

# In Situ Transesterification from Soybean Seed Using Mechanochemical Methods toward Producing Biodiesel

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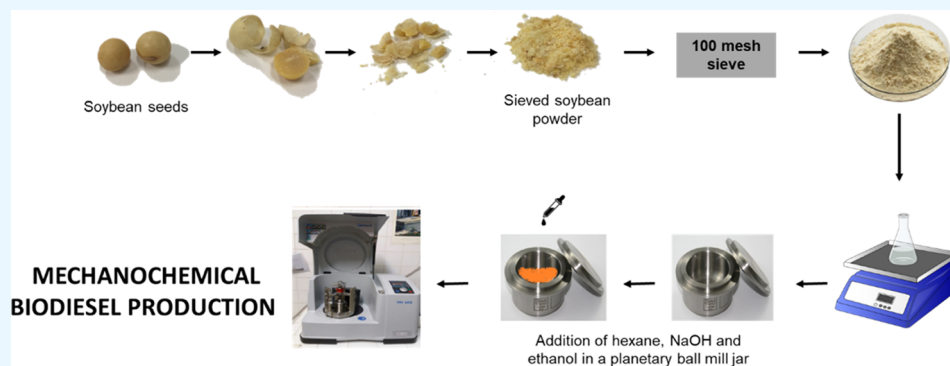


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**ABSTRACT:** The research and development of new routes of biodiesel synthesis have been increasingly in line with the principles of green chemistry. In this sense, mechanochemistry is a promising technique, able to ally the energetic potential with reductions in the use of solvents and steps of treatment of the sample and the purification of the product. To date, this is the first work using mechanochemistry directly in extracting soybean oil from its seed and the *in situ* transesterification reaction by applying a reactive soybean oil extraction process. The presence of *n*-hexane was studied in different molar proportions (relative to the oil content), and a low solvent consumption in a 3:1 ratio was adopted. Mechanochemistry favored oil diffusion in the *n*-hexane solvent, resulting in a mean triglyceride content equal to 90%, against 66% obtained in the tests without spheres in the planetary ball mill. The catalyst content was also evaluated, and 4% NaOH (weight, concerning the oil) was the concentration that presented less residue of nontransesterified glycerides in the samples for ethyl ester preparation. Additionally, the protein content was determined on the residual soybean cake, with no loss of nutritional potential when subjected to the mechanochemical process.

## 1. INTRODUCTION

Biodiesel is an interesting alternative for diversifying the automotive fuel matrix, reducing global dependence on fossil oil, and contributing to environmental protection.<sup>1</sup> Considering the high production costs, efforts have been shifted to seeking a reduction in the price of biodiesel production to make it more competitive, involving profitable production, efficient agricultural subsidies, more sustainable production processes, and better use of coproducts.<sup>2,3</sup>

Biodiesel production is based on a direct transesterification reaction between triglycerides (e.g., from vegetable oils) and primary alcohols, mainly methanol and ethanol. Alternatively, the oily matrix (a seed, for example) can be subjected to direct contact with alcohol without prior oil production. Thus, simultaneous oil extraction and transesterification reactions can be performed in a single-step reactive extraction. This type of approach converges with green chemistry because, in general, it results in a lower generation of process residues and lower energy consumption.<sup>4,5</sup>

Several studies that adopt reactive extraction in biodiesel production are found in the literature. Some raw materials studied are solid oleaginous materials such as *Jatropha curcas* seeds, castor beans, canola, cotton, crambe, and coconut residues. In these works, reaction variables for the *in situ* transesterification reaction were evaluated, such as the molar ratio of alcohol to oil, catalyst ratio, medium agitation effect, temperature, pressure, the influence of ultrasonic cavitation, and also supercritical conditions.<sup>6–12</sup>

In the direct transesterification of oils or fats, the reaction is typically catalyzed and occurs at the interface between triglycerides and alcohol. To obtain higher conversion rates,

