

## USE OF HETEROGENEOUS CATALYSTS IN METHYLIC BIODIESEL PRODUCTION INDUCED BY MICROWAVE IRRADIATION

Evandro L. Dall'Oglio<sup>\*a</sup>, Paulo T. de Sousa Jr.<sup>a</sup>, Pedro Tiago de Jesus Oliveira<sup>a</sup>, Leonardo Gomes de Vasconcelos<sup>a</sup>, Carlos Adriano Parizotto<sup>a</sup> and Carlos Alberto Kuhnen<sup>b</sup><sup>a</sup>Departamento de Química, Universidade Federal do Mato Grosso, Av. Fernando Corrêa da Costa s/n, Cidade Universitária, Cuiabá – MT, Brasil<sup>b</sup>Departamento de Física, Universidade Federal de Santa Catarina, Campus Universitário Trindade, Florianópolis – SC, Brasil

Recebido em 10/06/2013; aceito em 23/11/2013; publicado na web em 26/02/2014

The effect of different heterogeneous catalysts on the microwave-assisted transesterification of sunflower oil for the production of methylic biodiesel in a monomode microwave reactor is described. The experiments were carried out at 70 °C with a 16:1 methanol-sunflower oil molar ratio and different heterogeneous basic and acidic catalysts. The results showed that the microwave-heated reactions occur up to four times faster than those carried out with conventional heating. The reactions were performed with 24 catalysts; pure calcium oxide (CaO) and potassium carbonate, either pure or supported by alumina ( $K_2CO_3/Al_2O_3$ ), were the most efficient catalysts.

Keywords: heterogeneous catalysts; transesterification; microwave irradiation.

## INTRODUCTION

The environmental and economic issues raised by the rapid growth of the global population coupled with industrial and technological developments and the rapid depletion of limited fossil fuel resources are all driving factors for the search for new renewable sources of energy.<sup>1-3</sup> Biodiesel, which is synthesized from vegetable oil, is one such source and is a realistic alternative to diesel fuel since it is produced from renewable resources and has lower emissions than petroleum diesel. Biodiesel consists of fatty acid alkyl esters mainly derived from vegetable oils and some animal fats and is biodegradable, non-toxic, and non-inflammable. Furthermore, it has a good combustion-emission profile, producing less carbon monoxide and unburned hydrocarbons than fossil fuels, and its burning does not result in sulfur dioxide production. Biodiesel is a very promising alternative fuel since the technologies related to other alternative fuel sources are still developing and expensive.<sup>1</sup>

The methods most commonly used for biodiesel production involve transesterification reactions. They are performed under basic or acidic conditions and involve the reaction of alkyl alcohols with vegetable oils or animal fats to yield monoalkyl esters and glycerol. The catalysts typically used in the transesterification process are homogeneous alkaline catalysts such as NaOH or KOH<sup>1,2</sup> and acid catalysts such as  $H_2SO_4$  or HCl.<sup>1,4</sup> The alkaline catalyzed transesterification process is usually the method adopted for large scale biodiesel production. If a high concentration of free fatty acids is present, as in low cost raw materials or waste frying oils, then an acid catalyst must be employed.<sup>1</sup> NaOH or KOH are commonly used as base catalysts, but some difficulties, such as soap formation, can arise during biodiesel production. This is an undesirable side reaction because it partially consumes the catalyst, decreases the biodiesel yield, and complicates the separation and purification steps. Moreover, the difficulty associated with recycling and generating large amounts of waste make these traditional catalysts less favorable. Acidic catalysts are also used for the transesterification reaction. Despite the increased biodiesel yield when low-priced raw materials such as frying oils are

used, homogeneous acid catalyzed reactions are much slower than the alkali catalyzed reactions, requiring higher temperatures and pressures.<sup>5,6</sup> Some of the inherent difficulties of this process can be avoided using heterogeneous catalysis rather than homogeneous base or acid catalysts for biodiesel production.

In fact, there are several advantages to heterogeneous catalysts.<sup>1,2</sup> They are reusable, noncorrosive, and may improve the biodiesel yield and purity, showing a greater tolerance for water and free fatty acids (FFAs) in the feedstock. Finally, the use of a heterogeneous catalyst allows for a simpler purification process for glycerol, facilitating its separation from the biodiesel product. Many studies describing the use of different heterogeneous catalysts for the transesterification of oils have been recently reported in the literature.<sup>7-17</sup> For example, alkaline earth metal oxide catalysts can catalyze transesterification reactions. The order of effectiveness for the alkaline earth metal oxide catalysts is  $BaO > SrO > CaO > MgO$  for the transesterification of *Camelina sativa* oil in methanol.<sup>16</sup> However, BaO is noxious and can be dissolved by methanol, and, therefore, it is not suitable for biodiesel production. SrO,<sup>12,18</sup> MgO,<sup>16,19</sup>  $K_2CO_3/Al_2O_3$ , KOH/ $Al_2O_3$ ,<sup>9,20</sup> CaO,<sup>7,10,17,21</sup> KI/ $Al_2O_3$ ,<sup>9</sup> CaO/ $TiO_2$ ,<sup>22</sup> montmorillonite,<sup>23</sup>  $H_2SO_4/TiO_2$ ,<sup>24</sup> calcium zincate,<sup>25</sup> and  $La_2O_3$ <sup>26</sup> have all been used as heterogeneous catalysts for the production of biodiesel with high conversion, but they all had low reaction rates when conventional heating was applied. To overcome the characteristic reaction drawbacks associated with conventional heating in heterogeneous base or acid catalyzed transesterification of triacylglycerides, i.e., long reaction times, our group has been using microwave radiation to increase the reaction rates.<sup>27</sup>

