Catalysis Today 166 (2011) 116–122

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Biodiesel from waste frying oil. Two step process using acidified SiO_2 for esterification step

Grisel Corro[a,*], Nallely Tellez[a], Teresita Jimenez[a], Armando Tapia[a], Fortino Banuelos[a], Odilón Vazquez-Cuchillo[b]

[a] Instituto de Ciencias, Benemerita Universidad Autonoma de Puebla, 4 sur 104, Puebla, Puebla 72000, Mexico
[b] Departmento de Ecomateriales y Energía, Universidad Autónoma de Nuevo León, Nuevo León 66451, Mexico

ARTICLE INFO

Article history:
Available online 6 October 2010

Keywords:
Biodiesel
Waste frying oil
Heterogeneous acid catalyst
Esterification

ABSTRACT

Biodiesel was produced from waste frying oil (WFO) by the two step catalyzed process. The free fatty acids (FFA) were first esterified with methanol catalyzed by SiO_2 pretreated with HF. The catalyst was characterized by its acid surface sites, FTIR, SEM, and, its CO_2 and H_2O adsorption reactivity. This catalyst was easy to recover, was not hydrated or carbonated, was not dissolved by the reactants or the products of the reaction, showed a high activity for the FFA esterification and presented high stability. After 10 esterification runs, the catalyst activity remained unchanged. During the second step, the triglycerides in WFO were transesterified with methanol catalyzed by NaOH. The biodiesel obtained was characterized by its physical properties and its chemical composition. Gas chromatography and mass spectrometry analysis revealed that the process proposed in this investigation led to a biodiesel containing 96% methyl esters.

1. Introduction

Biodiesel, as an alternative fuel, is derived from a renewable, domestic resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has more favorable combustion emission profile, such as low emissions of carbon monoxide (CO), particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect [1,2]. Biodiesel is less volatile and safer to transport than petroleum diesel [3]. These characteristics of biodiesel make it a good alternative to petroleum based fuel and have led to its use in many countries.

Biodiesel production costs are rather high compared to petroleum-based diesel fuel [4]. There are two main factors that affect the cost of biodiesel: the cost of raw materials and the cost of processing. Processing cost could be reduced through simplified operations and eliminating waste streams.

Exploring ways to reduce the high cost of biodiesel is of much interest in recent biodiesel research. The use of waste frying oil (WFO) instead of virgin oil to produce biodiesel is an effective way to reduce the raw material cost because it is estimated to be about half the price of virgin oil [5–7]. In addition, using WFO could also help to solve the problem of waste oil disposal [8].

The most common way to produce biodiesel is by transesterification which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol (Fig. 1, reaction 2). Triglycerides, as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol structure. When triglycerides react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the methanol to yield fatty acid methyl esters (FAME). Glycerol is produced as a by-product.

For biodiesel production, chemically catalyzed processes, including alkali catalyzed and acid catalyzed ones have proved to be more practical than the enzyme catalyzed process. An alkali catalyzed process can achieve high purity and yield of biodiesel product in a short time (30–60 min) [9–11]. However, it is very sensitive to the purity of the reactants. Well refined vegetable oils with low amounts of free fatty acid (FFA) can be used as the reactant in this process [12]. When waste frying oil (WFO) with more than 10 wt% FFA is used, an acid catalyzed process is preferred, but it requires more excess of methanol, high pressure (170–180 kPa) and high cost stainless steel equipment. Moreover, the yield of the product is low when sulfuric acid is used as the catalyst [12–14].

A combined process with acid catalyzed pretreatment was developed to synthesize biodiesel from WFO. The first step is to esterify the FFA with methanol by acid catalysis. When the FFA content is lower than 0.5 wt%, the acid is drained, and the solid alkali

---

[*] Corresponding author. Tel.: +52 222 22955 00 7294; fax: +52 222 22955 00 7294.
E-mail address: cs001380@siu.buap.mx (G. Corro).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.09.011

