Transformation of triglycerides to fatty acid methyl esters with hydrophilic sulfonated silica (SiO$_2$-SO$_3$H) as catalyst and quaternary ammonium salts in toluene or DMSO

Sandro L. Barbosa,* Adeline C. Pereira Rocha,* David Lee Nelson,* Milton de S. Freitas,* Antônio A. P. Fulgêncio Mestre,* Stanlei I. Klein,* Giuliano C. Clososki,* Franco J. Caires,* Danilo L. Flumignan*‡, Leticia Karen dos Santos,* Alexandre P. Wentz,* Vânya M. Duarte Pasa,* Regiane D. Fernandes Rios*‡

aDepartment of Pharmacy, Universidade Federal dos Vales do Jequitinhonha e Mucuri-UFVJM, R. da Glória, 187, CEP-39.100-000, Diamantina/MG, Brazil. e-mail: sandro.barbosa@ufvjm.edu; adeline.rocha@ufvjm.edu.br; dleenelson@gmail.com; milton.freitas@ufvjm.edu.br; antonio.alexandre@ufvjm.edu.br

bDepartment of General and Inorganic Chemistry, Institute of Chemistry, São Paulo State University-Unesp, R. Prof. Francisco Degni 55, Quitandinha, CEP-14.800-900 Araraquara/SP, Brazil; e-mail: stanleiklein@gmail.com

cDepartment of Physics and Chemistry, Faculdade de Ciências Farmacêuticas de Ribeirão Preto, São Paulo University-USP, Av. do Café s/n, CEP-14.040-903 Ribeirão Preto/SP, Brazil; e-mail:gclososki@yahoo.com.br; fjcaires@usp.br

dInstituto Federal de Educação, Ciência e Tecnologia de Mato Grosso - IFMT - Campus Cuiabá, Departamento das Áreas de Base Comum (DABC), Rua Profa. Zulmira Canavarros, 95, Centro, 78005-200, Cuiabá - MT, Brazil; e-mail: dfllumig@yahoo.com.br; leticiaksantos@yahoo.com.br

eInstitute of Chemistry, Center for Monitoring and Research of the Quality of Fuels, Biofuels, Crude Oil and Derivatives – CEMPEQC, São Paulo State University (UNESP), 14800-900, Araraquara, SP, Brazil.

fCentro universitário SENAI-CIMATEC, Av. Orlando Gomes, 1845, Piatã, 41650-010, Salvador, BA, Brazil; e-mail: alexandre.wentz@fieb.org.br

gChemistry Department, Laboratório de Ensaios de Combustíveis - LEC-DQ/ ICEX, Universidade Federal de Minas Gerais - UFMG, Av. Antônio Carlos, 6627, 31270-901, Belo Horizonte/MG, Brazil; e-mail: vmdpasa@gmail.com; regiane.debora@yahoo.com.br

*Corresponding author. Tel.: +55-38-35321234; fax: +55-38-35321234; e-mail: sandro.barbosa@ufvjm.edu.br
Abstract: Triglycerides of waste cooking oil reacted with methanol in refluxing toluene to yield mixtures of diglycerides, monoglycerides and fatty acid methyl esters (FAMEs) in the presence of 20% (w/w) catalyst/oil using the hydrophilic sulfonated silica (SiO$_2$-SO$_3$H) catalyst alone or with the addition of 10% (w/w) co-catalyst/oil [(Bu$_4$N)[BF$_4$] or Aliquat 336]. The addition of the ammonium salts to the catalyst lead to a decrease in the amounts of diglycerides in the products, but the concentrations of monoglycerides increased. Mixtures of [(Bu$_4$N)[BF$_4$]/catalyst were superior to catalyst alone or Aliquat 336/catalyst for promoting the production of mixtures with high concentrations of FAMEs. The same experiments were repeated using DMSO as the solvent. The use of the more polar solvent resulted in excellent conversion of the triglycerides to FAME esters with all three-catalyst media. A simplified mechanism is presented to account for the experimental results.

