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# Valorization of Waste Cooking Oil into Biodiesel over Heteropolyacids Immobilized on Mesoporous Silica — A Kinetic Study

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Additional information is available at the end of the chapter

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## 1. Introduction

Biodiesel is a source of energy derived from renewable sources, which can be a substitute for diesel fuel. It is biodegradable, and it has limited greenhouse gas emissions because of the closed CO<sub>2</sub> cycle and a lower combustion emission profile (especially SO<sub>x</sub>). Biodiesel consists of fatty acid alkyl esters (usually methyl esters, FAME) derived from either the transesterification of triglycerides and/or the esterification of free fatty acids (FFAs) with low molecular weight alcohols [1-3].

Traditionally, the production of biodiesel is carried out in the presence of a homogeneous base catalyst; however, effluent disposal leads to environmental problems and economical inconveniences. These problems can be overcome by the use of heterogeneous catalysts. Another problem with commercial production of biodiesel is the high cost of raw materials. In order to overcome this problem, waste oils and fats can be used as feedstocks [4-7]. However, waste cooking oils contain a high amount of free fatty acids, which is a problem for biodiesel production by the traditional process (homogeneous alkali-catalyzed transesterification) [8,9]. Different solid acids such as resins with sulfonic acid groups [10-14], zeolites [15-17], solid super acid catalysts [18] and carbonaceous catalysts [19] have been used as catalysts in the conversion of waste cooking oil containing a high amount of free fatty acids into biodiesel.

Heteropolyacids (HPAs) have several advantages as catalysts, which make them economically and environmentally attractive. On the one hand, HPAs have a very strong Bronsted acidity, approaching the superacid region; on the other, they are efficient oxidants, exhibiting fast reversible multielectron redox transformations under rather mild conditions. Their acid-base and redox properties can be varied over a wide range by changing the chemical composition.

Solid HPAs possess a discrete ionic structure, comprising fairly mobile basic structural units, e.g., heteropolyanions and counter cations ( $H^+$ ,  $H_3O^+$ ,  $H_5O_2^+$ , etc.) unlike the network structure of, e.g., zeolites and metal oxides [20-22]. HPAs have low specific surface areas ( $1-10\text{ m}^2/\text{g}$ ). In order to increase the specific area of HPAs or, even better, to increase the number of accessible acid sites of the HPAs, a variety of supports like activated carbon [23-26], silica [27-32], zeolite [33-38] and polymeric matrix [39-43] have been used as support to immobilize HPAs.

HPAs and HPAs supported on different supports have been used as acid catalysts for biodiesel production [44-48].

Transesterification of waste cooking oil with high acid value and high water content was performed using heteropolyacid  $H_3PW_{12}O_{40}\cdot 6H_2O$  (PW) as homogeneous catalyst. PW was found to be the most promising catalyst, which exhibited the highest ester yield (87%) for transesterification of waste cooking oil and an ester yield of 97% for esterification of long-chain palmitic acid. The PW acid catalyst showed higher activity under the optimized reaction conditions compared with the conventional homogeneous catalyst sulfuric acid, and it can easily be separated from the products by distillation of the excess methanol and can be reused several times [45].

Biodiesel production in the presence of 20 wt% myristic acid from soybean oil was carried out over heteropolyacid immobilized on mesoporous  $Ta_2O_5$  materials. Different catalysts were prepared. The network structures of the hybrid materials and the functions of the incorporated alkyl groups on the catalytic activity of the materials have been put forward [46].

Biodiesel synthesis from waste cooking oil was carried out over 12-tungstosilicic acid on SBA-15. The heteropolyacid was prepared using impregnation method. The effect of different reaction parameters like percentage loading, catalyst amount, mole ratio, time and temperature were studied for the supreme conversion. The catalyst was recycled up to four times after simple workup without notable loss in the activity [48].

In this work, we report the transesterification of waste cooking oil with different alcohols over heteropolyacids immobilized on SBA-15. We also studied the effect of free fatty acid addition into waste cooking oil. A kinetic model is proposed.

