

Sodium Glyceroxide: An Efficient Homogeneous Alkaline Catalyst for Biodiesel Synthesis

Samuel J. Santos,^{✉*a,b} João V. Braun,^{a,b} Guilherme C. Espíndola,^b Josué A. da Silva,^b
Rodrigo E. Renner^b and Luiz A. M. Fontoura^{✉*a,b}

^aDepartamento de Engenharia de Processos, Fundação de Ciência e Tecnologia (CIENTEC),
Av. das Indústrias, 2270, 94930-230 Cachoeirinha-RS, Brazil

^bCursos de Química e de Engenharia Química, Universidade Luterana do Brasil (ULBRA),
Av. Farroupilha, 8001, 92425-900 Canoas-RS, Brazil

Biodiesel is obtained from the alcoholysis of triglycerides and has been used as a renewable alternative to diesel. Though the methanolysis of triglycerides in the presence of MeONa catalyst has been widely used, searching for alternatives that may improve the competitiveness of the production chain is still a challenge. The aim of this work was to evaluate sodium glyceroxide as a catalyst in the methanolysis of soy oil. Sodium glyceroxide was obtained from glycerol and NaOH in ethanol, and characterized by thermogravimetric analysis (TGA), X-ray powder diffraction (XRD) and, Fourier transform infrared (FTIR) spectroscopy. The transesterification reaction was optimized after two sets of experiments based on the Doehlert matrix experimental design. In the first one, the influence of the molar ratio of methanol/triglyceride, and the amount of catalyst (m/m with respect to the triglyceride) were studied. In the second set, the temperature, and the reaction time were studied. The best conditions were found as 12:1 molar ratio, 2% of catalyst, 50 °C, and 60 min. The conditions were applied in the transesterification of canola and sunflower oils, and tallow. All the biodiesels were obtained with an ester content superior to 98%, free from methanol and triglycerides. Specific mass, viscosity, and pour point were determined and met the international specifications.

Keywords: biofuel, biodiesel, sodium glyceroxide, transesterification, Doehlert matrix

Introduction

The first patent for biodiesel preparation and use as a fuel was claimed in 1937 by G. Chavane, a researcher from the University of Brussels.¹⁻³ Petroleum, however, was the major fuel source throughout the 20th century, and still nowadays. Especially after the oil embargo in 1973, alternatives to petroleum derivatives have been sought, firstly, for political, security and economic interests, and more recently, for environmental concerns.³⁻⁵ In 2021, Indonesia was the world's largest biodiesel producer with a production of 9.5 billion liters, followed by Brazil and the United States, which produced 6.9 and 6.2 billion liters, respectively.⁶

Biodiesel is a biofuel mainly used as a partial substitute for diesel in compression ignition engines. Compared to its non-renewable counterpart, biodiesel has several properties

enhanced, as the higher cetane number, lubricity, and flash point.⁷⁻¹¹ In addition, it is free from sulfur compounds, which are responsible for contributing to acid rain,^{7,10} and its combustion is more complete, reducing carbon monoxide and particulate matter emissions. Furthermore, it has been attributed to biodiesel a lower contribution to the greenhouse effect since it is made from biomass.¹⁰ However, there are some disadvantages. The combustion temperature is higher, promoting the NO_x emission, and the heat value is lower.¹⁰ In addition, the oxidation stability is lower,⁷⁻¹² and the so-called cold flow properties are worse.^{7-11,13}

Biodiesel is comprised of a blend of fatty esters, which are obtained by triglycerides (TG) alcoholysis. Most commercial oils and fats of vegetable or animal origin can be used as a source of triglycerides,¹¹ and palm, soy and canola have been the most utilized ones over the world.¹⁴ Any short chain alcohol can be used, and methanol is, by far, the lead one due its lower price compared to others, such as ethanol. Long chain alcohols are not employed since they can modify biodiesel properties such as viscosity and

*e-mail: samuel.j.santos@hotmail.com; lmazzini@uol.com.br
Editor handled this article: Albertina Moglioni (Associate)



specific mass, among others, resulting in a fuel that would not be within specifications.¹⁵⁻¹⁷

In order to reach high conversions of triglycerides into biodiesel within a suitable reaction time, a catalyst must be used. Homogeneous catalysts are more widely used since lower loadings are necessary and higher reaction rates can be observed.¹⁸ Alkaline catalysts, such as metal hydroxides and alkoxides are often employed. Hydroxides, even though cheaper, produce water and soap, so the yield is lower and the biodiesel isolation and purification, more complex. In general, molar ratios of MeOH/triglycerides from 6 to 12:1, and 0.5 to 1.5% of catalyst (m/m with reference to the triglycerides) are required. If fatty acids are present in the feedstock, alkaline catalysis must be avoided, since it is consumed and soap is produced. In this case, acid catalysts such as H₂SO₄, H₃PO₃, and sulfonic acids have been used. In such cases, higher molar ratios, up to 30:1, and catalyst amounts, from 1 to 4% are reported and the reaction times are usually longer.^{14,18} Homogeneous catalysts, although efficient, require biodiesel purification steps, with water consumption and waste production.¹⁸ Alternatively, heterogeneous catalysts offer the possibility of recuperation and reuse. On the other hand, conversions are scarcely as high as those found in homogeneous catalysis. Metal oxides such as CaO, and hydrotalcites, are alkaline examples, while zeolites and heteropolyacids, acid ones.^{14,19,20} Sodium methoxide, a homogeneous catalyst, is probably the most used one over the world for biodiesel production, producing fatty esters with high yield and rate. On the other hand, it is generally sold as a solution in MeOH, which is expensive and hazardous.^{21,22} Glycerol is a polyol and, as any other alcohol, is a Bronsted acid and can form salts. In fact, metal glyceroxides have been described in literature²²⁻³¹ as catalysts for the biodiesel production by triglycerides transesterification. Depending on the metal, glyceroxides salts can be soluble or not in the reaction mixture. Their properties are substantially dependent on the metal ion size, electronegativity, and coordination number. In some cases, the glycerol conjugated base can act as a mono, bi or tridentate ligand.²⁹

