperature, catalyst amount, oil-alcohol ratio, and reaction time used in our experiments. The main specific findings of the work were:

- All formulations had a high base strength (11.0-18.4), which was comparable to several other solid catalysts reported in the literature;

- Potassium-based geopolymers had the highest basicity, followed by sodium- and sodium-potassium geopolymer catalysts;
- The basicity of all formulations decreased gradually as the calcination temperature increased from 110 to 700°C following the same trends observed for SSA;
- The amount of Na and K leached during the actual transesterification reaction of soybean oil and methanol at 75°C for 4 h was 5.01 and 4.10% in mass, respectively, which is insufficient to sustain a homogeneous catalytic process;
- When compared to the homogeneous catalysts NaOH and KOH, the contamination of biodiesel with Na and K present in the geopolymers was 81–93% lower. The findings support the hypothesis of the heterogeneous catalytic mechanism of geopolymers used in biodiesel synthesis.

ORCID

Renata Botti https://orcid.org/0000-0003-4279-0613
Giorgia Franchin https://orcid.org/0000-0002-4419-827X
Paolo Colombo https://orcid.org/0000-0001-8005-6618

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