Microwave irradiation has been used as an alternative heating system for transesterification over the past few years and is reputed to have a high synthesis potential.<sup>28</sup> In this regard, the application of microwave heating has been reported as a fast and easy method to obtain biodiesel via homogeneous acid catalyzed reactions,<sup>27</sup> homogeneous alkaline catalyzed reactions,<sup>29-36</sup> and heterogeneous catalyzed reactions.<sup>37-42</sup> Heterogeneous or homogeneous catalytic transesterification of triglycerides induced by microwaves may be a viable alternative technology for ethylic biodiesel production, especially in Brazil, one of the world's largest producers of ethanol. The transesterification reaction consists of three equivalent, consecutive, and

\*e-mail: dalloglio.evandro@gmail.com

reversible reactions. The overall reaction occurs in three steps. The triglyceride (TG) is converted stepwise to a diglyceride (DG), monoglyceride (MG), and, finally, glycerol (GL) and an alkyl ester. At each stage one molecule of alkyl ester is produced. In this study, the effects of various heterogeneous catalysts on the microwave-assisted transesterification of sunflower oil for the production of methyl biodiesel in a monomode microwave reactor were investigated. The transesterification reactions were carried out with the following supported and non-supported catalysts: KI/Al<sub>2</sub>O<sub>3</sub>, KOH/Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, CaO, CaO/Al<sub>2</sub>O<sub>3</sub>, CaO/MnO<sub>2</sub>, CaO/TiO<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>/ZnSO<sub>4</sub>, KOH/ZnSO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>/TiO<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> (base), Al<sub>2</sub>O<sub>3</sub> (acid), CuSO<sub>4</sub>, Al<sub>2</sub>Cl<sub>3</sub>, MgO, MnO<sub>2</sub>, montmorillonite, purolite, CaCl<sub>2</sub>, FeCl<sub>2</sub>, ZnCl<sub>2</sub>, TiO<sub>2</sub>, and ZnSO<sub>4</sub>.

## EXPERIMENTAL SECTION

### Materials

Refined commercial sunflower oil purchased from a supermarket in Cuiabá, Mato Grosso State, Brazil was used in this study. The main chemical composition (fatty acid composition, wt%) of sunflower oil is reported in the literature,<sup>43,44</sup> and its density<sup>43</sup> and mean molecular weight<sup>44</sup> are 0.92 g cm<sup>-3</sup> and 861,22 g mol<sup>-1</sup> respectively.

Methanol (99.8%), CDCl<sub>3</sub> (99.8%), and neutral Al<sub>2</sub>O<sub>3</sub> were purchased from Tedia, Cambridge Isotope Laboratories, Inc. and Vetec, respectively. The supported catalysts, KI/Al<sub>2</sub>O<sub>3</sub>, KOH/Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, CaO/Al<sub>2</sub>O<sub>3</sub>, CaO/MnO<sub>2</sub>, CaO/TiO<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>/ZnSO<sub>4</sub>, KOH/ZnSO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub>/TiO<sub>2</sub>, were obtained via sedimentation followed by calcination of the catalyst active mass on the mounting surface, as described below.

Reagent A was diluted in a sufficient amount of water to obtain a saturated solution. This was followed by addition of reagent B and stirring for homogenization. The mixture was subsequently dried in an oven and calcined in a muffle furnace. The reaction conditions are described in Table 1.

**Table 1.** Reaction conditions for Catalyst Preparation. N.A.: Does not apply

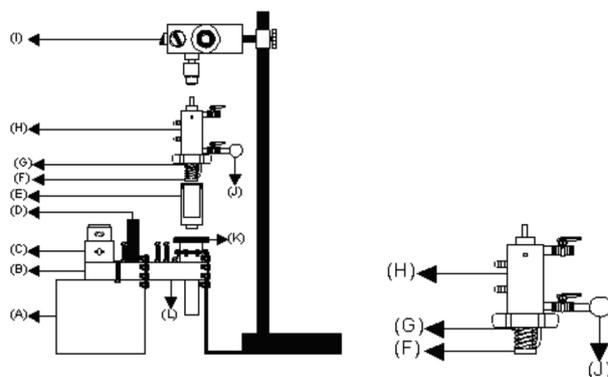
Reagent A(g)/Reagent B(g)	Oven (°C) / Time (h)	Muffle (°C) / Time (h)
KI (10.0)/ Al <sub>2</sub> O <sub>3</sub> (50.0)	120/12	500/3
KOH (10.0)/ Al <sub>2</sub> O <sub>3</sub> (50.0)	120/12	500/3
K <sub>2</sub> CO <sub>3</sub> (10.0)/ Al <sub>2</sub> O <sub>3</sub> (50.0)	120/12	550/2
CaO (2.5)/ Al <sub>2</sub> O <sub>3</sub> (7.5)	N.A.	1050/2
CaO (7.8)/ Al <sub>2</sub> O <sub>3</sub> (12.2)	N.A.	1050/2
CaO (9.4)/TiO <sub>2</sub> (10.6)	N.A.	1050/2
K <sub>2</sub> CO <sub>3</sub> (10)/ZnSO <sub>4</sub> (50)	120/24	550/5
KOH(10)/ZnSO <sub>4</sub> (50)	120/24	550/5

H<sub>2</sub>SO<sub>4</sub>/TiO<sub>2</sub> was prepared by the addition of TiO<sub>2</sub> (50.0 g) to a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (500.0 mL). After 24 h the mixture was filtered and calcined for 3 h at 550 °C in a muffle furnace. The other heterogeneous catalysts, CaO, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> (base), Al<sub>2</sub>O<sub>3</sub> (acid), CuSO<sub>4</sub>, Al<sub>2</sub>Cl<sub>3</sub>, MgO, MnO<sub>2</sub>, Montmorillonite, Purolite, CaCl<sub>2</sub>, FeCl<sub>2</sub>, ZnCl<sub>2</sub>, TiO<sub>2</sub>, and ZnSO<sub>4</sub>, were dried in an oven at 150 °C for 2 h.

### Equipment

The transesterification reactions carried out under microwave irradiation were performed in the monomode reactor outlined in Figure 1.