Calcium diglyceroxide synthesis, characterization, and catalytic activity in the methanolysis of soy oil have been described by Kouzu *et al.*²³ in 2010. Calcium diglyceroxide is a white solid obtained by refluxing glycerol and CaO in MeOH. More recently, Lisboa *et al.*²⁹ have deepened the study presenting the syntheses and the analyses of mono, and di-glyceroxide, and their use, and reuse, as heterogeneous catalyst in soy oil transesterification. Calcium diglyceroxide has been also applied in the transesterification reaction of other feedstock such as castor,²⁵ and sunflower²⁶ oils. In 2015, Ferrero *et al.*³¹ reported some additional results

applying Ca glyceroxide, and pointed out the fact that, as the catalyst is heterogeneous, the transesterification is a three-phase reaction, which causes mass transfer difficulties, and, for this reason, the reaction rate decrease. In addition, some catalyst loss was observed since some Ca soap is produced. Reinoso *et al.*²⁷ have described the use of zinc glyceroxide as the catalyst in the synthesis of methyl soy biodiesel. The salt was prepared by reacting glycerol with zinc acetate under pressure at 160 °C in the presence of water. Lithium, and potassium glyceroxides syntheses and characterization have been reported by Wang *et al.*,²² and Pradhan *et al.*,³² respectively. Sodium glyceroxide, by its turn, has been reported by Bradley *et al.*,²⁸ and Korchak *et al.*³⁰ In all cases, the salts were prepared by the reaction of the metal hydroxide with glycerol in aqueous solution. The solid salts were isolated after water distillation under reduced pressure, that is energy and time consuming.

In order to facilitate the solvent elimination in the synthesis of sodium glyceroxide, we decide to carry out the reaction in ethanol instead of water. Surprisingly, at room temperature, a white salt precipitated as soon as glycerol was added over NaOH ethanolic solution. The quick, simple, cheap, and easy procedure, to the best of our knowledge, has not been reported before.

Apart from the alcohol, the catalyst, and the triglyceride source, transesterification is also strongly affected by the reaction time and temperature.³³ In order to ensure the highest yield and ester content in the product, those variables must be optimized.

In this paper, we present not only the sodium glyceroxide preparation and characterization, but its use as an alkaline homogeneous catalyst in the methanolysis of soy oil as well. The transesterification reaction was optimized after two sets of experiments based on the Doehlert matrix. In the first one, the influence of the molar ratio (M_R) of methanol and triglyceride, and the amount of catalyst (W_{CAT}) were studied. In the second, time (t) and temperature (T) were studied. The optimum conditions were also applied to the synthesis of canola, sunflower, and tallow methyl biodiesels.

Experimental

The Doehlert matrix is a multivariate experimental design that enables the study of the effect of two or more variables over a target outcome. When applied to two variables x and y , the design combines five values of the former set as -1.000 , 0.500 , 0.000 , 0.500 and 1.000 , with three of the latter, -0.866 , 0.000 , and 0.866 , so that a set of seven different experimental conditions is defined. The values -1.000 and -0.866 correspond to the lower limits assigned to the variables x and y , respectively. The values

1.000 and 0.866, by the other side, correspond to the upper ones. The in-between intervals must be uniform. The matrix can be seen as a regular hexagon, and the six vertices and the central point are the seven reaction conditions, Figure 1.³⁴⁻³⁷ Widely employed in analytical chemistry,³⁵⁻³⁷ the Doehlert matrix has been seldom used in reactions optimization, let alone in the transesterification of triglycerides.³⁸⁻⁴⁰

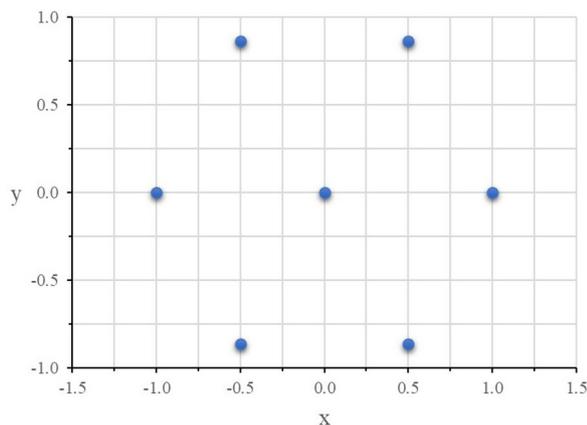


Figure 1. Doehlert matrix design for two variables x and y .

Sodium glyceroxide synthesis

40 g (1.0 mol) of NaOH (Dinâmica, São Paulo, Brazil) were dissolved in 950 mL of absolute EtOH (Êxodo, Sumaré, Brazil) at room temperature with magnetic stirrer. Once the solubilization was complete, a solution of 138 g (1.5 mol) of glycerol (Vetec, Duque de Caxias, Brazil) and 50 mL of EtOH was poured over the alkali solution. After a few seconds, the precipitation of a white solid was observed. The mixture was stirred for 10 min more, and filtered under reduced pressure. The white solid was washed with cold absolute EtOH (3×15 mL) and dried in a desiccator under reduced pressure. The thermogravimetric analysis (TGA) was carried out in a PerkinElmer TGA-7 analyzer (Waltham, USA) in N_2 atmosphere from 30 °C (1 min) to 700 °C at a heating rate of 10 °C min^{-1} . The same procedure was repeated under oxidant atmospheric conditions. The X-ray powder diffraction (XRD) measurements were carried out with a PHILIPS diffractometer X'PERT (Malvern, United Kingdom) with Cu $K\alpha$ radiation operating with 40 kV from 5 to 60° (2θ). The infrared (IR) attenuated total reflectance (ATR) spectrum was recorded on a Shimadzu spectrometer, model IRAffinity-1 (Kyoto, Japan) from 4000 to 600 cm^{-1} , 8 scans, and 0.5 cm^{-1} resolution.

Transesterification

Two sets of experiments designed by a Doehlert matrix were carried out. The weight of sodium glyceroxide (W_{CAT}),

the volumes of methanol (V), the temperatures (T), and the reaction times (t) are presented in Table 1. The first matrix is composed of entries 1 to 9, in which the MeOH/TG molar ratio (M_R), and the relative catalyst/TG weight ratio (W_R) are the x and y Doehlert's parameters, respectively. The second matrix is composed of entries 10 to 18, where, on the other hand, temperature (T), and time (t) are the x and y Doehlert's parameters, respectively.