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the contact between these two low-miscible phases should be maximized. In most studies that address biodiesel production on a laboratory scale, mechanical agitation is coupled to heating of the reaction medium to maximize mass transfer. An increase in the temperature causes a reduction of the oil's viscosity, increasing its interaction with the alcohol and the catalyst, accelerating the reaction, and improving the yield.<sup>13</sup>

With the advent of new process technologies, alternative energy sources have gone beyond conventional heating and have been applied to overcome problems of mass and heat transfer and to accelerate the rate of conversion of triglycerides into biodiesel. In this context, ultrasonic energy and microwave radiation are examples of such alternatives applied to biodiesel production.<sup>14–17</sup> However, mechanochemistry is the new frontier as an alternative source of energy, aiming for higher yields in a shorter time and at mild conditions of temperature and pressure, and mechanical grinding has been used for breaking of bonds and for allowing reactions with minimal or without solvent addition.<sup>18,19</sup> It is worth pointing out that the possibility of promoting reactions under these conditions, including solvent absence, is one of the reasons for the increase of mechanochemistry applications, which favors its suitability to green chemistry. Atom economy, energy efficiency, and inherently safer chemistry for accident prevention are other green chemistry principles applicable to mechanochemistry.<sup>20,21</sup>

Toward biodiesel production, the use of mechanochemistry applied for the synthesis of fatty acid alkyl esters (FAAEs) has been limited to sample preparation and the synthesis of catalysts (mostly heterogeneous).<sup>22–30</sup> Despite there being a recent report on the mechanochemical process for biodiesel production by the transesterification of vegetable oil with methanol,<sup>31</sup> to the best of our knowledge, mechanochemistry has not been applied to the extraction of vegetable oils from the raw material and *in situ* transesterification to obtain FAAEs.

The present work inserts mechanochemistry as an alternative energy source for soybean oil extraction from its seeds toward reactive extraction (*in situ* transesterification), aiming for FAAE synthesis. In addition, this work addresses some of the principles of green chemistry, such as the direct use of soybean, eliminating the extraction stage of the oil through an independent process, and reducing time and solvent consumption. The experiments used ethanol to form fatty acid ethyl esters (FAEEs), aiming for an approximation with green chemistry principles. Beyond this, the nutritional potential of the residual soybean cake in terms of protein content was also evaluated.

## 2. EXPERIMENTAL SECTION

**2.1. Reagents and Samples.** Soybean seeds were acquired from a local market in Salvador, Bahia, Brazil. The seeds were ground with a domestic blender until the obtention of a fine powder and then dried in a laboratory oven at 115 °C for 15 min to remove the moisture. Commercial soybean oil (also acquired from a local market) was used for comparative purposes.

The following reagents and standards were used: *n*-hexane (Merck, ≥96%), absolute ethanol (Qumica Moderna, ≥99.3%), pyridine (JT Baker, ACS grade), sodium hydroxide (Neon), sodium chloride (Quimidrol), anhydrous sodium sulfate (Synth), heptadecanoate methyl ester (Spectrum), and certified reference materials (Accustandard): triolein, diolein, and monoolein in pyridine.

## 2.2. Instruments, Operational Procedures, and Data Analysis.

**2.2.1. Gas Chromatography.** Gas chromatography with a flame ionization detector (CP-3800, Varian), equipped with a Restek MXT-Biodiesel capillary column (5% phenyl, 95% methylpolysiloxane, 10 m × 0.32 mm × 0.1 μm), was used for the analysis of the samples obtained from transesterification reactions as well as for commercial and Soxhlet-extracted soybean oil analysis. The analysis conditions were as follows: 20:1 split ratio; 1 μL sample injection volume; and injector and detector temperatures of 280 and 380 °C, respectively. The oven program was as follows: 80 °C for 1 min, 7 °C min<sup>-1</sup> ramp until 300 °C, 30 °C min<sup>-1</sup> ramp until 370 °C, maintained for 10 min. Helium was used as the carrier gas at 1.6 mL min<sup>-1</sup>.<sup>32</sup>

**2.2.2. Planetary Ball Mill.** A planetary ball mill (Retsch, model PM-100) was used for oil extraction and *in situ* transesterification at 350 rpm for 30 min. Reverse sensing was applied at half of the time. The stainless steel reaction vessel was loaded with spheres of the same material, when applicable to the tests performed.