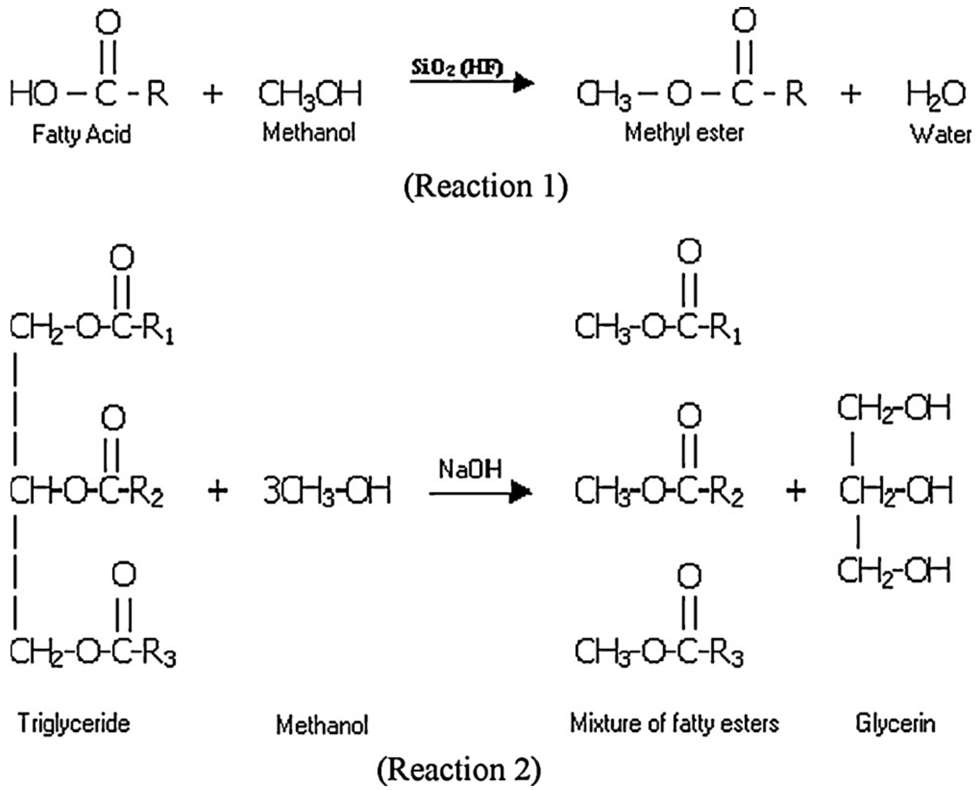

Fig. 1. Biodiesel (fatty acid methyl esters) production by: FFA esterification catalyzed by SiO_2(HF) (reaction 1); triglycerides (TG) transesterification catalyzed by NaOH (reaction 2).

is introduced into the system to complete the transesterification [12,15]. However, the drawbacks of this combined process include: effluent of acid, no recovery of the catalyst and high cost of reaction equipment [16]. To overcome this problem, a novel method has been developed by Wang et al. [17] for the production of biodiesel from WFO of high acid value (75 mg KOH/g), by a two step catalysis process. At first step, a solid acid catalyst (ferric sulfate) was introduced to catalyze the esterification reaction in which the FFA in the WFO reacted with methanol. At the second step, potassium hydroxide was added to catalyze the transesterification reaction in which the triglyceride (TG) reacted with methanol. This process showed advantages of no acid wastewater. Moreover, the catalyst was recovered and reused for several runs. However, during high temperature esterification of FFA, water is generated as a product of the reaction. This water may dissolve a part of the ferric sulfate leading to a loss of the catalyst and to the presence of sulfates in the biodiesel. During this biodiesel combustion in the engine, sulfates may generate the polluting SO_2 in the exhaust gas.

Now, in previous studies, we found that pretreatment of SiO_2 with different strong acids (H_2SO_4, HCl, HNO_3, and HF), resulted in a strong generation of acid surface sites. SiO_2 pretreated with HF presented the highest number of acid surface sites in the catalysts studied. Thereafter, in this investigation, we wanted to study the activity of SiO_2 pretreated with HF for the esterification of FFA in the WFO obtained from restaurants which without suitable treatment available, would be discharged and cause environmental pollution. The process proposed for the production of biodiesel is schematized in Fig. 1.

2. Materials and methods

2.1. Waste frying oil

The waste frying oil (WFO) was a mixture of different vegetable oils, provided by a local restaurant. Particles remaining in the WFO were removed by filtration before the esterification reaction. The analysis of the FFA chemical composition of this oil was performed with a gas chromatograph–mass spectrometer HP 6890, provided with a 5973 Network Agilent Technology detector. The employed standard method in the analysis of the FFA was the NMX-F-017-SCFI-205.

2.2. Catalysts

2.2.1. Catalysts preparation

The SiO_2–F6 (Baker 99.9%) was impregnated with the appropriate amount of HF solution to obtain a 10 wt% HF in the SiO_2. The suspension was stirred at room temperature for 1 h. After drying, at 120 °C overnight, the catalyst, called SiO_2(HF), was calcined in air at 500 °C for 12 h. A reference SiO_2 sample was prepared in the same way using only water. High temperature calcination process was performed on the catalysts, in order to reduce its porosity, thus to lower the probability of water adsorption in its surface.

2.2.2. Catalyst characterization

Surface areas and pore volumes of the SiO_2 and the SiO_2HF were determined on an ASAP 2010 analyser using UHP N_2 adsorption at −196 °C. Prior to surface area analysis, the catalyst samples were degassed at 150 °C and 10^{-3} mmHg for 5 h. Textural data are given in Table 2.

The catalysts microstructure analysis was performed on a scanning electron microscopy SEM, JEOL 6490L using a carbon-coated copper micro grid covered with a gold film. FTIR spectra were recorded from 800 to 3500 cm^{-1} on a Bruker Vertex 70 spectrometer. Spectra were recorded with a resolution of 5 cm^{-1} and 100 scans.

In order to measure the CO_2 and H_2O adsorbed from the atmosphere over the catalysts, a sample (200 mg) was placed in a continuous flow tubular quartz reactor placed in a programmable furnace. Measurements over the catalysts were performed using

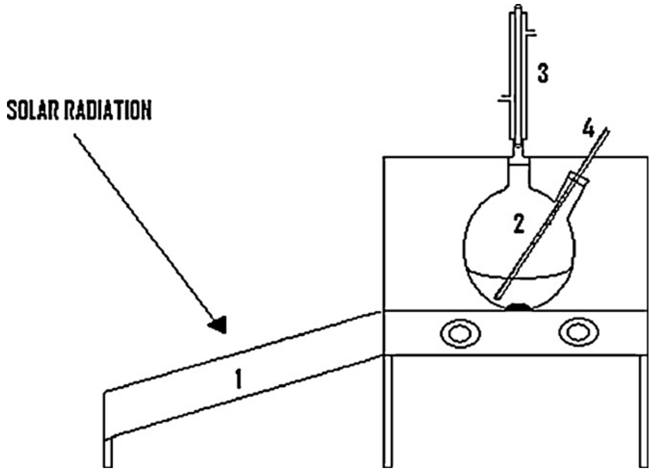

Fig. 2. Schematic layout of the biodiesel reactor: (1) heat conductor; (2) glass flask; (3) condenser; (4) thermocouple.