The generic procedure is described below. In a beaker, W g of sodium glyceroxide were dissolved in V mL of MeOH (Êxodo, Sumaré, Brazil). Then, the solution was transferred into a 1 L glass reactor equipped with a mechanical stirrer and a reflux condenser in a thermostatically controlled water bath at T °C, over 300 g of soy oil (Soya, Gaspar, Brazil). The reaction mixture was kept stirring (1000 rpm) for t min. After that, the mixture was transferred to a rotary evaporator to distillate the remaining MeOH. Then, the two-phase mixture was transferred to a separatory funnel, where the lower phase, glycerol, was discarded, and the upper layer, biodiesel, was washed with hot water (70 °C, 3×100 mL). Finally, biodiesel was again transferred to a rotary evaporator under reduced pressure, in order to eliminate the volatiles.

Biodiesel characterization

The fatty ester contents were determined by gas chromatography (Shimadzu GC 2010, Kyoto, Japan).^{41,42} Fatty esters profiles were estimated as described by Schaumlöffel *et al.*⁴³ by 1H nuclear magnetic resonance (NMR) in triplicate. The methanol content was determined by 1H NMR as described by Santos *et al.*⁴⁴ by standard addition quantification method (limit of detection 0.02%). Triglycerides were tracked by the dd at δ 4.30 (limit of detection 0.05%).⁴⁵ Iodine⁴⁶ and saponification⁴⁷ values were determined by 1H nuclear magnetic resonance (NMR) in triplicate. Spectra were acquired in a Varian Mercury 400 MHz spectrometer (Palo Alto, USA), and are presented in the Supplementary Information (SI) section. The samples were prepared by dissolving 30 mg of biodiesel in 0.5 mL of $CDCl_3$ (D 99.8%, 0.1% tetramethylsilane (TMS), Cambridge, Andover, USA). Specific masses (ρ) were determined at 20 °C with a hygrometer (0.7 to 1 g mL^{-1} (Incoterm, model 5598, Porto Alegre, Brazil) as described in the ASTM D1298-12 standard method (triplicate).⁴⁸ Kinematic viscosities (ν) were determined at 40 °C in a Cannon-Fenske 75 tube (Laborglass, São Paulo, Brazil, k 0.0066105 $m^2 s^{-2}$) as described in the ASTM 445-06 standard method (triplicate).⁴⁹ Pour points (PP) were determined in a PP Meter (IBP, Porto Alegre, Brazil) as described in the ASTM D97-17 standard method (duplicate).⁵⁰

Table 1. Transesterification experimental conditions: relative catalyst/TG weight ratio (W_R), catalyst weight (W_{CAT}), MeOH/TG molar ratio (M_R), MeOH volume (V_{MeOH}), temperature (T), reaction time (t), experimental (EXP) and calculated (CALC) fatty esters content (C_{FE})

entry	W_R / %	W_{CAT} / g	M_R	V_{MeOH} / mL	T / °C	t / min	C_{FE}^{EXP} / %	C_{FE}^{CALC} / %
1	2.0	6.0	12.0	170	65	60	98.3 ± 1.2	98.2
2	2.0	6.0	12.0	170	65	60	98.1 ± 3.2	98.2
3	2.0	6.0	12.0	170	65	60	98.2 ± 1.8	98.2
4	2.0	6.0	6.0	85	65	60	97.4 ± 3.4	97.6
5	2.5	7.5	9.0	127	65	60	97.1 ± 2.1	96.9
6	2.5	7.5	15.0	212	65	60	96.6 ± 0.0	96.8
7	2.0	6.0	18.0	255	65	60	96.1 ± 5.2	95.9
8	1.5	4.5	15.0	212	65	60	94.2 ± 1.8	94.4
9	1.5	4.5	9.0	127	65	60	96.0 ± 0.9	95.8
10	2.0	6.0	12.0	170	60	50	98.8 ± 0.3	98.5
11	2.0	6.0	12.0	170	60	50	97.8 ± 0.4	98.5
12	2.0	6.0	12.0	170	60	50	98.8 ± 1.7	98.5
13	2.0	6.0	12.0	170	30	50	93.6 ± 1.2	93.0
14	2.0	6.0	12.0	170	45	65	97.1 ± 0.9	97.9
15	2.0	6.0	12.0	170	75	65	98.9 ± 2.5	98.3
16	2.0	6.0	12.0	170	90	50	99.1 ± 1.7	99.7
17	2.0	6.0	12.0	170	75	35	94.4 ± 1.7	93.8
18	2.0	6.0	12.0	170	45	35	87.2 ± 3.2	87.8

Results and Discussion

Sodium glyceroxide was obtained from glycerol and sodium hydroxide in ethanol, Scheme 1. Glycerol was used in excess (150 mol%) in order to avoid hydroxide as an impurity in the product. EtOH was used as the solvent since it dissolves the base and facilitates the homogenization of the reactants. The product precipitates as a plentiful white solid.

Glycerol is about 40 times more acidic than EtOH, and its sodium salt is insoluble in this solvent.⁵¹ The reaction was first carried out in MeOH, but no precipitate was observed, which can be attributed to the higher polarity of the solvent.