**2.2.3. Infrared Spectroscopy.** Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR, Shimadzu IR-Afinity) was used to qualitatively analyze the soybean oil or FAAE mixtures. Infrared spectra were obtained from 4000 to 600 cm<sup>-1</sup> after programming 20 scans and correcting the atmosphere to eliminate spectral interferences. In the spectrum, it was sought to observe the characteristic bands of esters, either the starting oil (in the form of mono-, di-, or triglycerides) or the alkyl ester obtained by transesterification.

**2.2.4. Data Analysis.** Chromatographic data analysis was based on ASTM D-6584-17 (the standard test method for the determination of total monoglycerides, total diglycerides, total triglycerides, and free and total glycerin in B-100 biodiesel methyl esters by gas chromatography). The relative mass (%) of glycerides in the samples was calculated by eq 1:<sup>33</sup>

$$Gli = \left[ \frac{w_{IS}}{a_{Gli}} \right] \cdot \left( \left[ \frac{A_{Gli}}{A_{IS}} \right] - b_{Gli} \right) \cdot \left[ \frac{100}{w_s} \right] \quad (1)$$

where Gli is the relative mass of each glyceride in the sample (%), being monoglyceride, diglycerides, or triglycerides;  $A_{Gli}$  is the peak area of each glyceride;  $A_{IS}$  is the internal standard peak area;  $w_s$  is the weighted mass used for preparing the injected sample (g);  $w_{is}$  is the weighted mass of the internal standard added to the sample (g); and  $a_{Gli}$  and  $b_{Gli}$  are the slope and intercept, respectively, of the calibration curve of each glyceride.

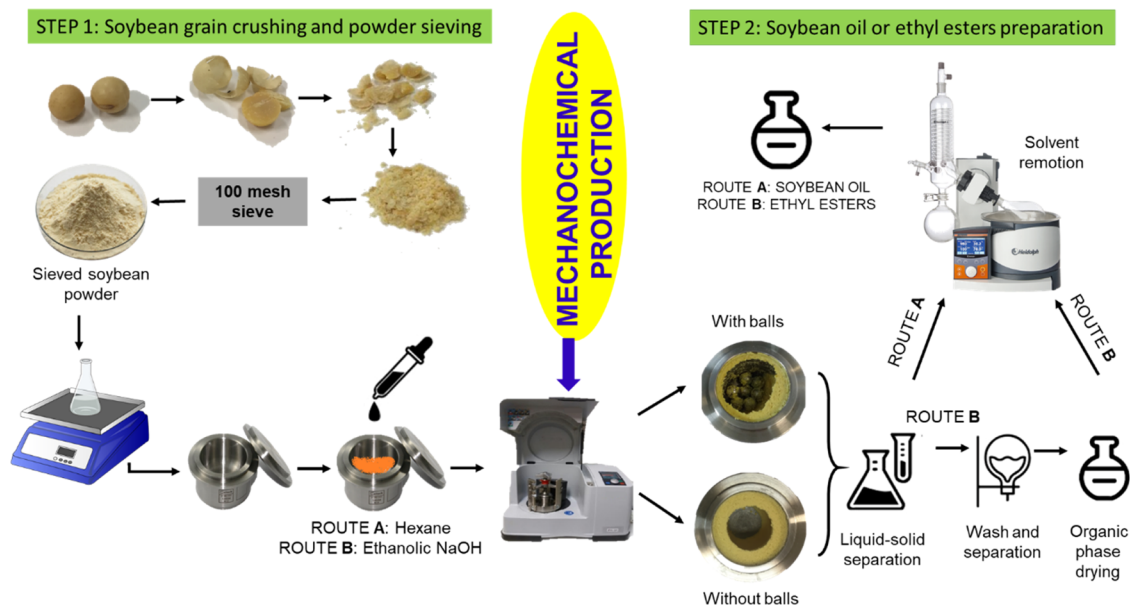
Equation 2 was used to calculate the FAEE (%) in samples from chromatographic peaks:<sup>34–37</sup>