a N_2 (UHP) volume flow rate of $100\,cm^3\,min^{-1}$. The reactor out flow was analyzed using a gas chromatograph equipped with a thermal conductivity detector and a Porapak Q packed column. Programmed thermo-desorption measurements of CO_2 and H_2O were taken as the temperature was increased stepwise at temperatures from 25 to 400 °C in order to follow the process of decarbonation and dehydration of the solid.

The number of catalytically available Lewis acid sites of SiO_2 and SiO_2(HF) catalysts was determined by the titration method proposed by Lopez et al. [18].

2.3. First step: FFA esterification with methanol

2.3.1. Optimization of the reaction conditions

The reaction of FFA esterification with methanol catalyzed by SiO(HF) and SiO_2 was carried out in a laboratory scale reactor represented in Fig. 2. This reactor consisted of a round bottom, two necked flask for the condenser and for placing the thermometer to observe the reaction temperature and a magnetic stirrer arrangement. The working capacity of the flask is 1 l. The reactor was placed in a home built solar heater provided with an air temperature controller. Desired temperatures were obtained using only solar radiation as energy source. The experiments were performed at a constant temperature in a range from 40 °C to 70 °C. The reactants were methanol (Aldrich, 99%) and WFO. The molar ratio of WFO and methanol was adjusted as 1:30 according to the literature [19].

The catalyst concentration range used was from 2 to 8 wt % of the initial WFO mass. The experiments were performed at a constant temperature in a range from 40 °C to 70 °C. The reaction was allowed to proceed for a specified time (1–8 h). The speed of stirring was 600 rpm. After the specified time of reaction, the mixture was left to settle to separate into two layers. The lower oil layer was composed by the methyl esters produced by the FFA esterification, the unreacted triglyceride (that was further subjected to the transesterification reaction) and the solid insoluble catalyst that was recovered for further use. The upper layer was methanol and the water produced during reaction 1.

Catalysts durability tests were performed by repeating the esterification reaction 10 times with the used catalyst. Catalysts separated from the previous reaction mixture were used again without any further washing pretreatment.

2.3.2. Acid number determination

The acid number of the initial WFO or after the FFA esterification reaction was determined according to the ASTM D 664 international standard method. In this method, the sample was dissolved in a mixture of toluene and isopropanol. The mixture was then titrated potentiometrically with an alcoholic KOH solution. The acid number was the quantity of mg KOH/g of sample required to titrate the sample to the neutral point.

The acid number was determined according to Eq. (1):

$$N_{acid} = 56.1 \times M\frac{A - B}{W} \tag{1}$$

where M is the concentration of KOH; A is the volume of KOH used to reach the neutral point corresponding to basic buffer; B is the volume corresponding to A for the blank titration; W is the mass of the sample.

2.3.3. Determination of the %conversion of FFA.

The conversion of the FFA is defined as the fraction of FFA that reacted during the esterification with methanol. The conversion of FFA ($\%C_{FFA}$) was determined from the acid number ratio using the following equation:

$$\%C_{FFA} = \frac{A_i - A_f}{A_i} \times 100 \tag{2}$$

where A_i is the initial acid number of the WFO; A_f is the final acid number of the WFO after the FFA esterification reaction.

2.4. Second step: alkali catalyzed transesterification of WFO

2.4.1. Reaction conditions

For oil samples with FFA below 2.0%, alkaline transesterification is preferred over the acid catalyzed transesterification, as the former is reported to proceed about 4000 times faster than the later [20].

The mixture of the esterified FFA and the unreacted triglyceride was transferred to a 250 ml one neck flask. Six times the stoichiometric amount of methanol required for total conversion of triglyceride and 1.0 wt% of NaOH were added as proposed by Zhang et al. [12]. The reaction was performed at 60 °C for 2 h under stirring at 600 rpm. The mixture was left to settle overnight to separate in two layers. The upper layer was the FAME and the lower layer was the mixture of methanol, water and glycerol as indicated in Fig. 1, reaction 2. The FAME obtained was washed with hot water (80 °C) and dried under stirring at 100 °C for 2 h, using the solar heater as energy source.

2.4.2. Chemical analysis of the biodiesel produced

The fatty acid methyl esters (FAME) content in the biodiesel obtained was measured by GC analysis according to the EN 14103 test method, using a GC-2014 Shimadzu chromatograph provided with a FID detector. The biodiesel sample was added to the standard solution containing methyl heptadecanoate. The mixed sample was analyzed by GC. The fatty acid methyl esters content (FAME) was determined using the following equation:

$$\mathrm{FAME}\,(\%) = \frac{\sum A - A_s}{A_s} \times \frac{C_s V_s}{m} \times 100 \tag{3}$$

where $\sum A$ is the sum of peak areas of methyl esters (C14:0–C24:1); A_s is the peak area of methyl heptadecanoate; C_s is the concentration of methyl heptadecanoate; V_s is the volume of standard solution; m is the amount of biodiesel sample.The linolenic acid methyl ester content L is calculated using Eq. (4):

$$L\,(\%) = \frac{A_L}{\sum A - A_{EI}} \times 100 \tag{4}$$

where $\sum A$ is the total peak area from the FAME (C14:0-C24:1); A_{EI} is the peak area of methylheptadecanoate; A_L is the peak area of linolenic acid methyl ester.