Sodium glyceroxide was characterized by TGA in N_2 and in air atmosphere from 30 to 700 °C. The thermograms are presented in Figure 2. In both cases, three events are observed. The first one, at 120 °C, with weight loss of about 28% can be attributed to ethanol in the crystal $Na(C_3H_7O_3) \cdot C_2H_6O$. The second and the third ones at 260

and 485 °C, respectively, correspond to the $Na(C_3H_7O_3)$ decomposition to Na_2CO_3 , leaving 33% of the initial weight. It is important to point out that 1 mol of sodium glyceroxide decomposes to 0.5 mol of sodium carbonate. Reyero *et al.*²⁶ and Kouzu *et al.*²³ have reported the thermal decomposition of calcium diglyceride to calcium carbonate in two steps

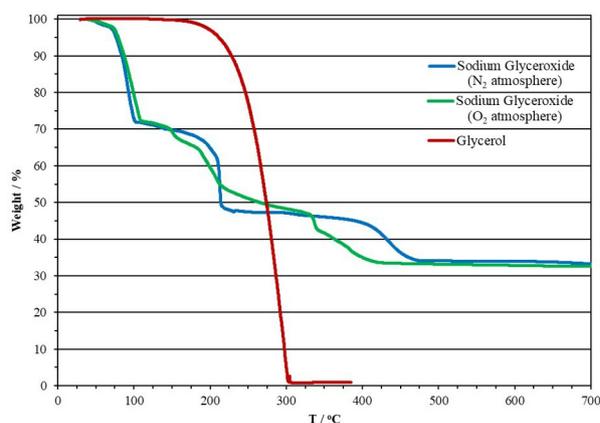
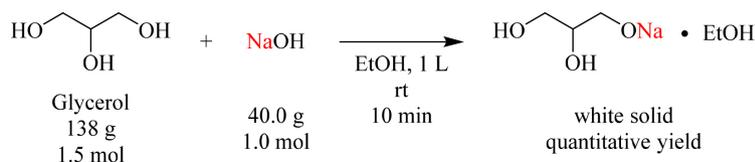


Figure 2. Sodium glyceroxide and glycerol thermograms.



Scheme 1. Sodium glyceroxide synthesis from glycerol and NaOH.

as well. The glycerol thermogram is also presented. A single event is observed because of its phase transition (boiling point 290 °C). Sodium glyceroxide was also obtained from raw glycerol produced in the soy oil transesterification, and, in this case, the same yield and identical thermogram were found.

The Fourier transform infrared (FTIR) spectrum, Figure 3, shows a large band at 3300 cm^{-1} attributed to the OH stretching of glyceroxide and ethanol of crystallization. From 2950 to 2850, the bands of H–C (sp^3) stretching are observed. Two intense bands at 1670 and 1470 cm^{-1} can be assigned to OH bending, and, finally, at 1125 and 1060 cm^{-1} to the C–O stretching. Similar attributions have been reported by León-Reina *et al.*,²⁴ Reyero *et al.*,²⁶ Reinoso *et al.*,²⁷ and Cheng *et al.*⁵² for calcium and zinc glyceroxides' IR spectra.²⁷

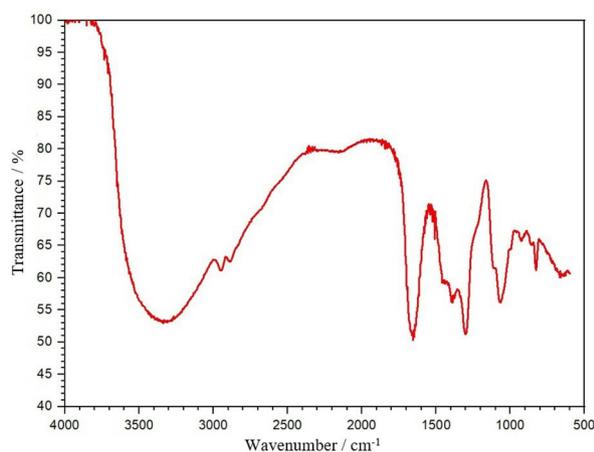


Figure 3. FTIR-ATR of sodium glyceroxide.

The XRD, Figure 4, shows an intense signal at 2θ equal to 7° . Schatte *et al.*^{53,54} in two independent studies, have described sodium⁵³ and potassium⁵⁴ glyceroxide crystal structures from the XRD analyses. In both cases, the ligand and the metal are present in 1:1 ratio in the complex salt. The metal is surrounded by four different glyceroxides units, coordinated by the ionized oxygen of one, and by hydroxyl groups of the others. In the Na salt, authors have suggested a primary hydroxyl group ionized. In the K salt, by its turn, a secondary one. Similar results have been reported by Bradley *et al.*²⁸ in the sodium glyceroxide characterization. In the present study, the thermogravimetric analysis pointed out ethanol in the solid beside the salt in the 1:1 ratio, and, so, the crystal structures presented before are not applicable. A crystallographic description from the XRD is outside the scope of this work.

The reaction variables were studied in two steps applying Doehlert experimental design. In the first matrix, MeOH/TG molar ratio (M_R) and relative catalyst/TG weight ratio (W_R) were optimized. In the second, temperature (T)

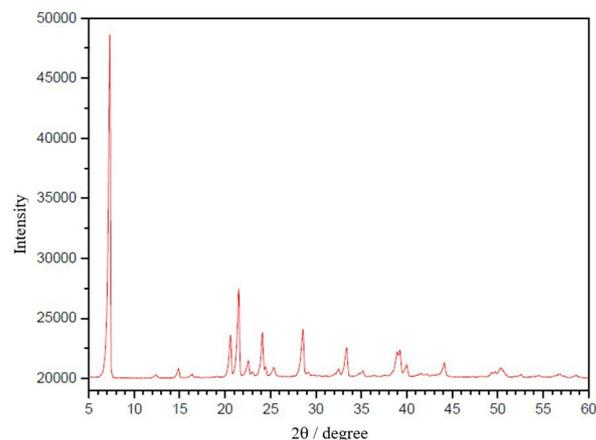


Figure 4. XRD of sodium glyceroxide.

and time (t) were the targets. M_R was set in five levels from 6 to 18:1, and W_R , by its turn, in three levels from 1.5 to 2.5% (m/m, catalyst with respect to the triglyceride). The reactions were carried out at 65 °C for 60 min. The results, expressed as the fatty esters contents (C_{FE}) are presented in Table 1 (entries 1-9), and were found from 94 to 98%. The data were analyzed in the spreadsheet developed by Teófilo and Ferreira.⁵⁵ The experimental results provided the equation 1, which establishes the effect of the two variables on the C_{FE} . In the equation, x and y are the Doehlert parameters for M_R (−1.0, −0.5, 0.0, +0.5, +1.0) and for W_R (−0.87, 0.0, +0.87), respectively.³⁴

$$C_{FE} = 98.20 - 0.82x + 1.01y - 1.45x^2 - 2.48y^2 + 0.75xy \quad (1)$$

The response surface is presented in Figure 5, which was created from equation 1. The global maximum was found with M_R and W_R equal to 12:1 and 2.0%, respectively. An increment in any variable, especially in M_R , makes the C_{FE} lower. It is worth noting that the alcohol addition dilutes