$$FAEE (\%) = \frac{(\sum A_{FAEE} - A_{IS}) \cdot c_{IS} \cdot V_{IS}}{A_{IS} \cdot w_s} \times 100 \quad (2)$$

where  $A_{FAEE}$  is the peak area of each fatty acid ethyl ester present in the sample;  $A_{is}$  is the internal standard peak area;  $c_{is}$  is the internal standard concentration in the sample;  $v_{is}$  is the internal standard volume added to sample; and  $w_s$  is the weighted mass used for preparing the injected sample.

The weight yield (%) was calculated by eq 3:<sup>6,9</sup>

$$\text{weight yield (\%)} = \frac{w_{oil}}{(0.2 \times w_{soy})} \times 100 \quad (3)$$



**Figure 1.** Steps of mechanochemical oil extraction and *in situ* transesterification from soybean seeds. Images sourced from (1) laboratory glassware: Vecteezy.com (<https://www.vecteezy.com/free-vector/laboratory-glassware>), (2) laboratory balance: DBCLS CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0>), via Wikimedia Commons, and (3) rotaevaporator: Vap2012, CC BY-SA 3.0 (<https://creativecommons.org/licenses/by-sa/3.0>), via Wikimedia Commons. The remainder of the images were taken by the authors.

where  $w_{\text{oil}}$  is the weight of the oil product (g) and  $w_{\text{soy}}$  is the weight of the soybean meal used (g).

**2.3. Ball-Milling Soybean Oil Extraction.** In this work, it was considered that the oil content of soybean is 20%.<sup>38</sup> To evaluate soybean oil extraction through a ball mill, replicates of the procedure were made in the presence and absence of the spheres in the grinding jar. A mass of 10 g of grounded soybeans, previously sieved (100 mesh), was inserted in a 50 mL stainless steel grinding jar with seven spheres of 10 mm diameter (when applicable). *n*-hexane was added to the medium in different molar proportions (relative to the oil content) toward the assessment of the cosolvent ratio: 3:1 (0.94 mL), 13:1 (3.8 mL), and 33:1 (9.4 mL). The grinding jar was appropriately placed in a planetary ball mill. After extraction, the soybean cake, grinding jar, and spheres (when applicable) were washed with 10 mL of *n*-hexane before filtration and solvent elimination under vacuum. The efficiency of soybean oil extraction was evaluated by the concentration of glycerides in the obtained oil (monoolein, diolein, and triolein).

For comparison purposes, Soxhlet oil extraction from grounded soybean was made with 250 mL of *n*-hexane for 7 h, according to a standardized method published by Adolfo Lutz Institute.<sup>39</sup> Purified and degummed commercial soybean oil and those oils obtained from mechanochemical and Soxhlet extractions were analyzed by infrared spectroscopy and gas chromatography.

**2.4. Ball-Milling *In Situ* Transesterification.** After the proportion of *n*-hexane was established for oil extraction, the influence of mechanochemistry on *in situ* transesterification was evaluated. First, a univariate study of the effect of the catalyst content (NaOH) was performed using a planetary ball mill. The evaluated concentrations of NaOH were 2, 4, 6, and 8% (weight, concerning the oil). For each test, 10 g of grounded and sieved soybean was inserted in a 50 mL stainless steel grinding jar with seven spheres of 10 mm diameter (when applicable). The recommended volume of *n*-hexane was added

to soybean with a micropipette, with 3.2 mL of NaOH solution in ethanol. The alcohol/oil molar ratio was fixed at 25:1, and the NaOH content varied according to the test condition. The grinding jar was placed in a planetary ball mill. After the reaction, the soybean residue, grinding jar, and spheres were washed with 10 mL of *n*-hexane before filtration under vacuum. The filtrate was washed thrice with saturated sodium chloride solution to purify fatty acid ethyl esters (FAEEs) before moisture removal with anhydrous sodium sulfate. Finally, vacuum was applied for solvent elimination, and the soybean cake was kept in a closed jar for further determination of protein content by Kjeldahl analysis. Figure 1 resumes the steps in the experiments described in Sections 2.3 and 2.4.

