

Transesterification of triglycerides in high and low quality oil feeds over an HT2 hydrotalcite catalyst

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Abstract

The use of a heterogeneous catalyst, in the transesterification reaction of refined and acidic cottonseed oil for the production of methyl-esters (biodiesel) has been studied. The basic Mg–Al–CO₃ hydrotalcite catalyst used showed a high activity for methanolysis and esterification reactions in a refined and an acidic cottonseed oil as well as in a representative high water content animal fat feed. The experiments were performed in a temperature range between 180 and 210 °C, in a batch reactor. The methanol to vegetable oil molar ratio was 6 to 1, while the catalyst concentration was fixed at 1 wt.% of the oil mass. Non-calcined and calcined forms of the catalyst were tested. The activity of the calcined catalyst was lower than the initial activity of the non-calcined catalytic system but it appeared the same with the reused non-calcined system.

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1. Introduction

The ever increasing need for using alternative renewable fuels instead of petroleum cuts, like diesel, in transportation is based on very important environmental, economical and strategic reasons. One promising biofuel, which has similar properties to conventional petro-diesel, is biodiesel.

Biodiesel derives from renewable energy sources, such as vegetable oils and animal fats. It has similar and sometimes better physical and chemical properties than petro-diesel fuel, like higher flash point, ultra-low sulphur concentration, better lubricating efficiency owing to the contained oxygen, and better cetane number (Anastopoulos et al., 2001; Goodrum and Geller, 2005; Nabi et al., 2006). The direct use of biodiesel or its blends with diesel has positive influence to the exhaust gases compared to diesel (Knothe et al., 2006; Nabi et al., 2006; Schumacher et al., 1996).

Biodiesel is produced through the transesterification of triglycerides which are the main component of vegetable oils and animal fats or the esterification reaction of the free fatty acids present in low quality vegetable oils. Methanol is usually used as alcohol because of its low cost and its chemical and physical advantages. Transesterification reaction is catalyzed from bases, oxides and enzymes at low or high temperatures. The mostly used process in industrial praxis today is based on strong base catalysts (e.g. NaOH, KOH and CH₃ONa) dissolved in methanol (Ma and Hanna, 1999; Meher et al., 2006). In some circumstances strong acids (e.g. H₂SO₄) (Al-Widyan and Al-Shyoukh, 2002) are also used. When a hydroxide is used as catalyst the reaction takes place near to methanol boiling point, in between 60 and 64 °C. The reaction time is about 1 h while the molar methanol to oil ratio is kept close to 6 to 1 (Fukuda et al., 2001; Srivastava and Prasad, 2000). One of the disadvantages of the classic method is the presence of catalyst in the products. The purifying process of the ester and glycerine phase increases the production cost and also produces wastes. An additional problem that is

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Nomenclature

ACO (–) acid cottonseed oil
 AD ($\text{kg}_{\text{OA}}/\text{kg}_{\text{Oil}}$) acidity
 AFF (–) animal fat feedstock
 AV ($\text{mg}_{\text{KOH}}/\text{gr}_{\text{Oil}}$) acid value
 DGs (–) diglycerides
 FFAs (–) free fatty acids
 GL (–) glycerin

HACO (–) high acidity and water content cottonseed oil
 MEs (–) methyl-esters
 MGs (–) monoglycerides
 OA (–) oleic acid
 RCO (–) refined cottonseed oil
 TGs (–) triglycerides

connected with the use of hydroxide catalysts is the undesirable reaction of the catalyst with the free fatty acids which are contained in low quality oils (e.g. waste and used frying oils), to form soaps (Ma and Hanna, 1999).

For this reason pre-treatment of these oils is demanded to remove the free fatty acids and the possible small amounts of water. When strong acids are used soap formation is avoided but for reaction temperature 60–64 °C a molar alcohol to oil ratio 30 to 1 is demanded to complete the reaction within 50 h (Al-Widyan and Al-Shyoukh, 2002; Lotero et al., 2005).