Keywords: hydrophilic sulfonated silica catalyst; Aliquat 336; tetrabutylammonium tetrafluoroborate; transesterification; fatty acid methyl esters, DMSO.
1. Introduction

In the search for an environmentally friendly method for biodiesel synthesis by transesterification of triglycerides, several alternatives for the development of solid acid catalysts have been studied. In principle, solid catalytic mixtures with large pores through which bulky triglycerides can access as many acidic sites as possible were sought. These sites should be highly stable, and large pores should also allow esterification of free fatty acids that are also present in vegetable oils [1].

Recently, the propyl sulfonic acid-functionalized silica, SiO$_2$-Pr-SO$_3$H, was synthesized from commercial silica gel and 3-mercaptopropyltriethoxysilane, followed by the oxidation of SiO$_2$-Pr-SH to SiO$_2$-Pr-SO$_3$H with H$_2$O$_2$. The functionalized silica was applied as an alternative to traditional sulfuric acid or sulfonic resins for catalyzing chemical transformations [2-6]. Although it was employed for the preparation of biodiesel by the methanolic esterification of free fatty acids (FFAs) present in vegetable oils [7], in simulated oils [8], and in beef tallow [9], there is no report of the use of sulfuric acid-functionalized silicas for the production of biodiesel from triacylglycerides under atmospheric pressure.

As part of an ongoing study of the use of SiO$_2$-SO$_3$H for clean synthesis [10-13], we report herein the direct preparation of fatty acid methyl esters (FAMEs) using methanol, waste cooking oil, and the hydrophilic SiO$_2$-SO$_3$H as a catalyst, alone or in combination with the quaternary ammonium salts Aliquat 336 or (Bu$_4$N)(BF$_4$) in refluxing toluene or in DMSO (Fig. 1).

![Fig. 1. Schematic synthesis of FAME and glycerol.](image)

2. Experimental

All the reactions were performed in air under atmospheric pressure and monitored by TLC with pre-prepared plates (Silica Gel 60 F 254 on aluminum).

2.1. Waste cooking oil and biodiesel analysis
The official methods proposed by ISO 12966 were used to determine the compositional profile by gas chromatography with a flame ionization detector (GC-FID) (Shimadzu GC-2010). The chromatographic system used to separate and identify FFAs (wt%) included a cross-bound polyethyleneglycol capillary column (Supelco SP 2560, 100m x 0.25mm x 20 µm). The initial temperature was 60 °C for 2 min; the temperature increased to 220 °C at 10 °C.min⁻¹, and finally, to 240 °C at 5 °C.min⁻¹, where it was held for 7 min. The injector and detector temperatures were 350 °C, and the sample (0.5 µL injected) was dissolved in 99% iso-octane.

The European Standards (EN 14103) and the Brazilian Technical Standards Association (ABNT NBR 15908) were used to quantify FAMEs and remaining mono, di and triglycerides (MG, DG, TG) in the biodiesel. For quantification of FAMEs, a Thermo Trace GC-Ultra chromatograph was used, equipped with a flame ionization detector and a Thermo Scientific TR-BD (FAME) Capillary GC Column (L × I.D. 30 m × 0.25 mm, df 0.25 µm) containing a polyethylene glycol stationary phase, according to the EN 14103 analytical procedure. Pure methyl nonadecanoate (C19:0, Sigma-Aldrich) was used as an internal standard to normalize the peak areas of the chromatograms. The integration was achieved from the methyl hexanoate (C6:0) peak to that of the methyl nervonate (C24:1), including all the peaks identified as fatty acid methyl esters. To analyze the FAME samples, approximately 100 mg (accuracy ± 0.1 mg) of homogenized sample and approximately 100 mg (accuracy ± 0.1 mg) of nonadecanoic acid methyl ester were weighed in a 10 mL vial and diluted with 10 ml of toluene before the injection into the equipment. All the samples were prepared in duplicate. Chromatographic conditions are described as follows: (a) column temperature: 60 °C held for 2 min, programmed at 10 °C.min⁻¹ to 200 °C, then programmed at 5 °C.min⁻¹ to 240 °C; the final temperature was held for 7 min; (b) injector and detector temperature: 250 °C; (c) helium carrier gas flow rate: 1-2 ml.min⁻¹, a minimum flow rate of 1 ml.min⁻¹ was warranted when operating at the maximum temperature; (d) injected volume: 1 µl and (e) split flow: 100 mL.min⁻¹.