**2.5. Kjeldahl Analysis.** The soybean cake was subjected to Kjeldahl analysis after reactive extraction, as described in Section 2.3. The same procedure was applied to the ground soybean before the reactive extraction process. From this analysis, it was evaluated whether the *in situ* transesterification process through the ball-milling technique resulted in protein content loss of the feedstock. A nitrogen distiller (TECNAL TE-036/1, Brazil) and digester (TECNAL TE-007A, Brazil) were used, according to the procedure published by Adolfo Lutz Institute.<sup>40</sup> Protein content (%P) was calculated by eqs 4 and 5, where 5.71 refers to a factor applied to soybean:<sup>41</sup>

$$\%N = \frac{(V_{\text{HCl}} - V_{\text{b}}) \cdot c_{\text{HCl}} \cdot f \cdot 14 \times 100}{w_s} \quad (4)$$

$$\%P = \%N \times 5.71 \quad (5)$$

where %N is the total nitrogen content of samples,  $V_{\text{HCl}}$  and  $c_{\text{HCl}}$  are the volume and concentration of hydrochloric acid (titrating solution), respectively,  $f$  is the solution factor (1.2), and  $w_s$  is the sample weight.

## 3. RESULTS AND DISCUSSION

**3.1. Soybean Oil Extraction.** Under the mechanochemical conditions (50 mL stainless steel jar, seven spheres of 10

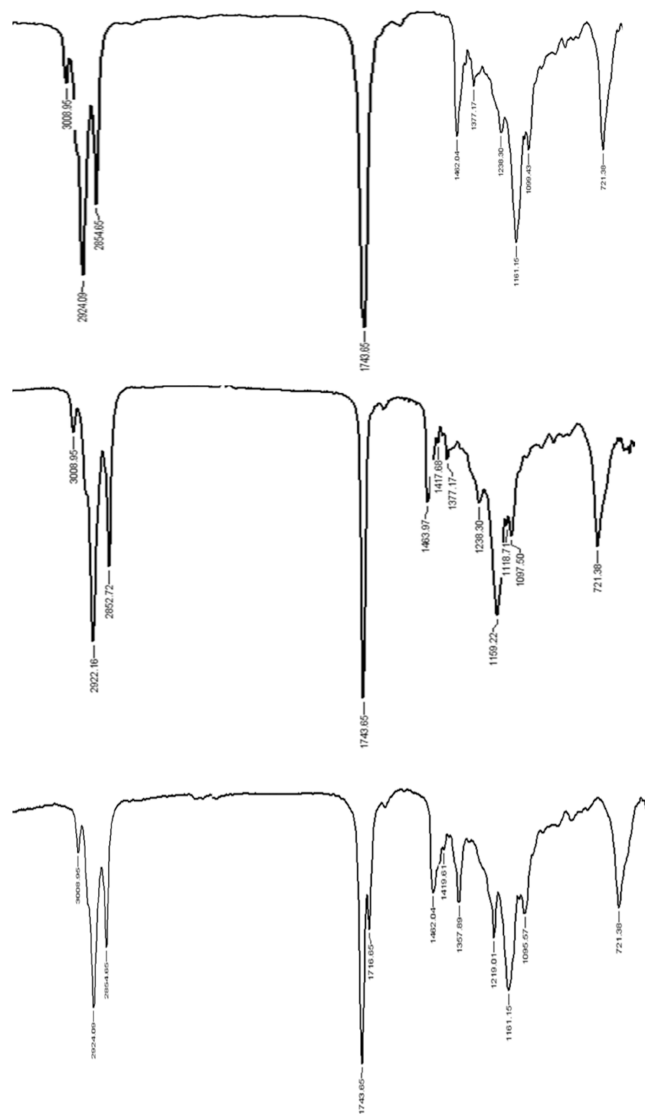


**Table 1. Yields of Diglycerides and Triglycerides from Mechanochemical Soybean Oil Extraction with Different *n*-Hexane Molar Proportions ( $n = 3$ )**