The apparatus consists of a Teflon reactor, working as a



**Figure 1.** Monomode reactor: (A) High voltage system; (B) Inox 304 Launcher WR 340; (C) Magnetron valve; (D) MicroFan; (E) Teflon reactor; (F) Teflon stirring paddle; (G) Cooling coil (304 stainless steel); (H) Condenser; (I) Mechanical stirrer; (J) Insertion point of thermocouple type PT 100; (K) Connection flange; (L) Waveguide WR340 (304 stainless steel)

monomode resonant cavity, supplied with electromagnetic irradiation by a magnetron valve emitting at 2.45 GHz with a nominal power of 800 W and equipped with a high voltage system that supplies the magnetron, condenser coupled with a thermal bath (not shown in Figure 1), and mechanical stirrer. Nine calorimetric measurements were carried out (each one in triplicate) to determine the effective power emitted by the magnetron and absorbed by the sample (40 mL of water irradiated for 20 seconds) in the monomode reactor. The result obtained for the effective power absorbed by the sample was 470 W (average over nine measurements). The details of the construction, calorimetric measurements, and applicability of the monomode, 5 L, and 100 L multimode reactors will be published elsewhere.

<sup>1</sup>H NMR analyses were performed in a VARIAN mercury 300 NMR apparatus at the Department of Chemistry at the Federal University of Mato Grosso State (UFMT), Brazil.

### Transesterification process

The transesterification reactions were induced by microwave dielectric heating and catalyzed using the heterogeneous catalysts prepared in this study. Sunflower oil (24 mL or 22 g), catalyst (0.9, 1.8, 2.5, and 3.6 g), and methanol (16 mL) were poured into the reactor. The mass of the above supported catalysts corresponded to 2.5, 5.0, 6.9, and 10 wt% of the entire mass of oil and methanol. The catalyst-methanol-oil mixture was stirred (260 rpm) to ensure complete mixing, and that was followed by microwave irradiation (25–120 min) and catalyst removal by centrifugation. The temperature was 70 °C for all reactions. The excess methanol was distilled (50 °C) under reduced pressure, and the biodiesel was separated from glycerol by decantation, which was followed by washing with water (3 x 10 mL). The transesterification reactions were monitored by <sup>1</sup>H NMR spectroscopy according to the literature.<sup>45</sup> The chemical shifts were referenced to CDCl<sub>3</sub>. The amount of soap formation was determined by means of the AOCS Cc 17-95 standard.

## RESULTS AND DISCUSSION

### Screening of the catalyst

A screening of catalytic activity of the 24 supported and non-supported heterogeneous catalysts for sunflower oil transesterification was performed. Sixteen milliliters of methanol were chosen as the reference volume for all of the reactions, i.e., a methanol-oil molar ratio of 16:1, which is in agreement with the literature,<sup>9</sup> which reports

an optimum molar ratio of 15:1. At values above this molar ratio, the addition of methanol had no significant effect on the conversion.<sup>9</sup>

The same reaction conditions were employed for each catalyst, allowing for direct comparisons. Appreciable conversions (above 30%) were only obtained for a few catalysts, and the remainder afforded conversions of less than 1%. The results are summarized in Table 2.

**Table 2.** Catalytic activity in the conversion of sunflower oil to methyl esters induced by microwave irradiation. Reaction conditions: methanol-oil molar ratio, 16:1; catalyst amount, 10 wt.% ; reaction time, 2 h; reaction temperature, 70 °C

Catalyst	Catalyst-active mass (g)	Conversion (%)
K <sub>2</sub> CO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.72	100
KOH/Al <sub>2</sub> O <sub>3</sub>	0.72	100
CaO	3.60	100
KI/Al <sub>2</sub> O <sub>3</sub>	0.72	54.6
CaO/MnO <sub>2</sub>	2.34	49.2
CaO/Al <sub>2</sub> O <sub>3</sub>	1.19	46.2
CaO/TiO <sub>2</sub>	3.17	36.6
MgO	3.60	< 1
Montmorillonite	3.60	< 1
H <sub>2</sub> SO <sub>4</sub> /TiO <sub>2</sub>	1.80	< 1

It should be noted that the reaction conditions were not optimized to maximize the conversion for each catalyst; however, the adopted procedure provided a way to compare the effectiveness of the catalysts employed. The data for the 24 catalysts in Table 2 show that most of the catalysts exhibited no activity under microwave irradiation. Alumina-supported potassium carbonate and potassium hydroxide, as well as calcium oxide, exhibited prominent results with reaction conversions greater than 98%. The catalytic activities of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, KOH/Al<sub>2</sub>O<sub>3</sub>, and KI/Al<sub>2</sub>O<sub>3</sub> seem to be enhanced by microwave irradiation, since under conventional heating these catalysts only afford yields of 48.0%, 80.2%, and 87.4%, respectively, with a 15:1 methanol-soybean oil molar ratio, 2 wt% catalyst, and reaction time of 6 h.<sup>9</sup> Furthermore, approximately 40% conversion was reported for experiments performed in a batch autoclave<sup>20</sup> when 2 wt% alumina/silica supported K<sub>2</sub>CO<sub>3</sub> was used as the catalyst. This was for biodiesel synthesis from sunflower oil and methanol (30:1 molar ratio) at 80 °C for 2 h. The same authors reported high conversions (>90%) when higher temperatures were used (>120 °C).<sup>20</sup>

On the other hand, when CaO was employed with conventional heating under different reaction conditions, poor reaction yields (30% to 40%) were obtained.<sup>10,16</sup> When activated calcium oxide (1 wt%) was employed in the sunflower oil transesterification reaction with methanol (13:1 molar ratio) at 60 °C for 2 h, a conversion of 85% was reported.<sup>21</sup> More recently the transesterification reaction of sunflower oil with ethanol<sup>25</sup> was studied using calcined calcium zincate as a solid base catalyst (3 wt%) at 78 °C, resulting in yields higher than 95% after 3 h. These examples leave no doubt that the catalytic activity of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and CaO are enhanced by microwave irradiation when compared to conventional heating.