Table 1
FFA content in WFO.

Compound	Content (%)
n-Hexadecanoic acid	8.42
Tetradecanedioic acid	3.27

The determination of the free, bound, and total glycerin, and mono, di, and triglycerides, was made according to the ASTM D 6584 test method, using the EZStart Chromatography Software provided by Shimadzu.

2.4.3. *Biodiesel density and kinematic viscosity determinations*

Density of the samples was calculated from the following equation:

$$\rho = \rho_{\mathrm{ref}} \cdot g_s \qquad (5)$$

where ρ is the density; ρ_{ref} is the reference density; g_s is the specific gravity.

The kinematic viscosity of the produced biodiesel was measured according to the ASTM D 445 international standard method. The test was performed at 40 °C by measuring the time required for a volume of liquid to flow under gravity through a Cannon–Fensake style glass capillary tube.

3. Results

3.1. *Waste frying oil analysis*

The FFA chemical composition analysis performed by GCMS of the WFO is reported in Table 1. This table shows 11.69% content of FFA in the WFO used in this investigation.

3.2. *Catalysts characterization*

The method proposed by Lopez et al. [18] to determine acid sites on resins, was applied in this investigation to measure surface acid sites on SiO_2 and SiO_2HF according to the following proposed reactions:

$$SiO_2 + H_2O \leftrightarrow SiO_2\text{–}OH + H^+ \qquad (3)$$

$$SiO_2HF + H_2O \leftrightarrow SiO_2HF\text{–}OH + H^+ \qquad (4)$$

In this case, no ion exchange might have taken place with NaCl as proposed by Lopez et al. Thus, the number of acid sites was determined by titration of the protons with NaOH. The catalyst characterization data is summarized in Table 2. In this table, it can be seen that the HF pretreatment of SiO_2 resulted in a strong increase in the acid sites g cat^{-1}.

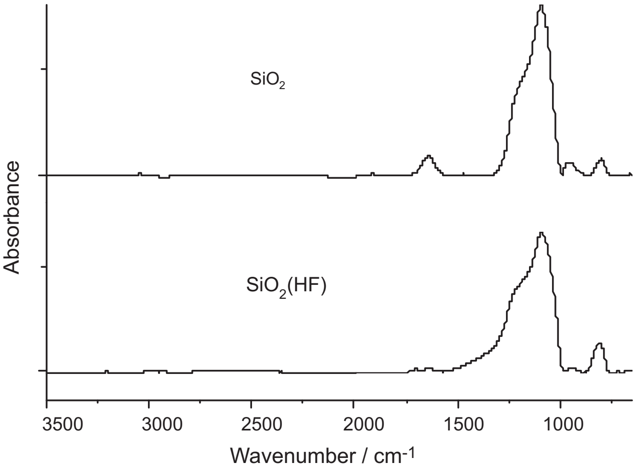

Fig. 3. FTIR spectra of the SiO_2 and SiO_2(HF) catalysts.

Programmed thermo-desorption measurements performed on SiO_2 and SiO_2HF showed no CO_2 or H_2O desorption from 25 to 400 °C, as reported in Table 2. Moreover, the FTIR spectra obtained from the SiO_2 and SiO_2(HF) catalysts shown in Fig. 3, revealed the absence of the absorbance signals at 3335 cm^{-1} and 1400 cm^{-1} corresponding to water and at 2360 cm^{-1} due to CO_2 adsorption. These results can be explained on basis of the amorphous nature of the fused silica (SiO_2 F-6) used for the preparation of the catalysts. This form of SiO_2 may not adsorb CO_2 or H_2O as the silica gel, whose high surface area (around 800 m^2/g) and average pore size of 24 Å allow it to adsorb water readily.

Table 2
Catalyst characterization data.

Property	Catalyst	
	SiO_2	SiO_2 (HF)
Acid sites g cat^{-1}	$<10^5$	3.2×10^{21}
CO_2 desorption 25–400° C	0	0
H_2O desorption 25–400° C	0	0
Specific surface area (m^2 g cat^{-1})	400	158
Total pore volume (ml/g) (pores < 4272 Å diameter)	0.63	0.30

In Table 2, it can also be seen that SiO_2HF presents lower values for specific surface area and total pore volume (pores with diameters smaller than 4272 Å) related to SiO_2. These results suggest that SiO_2 pretreatment with HF at high temperature might have generated a new form of SiO_2. This assumption is supported by the SEM images of SiO_2 and SiO_2HF shown in Figs. 4 and 5. Results observed in these figures suggest that after the high temperature pretreatment of SiO_2 impregnated with HF, a sintered form of the original SiO_2, was generated.

3.3. *Biodiesel production*

3.3.1. *First step (FFA esterification)*

To determine the optimal conditions for FFA esterification reaction catalyzed by SiO_2(HF), we examined the effect of the reaction temperature, reaction time, and catalyst/WFO mass ratio.