## 2. Waste cooking oil raw converted to biofuel

The McDonald's Corporation is the world's largest chain of fast-food restaurants, serving around 68 million customers daily in 119 countries across 35,000 outlets [49]. The waste cooking oil in about 90% of McDonald's restaurants is used for after-market uses, including biodiesel. The used cooking oil from the restaurants is collected, recycled into biodiesel, and put back into distributors' trucks to fuel their deliveries to McDonald's restaurants. In a few countries, McDonald's waste cooking oil are a closed-loop system. Since 2013, McDonald's developmental licensee in the United Arab Emirates operates a 100% closed-loop biodiesel system. More than 25,000 liters of waste cooking oil are being collected from McDonald's approximately 108 restaurants each month and converted into biodiesel. Waste cooking oil is stored at the

restaurants in a specially designed container. 1.75 million liters of biodiesel have been generated from waste cooking oil and used to power the distribution fleet. Excess biodiesel can be sold, helping other companies reduce their transportation impacts. In the United Kingdom (in 2013), McDonald's replaced more than 3 million liters of diesel fuel with biofuel made from used cooking oil collected at approximately 1,200 restaurants. Across markets in Europe, the waste cooking oil from more than 80% of the McDonald's Europe restaurants is being converted into biodiesel. In Brazil 19 restaurants are participating in a closed-loop system that has recycled more than 187,000 liters of used cooking oil into 65,000 liters of biodiesel since 2009, for use in five trucks that deliver to the restaurants [50].

### 3. Experimental

#### 3.1. Catalyst preparation

Mesoporous silica SBA-15 was prepared according to the literature [51]. An ethylene oxide (EO)/propylene oxide (PO) triblock copolymer (P123) with composition EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> and with an average molecular weight of 5800 was used as the template. The synthesis consisted of 2.0 g of triblock P123 dissolved in 60 cm<sup>3</sup> of 2 mol.dm<sup>-3</sup> aqueous HCl and 15 cm<sup>3</sup> of distilled water under stirring. Then, 4.4 g of tetraethyl orthosilicate (TEOS) was added dropwise to the solution at room temperature. The mixture was stirred for 24 h at 313 K, and then the temperature was raised to 373 K and kept at 373 K for another 24 h in a Teflon-lined autoclave. Finally, the resulting precipitate was filtered, washed carefully with distilled water, air-dried, and calcined at 773 K in air for 5 h to remove the template and to obtain the final product SBA-15.

The heteropolyacid was immobilized on SBA-15 by the grafting technique. The grafting of tungstophosphoric acid (PW) was carried out by mixing 2.0 g dried SBA-15 with 3-aminopropyltriethoxysilane (23.4  $\mu$ L) containing freshly distilled toluene refluxing for 48 h. The obtained solid material was immersed in an aqueous solution of PW with stirring for 5 h. The solid was then dried in vacuum to obtain the heteropolyacid anchored mesoporous catalyst [52].

#### 3.2. Catalyst characterization

The textural characterization of the catalysts was based on the nitrogen adsorption isotherm, determined at 77 K with a Micromeritics ASAP 2010 apparatus.

The FTIR spectra were recorded with a Bio-Rad FTS 155 instrument.

The amount of W in silica catalysts was measured by dissolving the catalyst in H<sub>2</sub>SO<sub>4</sub>/HF 1:1 (v/v) and analyzing the obtained solution using inductively coupled plasma analysis (ICP), which was carried out in a Jobin-Yvon ULTIMA instrument.

The X-ray diffraction (XRD) patterns of the heteropolyacid, silica and catalysts were obtained by using a Bruker powder diffractometer with built-in recorder, using Cu K $\alpha$  radiation, nickel filter, 30 mA and 40 kV in the high voltage source, and scanning angle between 0.7° and 5° of 2 $\theta$  at a scanning rate of 1°/min.