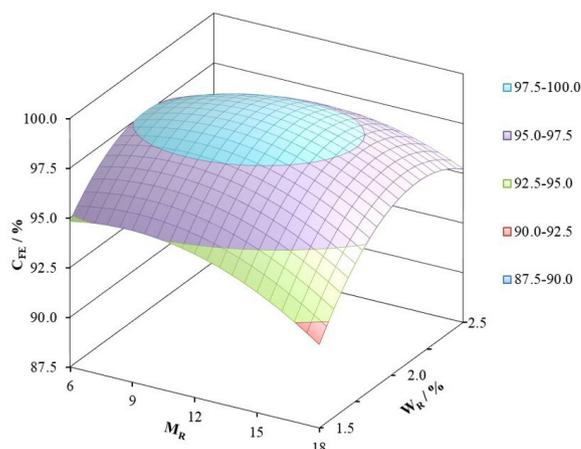


Figure 5. Response surface: calculated fatty esters content (C_{FE}) versus MeOH/TG molar ratio (M_R), 6 to 18:1, and relative catalyst/TG weight ratio (W_R), 1.5 to 2.5%.

the catalyst. On the other hand, the catalyst conjugate base is glycerol, the transesterification reaction coproduct, which may interfere in the chemical equilibrium.

The calculated fatty esters content values ($C_{FE\text{ CALC}}$) were plotted against the experimental ones ($C_{FE\text{ EXP}}$). A straight line with inclination of 0.9869 and a correlation coefficient of 0.9934 was obtained. The residues were found to be between -0.2 and 0.2% , not higher than the experimental error.

Once established the M_R and W_R , t and T were assessed. The first variable was set in five levels from 30 to 90 min. The second one, by its turn, in three levels from 35 to 65 °C. The M_R and W_R were set as 12:1 and 2.0%, respectively. The results, expressed as the fatty esters contents (C_{FE}), are presented in Table 1 (entries 10-18), and were found from 87 to 99%. The response surface is presented in Figure 6, which was created from equation 2. In the equation, x and y are the Doehlert parameters for T ($-1.0, -0.5, 0.0, +0.5, +1.0$) and for t ($-0.87, 0.0, +0.87$), respectively.³⁴

$$C_{FE} = 98.5 + 3.33x + 4.16y - 2.15x^2 - 4.75y^2 + 3.12xy \quad (2)$$

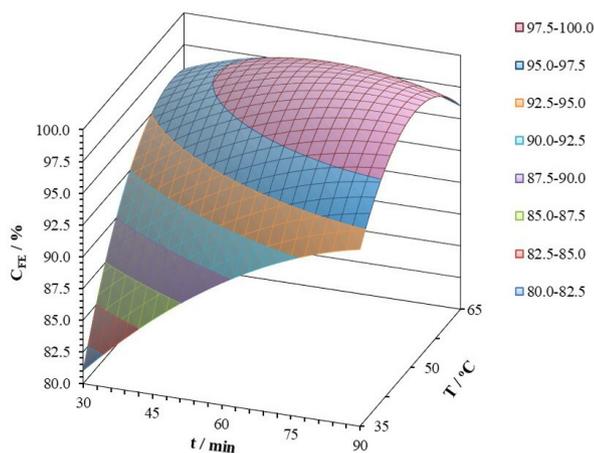
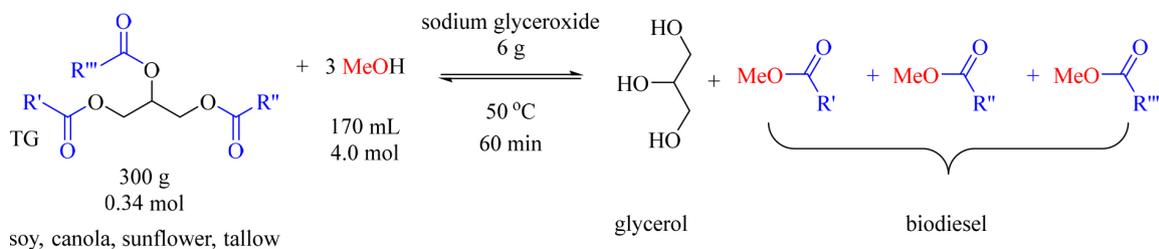


Figure 6. Response surface: calculated fatty esters content (C_{FE}) versus time (t , 30 to 90 min), and temperature (T , 35 to 65 °C).

The surface shows clearly that the higher the temperature, or the time, the higher the C_{FE} but it falls slightly when both variables are close to their maximum



Scheme 2. Synthesis of methyl biodiesel from soy, canola, and sunflower oils, and from tallow catalyzed by sodium glyceroxide.

values. The temperature may affect methanol liquid-vapor equilibrium, especially at longer times when the alcohol was partially consumed. All the reaction conditions under the pink surface produce a biodiesel with ester content higher than 97.5% and, thus, meet the official specifications. Once more, the calculated C_{FE} values were plotted against the experimental ones. A straight line with inclination of 0.9781 and a correlation coefficient of 0.9890 was obtained. The residues were found to be between -0.6 and 0.7% .

The reaction was carried out again at the optimum conditions: 12:1 molar ratio, 2.0% catalyst, 50 °C, and 60 min, Scheme 2. In addition, the methodology was also employed in the transesterification of tallow, and canola and sunflower oils. The biodiesel properties are presented in Table 2.

The fatty ester contents were found to be 98% or higher, and contaminations such as methanol, and triglycerides were not detected. If the purification steps are efficient, methanol is not supposed to be present in the final biodiesel. If present, it reduces the viscosity, the specific mass, and the flash point. As any alkaline catalyst, sodium glyceroxide shall not be used in acidic medium. The oils and the lard were commercial, so the free fat acid contents were negligible. Although it is out of the scope of this paper, we have already used sodium glyceroxide in the transesterification of raw oils (peanut, butia, imperial palm), and fats (bovine, chicken, duck, sheep) with conversions higher than 98% as well.