For the quantification of the glycerides (MG, DG, and TG), a Shimadzu GC2010 chromatograph equipped with a flame ionization detector was used according to the ASTM D6584 analytical procedure. The chromatographic system was configured to separate and identify MG, DG and TG with a CrossbondTM 5% Phenyl/95% dimethypolysiloxane capillary column (Zebron ZB-5HT, 30 m x 0.32 mm x 0.1 mm - Phenomenex, Torrence, CA) with on-column injection. The initial temperature in the capillary column was 50 °C (1 min); the temperature increased to 180 °C at 15 °C/min, to 230 °C at 7 °C/min, and finally to 380 °C at 20 °C/min, where it was held for 10 min. The injector and detector temperatures were 380 °C, and the
sample (0.5 mL injected) was prepared using heptane 99%. $^1$H- and $^{13}$C-NMR spectra were recorded on Bruker Avance 400 and Avance 500 spectrometers. These data are included in the supplementary material.

2.2. Raw materials and chemicals

Waste cooking oil was donated by the university restaurant. All the other reagents (analytical grade), including dry toluene, DMSO and methanol, were supplied by Vetec, São Paulo, Brazil.

2.3. Preparation of the silica gel and sulfonated silica (SiO$_2$-SO$_3$H)

The preparation of silica gel and the sulfonated silica SiO$_2$-SO$_3$H catalyst have been reported previously [10-13].

2.4. Typical procedures

2.4.1. Reacting the triglycerides from waste cooking oil with methanol using the SiO$_2$-SO$_3$H catalyst.

Waste cooking oil (11.2520 g; 12.8856 mmol), methanol (22.50 mL, 17.8431 g, 556.90 mmol), toluene (244.0 mL) and the catalyst SiO$_2$-SO$_3$H (2.2504 g; 20% w/w of waste cooking oil) were mixed in a 500-mL round bottom flask equipped with a reflux condenser, and the mixture was refluxed for 72 h at 110 °C. The mixture was cooled, and the solid catalyst was filtered. The methanol and toluene were evaporated separately on a rotary evaporator, purified by distillation and used in new reaction processes within this study. The organic layer was decanted into a separatory funnel, where the biofuel-containing upper phase was separated from the lower phase containing glycerol by decantation. The recovered glycerol was treated as previously described [11a]. The biofuel phase was dissolved in hexane (50 mL), extracted with 20 mL of a saturated solution of NaCl, dried with MgSO$_4$ and concentrated.

The same procedure was repeated using DMSO as the solvent with heating at 110 °C for 72 h. After cooling, the solid catalyst was filtered, and the excess methanol and DMSO were removed on a rotary evaporator under high vacuum. The glycerol was separated from the oil with a separatory funnel. The biodiesel was diluted in hexane, and the mixture was treated as described above. The biodiesel was finally dried under high vacuum for 5 h.

The catalyst was transferred to a muffle furnace, heated for 2 h at 200 °C, cooled and stored in a desiccator before reuse. The glycerol was purified by adsorption using activated charcoal, and it was used in the synthesis of ketals [11].
2.4.2. Reacting the triglycerides from waste cooking oil with methanol with the SiO$_2$-SO$_3$H catalyst and $[(\text{Bu}^4\text{N})(\text{BF}_4)]$.

Waste cooking oil (11.2520 g; 12.8856 mmol), methanol (22.50 mL, 17.8431 g, 556.90 mmol), toluene (244.0 mL), $[(\text{Bu}^4\text{N})(\text{BF}_4)]$ (1.1252 g or 10% w/w of waste cooking oil) and the catalyst SiO$_2$-SO$_3$H (2.2504 g, 20% w/w of waste cooking oil) were mixed in a 500-mL round bottom flask equipped with a reflux condenser and refluxed at 110 °C for 72 h. The mixture was cooled, and the solid catalyst was filtered. The methanol and toluene were eliminated on a rotary evaporator, and the organic layer was decanted into a separatory funnel, where the upper phase containing biofuel was separated from the lower phase containing glycerol and $[(\text{Bu}^4\text{N})(\text{BF}_4)]$ by decantation. The FAME phase was dissolved in hexane (50 mL) and extracted with 20.0 mL of a saturated solution of NaCl, dried with MgSO$_4$ and concentrated.