In Fig. 6, the evolution of the FFA conversion as a function of the esterification temperature shows that the FFA conversion increases with temperature. From 60 °C to70 °C a very slight increase in FFA conversion was detected. Fig. 5 shows the effect of the reaction time on the FFA conversion. In this figure, it can be observed that

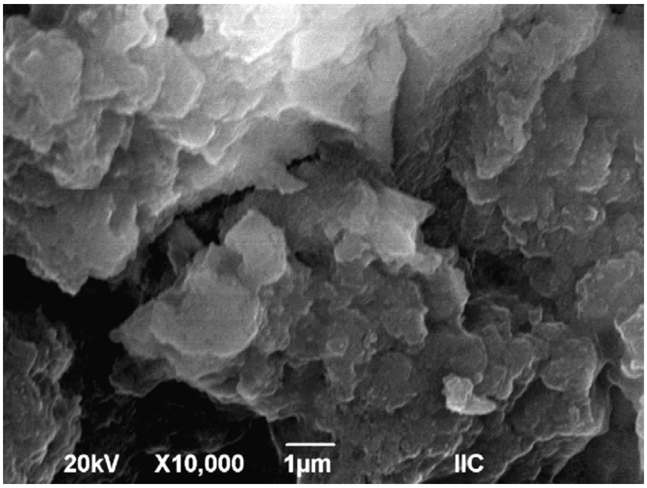

Fig. 4. SEM micrograph of SiO_2 sample (20,000×).

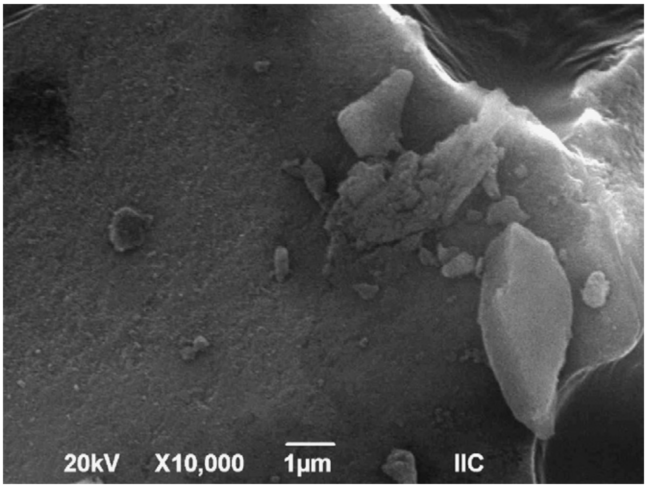

Fig. 5. SEM micrograph of SiO_2HF sample (20,000×).

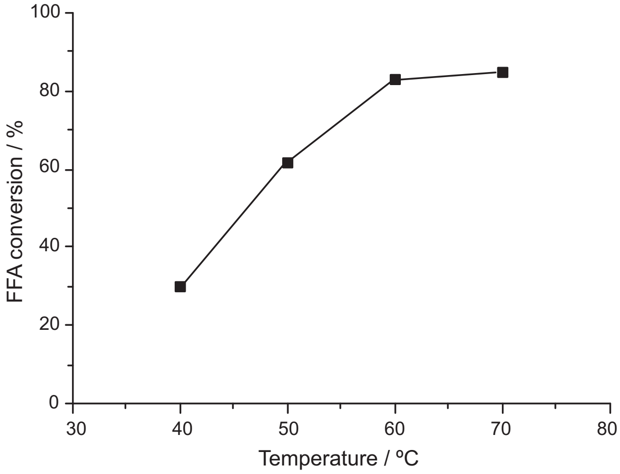

Fig. 6. Effect of temperature on FFA esterification catalyzed by SiO_2(HF). Reaction conditions: methanol/WFO ratio = 1/30; catalyst/WFO mass ratio = 4%; time = 4 h.

after 4 h of reaction in the specified conditions, FFA esterification remained rather constant. Fig. 6 shows the evolution of the FFA esterification yield as a function of the catalyst/WFO mass ratio. This figure revealed that the optimal catalyst/WFO mass ratio for the reaction is 4%.

The results presented in Figs. 6–8 led us determine the optimal conditions for the FFA esterification catalyzed by SiO_2(HF). Thus, the reaction was performed in the presence of 4 g SiO_2(HF) in 100 g WFO, at 70 °C for 4 h.

The effect of the catalyst on FFA conversion is shown in Table 3. The SiO_2 and SiO_2(HF) can catalyze methanolysis of FFA but cannot catalyze the transesterification of triglycerides, so the acid value can be calculated for the conversion of FFA. In this table it can be seen the effect of the catalysts on the FFA esterification with methanol at the optimal reaction conditions determined in this investigation. The conversion of FFA was 86% when SiO_2(HF) was used as the catalyst. The acid value of the WFO decreased substantially in the presence of SiO_2(HF). However, the use of SiO_2 for the esterification reaction resulted in very low FFA conversion. Therefore, only SiO_2(HF) was studied for FFA esterification and therefore, only the products obtained after this process were investigated for the transesterification of triglycerides with NaOH (Fig. 1, reaction 2).

Table 3
Effect of the catalysts on the WFO acid value after the FFA esterification. Initial WFO acid value: 15.8 mg KOH/g.