The results allow us to affirm that sodium glyceroxide can be considered as effective as sodium methoxide, the most used catalyst in industry, that is, it can promote the conversion of triglycerides into biodiesel with low load, in mild conditions, in short time, with high yield, and high fatty esters content. In contrast, the first is obtained from cheaper chemical inputs, NaOH and glycerol, and is safer and easier to manipulate than the last one. It should be mentioned that glycerol is obtained as the coproduct in the biodiesel synthesis by the transesterification reaction, which can be used in the catalyst synthesis, as presented before. It is worth mentioning that NaOH, although cheap, produces water and soap, leading to lower conversions, and

emulsions that make the biodiesel and glycerol separation difficult and time demanding.

NMR spectra data provide the fatty esters profiles as molar fraction of saturated, mono-, di-, and tri-unsaturated chains. As expected, soy and sunflower biodiesels were found to be composed mainly of di-unsaturated esters, while canola and tallow biodiesels, mono, and saturated ones, respectively. The results are in accordance with those reported in the literature.⁵⁶ The spectra are presented in the SI section.

Among the properties presented in Table 2, some are part of the standard specifications in the USA, Europe, or Brazil. In those cases, the four biodiesels matched the specifications. The only exception is the iodine value of the soy biodiesel, 128 g I₂ per 100 g, which, although considered a typical result, is not in accordance with the European standard, in which it must not exceed 120 g I₂ per 100 g. Specific mass, viscosity, pour point, iodine value, and the composition agree with the values reported in the literature.⁵⁷

The ν and ρ are quite similar for the biodiesels derived from the three oils. The biodiesel from tallow, however, is more viscous, but less dense, which is attributed to its higher content of saturated fatty esters (56%). For the same reason, it is expected to present the lowest iodine value (I_V), 42 g I₂ per 100 g. Saponification values (S_V) were found in the narrow range of 191 and 198 mg KOH per g. It is worth noting that the higher the average molar mass, the lower the S_V, which was observed in the tallow biodiesel. The pour point is highly dependent on the biodiesel composition,

and was found to be within the range of –6, canola, to +15 °C, tallow, in the same crescent order as the saturated fatty esters contents.

Conclusions

Sodium glyceroxide was easily obtained from glycerol and NaOH in ethanolic solution at room temperature, characterized by thermogravimetric analysis, FTIR and XRD, and employed as alkaline homogeneous catalyst in the methyl transesterification of soy oil. The reaction was optimized by a Doehlert design. Firstly, the effect of the molar ratio MeOH/TG and the catalyst amount were studied, and the optimum conditions were found as 12:1 and 2%, respectively. After, the temperature and the reaction time were also optimized, and the best conditions established as 50 °C and 60 min. The procedure was also applied to the biodiesel synthesis from canola oil, sunflower oil, and tallow. Fatty esters content, specific mass at 20 °C, kinematic viscosities at 40 °C, triglycerides and methanol contents matched the specifications in all cases. In addition, saponification, and iodine values, pour point, and composition were estimated and agree with the values reported in the literature.

Supplementary Information

Supplementary information is available free of charge at <http://jbcs.sbq.org.br> as PDF file.

Table 2. Fatty esters (C_{FE}), triglycerides (C_{TG}), and methanol (C_{MeOH}) contents, specific mass at 20 °C (ρ), kinematic viscosity at 40 °C (ν), pour point (PP), average molar mass (M_M), iodine (I_V) and saponification (S_V) values, and composition (CX:Y)

	Soy	Canola	Sunflower	Tallow	USA ⁵⁸	Europe ⁵⁹	Brazil ⁶⁰
Aspect	clear	clear	clear	clear			clear
C _{FE} / %	99 ± 1	99 ± 1	100 ± 1	98 ± 2	–	96.5	96.5
C _{TG} / %	nd	nd	nd	nd	–	0.20	0.20
C _{MeOH} / %	nd	nd	nd	nd	0.20	0.20	0.20
ρ / (kg m ⁻³)	880 ± 1	880 ± 1	881 ± 1	865 ± 1	–	860 - 900	850-900
ν / (mm ² s ⁻¹)	4.29 ± 0.08	4.20 ± 0.03	4.29 ± 0.04	4.77 ± 0.02		3.5 – 5.0	3.0-6.0
PP / °C	0	–6	–3	15	–	–	–
M _M / (g mol ⁻¹)	290 ± 2	291 ± 6	293 ± 3	284 ± 4	–	–	–
I _V / (g I ₂ per 100 g)	128 ± 2	110 ± 1	128 ± 1	42 ± 3	–	120	report
S _V / (mg KOH per g)	194 ± 2	193 ± 4	191 ± 2	198 ± 3	–	–	–
CX:0 / %	19 ± 5	11 ± 2	13 ± 5	56 ± 2			
CX:1 / %	25 ± 3	57 ± 2	29 ± 4	42 ± 2			
CX:2 / %	51 ± 2	25 ± 3	58 ± 1	2.4 ± 0.1			
CX:3 / %	5 ± 1	6 ± 1	nd	nd			

Saturated (CX:0), mono-unsaturated (CX:1), di-unsaturated (CX:2) and tri-unsaturated (CX:3) fatty esters, not detected (nd).

Acknowledgments

The authors thank Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS), Bianchini S/A, Refinaria Alberto Pasqualini (REFAP), and Dorf Ketal Brasil.

Author Contributions

Samuel J. Santos was responsible for data curation, investigation, resources, software, writing (original draft, review and editing); Luiz A. M. Fontoura for data curation, formal analysis funding acquisition, investigation, project administration, resources, software, writing original (draft, review and editing); João V. Braun and Guilherme C. Espíndola for conceptualization, data curation, formal analysis funding acquisition, investigation, writing original draft; Josué A. da Silva and Rodrigo E. Renner for investigation.