Transmission electron microscopy (TEM) analyses were performed on a Hitachi S-2400 scanning electron microscope, at a current voltage of 25 kV.

Catalyst acidity was measured by means of potentiometric titration [53].

3.3. Catalytic experiments

The catalytic experiments were carried out in a stirred batch reactor at 60°C. In a typical experiment, the reactor was loaded with 30 mL of methanol and 0.2 g of catalyst. Reactions were started by adding 2.5 ml waste cooking oil (WCO).

Stability tests of the catalyst were carried out by running four consecutive experiments, using the same reaction conditions. Between the catalytic experiments, the catalyst was separated from the reaction mixture by filtration, washed with acetone and methanol and dried at 70° C overnight.

In order to study the reusability, the PW-NH<sub>2</sub>-SBA-15 catalyst was filtered from the reaction mixture. After this operation, it was soaked in hexane overnight and it was dried overnight.

Undecano was used as the internal standard. Samples were taken periodically and analyzed by GC, using a Hewlett Packard instrument equipped with a 30 m x 0.25 mm HP-5 column.

4. Results and discussion

4.1. Catalyst characterization

SBA-15 and PW-NH<sub>2</sub>-SBA-15 catalysts showed a typical IV adsorption isotherm with H1 hysteresis loop as defined by IUPAC. It was observed that the specific surface area and total pore volume of SBA-15 decreased with the immobilization of PW on SBA-15 (Table 1).

	PW load <sup>a</sup> (wt%)	Surface area <sup>b</sup> (m <sup>2</sup> /g)	V <sub>Tc</sub> (cm <sup>3</sup> /g)
SBA-15	-	1050	1.38
PW-NH <sub>2</sub> -SBA-15	5.6	735	0.62

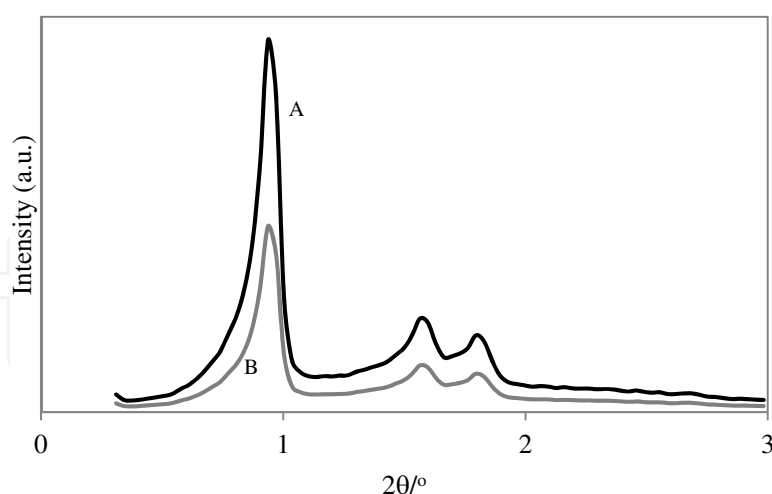
<sup>(a)</sup>HPA load determined by ICP analysis

<sup>(b)</sup> BET

<sup>(c)</sup> (p/p°) = 0.98

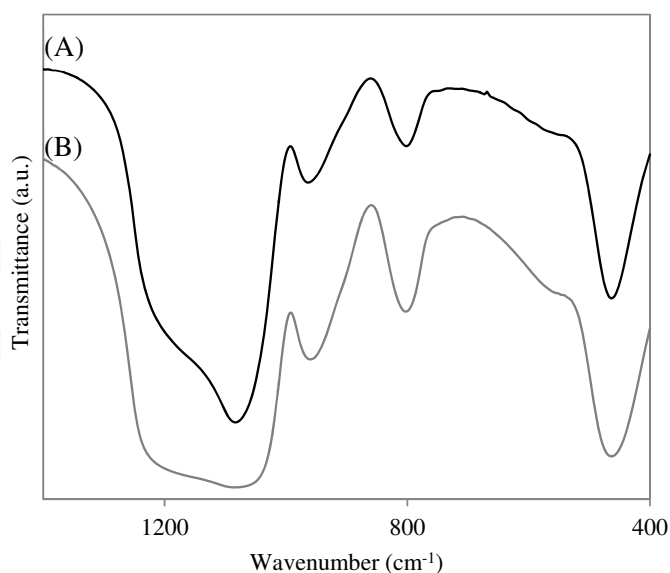
Table 1. Physicochemical characterization of SBA-15 and PW-NH<sub>2</sub>-SBA-15