Catalyst	Run number	Final acid value (mg KOH/g WFO)	FFA conversion (%)
Without catalyst	1	15.8	0
SiO_2	1	15.0	10
SiO_2 (HF)	1	2.3	86
SiO_2 (HF)	10	2.4	85

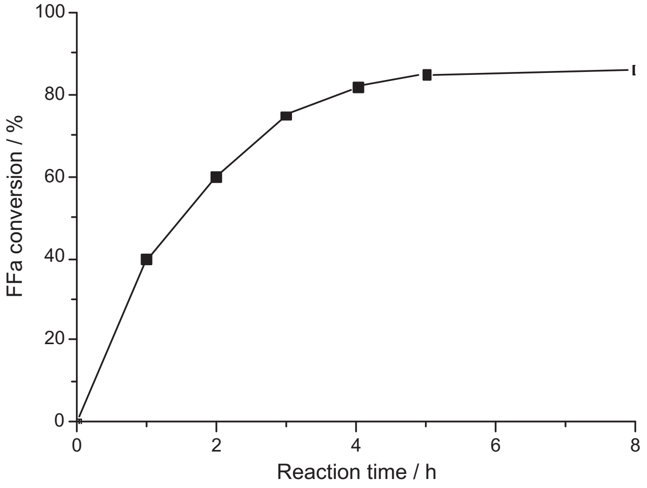

Fig. 7. FFA conversion evolution catalyzed by SiO_2(HF) as a function of reaction time. Reaction conditions: methanol/WFO ratio = 1/30; catalyst/WFO mass ratio = 4%; temperature = 70 °C.

In Fig. 9 it can be seen the FFA esterification evolution over SiO_2(HF) as a function of the number of runs at the optimal determined reaction conditions. This figure shows that after 10 runs, the activity of the catalyst for the FFA esterification remained rather unaffected.

3.3.2. Second step: alkali catalyzed transesterification of WFO

The biodiesel obtained from the NaOH catalyzed transesterification of WFO with methanol after the FFA esterification catalyzed by SiO_2(HF) with methanol was characterized by its physical and chemical properties. The results are shown in Table 4.

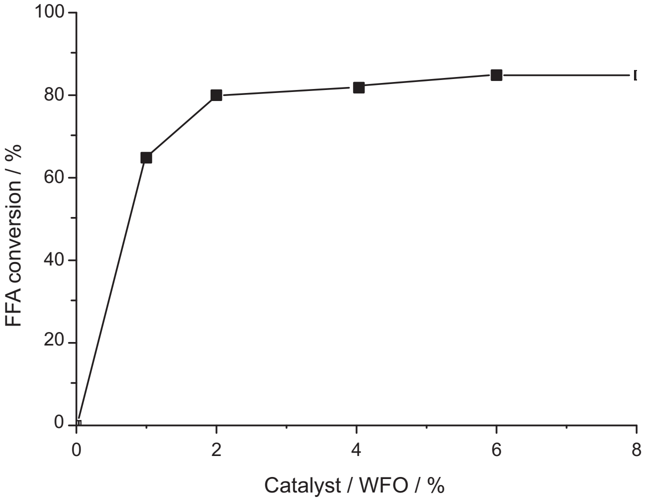

Fig. 8. Effect of catalyst/WFO mass ratio on the FFA esterification catalyzed by SiO_2(HF). Reaction conditions: methanol/WFO ratio = 1/30; reaction time = 4 h; temperature = 70 °C.

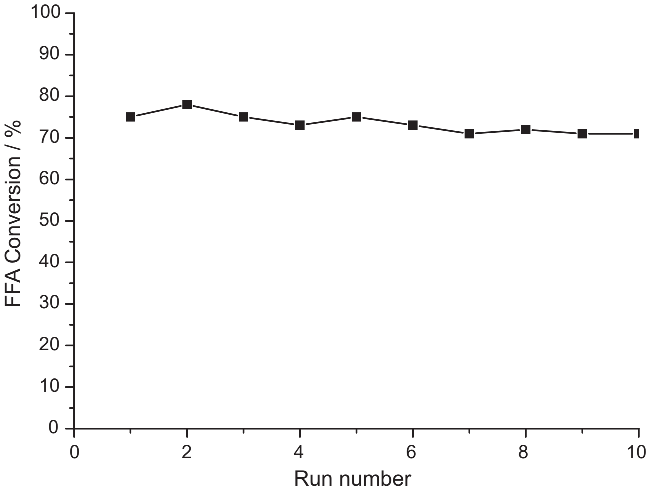

Fig. 9. FFA %conversion evolution as a function of the run number over SiO_2(HF) catalyst.

Table 4
Biodiesel composition determined by gas chromatography (according to the EN 14,103 test method).

Compound	Content (%)
Methyl butyrate	0.04
Methyl hexanoate	0.11
Methyl octanoate	0.08
Methyl tridecanoate	0.08
Methyl pentadecanoate	0.02
Methyl palmitate	0.45
Methyl palmitoleate	8.02
Methyl heptadecanoate	0.08
Methyl elaidate	87.14
Methyl oleate	3.44
Methyl linolaidate	0.08
Other compounds	0.46
Total	100

The FAME in the biodiesel obtained was analyzed using gas chromatography. The chromatogram obtained from the analysis of the biodiesel is represented in Fig. 10. The quantitative and qualitative analysis of the compounds contained in the biodiesel are listed in Table 4. The contents of monoglyceride, diglyceride, triglyceride, free, bound and total glycerin determined according to the ASTM D 6584 test method, are reported in Table 5. In this table it can be observed that the biodiesel obtained presented very low values of these molecules.