Due to the inherent problems of the currently used processes, research on solid catalysts for triglycerides transesterification is carried out and a number of studies describing rival catalysts performance have appeared in the literature. The main advantage in using solid catalysts is their much easier separation from the reacting system. A Na/NaOH/ γ - Al_2O_3 heterogeneous base catalyst was used from Kim et al. (2004) for the transesterification of soybean oil with methanol at 60 °C. The results of this study were encouraging indicating conversions of about 80% when a molar methanol to soybean oil ratio equal to 6 to 1 was used and about 95% when this ratio reached 9 to 1 in the presence of *n*-hexane as co-solvent. A series of NaX faujasite zeolite, ETS-10 zeolite and metal catalysts were studied from Suppes et al. (2004) for the transesterification of refined soybean oil containing ~2.6 wt.% free fatty acids. The best results were derived at 100 °C with the ETS-10 catalyst, the conversion reaching 92% in 3 h. However, when the ETS-10 catalyst was used for the transesterification of triglycerides containing 27% free fatty acids there was a quench of the catalyst activity. The free fatty acids substantially quenched the reaction and conversions to methyl-esters remained below 13.7% after 4 h of reaction. This data indicates that free fatty acids can inhibit solid catalysts relying on basic sites. Wenlei et al. (2006) have presented a process for the methanolysis of soybean oil to methyl-esters using calcined Mg–Al hydrotalcites as solid base catalysts. The reaction was carried out at reflux of methanol, with a molar ratio of soybean oil to methanol of 15 to 1 and a catalyst amount of 7.5%. After a reaction time of 9 h the oil conversion was found 67%. The same type of catalyst was studied from Cantrell et al. (2005) for the liquid phase transesterification of glyceryl tributyrates with methanol for biodiesel production at 60 °C with

encouraging results. Results on the transesterification of refined soybean oil, containing 0.1 wt.% free fatty acids, at high temperatures in the presence of calcined HT4 hydrotalcite catalyst (Mg to Al molar ratio 4 to 1 or Al/(Al + Mg) theoretical molar ratio ~0.2) have been reported by Di Serio et al. (2006). A small amount of catalyst (1 wt.% of the vegetable oil mass) was used but the reaction was performed with a high methanol to vegetable oil molar ratio (12 to 1). High conversions were achieved at 180 and 200 °C while it is also mentioned that the catalysts performance was not affected by the presence of 1 wt.% (10,000 ppm) of water into the reaction mixture. In a recent patent Siano et al. (2006) give first results on the triglycerides and free fatty acids conversion over a fresh calcined HT4 hydrotalcite (10 wt.% of the vegetable oil) reporting an experiment which was performed in a batch reactor at 180 °C with an acid oil containing 27 wt.% free fatty acids and a methanol to vegetable oil molar ratio 6 to 1. A satisfactory conversion of free fatty acids to methyl-esters was achieved with final acidity 5.7 wt.% but a poor conversion of triglycerides (44%) after 180 min reaction time was observed.

The aim of this work is to address the important contemporary problem of using a solid catalyst system for processing refined vegetable oils but also cheaper raw materials usually characterized as wastes (frying oils, low quality acid vegetable oils or high water content oils and waste animal fats). The perspective of developing an economically efficient and flexible biodiesel production method is supported by the use of the same efficient catalyst to convert triglycerides in a wide range of raw materials.

2. Experimental section

2.1. Materials

Refined (RCO) and acid cottonseed oil (ACO) as well as a high acidity and water content cottonseed oil (HACO) and an animal fat feedstock (AFF) were used as raw materials. The acidity (AD) of the acid cottonseed oil was about 9.5 wt.% (Acid value: AV 18.86 $\text{mg}_{\text{KOH}}/\text{gr}_{\text{Oil}}$) while the acidity of the refined one was about 0.15 wt.% (AV 0.29 $\text{mg}_{\text{KOH}}/\text{gr}_{\text{Oil}}$). The water content of these feedstocks was 840 and 3250 mg/kg, respectively. The high acidity cotton-