X-ray diffraction patterns of the SBA-15 and PW-NH<sub>2</sub>-SBA-15 catalysts are shown in Figure 1. All three reflections are still detectable after PW immobilization, suggesting that hexagonal pore structure of the support is retained.



**Figure 1.** X-ray diffractograms of SBA-15 (A) and PW-NH<sub>2</sub>-SBA-15 (B).

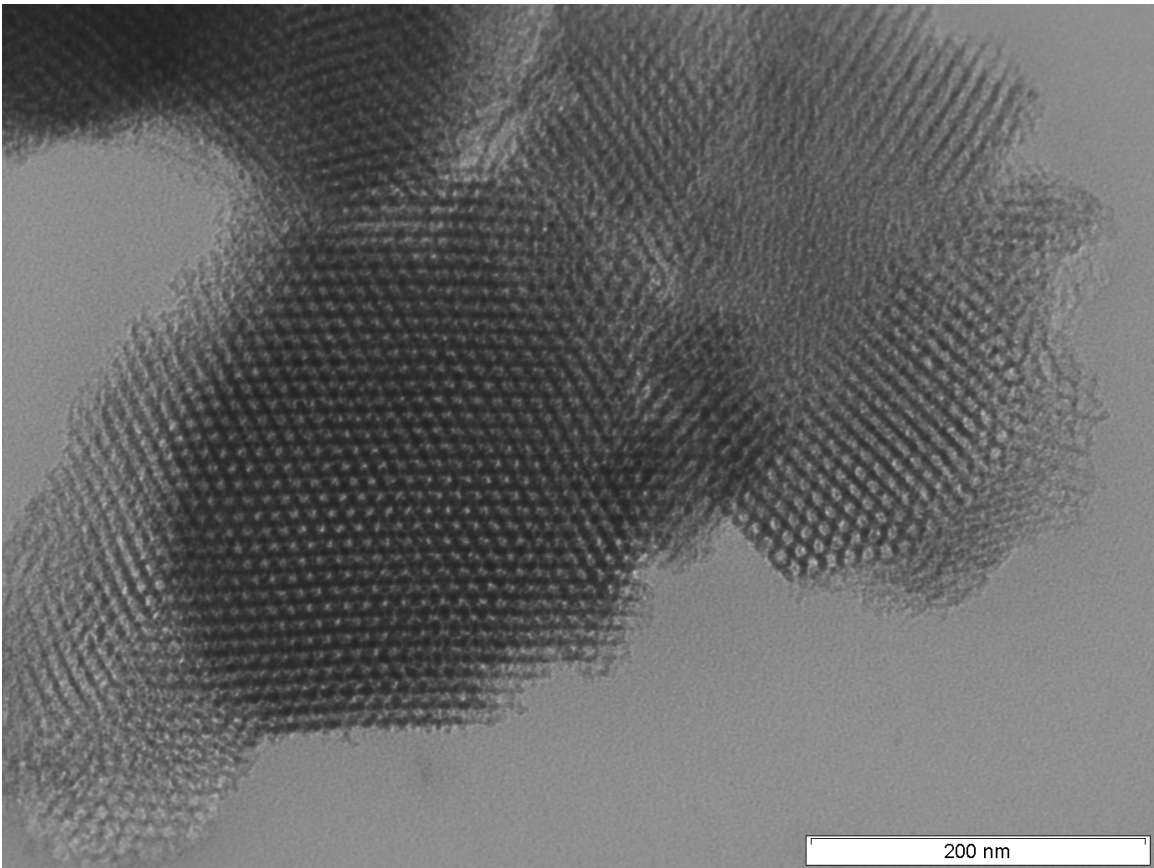
Figure 2 shows the FT-IR spectra of SBA-15 and PW-NH<sub>2</sub>-SBA-15 samples. For SBA-15 bands were observed at 1084, 812 and 476 cm<sup>-1</sup>, which are attributed to asymmetric stretching, symmetric stretching and bending modes of Si-O-Si, respectively. For PW-NH<sub>2</sub>-SBA-15 catalyst the characteristic bands of SBA-15 are present along with the bands at 1083, 982, 890 and 808 cm<sup>-1</sup>, which are the fingerprint of Keggin structure of HPW. However, some bands typical of the Keggin-type HPA structures are overlapped or partially overlapped with the bands of the SBA-15 matrix framework, probably due to the low loading of PW. Similar results were also observed by Liu et al. [52].