References

1. Pahl, G.; *Biodiesel, Growing a New Energy Economy*, 1st ed.; Chelsea Green: White River Junction, 2005.
2. Pousa, G. P. A. G.; Santos, A. L. F.; Suarez, P. A. Z.; *Energy Policy* **2007**, *35*, 5393. [Crossref]
3. de Oliveira, F. C.; Coelho, S. T.; *Renewable Sustainable Energy Rev.* **2017**, *75*, 168. [Crossref]
4. Demirbas, A.; *Energy Convers. Manage.* **2008**, *49*, 2106. [Crossref]
5. Cremonese, P. A.; Feroldi, M.; Nadaletti, W. C.; de Rossi, E.; Feiden, A.; de Camargo, M. P.; Cremonese, F. E.; Klajn, F. F.; *Renewable Sustainable Energy Rev.* **2015**, *42*, 415. [Crossref]
6. Statista; *FAME Biodiesel Production Volume Worldwide from 2020 to 2022, by Key Country/Region*, <https://www.statista.com/statistics/1297107/fame-biodiesel-production-worldwide-by-key-country>, accessed in January 2024.
7. Singh, D.; Sharma, D.; Soni, S. L.; Sharma, S.; Kumari, D.; *Fuel* **2019**, *253*, 60. [Crossref]
8. Yasar, F.; *Fuel* **2020**, *264*, 116817. [Crossref]
9. Folayan, A. J.; Anawe, P. A. L.; Aladejare, A. E.; Ayeni, A. O.; *Energy Rep.* **2019**, *5*, 793. [Crossref]
10. Sakthivel, R.; Ramesh, K.; Purnachandran, R.; Shameer, P.; *Renewable Sustainable Energy Rev.* **2018**, *82*, 2970. [Crossref]
11. Knothe, G.; Razon, L. F.; *Prog. Energy Combust. Sci.* **2017**, *58*, 36. [Crossref]
12. Kumar, N.; *Fuel* **2017**, *190*, 328. [Crossref]
13. Hazrat, M. A.; Rasul, M. G.; Mofijur, M.; Khan, M. M. K.; Djavanroodi, F.; Azad, A. K.; Bhuiya, M. M. K.; Silitonga, A. S.; *Frontiers in Energy Research* **2020**, *8*, 598651. [Crossref]
14. Changmai, Bi.; Vanlalveni, C.; Ingle, A. P.; Bhagat, R.; Rokhum, L.; *RSC Adv.* **2020**, *10*, 41625. [Crossref]
15. Wenchao, W.; Fashe, L.; Ying, L.; *J. Mater. Res. Technol.* **2020**, *9*, 2727. [Crossref]
16. Jayaraman, J.; Alagu, K.; Appavu, P.; Joy, N.; Mariadhas, A.; *Energy Fuels* **2020**, *34*, 9763. [Crossref]
17. de Oliveira, V. F.; Parente Jr., E. J. S.; Manrique-Rueda, E. D.; Cavalcante, C. L.; Luna, F. M. T.; *Chem. Eng. Res. Des.* **2020**, *160*, 224. [Crossref]
18. Fattah, I. M. R.; Ong, H. C.; Mahlia, T. M. I.; Mofijur, M.; Silitonga, A. S.; Rahman, S. M. A.; Ahmad, A.; *Front. Energy Res.* **2020**, *8*, 101. [Crossref]
19. Gupta, J.; Agarwal, M.; Dalai, A. K.; *J. Ind. Eng. Chem.* **2020**, *88*, 58. [Crossref]
20. Ravi, A.; Gurunathan, B.; Rajendiran, N.; Varjani, S.; Gnansounou, E.; Pandey, A.; You, S.; Raman, J. K.; Ramanujam, P.; *Environ. Technol. Innovation* **2020**, *19*, 100906. [Crossref]
21. Pradhan, S.; Shen, J.; Emami, S.; Mohanty, P.; Naik, S. N.; Dalai, A. K.; Reaney, M. J. T.; *J. Ind. Eng. Chem.* **2017**, *46*, 266. [Crossref]
22. Wang, E.; Shen, J.; Wang, Y.; Tang, S.; Emami, S.; Reaney, M. J. T.; *Fuel* **2015**, *160*, 621. [Crossref]
23. Kouzu, M.; Hidaka, J. S.; Wakabayashi, K.; Tsunomori, M.; *Appl. Catal., A* **2010**, *390*, 11. [Crossref]
24. León-Reina, L.; Cabeza, A.; Rius, J.; Maireles-Torres, P.; Albarubio, A. C.; López Granados, M.; *J. Catal.* **2013**, *300*, 30. [Crossref]
25. Sánchez-Cantú, M.; Reyes-Cruz, F. M.; Rubio-Rosas, E.; Pérez-Díaz, L. M.; Ramírez, E.; Valente, J. S.; *Fuel* **2014**, *138*, 126. [Crossref]
26. Reyero, I.; Arzamendi, G.; Gandía, L. M.; *Chem. Eng. Res. Des.* **2014**, *92*, 1519. [Crossref]
27. Reinoso, D. M.; Damiani, D. E.; Tonetto, G. M.; *Appl. Catal., B* **2014**, *144*, 308. [Crossref]
28. Bradley, D.; Levin, E.; Rodriguez, C.; Williard, P. G.; Stanton, A.; Socha, A. M.; *Fuel Process. Technol.* **2016**, *146*, 70. [Crossref]
29. Lisboa, F. S.; Ferreira, E. B.; Silva, F. J. L. B.; Silva, F. R.; *React. Kinet., Mech. Catal.* **2023**, *136*, 851. [Crossref]
30. Korchak, M.; Bliznjuk, O.; Nekrasov, S.; Gavriush, T.; Petrova, O.; Shevchuk, N.; Strikha, L.; Kostyrkin, O.; Semenov, E.; Saveliev, D.; *East.-Eur. J. Enterp. Technol.* **2022**, *5*, 15. [Crossref]
31. Ferrero, G. O.; Almeida, M. F.; Alvim-Ferraz, M. C. M.; Dias, J. M.; *Energy Convers. Manage.* **2015**, *89*, 665. [Crossref]
32. Pradhan, S.; Shen, J.; Emami, S.; Naik, S. N.; Reaney, M. J. T.; *Eur. J. Lipid Sci. Technol.* **2014**, *116*, 1590. [Crossref]
33. Schuchardt, U.; Sercheli, R.; Vargas, R. M.; *J. Braz. Chem. Soc.* **1998**, *9*, 199. [Crossref]
34. Doehlert, D. H.; *J. R. Stat. Soc., Series C* **2013**, *19*, 231. [Crossref]
35. Araujo, P.; Janagap, S.; *J. Chromatogr. B: Anal. Technol. Biomed. Life Sci.* **2012**, *910*, 14. [Crossref]