Table 1
Composition of the base cottonseed oil

Fatty acids type	Form	Formula	% (kg/kg)
Palmitic	16:0	C ₁₆ H ₃₂ O ₂	22.96
Palmitoleic	16:1	C ₁₆ H ₃₀ O ₂	0.90
Stearic	18:0	C ₁₈ H ₃₆ O ₂	2.30
Oleic	18:1	C ₁₈ H ₃₄ O ₂	16.70
<i>trans</i> -Oleic	18:1	C ₁₈ H ₃₄ O ₂	0.10
Linoleic	18:2	C ₁₈ H ₃₂ O ₂	55.40
<i>trans</i> -Linoleic	18:2	C ₁₈ H ₃₂ O ₂	0.02
Linolenic	18:3	C ₁₈ H ₃₀ O ₂	0.20

seed oil included 43 wt.% free fatty acids and 3.5 wt.% water while the crude animal fat feedstock contained 55 wt.% triglycerides and 45 wt.% water. The acid and high acidity cottonseed oil were prepared in our laboratory. In Table 1, the composition of the base cottonseed oil used in this study is shown.

HACO and AFF were used to investigate the impact of the presence of free fatty acids and water in the feed on the reaction time and the catalyst activity. For transesterification reaction analytic grade (purity 99.9%) methanol (Sds) was used.

2.2. Catalyst preparation

For the promotion of the reaction a basic solid Mg–Al–CO₃ hydrotalcite catalyst (HT2) in powder form was used. The preparation of Mg–Al–CO₃ hydrotalcite was achieved by following the proposed method of Reichle (1985) and Cavani et al. (1991). The catalyst preparation was attempted into a three neck flask equipped with mechanical stirrer and a dropping funnel. Two aqueous solutions were first prepared. The first was a solution of 25.6 g Mg(NO₃)₂ · 6H₂O (0.10 mol) and 18.75 g Al(NO₃)₃ · 9H₂O (0.050 mol) in 70 ml distilled water. The second was a solution of 50% aqueous NaOH (0.350 mol), 10 g Na₂CO₃ (anhydrous, 0.094 mol) in 100 ml distilled water. The quantities were fixed so that the final product has an Mg to Al atomic ratio equal to 2 to 1.

The first solution was put into the flask where the second one was added into a period time of 4 h. The mixture was vigorously agitated all the time. The temperature at that stage was kept at 27 ± 1 °C with the help of a water bath. After the addition ended and the Mg–Al–CO₃ hydrotalcite catalyst was formed the mixture was heated at 65 ± 1 °C for 20 h under mixing. The produced mixture was finally filtered, cleaned and dried (at 100–120 °C) yielding a fine white powder. This powder was used in most of experiments while its calcined form was also used for comparison. Calcination was performed at 350 °C for 6 h.

2.3. Batch reactor-process

The reaction was carried out in a Series 4560 Bench Top Mini Batch Reactor (Parr Instrument Company, Illinois, USA). The methanol to cottonseed oil molar ratio in the

reaction mixture was kept at 6 to 1 mol/mol and the catalyst concentration was fixed to 1 wt.% of the initial vegetable oil mass. For avoiding oxidation of the reactants, the experiments were performed at nitrogen atmosphere. This was achieved by stripping the reaction mixture with a nitrogen volume equal to 4 times the reactors space. All the experiments were performed in a temperature range from 180 to 210 °C while the initial pressure was monitored from 2200 to 2900 kPa, respectively.

As the catalyst was in fine powder form sampling during operation was not feasible. The samples were collected after very rapid cooling of the reactor using its integrated cooling system including an internal coil. Then, samples were taken by opening the reactor. The samples collected from the reactor were allowed to settle in a ventilator before analysis.

Since triglycerides (TGs), diglycerides (DGs), monoglycerides (MGs) and free fatty acids (FFAs) analysis relates only with the oily liquid phase of the sample and the results are presented as percentage of the total oily mass, the oily mass was purged from impurities that might affect the final measurements. So, the oily phase was stripped with N₂ at 50 °C for about 0.5 h in order to remove the excess of methanol (MeOH) and water produced during reaction. Then, the samples were centrifuged to separate the catalyst powder, glycerine (GL) and oily phase. The upper layer of the centrifuged sample consists of the oily phase (biodiesel), the lower one of the glycerine while in the middle, between the oily and the glycerine phase appears the catalyst.