In some cases, the opposite behavior could be observed when a catalyst was employed under conventional or microwave heating conditions. For example, MgO, montmorillonite, and H<sub>2</sub>SO<sub>4</sub>/TiO<sub>2</sub> showed no activity under microwave heating. However, under conventional heating, MgO (commercial and calcined) afforded conversions above 90% in the methanolysis of soybean oil at 200 °C for 1 h using 3.35 wt% catalyst and a methanol-oil molar ratio of 12:1.<sup>19</sup> Montmorillonite demonstrated poor activity under conventional heating (120 °C, 2 h) with a conversion of only 47% for crude *Pongamia*

*pinnata* oil (10:1 methanol-oil molar ratio).<sup>23</sup> H<sub>2</sub>SO<sub>4</sub>/TiO<sub>2</sub> provides a high conversion (over 90%) for cottonseed oil using a methanol-oil molar ratio of 12:1 and 2 wt% of catalyst (catalyst-oil) at 230 °C (8 h).<sup>24</sup> Microwave heating also seems to improve the CaO/TiO<sub>2</sub> catalyst performance, which under conventional heating (60 °C, 10 h) afforded 79% conversion of grapeseed oil with a 6:1 methanol-oil molar ratio,<sup>22</sup> whereas in the present study a 37% conversion was observed in 2 h, as shown in Table 2.

The results in Table 2 can be compared to recent literature reports on microwave-induced transesterification reactions using different heterogeneous catalysts. Verziu *et al.*<sup>38</sup> reported a methyl ester yield of 98% using a nanocrystalline MgO catalyst under microwave (70 °C, 40 min) and a 4:1 methanol-oil molar ratio. Hsiao *et al.*<sup>40</sup> demonstrated that the microwave has a greater efficiency than conventional heating with the catalytic activity of CaO achieving a conversion rate of 96.6% in the transesterification of soybean oil under microwave (1 h) using CaO nanopowder (3 wt%) and a 7:1 methanol-oil molar ratio. Earth alkaline metal oxides were used by Patil *et al.*<sup>39</sup> as catalysts to study the transesterification kinetics of *Camelina sativa* oil under conventional and microwave heating conditions. The best yields of fatty acid methyl esters were observed when BaO (94%) and SrO (80%) were used, and the optimum reaction conditions were a 9:1 methanol-oil molar ratio and catalyst concentrations of 1.5% (BaO) and 2% (SrO). Their findings indicated that BaO is the best catalyst with the reaction rate constantly increasing by two orders of magnitude in the microwave-assisted transesterification reaction compared to conventional heating. Furthermore, the conversion of soybean and cooked oil to biodiesel using SrO as the catalyst under microwave conditions with magnetic stirring was reported by Koberg *et al.*<sup>41</sup> who achieved 99.8% conversion using a methanol-oil molar ratio of 6:1.

### Effect of catalyst amount and irradiation time on biodiesel conversion

Based on the results shown in Table 2 we investigated the transesterification of sunflower oil to biodiesel using the catalysts K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, KOH/Al<sub>2</sub>O<sub>3</sub>, CaO, and KI/Al<sub>2</sub>O<sub>3</sub> in more detail. In all of the reactions a methanol-oil ratio of 16:1 was maintained. First, we examined the effects of the mass ratio of catalyst to oil and irradiation time on biodiesel yield. Figure 2 shows the effect of irradiation time on biodiesel conversion with three different concentrations of catalyst (2.5%, 5%, and 10%).

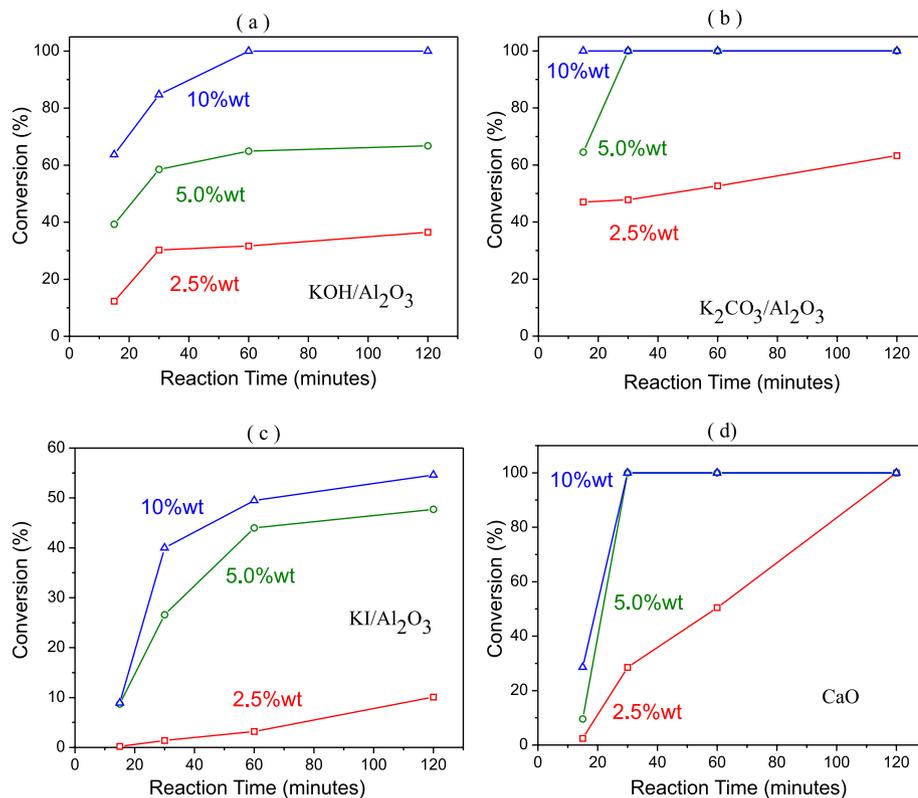
It can be observed in Figure 2 that for all the experiments with a catalyst concentration above 5% the conversion starts within a short time and then stabilizes. In particular, K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> exhibits a conversion of over 100% in over 15 min with 10% catalyst and over 30 min with 5% catalyst. Varying the amount of catalyst from 5% to 10% had no effect after 30 min when K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and CaO were used as catalysts (Figures 2b and 2d, respectively). However, an appreciable decrease in the conversion was observed under the same conditions when KI/Al<sub>2</sub>O<sub>3</sub> was employed (Figure 2c). Furthermore, in contrast to the conventional heating, it can be observed from Figure 2c that for microwave-assisted transesterification KI/Al<sub>2</sub>O<sub>3</sub> is not the best supported catalyst,<sup>9</sup> even in the presence of high catalyst concentrations and irradiation times (Figure 2a). These preliminary results suggest the use of 5% of the K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, CaO, and KOH/Al<sub>2</sub>O<sub>3</sub> catalysts with reaction times of 30 min.