**Figure 2.** FT-IR spectra of catalysts: (A) SBA-15 and (B) PW-NH<sub>2</sub>-SBA-15.

TEM image of PW-NH<sub>2</sub>-SBA-15 catalyst was carried out. The morphology of the support remains after immobilization of PW on SBA-15 (Fig. 3).





**Figure 3.** Transmission electron microscopy (TEM) image of PW-NH<sub>2</sub>-SBA-15.

Table 2 shows the initial electrode potential ( $E_i$ ) of the materials. The  $E_i$  indicates the maximum acid strength of the surface sites [53]. It can be observed that  $E_i$  increased with the amount of PW immobilized in SBA-15, which can be due to the increase in the amount of protons with PW loading of the SBA-15 support.

Sample	$E_i$ (mV)
SBA-15	+110
PW-NH <sub>2</sub> -SBA-15	+408

**Table 2.** Initial electrode potential (mV) of materials

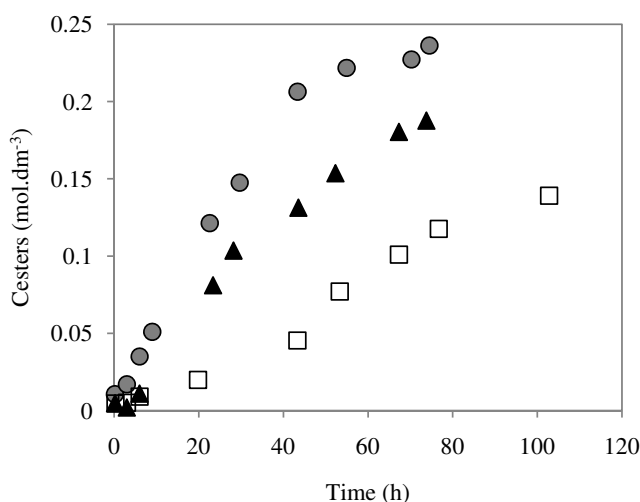
**4.2. Catalytic experiments**

The biodiesel production from WCO was carried out over PW-NH<sub>2</sub>-SBA-15 catalyst at 60°C. Different catalytic experiments were carried out at different stirring speeds to study the influence of external resistances to mass transfer. It was observed that experiments carried out with 700 rpm have got a good mix of the compounds and eliminate possible mass transfer problems.

### 4.3. Effect of the nature of alcohol

The alcohols most frequently used in biodiesel production are methanol and ethanol. Due to the low cost of methanol, this alcohol is the first choice for the esterification/transesterification reactions of WCO. However, for biodiesel production to be more environment friendly, ethanol is the ideal candidate for the synthesis of a fully biogenerated biodiesel, since ethanol is derived from agricultural products (renewable sources) [3].