The catalyst was transferred to a muffle furnace and heated for 2 h at 200 °C, cooled and stored in a desiccator before reuse. The glycerol was purified and separated from the $[(\text{Bu}^4\text{N})(\text{BF}_4)]$ after dilution in 20 mL of methanol and filtration in a column containing silica gel. The methanol was eliminated by evaporation on a rotary evaporator. The $[(\text{Bu}^4\text{N})(\text{BF}_4)]$ was extracted on a silica column and eluted with hexane (30 mL); the hexane was evaporated to recover the $[(\text{Bu}^4\text{N})(\text{BF}_4)]$. This procedure was repeated using DMSO as the solvent, and the recovery of the biodiesel was performed as described above.

2.4.3. Reacting the triglycerides from waste cooking oil with methanol with SiO$_2$-SO$_3$H catalyst and Aliquat 336

In a similar apparatus, waste cooking oil (11.2520 g; 12.8856 mmol), methanol (22.50 mL, 17.8431 g, 556.90 mmol), toluene (244.0 mL), Aliquat 336 (1.1252 g; 10% w/w of waste cooking oil) and the catalyst SiO$_2$-SO$_3$H (2.5040 g, 20% w/w waste cooking oil) were mixed in a 500 mL round bottom flask equipped with a reflux condenser and refluxed at 110 °C for 72 h. The mixture was then cooled, and the solid catalyst was filtered. The methanol and toluene were evaporated on a rotary evaporator, and the organic layer was decanted into a separatory funnel, where the upper phase containing FAME was separated from the lower phase containing glycerol and Aliquat by decantation. The biofuel phase was dissolved in hexane (50 mL) and extracted with 20.0 mL of a saturated solution of NaCl, dried with MgSO$_4$ and concentrated.

The catalyst was transferred to a muffle furnace, heated for 2 h at 200 °C, cooled and stored in a desiccator before reuse. The glycerol was purified and separated from the Aliquat after dilution in 20 mL of methanol and filtration through a column containing silica gel. The methanol was eliminated on a rotary evaporator.
The Aliquat was eluted from a silica column by hexane (30 mL), and the hexane was evaporated to recover the Aliquat. This procedure was repeated using DMSO as the solvent, and the recovery of the biodiesel was achieved as described above.

3. Results and Discussion

The compositional profile analysis of the commercial brand used in this work is described in Table 1. The main fatty acids in that oil were linolenic (C18:2) and oleic acids (C18:1); accordingly, the mean molecular weight of the fatty acids was determined to be 277.41 g.mol$^{-1}$, and the mean molecular mass of the triglycerides was 873.22 g.mol$^{-1}$. This profile was considered for calculating the molar ratio of waste cooking oil: methanol for the transesterification reaction.

Table 1. Fatty acid composition of the waste cooking oil used in the present work.

| Fatty acid         | Molecular Weight (g.mol$^{-1}$) | wt%  |
|--------------------|---------------------------------|------|
| Palmitic acid (C16:0) | 256.43                         | 10.41|
| Stearic acid (C18:0)  | 284.48                         | 3.91 |
| Oleic acid (C18:1)   | 282.46                         | 26.52|
| Linoleic acid (C18:2) | 280.45                         | 51.66|
| Linolenic acid (C18:3) | 278.43                         | 5.55 |
| Others              | -                              | 1.95 |
| Average Molecular Weight of Fatty Acids (g.mol$^{-1}$) | | 277.41 |
| Molar mass of triglycerides (g.mol$^{-1}$) | | 873.22 |

3.1. Transesterification of waste cooking oil using catalysis by SiO$_2$-SO$_3$H/toluene, SiO$_2$-SO$_3$H/Aliquat 336/toluene and SiO$_2$-SO$_3$H/[(Bu$^n$N)](BF$_4$)/toluene.