### Influence of catalyst amount and irradiation time on the formation of soap

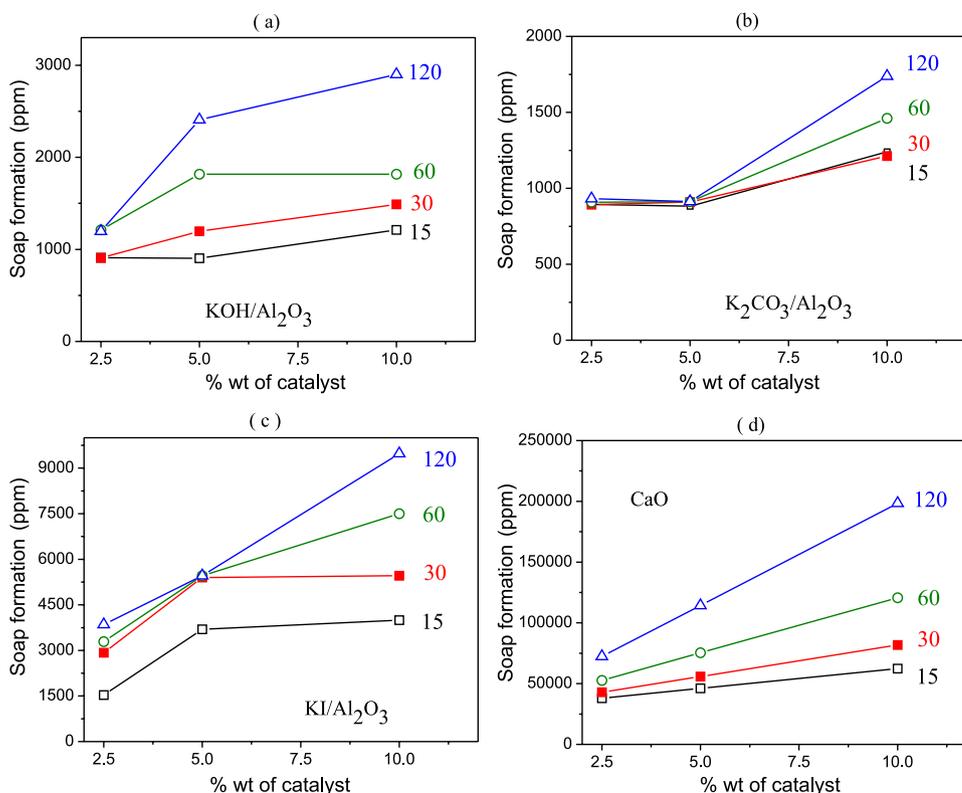
Soap formation (saponification) leads to the loss of catalyst and decreasing yields in the reaction products, and the greater the

amount of soap formation, the greater the consumption of oil. The loss of catalyst also reduces its reuse potential. Soap formation was determined after the conversion of sunflower oil to biodiesel, and the

results (ppm) are given as a function of the catalyst mass concentration and shown in Figure 3 for the  $\text{KOH}/\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ ,  $\text{KI}/\text{Al}_2\text{O}_3$ , and  $\text{CaO}$  catalysts after reaction times of 15, 30, 60, and 120 min.



**Figure 2.** Biodiesel yields and irradiation time using the heterogeneous catalysts:  $\text{KOH}/\text{Al}_2\text{O}_3$  (a),  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  (b),  $\text{KI}/\text{Al}_2\text{O}_3$  (c) and  $\text{CaO}$  (d). 16:1 methanol-oil molar ratio and 2.5%, 5% and 10% of catalyst concentration



**Figure 3.** Soap formation and catalyst amount for the heterogeneous catalysts  $\text{KOH}/\text{Al}_2\text{O}_3$  (a),  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  (b),  $\text{KI}/\text{Al}_2\text{O}_3$  (c) and  $\text{CaO}$  (d) with reaction times of 15, 30, 60 and 120 min. Methanol to oil molar ratio used was 16:1

Soap formation increases with irradiation time and quantity of catalyst, and this in turn leads to lower biodiesel conversion. Figure 3 shows that CaO produces larger amounts of soap compared to the other catalysts. For all the catalysts, there is an increase in soap formation over time. However, the amount of soap produced when 2.5 and 5% of  $K_2CO_3/Al_2O_3$  were employed remained constant and at a relatively low value. The catalysts  $KOH/Al_2O_3$  and  $KI/Al_2O_3$  have intermediate characteristics. They tend to show soap formation over time, but to a lower extent than calcium oxide. The high degree of soap formation observed with pure CaO may be related to its greater basic strength compared to the other supported catalysts. This is caused by the thermal decomposition of the carbonate and dehydroxylation of the OH groups during calcination.<sup>9</sup>