Figure 4 shows the effect of the nature of alcohol (methanol, ethanol and 1-propanol) on the fatty acid ester concentrations obtained over PW-NH<sub>2</sub>-SBA-15 catalyst, at 60°C. It was observed that the ester concentrations obtained with 1-propanol led to lower conversion, when compared with methanol and ethanol. Similar results were also observed by Sreeprasanth et al. [54], on the transesterification of rubber seed with ethanol over Fe-Zn-1 catalyst. This behavior can be explained not due to the reaction rate with ethanol is slower than with methanol, as ethyl nucleophile is less reactive than methyl nucleophile.



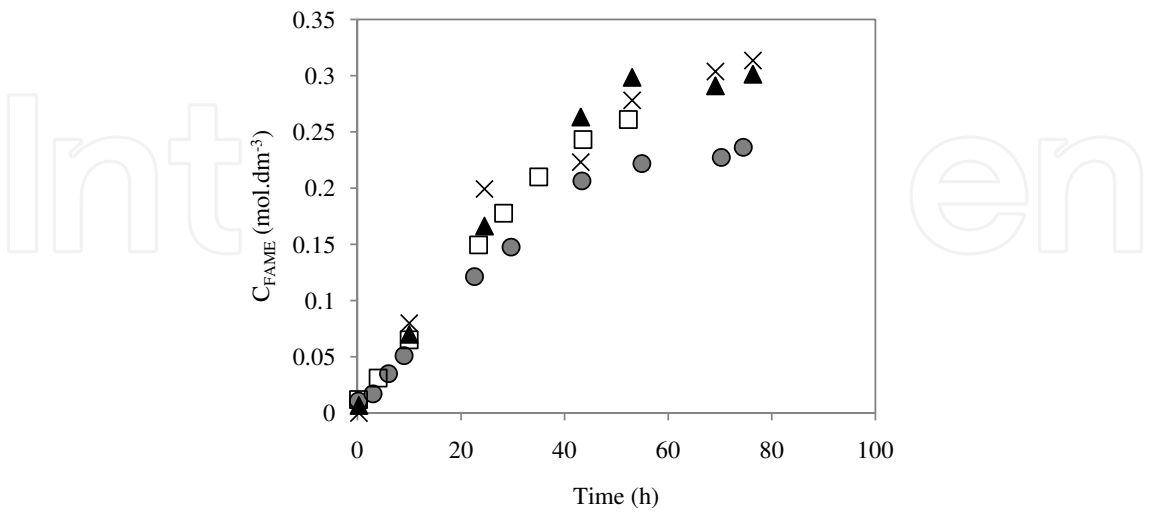
**Figure 4.** Biodiesel production from WCO with methanol over PW-NH<sub>2</sub>-SBA-15 catalyst. Effect of alcohol nature. FAME concentration (mol.dm<sup>-3</sup>) versus time (h): (○) Methanol; (▲) Ethanol; (□) 1-Propanol.

### 4.4. Effect of the initial amount of free fatty acid

In order to study the influence of the initial free fatty acid amount in the WCO, three different amounts of fatty acid (as a model) was added to the reaction mixture. The catalytic experiments were carried out at different amounts of initial palmitic acid in the WCO, over PW-NH<sub>2</sub>-SBA-15 catalyst, while the initial concentration of WCO (0.088mol.dm<sup>-3</sup>) and the catalysts loading (m=0.2 g) were kept constant. Figure 5 shows the influence of the initial amount of FFA in WCO on the biodiesel production. It was observed that the initial reaction rate increases with the amount of FFA. When the initial amount of FFA increases, a slight increase on the conversion was observed. Similar results were also observed by Marchetti and Errazu [16]. Therefore, this effect could also be seen on the total FAME production since the final amount