In the first phase of this study, a large excess of methanol dissolved in toluene was mixed with waste cooking oil and 20 wt% (based on the mass of waste cooking oil) of pure SiO$_2$-SO$_3$H, and the mixture was refluxed. On the basis of the TLC monitoring of the reaction, the total consumption of triglycerides occurred after 72 h; this period was maintained for all subsequent reactions with the mixtures of 20 wt% SiO$_2$-SO$_3$H with 10 wt% Aliquat 336 or 10 wt% [(Bu$^n$N)](BF$_4$). The FAMEs and glycerides (MG, DG, and TG) contained in the biodiesel phase were confirmed by GC-FID using the methods defined in EN 14103 and
ASTM D6584. The wt% composition of the mixture (FAMEs and glycerides) in the products is presented in Figure 1 and Table 2; they represent the average values of five different measurements. After 72 h, only the reactions containing SiO$_2$-SO$_3$H and [(Bu$_4$N)](BF$_4$) contained traces of unreacted triglycerides (Table 2). The choice of toluene as the solvent for the reactions and the use of quaternary ammonium salts as co-promoters were indicated by the recently discovered efficiency of the mixture toluene, [(Bu$_4$N)](BF$_4$) and SiO$_2$-SO$_3$H in the esterification of fatty acids with solketal [13]. The highest yield (64.2%) of FAMEs was obtained using the combination of (Bu$_4$N)](BF$_4$) with SiO$_2$-SO$_3$H.

Fig. 2. Composition of the waste cooking oil feedstock and the product mixture of each catalytic process (SiO$_2$-SO$_3$H/Aliquat, SiO$_3$-SO$_3$H and SiO$_2$-SO$_3$H/(Bu$_4$N)(BF$_4$)) involving methanol in refluxing toluene.

| Products          | Waste cooking oil | SiO$_2$-SO$_3$H/ Aliquat | SiO$_2$-SO$_3$H | SiO$_2$-SO$_3$H/(Bu$_4$N)](BF$_4$) |
|-------------------|-------------------|--------------------------|---------------|-----------------------------|
| Triacylglycerides % | 96.2              | 0                        | 0             | 0.7                         |
| Diacylglycerides %  | 2.80              | 9.5                      | 13.9          | 2.5                         |
| Monoacylglycerides % | 1                 | 35.6                     | 25.9          | 32.5                        |
Table 2. Numerical data for Fig. 2.

| FAME % | 0   | 54.9 | 60.2 | 64.2 |

In our previous experiences with esterification reactions catalyzed by SiO$_2$-SO$_3$H [10,13], we pointed out the importance of the cationic intermediates [RC(OH)$_2$]$^+$, which should be formed by the protonation of the acid at the catalyst surface; this charged species would disperse in solution where it would react with its alcohol counterpart [10]. We also pointed out that the addition of a quaternary ammonium salt to that type of mixture could change the polarity of the toluene phase, stabilizing those cationic intermediates, and leading to very good yields of, for instance, linoleic acid solketal ester [13]. The mechanism of the formation of biodiesel (FAMEs) using the solid catalyst can be oversimplified by the assumption that the majority of the chemical transformations will occur at the surface of the catalyst. With this assumption in mind, the three stages for the complete conversion of TG into long-chain methyl esters should occur as depicted in Fig 1. The first stage, denoted by V1, would probably be the rate-determining step due to the difficulty in connecting the long apolar chains of the TG molecules to the polar catalyst surface because of the sheer size of the molecule, with the inherent degrees of steric hindrance. The molecule’s reactive sites would have to reach the catalyst’s reactive sites: in the present case, this encounter would produce a cationic intermediate such that depicted in Fig. 3.

Fig. 3. Formation of a diglyceride from the initial protonation of a triglyceride by the solid catalyst.

Once the diglyceride is produced with the release of the methyl ester, the alcohol functional group of the DG would have the necessary properties to anchor, or at least, to facilitate the approach of this new reagent to the active centers of the solid catalyst [10]. Therefore, we can assume with certain confidence that the velocity of the V2 (Fig. 1) process is much faster than V1, which means that, once formed, the DG molecules trapped at or near the active centers of the catalyst surface would rapidly (in the time frame of the overall reaction) be converted into monoglycerides with the release of the second methyl ester. Within this reasoning, step V3 (Fig. 1) would be almost as delicate as V1, also requiring the fine tuning of the reaction parameters time, temperature, solvent and co-catalyst. Because the DG molecule was anchored at
the surface of the catalyst, the formation of the second alcohol functional group due to the transformation
DGs→to MGs should strengthen the forces binding that molecule to the highly hydrophobic catalyst
surface. It is reasonable to assume, at this stage, that the formation of glycerol in the process V3 could
possibly block the active center(s) where the actual process occurred because of the high affinity of the
catalyst for that kind of polar, H-bond-prone molecule.