2.4. Method of analysis

The analysis of TGs, DGs and MGs was performed by a Fisons 8530 HRGC MEGA 2 series gas chromatographer according to European biodiesel standards EN-14105. The carrier gas used was He. The temperature of the column was initially 220 °C and it was linearly increased up to 370 °C in a time period of 20 min (Plank and Lorbeer, 1995). For the calculations, Tricaprin (C₃₃H₆₂O₆) (GC grade) was used as internal calibrator.

The acidity (or acid value) of the samples was determined by a standard titration procedure according to EN-14104. A weighted amount of sample was dissolved into ethanol (purity 99.9%) and diethyl ether (purity 99.9%). To identify the pH change, some drops of phenolphthalein indicator were added into the solution. The titration was performed with 0.1 M KOH water solution.

The acidity of the oil was calculated by the following equation:

$$AD = \frac{C_{\text{sol,KOH}} V_{\text{sol,KOH}} MB_{\text{BOA}}}{m_{\text{oil}} \times 1000} 100 \text{ (wt.\%)} \quad (1)$$

The acid value of the oil was calculated by the following equation:

$$AV = \frac{C_{\text{sol,KOH}} V_{\text{sol,KOH}} MB_{\text{KOH}}}{m_{\text{oil}}} (\text{mg}_{\text{KOH}}/\text{gr}_{\text{oil}}) \quad (2)$$

3. Transesterification reaction

Transesterification reaction is a reversible reaction of triglycerides with an alcohol (e.g. methanol) to produce alcohol-esters (methyl-esters) and glycerine.

The reaction of transesterification includes three steps. First, triglycerides react with methanol Eq. (3) to produce methyl-esters and diglycerides which further react with methanol Eq. (4) to produce methyl-esters and monoglycerides. Finally, the monoglycerides react with methanol to give glycerine and methyl-esters (Eq. (5)):



If the oil contains free fatty acids, the esterification reaction of free fatty acids with methanol to produce water and methyl-esters according to Eq. (6) takes place in parallel with transesterification reactions:



4. Results and discussion

4.1. Catalyst performance

As shown in Table 2, triglycerides concentration decreases with reaction time and a total conversion is observed within 3 h when refined oil was used and within 1.5 h when the acid one was reacted at 210 °C. Diglycerides start to increase at the beginning of the reaction and finally they reduce to 2.3 wt.%. Monoglycerides concentration follows a continuous increasing progress to stabilize at about 13 wt.%. When an acid oil (ACO) is involved the concentration of free fatty acids decreases constantly to 2.0 wt.% as observed in Table 2.

Comparing the conversion time of 3 h for the catalytic transesterification of the refined oil (RCO) at 210 °C with the conversion time of over 10 h for the non-catalytic transesterification at 235 °C as given by *Diasakou et al. (1998)* we realize that the Mg–Al–CO₃ hydrotalcite signifi-

cantly catalyses the transesterification reaction. The basic advantage of this catalyst is its ability to transesterify triglycerides in the presence of acids which are reduced during processing due to their esterification with the present methanol. Thus, the present free fatty acids in the oil do not affect the activity of the catalyst as reported for the ETS-10 catalyst (*Suppes et al., 2004*) but they enhance the conversion rates acting as an acid homogeneous catalyst in parallel with the Mg–Al–CO₃ hydrotalcite catalyst.

In Fig. 1, the evolution of the transesterification reactions for the refined cottonseed oil is presented, while in Fig. 2 the corresponding evolution is given for the acidic oil at 200 °C. Triglycerides are rapidly converted in both cases while the presence of acids in the acidic raw material is observed to enhance the catalytic activity of the catalyst, as discussed before. Moreover, the concentration of the mono- and di-glycerides in the oil phase reaches an equilibrium value which depends on reaction temperature and reacting mixture composition. Acidity also decreases reaching an equilibrium value at the end of the reaction.