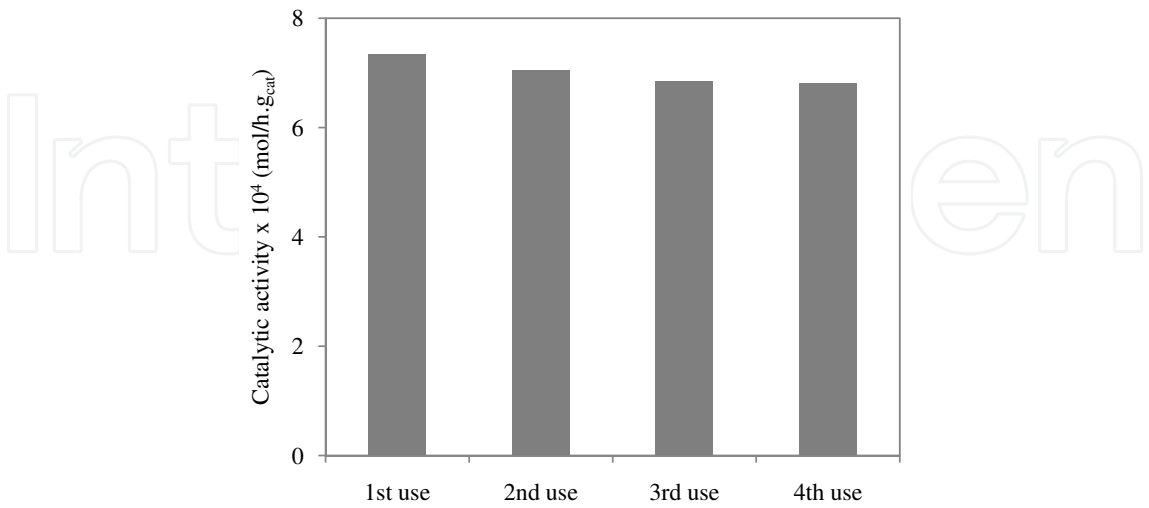
of biofuel will be produced from the triglycerides as well as from the fatty acids present in the reaction mixture.



**Figure 5.** Biodiesel production from WCO with methanol over PW-NH<sub>2</sub>-SBA-15 catalyst. Effect of the amount of palmitic acid. FAME concentration ( $\text{mol}\cdot\text{dm}^{-3}$ ) versus time (h): ( $\circ$ ) 0%; ( $\square$ ) 4%; ( $\blacktriangle$ ) 12 % ; ( $\times$ ) 27 %.

4.5. Catalyst stability

In order to study the catalytic stability of the PW-NH<sub>2</sub>-SBA-15, different batch runs with the same catalyst sample and under the same conditions were carried out. Figure 6 shows the catalytic activity of PW-NH<sub>2</sub>-SBA-15 at different batch runs. It was observed that the catalytic activity decreases only about 10%, after the fourth use.

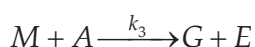
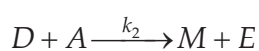
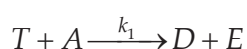


**Figure 6.** Catalytic stability of PW-NH<sub>2</sub>-SBA-15 catalyst in biodiesel production with methanol. The initial activities are taken as the maximum observed reaction rate, which was calculated from the maximum slope of the methyl ester kinetic curve.

#### 4.6. Kinetics modeling

A simple kinetic model can be established based on the following assumptions:

1. Isothermal and isobaric reaction conditions;
2. First order kinetics with respect to the reactants is assumed. The forward and reverse reactions follow second order overall kinetics;
3. Due to the excess of methanol used, the reverse reaction could be minimized and it was not considered in the reaction rate.
4. Triglycerides are consumed according to the consecutive reaction network:



where T represents triglycerides, D represents diglycerides, M represents monoglycerides, A represents alcohol, G represents glycerol and E represents esters of fatty acids;