In this reaction scenario, the co-catalyst should play multiple tasks: lower the repulsion forces of the bulky
TG molecules towards the catalyst surface to enhance the V1\textsubscript{init} process, stabilize the cationic intermediates
from V1\textsubscript{~}V3, and lower the attraction of glycerol to the active sites after completion of the V3 step,
effectively freeing those sites for the constructive continuation of the reactions V1-V2-V3 sequences. The
three systems under study are capable of breaking triglycerides by transesterification reactions with
methanol in refluxing toluene, but with slightly different behaviors, as is shown in the graph in Fig 2,
constructed using the data from Table 2.

The samples obtained from the 72-h reactions catalyzed by SiO\textsubscript{2}-SO\textsubscript{3}H alone contained no TGs but had
higher percentages at 13.9 % of DGs than the samples taken from the other reactions, a clear indication that
the addition of quaternary ammonium salts are important to accelerate the transformation of DGs→to MGs
(step V2 in Fig 1). Interestingly, the reactions with the lone catalyst resulted in the lowest percentage of
MGs (25.9 %), which could indicate that the ammonium salts are effective in stabilizing cationic species
derived from protonated MGs, which would slow down their conversion to FAME and glycerol (step V3
in Fig. 1).

The appearance of 0.7% TG in the samples derived from the system including the (Bu\textsubscript{4}N)(BF\textsubscript{4}) seems to
suggest that this co-catalyst slightly inhibits the V1 process of the binding of TG to an active center of the
solid catalyst and the formation of the DGs, either due to the poor interaction of the ammonium salt with
the bulky TGs, by the strong stabilization of a cation such as that in Fig. 3, thereby retarding the V1\textsubscript{final} step,
or both. However, the action of the (Bu\textsubscript{4}N)(BF\textsubscript{4}) in these systems seems to be beneficial, for only 2.5% of
DGs were found in the samples of those reactions (Table 2), indicating that the process, crudely described
above as V2, is indeed very fast with this mixed catalyst. Aliquat 336 and the (Bu\textsubscript{4}N)(BF\textsubscript{4}) were also tested
separately as catalysts for this transesterification reaction without the presence of the SiO\textsubscript{2}-SO\textsubscript{3}H; however,
no reaction was observed.
3.2. Transesterification of waste cooking oil using catalysis by SiO$_2$-SO$_3$H/DMSO, SiO$_2$-SO$_3$H/Aliquat 336/DMSO and SiO$_2$-SO$_3$H/[(Bu$_n$N)](BF$_4$)/DMSO.

In a recent study, DMSO was shown to be an efficient solvent for the SiO$_2$-SO$_3$H-catalyzed dehydration of fructose to 5-hydroxymethyl-2-furfural [14]. The interaction of DMSO with the catalyst led us to test the use of DMSO in transesterification reactions. Because of the inadequate results obtained using toluene with regard to the complete consumption of the di- and monoglycerides, the transesterification was performed using DMSO as the solvent in the second phase of the study. The remaining conditions for the reaction were the same as those used with toluene. The yields are presented in Table 3.

**Table 3.** Composition of the waste cooking oil feedstock and the product mixture of each catalytic process SiO$_2$-SO$_3$H/(Bu$_n$N)(BF$_4$), SiO$_2$-SO$_3$H/Aliquat 336, and SiO$_2$-SO$_3$H involving methanol in refluxing DMSO.

| Assay            | SiO$_2$-SO$_3$H/(Bu$_n$N)(BF$_4$) | SiO$_2$-SO$_3$H/Aliquat 336 | SiO$_2$-SO$_3$H |
|------------------|----------------------------------|----------------------------|----------------|
|                  | Result (% w/w) | Standard deviation | Result (% w/w) | Standard deviation | Result (% w/w) | Standard deviation |
| FAME             | 98.40            | 3.10               | 86.35          | 3.38             | 99.51           | 2.94              |
| Free glycerol    | 0.01             | 0.01               | 0.04           | 0.01             | 0.01            | 0.01              |
| Total glycerol   | 0.29             | 0.07               | 2.16           | 0.08             | 0.09            | 0.07              |
| Monoacylglycerol | 0.86             | 0.27               | 4.87           | 0.29             | 0.28            | 0.26              |
| Diacylglycerol   | 0.37             | 0.12               | 4.00           | 0.13             | 0.07            | 0.12              |
| Triacylglycerol  | 0.09             | 0.26               | 0.35           | 0.28             | 0.02            | 0.25              |