<i>n</i> -hexane, molar proportion	weight yield (%)	diglycerides (%)	triglycerides (%)
3:1	45 ± 4	0.66 ± 0.04	89.8 ± 0.6
13:1	50 ± 1	0.73 ± 0.08	88 ± 6
33:1	48.5 ± 0.7	0.74 ± 0.02	92 ± 4

**Table 2. Comparative Data of the Oil Extractions from the Ground Soybean Using a Mechanochemical Reactor with and without Spheres in the Presence of *n*-Hexane in a 3:1 Molar Proportion ( $n = 3$ )**

extraction technique	weight yield (%)	extraction time (min)	triglycerides (%)
with spheres	45 ± 5	30	89.8 ± 0.6
without spheres	29 ± 6	30	66 ± 12



**Figure 2.** ATR-FTIR spectra of mechanochemically extracted soybean oil (top), Soxhlet-extracted soybean oil (middle), and commercially available oil (bottom).

mm diameter, 350 rpm, 30 min), different *n*-hexane molar proportions were evaluated, in addition to evaluating if the

presence of grinding spheres, promoters of mechanical shocks, and energy influenced soybean oil extraction from soybean. Chromatography analysis showed that the mechanochemical oil extraction from the ground soybean was accomplished with satisfactory yields (Table 1). The triglyceride (TG) content corresponded to more than 88% of the glycerides in the extracted oil. The monoglyceride (MG) and diglyceride (DG) contents were minorities. The remainder compounds, observed as diverse and smaller-sized peaks in the chromatograms, can be attributed to free fatty acids or other matrix components since the oil has not undergone any process of neutralization and purification. Among the molar ratios of *n*-hexane, there was no significant difference between the contents of TG and DG in the extracts (Table 1). Thus, aiming at a lower solvent consumption, a 3:1 molar ratio of *n*-hexane was adopted to extract the oil from the meal.

To understand if the oil extraction resulted from mechanical shocks or an effect of agitation, a control experiment was investigated using the best conditions without spheres in the mill. A significant reduction in the TG content of the resulting oil extracted and a considerably higher standard deviation was observed (Table 2). Thus, the presence of the spheres contributed to a more homogeneous medium and better repeatability between the extractions, and the mechanical shocks derived from the spheres contributed positively to the extraction of the oil from the soybean meal, providing sufficient energy for oil diffusion through the solvent. The grinding jar became slightly hot due to the friction of the spheres with the soybean meal, the grinding jar's walls, and with themselves, and this temperature increase could help in oil diffusion.

The mechanochemical extraction of soybean oil was compared to that carried out using the Soxhlet technique (the conventional extraction process). The green chemistry metrics, namely, the *E* factor and the effective mass yield (EMY), were evaluated in these two processes.<sup>42</sup> The *E* factors obtained were 18 and 89 for mechanochemical and Soxhlet extractions, respectively. For the EMY, the results obtained were 12.5 and 1.2 for mechanochemical extraction and the Soxhlet technique, respectively. Even though the *E* factor of mechanochemical extraction was 5 times better than that of Soxhlet extraction, it is important to consider that the amount of the resultant soybean cake (a benign component in both processes) impacted the *E* factor more under mechanochemical conditions than in Soxhlet extraction. In this sense, the EMY can be a better metric to compare the green aspect of these extractions, which was 10 times more favorable to mechanochemical extraction. Despite a lower weight yield, mechanochemical extraction led to a triglyceride content comparable to Soxhlet extraction, requiring a 294 times lower molar ratio of extractive solvent in a period 14 times smaller among the tests performed. In addition, mechanochemical oil extraction is more straightforward, causing less exposure to organic vapors and requiring fewer steps. These aspects of mechanochemical extraction fit some principles of green chemistry, such as waste prevention, less hazardous/toxic materials, energy efficiency by design, and inherently safer processes.<sup>42</sup>