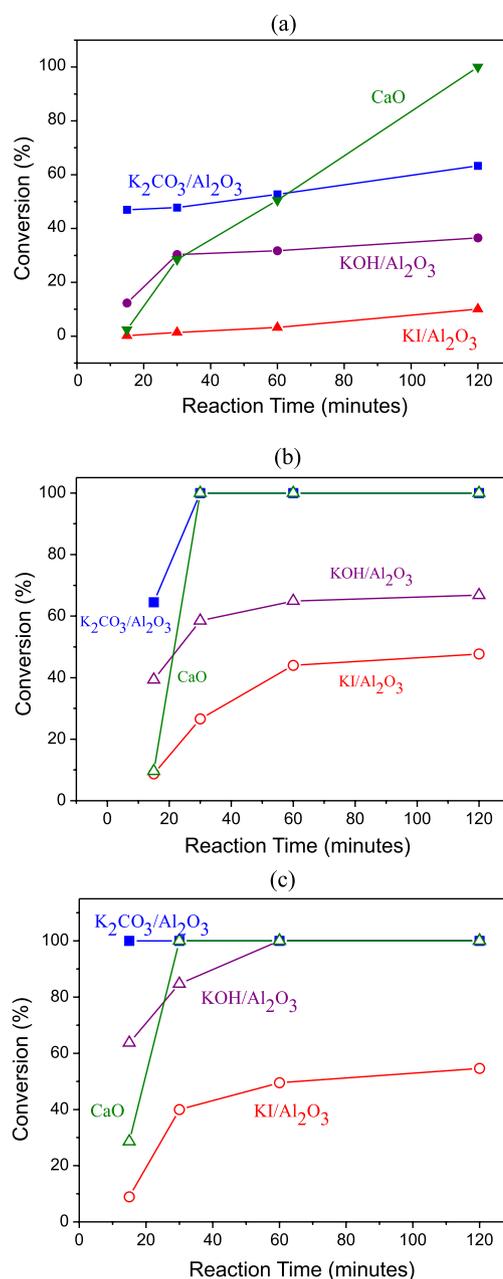
### Influence of the catalysts on biodiesel conversion

Figure 4 shows the biodiesel conversion as a function of the catalyst concentration and reaction time for the four best catalysts in this study.

As can be seen in Figure 4,  $K_2CO_3/Al_2O_3$  and CaO afford higher conversions in a shorter reaction time (15 min), regardless of their concentrations.  $KI/Al_2O_3$  and  $KOH/Al_2O_3$  catalysts had the poorest performance. For irradiation times of over 30 min and with 5% catalyst,  $K_2CO_3/Al_2O_3$  and CaO were comparable, showing high catalytic activity (100%) whereas  $KOH/Al_2O_3$  only showed an intermediate biodiesel conversion. Therefore  $K_2CO_3/Al_2O_3$  and CaO are the most suitable catalysts for biodiesel production through a microwave-assisted transesterification process employing sunflower oil. However, as shown in Figure 3, calcium oxide leads to higher soap formation. In an attempt to overcome this drawback, CaO was supported in  $Al_2O_3$ ,  $MnO_2$ , and  $TiO_2$ . The results for the biodiesel conversion and measured amount of soap formation are shown in Table 3. The reaction conditions are the same as those adopted for the experiments in Table 2.

There was an appreciable decrease in the amount of soap formation, particularly for CaO supported on alumina and titanium oxide, but a substantial decrease in biodiesel production also occurred. The observed decreases were attributed to the lower basic strength of the supported calcium oxide. This means that among the various catalysts studied  $K_2CO_3/Al_2O_3$  shows the best potential with a high conversion rate and low soap formation rate. Considering  $K_2CO_3/Al_2O_3$  the most promising catalyst, we decided to investigate the activity of the catalyst as a function of its repeated use. This is an important factor, especially from an economic point of view. In this regard, Carvalho *et al.*<sup>18</sup> recently reported on the stability of SrO for biodiesel production. Only a slight decrease in the ester conversion was seen after use six times, and this is in agreement with earlier results reported by Liu *et al.*<sup>12</sup> However, reusability is very important to also ensure that the active species are not leached from the solid support of the catalyst. For example, the reusability of alumina/silica supported  $K_2CO_3$  in the transesterification of sunflower oil was checked using the catalyst without any further purification and activation,<sup>20</sup> and a remarkable reduction in the conversion was observed, only 25.4% conversion after the second run. In a similar study on the transesterification of sunflower oil to biodiesel using  $La_2O_3/ZrO_2$  as a heterogeneous catalyst,<sup>25</sup> the reusability was investigated by washing the catalyst thoroughly with methanol and heating in a muffle oven at 600 °C for 2 hours prior to its next use. A reduction in the conversion to 55% was observed after five cycles, and the authors reported that this was probably due to the gradual loss of  $La_2O_3$  species.

To investigate the reusability of  $K_2CO_3/Al_2O_3$  in the methanolysis of sunflower oil under microwave irradiation, transesterification reactions were performed with 2.5 wt% catalyst and an irradiation



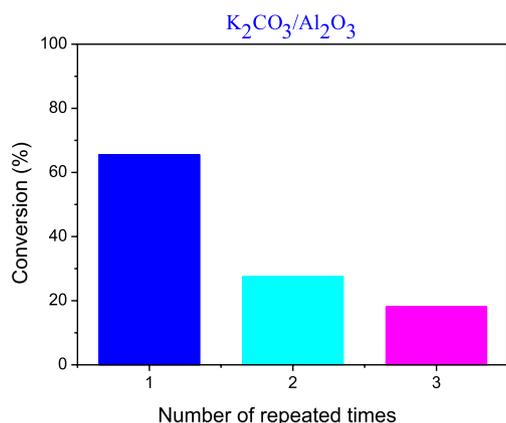
**Figure 4.** Biodiesel conversion against reaction times for each catalyst employing 2.5% (a), 5% (b) and 10% (c) of mass catalyst concentration (methanol-sunflower oil molar ratio of 16:1)

**Table 3.** Soap formation (ppm) and biodiesel conversion for CaO and supported CaO. Reaction conditions: methanol:oil (16:1 molar ratio); catalyst amount, 10 wt. %; reaction time, 2 h (70 °C)

Catalysts	Soap (ppm)	Conversion (%)
CaO/ $MnO_2$	129,612	49.2
CaO/ $TiO_2$	69,627	36.6
CaO/ $Al_2O_3$	78,108	46.2
CaO	198,385	100

time of 30 min with a methanol-oil molar ratio of 16:1. At the end of the reaction, the mixture was centrifuged, and the catalyst was separated for recycling. Recycling was accomplished by washing with hexane and anhydrous methanol, drying in an oven at 150 °C for 2 h, and followed by calcination for 3 h at 550 °C in a muffle furnace.