4.2. Glycerol phase removal

After the end of reaction (9 h) at 200 °C the final product was a mixture of diglycerides, monoglycerides, methyl-esters, methanol and glycerin. Considerable quantities of

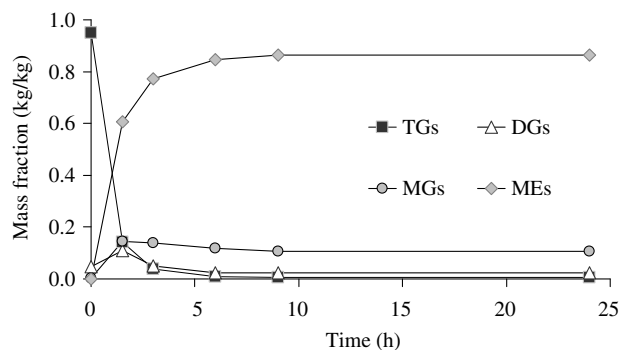


Fig. 1. Catalytic transesterification of refined cottonseed oil (RCO) at 200 °C. Methanol to oil molar ratio:6 to 1. 1 wt.% catalyst.

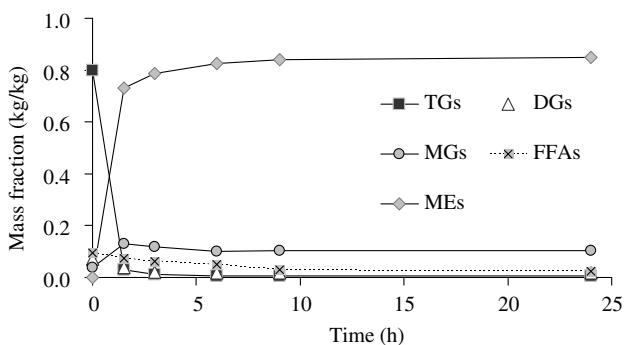


Fig. 2. Catalytic transesterification of acid cottonseed oil (ACO) at 200 °C. Methanol to oil molar ratio:6 to 1. 1 wt.% catalyst.

Table 2

Mass fraction of TGs, DGs, MGs and FFAs during progress of reaction at 210 °C for refined and acid cottonseed oil feed-stocks with molar ratio methanol to oil equal to 6 to 1 and 1 wt.% catalyst

Time (h)	0	1.5	3
<i>Acid oil</i>			
X_{TGs}	0.800	0.016	0.000
X_{DGs}	0.071	0.043	0.034
X_{MGs}	0.038	0.140	0.133
X_{FFAs}	0.094	0.020	0.020
<i>Refined oil</i>			
X_{TGs}	0.950	0.045	0.016
X_{DGs}	0.046	0.075	0.045
X_{MGs}	0.004	0.153	0.135

diglycerides (1.91 wt.%), monoglycerides (10.36 wt.%) and free fatty acids (2.96 wt.%) were measured in accordance with the equilibrium Eqs. (3)–(6). As a sequence the final product contains about 84 wt.% biodiesel. In order to rise biodiesel yields and overcome equilibrium constraints, glycerol phase was removed after separation of the mixture into glycerol-catalyst-oily phases in a separator flask. The upper oily phase was stripped with nitrogen in order to remove methanol and water residue. Finally, the remaining mixture reacted with fresh methanol (half of the initial quantity, i.e. 3 to 1 methanol to oil molar ratio) and fresh catalyst for another 3 h (1st GL removal in Fig. 3). The resulting oily phase contained less diglycerides (0.54 wt.%), monoglycerides (4.47 wt.%) and free fatty acids (1.37 wt.%). Better yields were achieved by a second glycerol phase removal stage (2nd GL removal in Fig. 3) that took place in the same way as the first one. The result was a product with 0.17 wt.% diglycerides, 1.97 wt.% monoglycerides, 1.01 wt.% free fatty acids and 96.16 wt.% methyl-esters. The same experiment was realized at 180 °C (Table 3) with similar results and 98.31 wt.% methyl-esters yield. The improved yield in methyl-esters is due to equilibrium which at lower temperatures favors the formation of esters.