Soybean oil obtained via mechanochemical extraction with *n*-hexane was compared to that obtained from Soxhlet extraction and commercially available oil through ATR-FTIR spectra (Figure 2). The obtained mechanochemical extracted oil spectrum was identical to the Soxhlet extract, indicating a

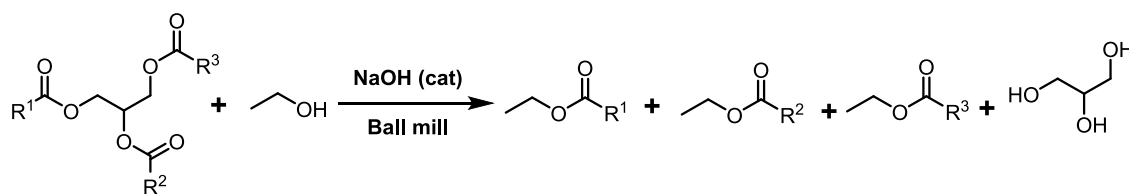


Figure 3. Mechanochemical *in situ* transesterification reaction.

Table 3. Results of the Contents of Monoglycerides (MG), Diglycerides (DG), Triglycerides (TG), and Fatty Acid Ethyl Esters (FAEEs) Present in Samples Obtained from *In Situ* Transesterification with Different Proportions of NaOH by Using a Mechanochemical Reactor with Spheres

NaOH (wt %)	average yield (%)	MG (%)	DG (%)	TG (%)	FAEE (%)
2	42.70 ± 0.58	2.06 ± 0.27	3.69 ± 0.20	54.98 ± 0.36	33.76 ± 0.95
4	37.4 ± 1.6	0.67 ± 0.03	0.45 ± 0.01	3.50 ± 0.19	77.53 ± 0.51
6	34.65 ± 0.61	0.66 ± 0.11	0.79 ± 0.07	6.41 ± 0.13	67.65 ± 0.02
8	63 ± 18	0.44 ± 0.29	1.5 ± 1.2	15 ± 11	68.6 ± 8.3

similar chemical composition. The ATR-FTIR spectrum of the commercial oil sample showed a band as a shoulder in 1700  $\text{cm}^{-1}$ , which is associated with the free fatty acid formed during the refining process. Common, typical bands present in the three oils are the original ester containing the glycerol-derived backbone:  $\text{C}_{\text{sp}^2}\text{-H}$  (3009  $\text{cm}^{-1}$ ) and  $\text{C}_{\text{sp}^3}\text{-H}$  stretches (2922–2924 and 2853–2855  $\text{cm}^{-1}$ ),  $\text{-C=O}$  (1743  $\text{cm}^{-1}$ ),  $\text{-COC-}$  (1159–1161  $\text{cm}^{-1}$ ), and  $\text{-CH}_2$  in the plane (721  $\text{cm}^{-1}$ ) and deformation of  $\text{-CH}_2$  (1462–1464  $\text{cm}^{-1}$ ), and  $\text{-CH}_3$  (1238  $\text{cm}^{-1}$ ).