The biodiesel conversion as a function of the reuse of  $K_2CO_3/Al_2O_3$  is shown in Figure 5.



**Figure 5.** Biodiesel conversion with the reuse of  $K_2CO_3/Al_2O_3$ . Reaction conditions: methanol:oil (16:1 molar ratio); catalyst amount, 2.5wt. %; reaction time, 30 min; 70 °C

The observed decrease in the biodiesel conversion shown in Figure 5 is in agreement with the previously reported results using alumina/silica supported  $K_2CO_3$ <sup>20</sup> and  $La_2O_3/ZrO_2$ <sup>25</sup> as heterogeneous catalysts for the methanolysis of sunflower oil under conventional heating. The reduction in the conversion observed in Figure 5 indicates decomposition of the  $K_2CO_3/Al_2O_3$  in each catalyzed transesterification reaction. That is, during the process, the  $K_2CO_3/Al_2O_3$  was solubilized, leading to a leaching of the support with a subsequent increase in soap formation, which diminishes the amount of catalyst available for biodiesel production. This is an indication that the alumina-supported potassium carbonate will likely produce the same amount of soap as pure  $K_2CO_3$ . Therefore, we carried out experiments with pure and  $Al_2O_3$ -supported  $K_2CO_3$  to test this hypothesis. The reactions were performed for 30 min in a 16:1 methanol-oil reactant molar ratio (70 °C). Table 4 shows the biodiesel conversion and amount of soap formation.

**Table 4.** Influence of the support on catalytic activity and soap formation of the  $K_2CO_3$ . Reaction conditions: methanol:oil molar ratio of 16:1; catalyst amounts of 5 wt.% and 10 wt.%; reaction time of 30 min at 70 °C

	Catalyst amount (g)	Active mass (g $K_2CO_3$ )	Conversion (%)	Soap (ppm)
$K_2CO_3$	0.72	0.72	98	4851
$K_2CO_3/Al_2O_3$	3.60	0.72	98	1216
$K_2CO_3$	0.36	0.36	98	4063
$K_2CO_3/Al_2O_3$	1.80	0.36	98	910

From the results presented in Table 4 it is clear that a reduction in the soap formation occurs with the supported  $K_2CO_3$ . Based on the results shown in Table 4, a reduction in soap formation was obtained by replacing the unsupported catalyst with the alumina-supported catalyst (77.6% with 5% catalyst and 75% with 10% catalyst). Therefore, the above results indicate that  $K_2CO_3/Al_2O_3$  can be used a limited number of times as a catalyst in the transesterification reaction under microwave heating. However, the production of a small amount of soap is unavoidable.

## CONCLUSION

The catalytic activities of 24 heterogeneous catalysts were

investigated in a microwave-assisted transesterification reaction for methylic biodiesel production using sunflower oil in a microwave monomode reactor. The effects of the catalyst amount and irradiation time on the biodiesel conversion were studied as well as the influence of the mass of the catalyst and irradiation time on the soap formation. Microwave-induced transesterification showed a four-fold reduction in the reaction time compared with conventional heating. High biodiesel conversions were obtained with  $K_2CO_3$ ,  $K_2CO_3/Al_2O_3$ , and CaO. The best results were obtained when 5%  $K_2CO_3/Al_2O_3$  and CaO, in a 16:1 methanol-oil molar ratio, were allowed to react for 30 min at 70 °C. CaO supported on alumina and titanium oxide showed an appreciable decrease in the amount of soap formation, but also a decrease in biodiesel production. Therefore,  $K_2CO_3/Al_2O_3$  was the most promising catalyst, with a relatively high conversion of oil to biodiesel and low rate of soap formation. The repeated activity of this catalyst was investigated, and a reduction in the biodiesel conversion due to the decomposition of the catalyst was observed. In conclusion, considering the 24 heterogeneous catalysts studied, it was found that the pure or alumina-supported  $K_2CO_3$  catalysts exhibited excellent catalytic activity for the transesterification of sunflower oil under microwave irradiation.

## SUPPLEMENTARY MATERIAL

<sup>1</sup>H NMR spectra (Figures 1S to 15S) for the related conversions are available free as pdf files at <http://quimicanova.sbq.org.br>.

## ACKNOWLEDGEMENTS

The authors wish to thank CNPq (National Council for Scientific and Technological Development – Brazil), FINEP (Funding Agency for Studies and Projects- Brazil), CPP (Pantanal Research Centre), and CAPES (Coordination for the Improvement of Higher Education – Brazil) for financial support.