36. Ferreira, S. L. C.; dos Santos, W. N. L.; Quintella, C. M.; Neto, B. B.; Bosque-Sendra, J. M.; *Talanta* **2004**, *63*, 1061. [Crossref]
37. Cerqueira, U. M. F. M.; Bezerra, M. A.; Ferreira, S. L. C.; Araújo, R. J.; da Silva, B. N.; Novaes, C. G.; *Food Chem.* **2021**, *364*, 130429. [Crossref]
38. Ruschel, C. F. C.; Ferrão, M. F.; dos Santos, F. P.; Samios, D.; *Quim. Nova* **2016**, *39*, 267. [Crossref]
39. Mendonça, D. R.; Andrade, H. M. C.; Guimarães, P. R. B.; Vianna, R. F.; Meneghetti, S. M. P.; Pontes, L. A. M.; Teixeira, L. S. G.; *Fuel Process. Technol.* **2011**, *92*, 342. [Crossref]
40. Valle, P. W. P. A.; Rezende, T. F.; Souza, R. A. A.; Fortes, I. C. P.; Pasa, V. M. D.; *Energy Fuels* **2009**, *23*, 5219. [Crossref]
41. Pereira, E.; Napp, A.; Braun, J. v.; Fontoura, L. A. M.; Seferin, M.; Ayres, J.; Ligabue, R.; Passaglia, L. M. P.; Vainstein, M. H.; *J. Chromatogr. B* **2018**, *1093-1094*, 134. [Crossref]
42. Braun, J. V.; dos Santos, V. O. B.; Fontoura, L. A. M.; Pereira, E.; Napp, A.; Seferin, M.; Lima, J.; Ligabue, R.; Vainstein, M. H.; *Quim. Nova* **2017**, *40*, 1111. [Crossref]
43. Schaumlöffel, L. S.; Fontoura, L. A. M.; Santos, S. J.; Pontes, L. F.; Gutterres, M.; *Fuel* **2021**, *292*, 120198. [Crossref]
44. Santos, S. J.; Dutra, C. E. M.; Fontoura, L. A. M.; *Quim. Nova* **2023**, *46*, 818. [Crossref]
45. de Jesus, M. P. M.; de Melo, L. N.; da Silva, J. P. v.; Crispim, A. C.; Figueiredo, I. M.; Bortoluzzi, J. H.; Meneghetti, S. M. P.; *Energy Fuels* **2015**, *29*, 7343. [Crossref]
46. Sarpal, A. S.; Silva, S. R.; Silva, P. R. M.; Monteiro, T. V.; Itacolomy, J.; Cunha, V. S.; Daroda, R. J.; *Energy Fuels* **2015**, *29*, 7956. [Crossref]
47. Ivanova, M.; Hanganu, A.; Dumitriu, R.; Tociu, M.; Ivanov, G.; Stavarache, C.; Popescu, L.; Ghendov-Mosanu, A.; Sturza, R.; Deleanu, C.; Chira, N. A.; *Foods* **2022**, *11*, 1466. [Crossref]
48. ASTM D1298-12: *Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method*; West Conshohocken, 2017. [Crossref]
49. ASTM D 445-23: *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids*; West Conshohocken, 2023. [Crossref]
50. ASTM D97-17: *Standard Test Method for Pour Point of Petroleum Products*; West Conshohocken, 2017. [Crossref]
51. Silverstein, T. P.; Heller, S. T.; *J. Chem. Educ.* **2017**, *94*, 690. [Crossref]
52. Cheng, H.; Wei, J.; Liang, M.; Dai, S.; Liu, X.; Ma, L.; Wang, H.; Lai, F.; *Front. Chem.* **2021**, *9*, 770247. [Crossref]
53. Schatte, G.; Shen, J.; Reaney, M.; Centre, S. S.; *Acta Crystallogr., Sect. E: Crystallogr. Commun.* **2010**, *66*, m634. [Crossref]
54. Schatte, G.; Shen, J.; Reaney, M.; Sammynaiken, R.; *Acta Crystallogr., Sect. E: Crystallogr. Commun.* **2011**, *67*, m141. [Crossref]
55. Teófilo, R. F.; Ferreira, M. M. C.; *Quim. Nova* **2006**, *29*, 338. [Crossref]
56. de Oliveira, D. M.; Ongaratto, D. P.; Fontoura, L. A. M.; Naciuk, F. F.; dos Santos, V. O. B.; Kunz, J. D.; Marques, M. V.; de Souza, A. O.; de Pereira, C. M. P.; Samios, D.; *Quim. Nova* **2013**, *36*, 734. [Crossref]
57. Sajjadi, B.; Aziz, A.; Raman, A.; Arandiyani, H.; *Renewable Sustainable Energy Rev.* **2016**, *63*, 62. [Crossref]
58. ASTM D6751-20a: *Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels*; West Conshohocken, 2017. [Crossref]
59. BS EN 14214:2012+A2:2019: *Liquid Petroleum Products, Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heating Applications, Requirements and Test Methods*; Brussels, 2019.
60. Agência Natural do Petróleo (ANP); Resolução ANP No. 920, de 4 de abril de 2023, *Estabelece a Especificação do Biodiesel e as Obrigações Quanto ao Controle da Qualidade a Serem Atendidas pelos Agentes Econômicos que Comercializem o Produto em Território Nacional*; Brasília, 2023. <https://www.legisweb.com.br/legislacao/?id=443945#:~:text=Estabelece%20a%20especifica%C3%A7%C3%A3o%20do%20biodiesel,o%20produto%20em%20territ%C3%B3rio%20nacional>, accessed in January 2024.

Submitted: February 13, 2023

Published online: January 25, 2024