**3.2. *In Situ* Mechanochemical Transesterification.** The *in situ* transesterification reaction (Figure 3) was applied to the mechanochemical synthesis of FAEEs. The soybean oil extracted by mechanical shocks from the spheres (step studied previously) was directly subjected to transesterification as the alkaline alcoholic solution was already inside the grinding jar. One of the main differences between *in situ* transesterification and the conventional biodiesel synthesis procedure (using the oil in its liquid form) is the system's heterogeneous characteristics regarding the material's presence in the solid state. According to Shuit and co-workers, the limiting stage of *in situ* transesterification is oil extraction from the matrix.<sup>43</sup> Justified by Fick's diffusion law, in which the oil extraction yield depends on the mass concentration gradient between the liquid and the matrix, many authors adopt a large amount of alcohol and cosolvent. For *in situ* transesterification of vegetable oils, better reactive extraction yields were obtained with very high alcohol:oil molar ratios, such as 100:1,<sup>7</sup> 250:1,<sup>6</sup> and up to 475:1.<sup>11</sup> It is worth mentioning that none of these procedures involve supercritical conditions.

In the present work, one goal was to establish an *in situ* transesterification condition where the proportion adopted is considerably lower than previously described, aiming at a lower consumption of reagents and the generation of process residues. Thus, from preliminary tests, it was observed that the ethanol:oil 25:1 (or 0.32  $\text{mL g}^{-1}$  soybean meal) molar condition, together with the use of the cosolvent, resulted in the good conversion of glycerides to FAEEs.

From Table 3, it is observed that there was a conversion of glycerides into FAEEs for all studied NaOH contents. As expected, for 2% NaOH, a more significant residue of nontransesterified glycerides was present in the samples. Consequently, fewer esters were observed. As the catalyst content was increased to 4 and 6%, there was a significant

reduction in glyceride residues and an increase in conversion to esters, maintaining good repeatability. With the highest level of NaOH, saponification was evident throughout the experimental procedure, including a large emulsion formed during washes and difficulties in purifying the product. Likewise, this assumption applies to the average weight yield of the product. These results agreed with other works which evaluated *in situ* transesterification of oilseeds for biodiesel synthesis.<sup>6,8</sup>

Under the studied conditions, the best catalyst proportion was 4%, resulting in a lower content of nontransesterified triglycerides, thus equivalent to the best content of FAEEs. A lower amount (2%) of NaOH resulted in the highest triglyceride content and inefficient FAEE conversion, and increased catalyst amounts (6 and 8%) afforded low or imprecise yields, respectively, and decreased the FAEE content (Table 3).

**3.3. Potential Nutritional Maintenance of Soybean after the Mechanochemical Transesterification.** The possible reuse of the soybean cake as animal feed, for example, would give an environmentally sustainable character to the process and benefit the biodiesel production cycle since it can insert the adequate management of this coproduct after the *in situ* mechanochemical transesterification reaction. The protein content in the soybean meal before and after *in situ* transesterification was determined to evaluate its protein content. The soybean before and after transesterification was subjected to Kjeldahl analysis in triplicates, and the protein content was calculated using eqs 4 and 5 with results of (40 ± 1)% and (49 ± 1)% for pretransesterification and post-transesterification, respectively. The higher protein content in the post-transesterification soybean cake can be associated with partial lipid extraction during the reaction. As the pretransesterification soybean has the total lipid content in its composition, a lower relative protein content is expected (considering the same sample weight). Thus, after the process of mechanochemical transesterification, the evaluation of the protein content of the soybean meal reveals that it can have a nutritional destination.

## 4. CONCLUSIONS

In the present study, *in situ* transesterification from soybean seed using mechanochemical methods was investigated. The mechanochemical process employing a planetary ball mill

allowed the oil extraction and *in situ* transesterification in the presence of ethanol and NaOH as a catalyst. The low *n*-hexane consumption and time required for the reactive extraction showed that the mechanochemical method is a promising technique, able to ally the energetic potential with reductions in solvents and steps of biodiesel production in agreement with the principles of green chemistry. In addition, the process led to obtaining a soybean cake without significant loss of protein content, which values the coproduct in the biodiesel production chain. Further study of the reaction kinetics, determining the amplification factor of the experimental parameters to scale up the process for pilot or industrial applications, can be considered a perspective for future evaluations.

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### Notes

The authors declare no competing financial interest.

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