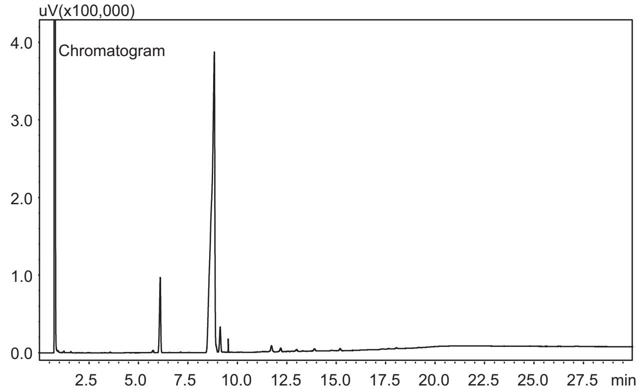

Fig. 10. Chromatogram of biodiesel obtained using SiO_2(HF) catalyst for esterification reaction and NaOH homogeneous catalyst for transesterification reaction.

4. Discussion

The pretreatment of SiO_2 with HF resulted in a strong increase of the surface acid sites, as shown in Table 2. Results in Table 3 show that the use of SiO_2(HF) for esterification resulted in a strong decrease of the content of FFA present in the WFO (86% FFA conversion) related to the use of untreated SiO_2 (10% FFA conversion). These results suggest that the Lewis acid sites of SiO_2(HF) generated during SiO_2 pretrated with HF are responsible of the high catalytic activity for FFA esterification. The decreased SiO_2 surface area should have resulted in a decrease in the SiO_2 activity for the esterification reaction. However, this is not the case. These results can be explained assuming that the strong increase in acid sites generated during the high temperature treatment of SiO_2 impregnated with HF, may largely compensate the loss in surface area.

Now, Liu et al. [21] found that Nafion supported on silica has comparable turnover frequencies (TOF) to H_2SO_4 and a similar reaction mechanism in esterification of the liquid acetic acid with methanol. The reaction occurs via a single site Eley–Rideal mechanism involving a nucleophilic attack between adsorbed carboxylic acid and unadsorbed alcohol as rate-determining step. The formation of a more electrophilic species also occurs with homogeneous and heterogeneous Lewis acid catalysts as the first step in the reaction mechanism [22]. In base of these results, we suggest the mechanism schematized in Fig. 11 for the FFA esterification with methanol catalyzed by SiO_2(HF).

(1) The mechanism follows 5 reaction steps:
(2) FFA adsorption on the acid site of SiO_2(HF).
(3) Formation of the Lewis' complex.

Table 5
Physical and chemical properties of FAME obtained from WFO, using SiO_2 (HF) as catalyst for esterification of FFA and NaOH as catalyst for transesterification of triglycerides with methanol.

Property	Units	Limit values allowed		Biodiesel SiO_2(HF)
		Min	Max	
Density at 15 °C	kg m^{-3}	860	900	870
Kinematic viscosity at 40 °C	$mm^2\ s^{-1}$	3.5	5.0	4.0
Acid number	mg KOH g^{-1}	–	0.5	0.38
Ester content	% (m m^{-1})	96.5	–	99.56
Esters with > 4 double bonds	% (m m^{-1})	–	1	0
Esters from linolenic acid	% (m m^{-1})	–	12.0	0
Monoglyceride	% (m m^{-1})	–	0.8	0.20
Diglyceride	% (m m^{-1})	–	0.2	0.08
Triglyceride	% (m m^{-1})	–	0.2	0.1
Free glycerin	% (m m^{-1})	–	0.02	0.01
Bound glycerin	% (m m^{-1})	–	0.23	0.07
Total glycerin	% (m m^{-1})	–	0.25	0.08

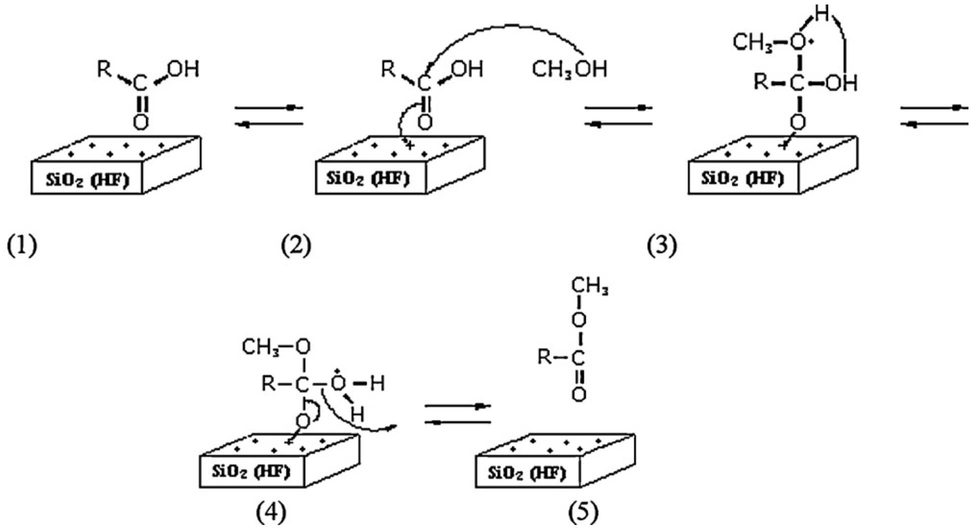

Fig. 11. Proposed mechanism for the FFA esterification catalyzed by SiO_2(HF).

(4) Formation of the methanol nucleophilic bonding.
(5) Formation of the new methylester and H_2O.
(6) Desorption of this methylester from the Lewis site and the cycle is repeated.