The yields of FAMEs obtained using DMSO as the solvent were significantly higher than those obtained with toluene with all the catalyst mixtures. The first possible explanation for this result is that the more polar DMSO would help to stabilize the protonated ester intermediate in the transesterification reaction. The second, less clear, possibility is that the more polar DMSO might facilitate the transport of the triglyceride and methanol to the catalyst surface. And finally, because the triglyceride is less soluble in DMSO than in toluene, there might be a greater tendency for it to be absorbed on the catalyst surface.
creating a concentration effect. There was essentially no difference in the yields obtained using SiO$_2$-SO$_3$H (99.51%) and SiO$_2$-SO$_3$H/(Bu$_4$N)(BF$_4$) (98.40%). The SiO$_2$-SO$_3$H/(Bu$_4$N)(BF$_4$) mixture was effective for the transesterification of triacylglycerols in DMSO and the esterification of free fatty acids with solketal [13]. These values are within the limits established by EN 14103-2011 (Min. 96.5%).

With regard to the concentration of total glycerol, the SiO$_2$-SO$_3$H (0.08%) and SiO$_2$-SO$_3$H/(Bu$_4$N)(BF$_4$) (0.23%) catalytic systems were within the limits specified by ASTM D6584-17 (Max. 0.25%), which also demonstrates the high degree of conversion of the tri-, di- and monoacylglycerols. The concentration of total glycerol obtained with the SiO$_2$-SO$_3$H/Aliquat 336 catalytic system (1.62%) indicates that this system is less adequate for catalyzing the transesterification of waste cooking oil.

The concentration of diglycerides in the product obtained using the SiO$_2$-SO$_3$H catalyst (0.07%) in DMSO was within the limits established by ASTM D6584-17 (Max. 0.20%), but those obtained using the SiO$_2$-SO$_3$H/Aliquat 336 (4.00) and SiO$_2$-SO$_3$H/(Bu$_4$N)(BF$_4$) (0.37%) systems were outside that limit. The concentration of monoglycerides observed using SiO$_2$-SO$_3$H (0.28%) as the catalyst was within the limit imposed by the ASTM D6584-17 (Max. 0.7%), whereas those obtained using the SiO$_2$-SO$_3$H/(Bu$_4$N)(BF$_4$) (0.86%) and SiO$_2$-SO$_3$H/Aliquat 336 (4.87%) catalytic systems were greater than the legal limit.

### 4. Conclusions

The sulfonated silica SiO$_2$-SO$_3$H and the mixtures of SiO$_2$-SO$_3$H with Aliquat 336 and with [(Bu$_4$N)](BF$_4$) were used successfully for the transesterification of waste cooking soy oil with methanol in refluxing toluene. Analysis of the quantities of triglycerides, diglycerides, monoglycerides and fatty acid methyl esters in the reaction’s products indicated different behaviors of the catalysts. Whereas the unmixed sulfonated silica was the fastest in promoting the transformation of monoglycerides to FAMEs, the mixed catalysts favored the transformation of diglycerides into monoglycerides. The salt (Bu$_4$N)(BF$_4$) showed a high efficiency in producing mixtures with high percentages of monoglycerides and FAMEs, despite its difficulty in promoting the initial approach of the triglyceride to the sulfonated catalyst surface. When DMSO was used in place of toluene under the same reaction conditions, the catalytic systems tested were effective for the transformation of tri-, di- and monoacylglycerols in FAME and glycerol. The results obtained using the sulfonated silica, SiO$_3$-SO$_3$H, and the SiO$_2$-SO$_3$H/(Bu$_4$N)(BF$_4$) in DMSO were within...
the standards established by the ASTM, indicating that these catalytic systems are effective for the transformation of low quality cooking oils.

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