The reaction rate of these three pseudo elementary reaction are expressed as:

$$r_1 = k_1 C_T \cdot C_A \quad (1)$$

$$r_2 = k_2 C_D \cdot C_A \quad (2)$$

$$r_3 = k_3 C_M \cdot C_A \quad (3)$$

For batch reactor the mole balance equations may be written as

$$\frac{dC_T}{dt} = -\frac{W}{V} (r_1) \quad (4)$$

$$\frac{dC_A}{dt} = -\frac{W}{V} (r_1 + r_2 + r_3) \quad (5)$$

$$\frac{dC_D}{dt} = \frac{W}{V} \cdot (r_1 - r_2) \quad (6)$$

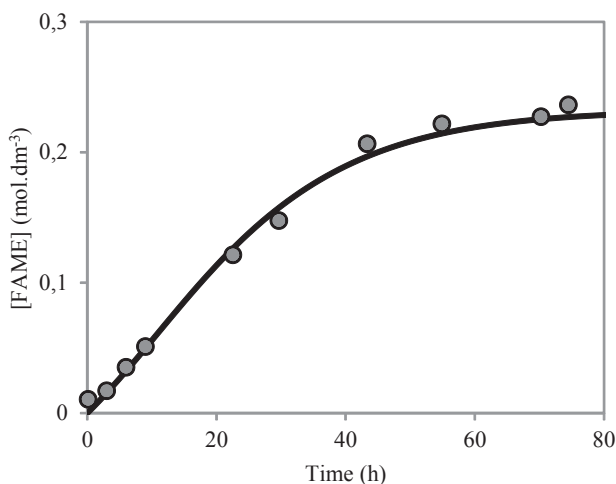
$$\frac{dC_M}{dt} = \frac{W}{V} \cdot (r_2 - r_3) \quad (7)$$

$$\frac{dC_G}{dt} = \frac{W}{V} (r_3) \quad (8)$$

$$\frac{dC_E}{dt} = \frac{W}{V} (r_1 + r_2 + r_3) \quad (9)$$

The differential equations system was integrated using the Euler Method. The optimization was carried out by the *SOLVER* routine in a *Microsoft Excel* spreadsheet.

Figure 7 shows the concentration of fatty acid methyl ester (FAME) *versus* time (h) on the transesterification of WCO with methanol. The solid line represents the model fitted to the data points. It was observed that the kinetic model fits experimental concentration data quite well. The model parameters,  $k_1$ ,  $k_2$  and  $k_3$ , have got the value of 0.00979, 0.01348 and 0.01956  $\text{dm}^6 \cdot \text{mol}^{-1} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ , respectively. It was observed that  $k_1 < k_2 < k_3$ , which can be explained due to the molecular size of monoglycerides, diglycerides and triglycerides and due to the textural characteristics of PW-NH<sub>2</sub>-SBA-15. The size of monoglycerides is smaller than that of diglycerides and triglycerides. Consequently, it is expected that, near the active sites of catalyst, the amount of monoglycerides is higher than the amount of diglycerides and triglycerides. As the reaction rate is dependent on reactant concentration, a high concentration of monoglycerides leads to high reaction rates.



**Figure 7.** Concentration of FAME ( $\text{mol} \cdot \text{dm}^{-3}$ ) versus time (h).

## 5. Conclusions

Biodiesel production from WCO with methanol was carried out over tungstophosphoric acid immobilized on SBA-15 by grafting technique, at 60°C. After PW immobilization, the morphology of the support remained.

In order to optimize the conditions, the influence of various reaction parameters, the nature of alcohol and the amount of initial free fatty acid on the transesterification of WCO in the presence of PW-NH<sub>2</sub>-SBA-15 catalyst were carried out. The catalytic stability of the material was also studied.

The esterification/transesterification of WCO with propanol and ethanol led to lower concentration of fatty acid esters than with methanol.

When different amounts of free fatty acids (palmitic acid) were added to the WCO, a slight increase on the concentration of FAME was observed.

In order to study the catalytic stability of PW-NH<sub>2</sub>-SBA-15 catalyst, four consecutive batch runs were carried out. It was observed that the catalytic activity of PW-NH<sub>2</sub>-SBA-15 tends to stabilize.

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