After 10 consecutive runs, the SiO_2(HF) catalyst showed the same activity for FFA esterification as shown in Fig. 9. Thus, the amount of catalyst during this reaction may remain unaffected. The catalyst may not be dissolved in the H_2O produced during esterification (Fig. 1, reaction 1) as it has been reported previously for other catalysts such as CaO [23]. This assumption is supported by the results obtained from the temperature programmed desorption experiments over SiO_2(HF). After 10 days of SiO_2(HF) exposure to room air, no desorbed H_2O or CO_2 were detected from 25 to 500 °C. Moreover, FTIR spectra of the catalysts (Fig. 2) showed no signals corresponding to adsorbed CO_2 and H_2O.

The transesterification reaction of the triclycerides in the WFO after the esterification process was performed with the NaOH homogeneous catalyst. Table 5 reports the various values determined from the analysis of the FAME produced. These values show that the process proposed in this investigation can generate biodiesel of a good quality. This process prevents the water waste streams, excess of methanol, high pressure and high cost stainless steel equipment used to eliminate the homogeneous acid catalyst that would be used for the FFA esterification step in the WFO.

5. Conclusions

Biodiesel production costs are rather high compared to petroleum based diesel fuel. The use of waste frying oil (WFO) as feedstock can lower the cost for biodiesel production.

This investigation showed that the use of SiO_2(HF) as esterification catalyst, resulted in a strong decrease of the free fatty acids present in the WFO used as feedstock for the biodiesel production. The high activity of this catalyst is explained on basis of the high number of acid sites present on its surface, which may be responsible of the first step FFA esterification reaction. Results showed that H_2O and CO_2 are not adsorbed over SiO_2(HF). Thus, this catalyst can be used for a high number of esterification cycles without being activated by hydration and carbonation. The second step transesterification reaction of triglycerides present in the WFO catalyzed by NaOH produced a biodiesel with a high content of methyl esters.

Acknowledgements

The authors acknowledge support from FOMIX-CONACYT-Gobierno del Estado de Puebla (Projectos 76981 y 130389), from PROMEP (Proyecto de Redes Tematicas de Colaboracion: Constuccion de un Laboratorio Solar, 2009-2011), and, from Vicerrectoria de Investigacion y Estudios Avanzados, BUAP (Proyecto 31 NAT/10).

References

[1] W. Korbitz, Renew. Energy 16 (1999) 1078–1083.
[2] A.K. Agarwal, L.M. Das, J. Eng. Gas Turbines Power 123 (2001) 440–447.
[3] U.R. Kreutzer, J. Am. Oil Soc. Chem. 61 (1984) 343–348.
[4] M. Di Serio, R. Tesser, L. Pengmei, E. Santacesaria, Energy Fuels 22 (2008) 2007–2014.
[5] A. Brito, M.E. Garin, A. Hernández, Energy Fuels 23 (2009) 2952–2958.
[6] G.W. Huber, S. Iborra, A. Corma, Chem. Rev. 106 (2006) 4044–4098.
[7] A. Demirbas, Energy Convers. Manage. 44 (2003) 2093–2109.
[8] D.G.B. Boocock, S.K. Konar, V. Mao, C. Lee, S. Buligan, J. Am. Oil Soc. Chem. 75 (1998) 1167–1172.
[9] P.R. Muniyappa, S.C. Brammer, H. Noureddini, Bioresour. Technol. 56 (1996) 19–24.
[10] M.P. Dorado, E. Ballesteros, F.J. Lopez, Energy Fuel 18 (2003) 1–16.
[11] G. Antolin, F.V. Tinaut, Y. Briceno, Bioresour. Technol. 83 (2002) 111–117.
[12] Y. Zhang, M.A. Dube, D.D. McLean, Bioresour. Technol. 86 (2003) 1–16.
[13] M.I. Al-Widyan, A.O. Al-Shyoukh, Bioresour. Technol. 85 (2002) 253–256.
[14] G.M. Tashtoush, M.I. Al-Widyan, Energy Convers. Manage. 45 (2004) 2697–2711.
[15] U. Schuchardt, R. Secheli, R.M. Vargas, J. Braz. Chem. Soc. 9 (1998) 199–210.
[16] Y. Zhang, M.A. Dube, D.D. McLean, Bioresour. Technol. 90 (2003) 229–240.
[17] Y. Wang, S. Ou, P. Liu, S. Tang, J. Mol. Catal. A 252 (2006) 107–115.
[18] D.E. Lopez, J.G. Goodwin Jr., D.A. Bruce, J. Catal. 245 (2007) 381–389.
[19] J.M. Marchetti, V.U. Miguel, A.F. Errazu, Fuel 86 (2007) 906–911.
[20] H. Fukuda, A. Kondo, H. Noda, J. Biosci. Bioeng. 92 (2001) 405–416.
[21] Y. Liu, E. Lotero, J.G. Goodwin Jr, J. Mol. Catal. A 245 (2006) 132–140.
[22] B. Bonelli, M. Cozzolino, R. Tesser, M. DiSerio, M. Garrone, E. Santacesaria, J. Catal. 246 (2007) 293–300.
[23] M. Lopez-Granados, M.D. Zafra-Poves, D. Martin-Alonso, F. Cabello-Galisteo, R. Moreno-Tost, J. Santamaria, J.L.G. Fierro, Appl. Catal. B 73 (2007) 317–325.