## REFERENCES

- Meher, L. C.; Sagar, D. V.; Naik, S. N.; *Renewable Sustainable Energy Rev.* **2006**, *10*, 248.
- Vicente, G.; Martínez, M.; Aracil, J.; *Bioresour. Technol.* **2007**, *98*, 1724.
- Dermibas, A.; *Prog. Energy Combust. Sci.* **2007**, *33*, 1.
- Lotero, E.; Liu, Y.; Lopez, D. E.; Suwannakarn, K.; Bruce Jr, D. A.; Goodwin, J.G.; *Ind. Eng. Chem. Res.* **2005**, *44*, 5353.
- Ma, F.; Hanna, M. A.; *Bioresour. Technol.* **1999**, *70*, 1.
- Agra, I. B.; Warnijat, S.; Wiratni; *WREC* **1996**, 1025.
- Meher, L. C.; Kulkarni, M. G.; Dalai A. K.; Naika, S. N.; *Eur. J. Lipid Sci. Technol.* **2006**, *108*, 389.
- Suppes, G. J.; Dasari, M. A.; Daskocil, E. J.; Mankidy, P. J.; Goff, M. J.; *Appl. Catal. A: Gen.* **2004**, *257*, 213.
- Xie, W.; Li, H.; *J. Mol. Catal. A: Chem.* **2006**, *255*, 1.
- Singh, A. K.; Fernando, S. D.; *Chem. Eng. Technol.* **2007**, *30*, 1716.
- Xie, W.; Peng, H.; Chena, L.; *J. Mol. Catal. A: Chem.* **2006**, *246*, 24.
- Liu, X.; He, H.; Wang, Y.; Zhu, S.; *Catal. Commun.* **2007**, *8*, 1107.
- Xie, W.; Yang, Z.; Chun, H.; *Ind. Eng. Chem. Res.* **2007**, *46*, 7942.
- Li, X.; Lu, G.; Guo, Y.; Guo, Y.; Wang, Y.; Zhang, Z.; Liu, X., Wang, Y.; *Catal. Commun.* **2007**, *8*, 1969.
- Singh, A. K.; Fernando, S. D.; *Energy Fuels* **2008**, *22*, 2067.
- Patil, P. D.; Deng, S.; *Energy Fuels* **2009**, *23*, 4619.
- Veljkovic, V. B.; Stamenkovic, O. S.; Todorovic, Z. B.; Lazic, M. L.; Skala, D. U.; *Fuel* **2009**, *88*, 1554.
- Carvalho, L. M. G.; Abreu, W. C.; Silva, M. G. O.; Lima, J. R. O.; Oliveira, J. E.; Matos, J. M. E.; Moura, C. V. R.; Moura, E. M.; *J. Braz. Chem. Soc.* **2013**, *24*, 550.

19. Di Serio, M.; Ledda, M.; Cozzolino, M.; Minutillo, G.; Tesser, R.; Santacesaria, E.; *Ind. Eng. Chem. Res.* **2006**, *45*, 3009; Di Serio, M.; Cozzolino, M.; Giordano, M.; Tesser, R.; Patrono, P.; Santacesaria, E.; *Ind. Eng. Chem. Res.* **2007**, *46*, 6379.
20. Lukić, I.; Krstić, J.; Jovanović, D.; Skala, D.; *Bioresour. Technol.* **2009**, *100*, 4690.
21. Granados, M. L.; Poves, M. D. Z.; Alonso, M. A.; Mariscal, R.; Galisteo, F.C.; Moreno-Tost, R.; Santamaría, J.; Fierro, J. L. G.; *Appl. Catal. B: Environ.* **2007**, *73*, 317.
22. Kawashima, A.; Matsubara, K.; Honda, K.; *Bioresour. Technol.* **2008**, *99*, 3439.
23. Karmee, S. K.; Chadha, A.; *Bioresour. Technol.* **2005**, *96*, 1425.
24. He, C.; Baoxiang, P.; Dezheng, W.; Jinfu, W.; *Front. Chem. Eng. China* **2007**, *1*, 11.
25. Rubio-Caballero, J. M.; Santamaría-Gonzalez, J.; Merida-Robles, J.; Moreno-Tost, R.; Alonso-Castillo, M. L.; Vereda-Alonso, E.; Jimenez-Lopez, A.; Maireles-Torres, P.; *Fuel* **2013**, *105*, 518.
26. Sun, H.; Ding, Y.; Duan, J.; Zhang, Q.; Wang, Z.; Lou, H.; Zheng, X.; *Bioresour. Technol.* **2010**, *101*, 953.
27. Dall'Oglio, E. L.; Sousa Jr., P. T.; Garofalo, M. N.; *Br PI 0403530-5*, **2004**.
28. Lidström, P.; Tierney, J.; Wathey, B.; Westman, J.; *Tetrahedron* **2001**, *57*, 9225.
29. Leadbeater, N. E.; Stencel, L. M.; *Energy Fuels* **2006**, *20*, 2281.
30. Azcan, N.; Danisman, A.; *Fuel* **2007**, *86*, 2639.
31. Azcan, N.; Danisman, A.; *Fuel* **2008**, *87*, 1781.
32. Hernando, J.; Leton, P.; Matia, M.P.; Novella, J. L.; Alvarez-Builla, J.; *Fuel* **2007**, *86*, 1641.
33. Barnard, T. M.; Leadbeater, N. E.; Boucher, M. B.; Stencel, L. M.; Wilhite, B. A.; *Energy Fuels* **2007**, *21*, 1777.
34. Groisman, Y.; Gedanken, A.; *J. Phys. Chem. C* **2008**, *112*, 8802.
35. Kumar, R.; Kumar, G. R.; Chandrashekar, N.; *Bioresour. Technol.* **2011**, *10*, 6617.
36. Refaat, A. A.; El Sheltawy, S. T.; *WSEAS Trans. Environ. Dev.* **2008**, *4*, 279.
37. Mazzocchia, C.; Modica, G.; Kaddouri, A.; Nannicini, R.; *C. R. Chim.* **2004**, *7*, 601.
38. Verziu, M.; Cojocaru, B.; Hu, J.; Richards, R.; Ciuculescu, C.; Filip, P.; Parvulescu, V. I.; *Green Chem.* **2008**, *10*, 373.
39. Patil, P. D.; Gude, V. G.; Pinappu, S.; Deng, S.; *Chem. Eng. J.* **2011**, *168*, 1296.
40. Hsiao, M.-C.; Lin, C.-C.; Chang, Y.-H.; *Fuel* **2011**, *90*, 1963.
41. Koberg, M.; Abu-Much, R.; Gedanken, A.; *Bioresour. Technol.* **2011**, *102*, 1073.
42. Patil, P. D.; Gude, V. G.; Camacho, L. M.; Deng, S.; *Energy Fuels* **2010**, *24*, 1298.
43. Leung, D. Y. C.; Wu, X.; Leung, M. K. H.; *Appl. Energy* **2010**, *87*, 1083.
44. Chaves, A. T. C. A.; *Dissertação de Mestrado*, Universidade federal da Paraíba, Brasil, **2008**.
45. Knothe, G.; *J. Am. Oil Chem. Soc.* **2000**, *77*, 489.