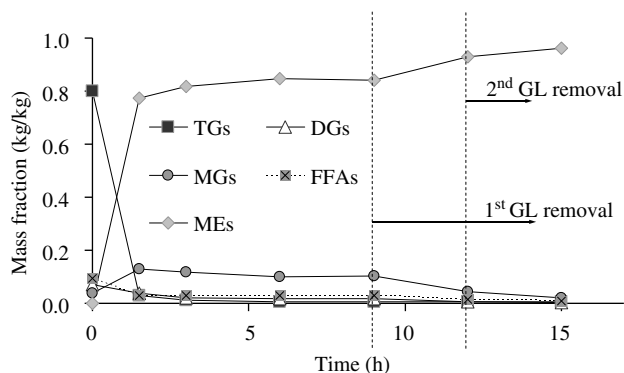


Fig. 3. Catalytic transesterification of acid cottonseed oil (ACO), at 200 °C. Methanol to oil molar ratio:6 to 1. Two glycerol phase removals.

Table 3
Catalytic transesterification of acid cottonseed oil, at 180 °C with molar ratio methanol to oil equal to 6 to 1 with two glycerol phase removals

Time (h)	Mass fraction % (kg/kg)				
	TGs	DGs	MGs	FFAs	MEs
<i>Acid cottonseed oil (180 °C)</i>					
0	80.04	7.09	3.75	9.41	0.00
1.5	8.72	8.03	11.87	3.67	67.71
3	3.12	3.91	11.05	3.46	78.46
6	1.02	1.61	7.46	3.01	86.90
9	0.75	1.21	7.27	2.96	87.81
12	0.51	0.29	2.65	1.38	94.98
15	0.11	0.11	1.39	0.08	98.31

4.3. Catalyst deactivation

An important factor in catalytic applications is the catalyst stability and decay with time. The catalyst stability and the comparison of the activity of the calcined and the non-calcined forms were checked with experiments performed at 200 °C with refined cottonseed oil (RCO), methanol to oil molar ratio equal to 6 to 1 and 1 wt.% catalyst. The results are shown in Fig. 4. After the first reaction for 9 h with fresh catalyst the catalytic powder was filtered and separated from the reaction mixture. Then the catalyst was washed with diethyl-ether to remove all the remaining reactants from the catalyst surface and pores, dried in air and reused for the next experiment for another 9 h with fresh reactants at the same conditions. From the data presented in Fig. 4, a moderate deactivation of the catalyst is observed which does not affect the time needed for total conversion of triglycerides.

The influence of calcination on Mg–Al–CO₃ hydrotalcite catalyst activity has also been examined. The calcined catalyst was used in an experiment carried out at the same conditions as those adopted to check deactivation of the non-calcined form. As observed in Fig. 4 the performance of the calcined form of Mg–Al–CO₃ catalyst was the same with that of the re-used one. This observation implies that the deactivation of the non-calcined powder was due to its thermal treatment during reaction at 200 °C.

4.4. Catalyst performance with high FFAs and water content feedstock

The effect of high free fatty acids and water concentrations on the catalyst activity was examined by performing experiments with the high acidity cottonseed oil (HACO) and the crude animal fat feedstock (AFF). The experiments were performed at 200 °C with an initial methanol to oil ratio 6 to 1 and 1 wt.% catalyst. The use of Mg–Al–CO₃ hydrotalcite catalyst for the transesterification and esterification reactions was successful. Within 3 h a 99% conver-

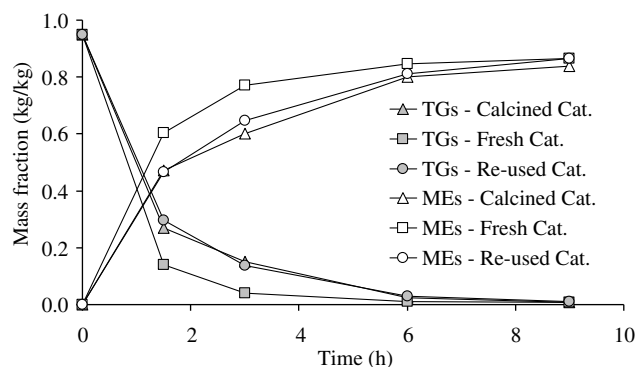


Fig. 4. Comparison of the performance of fresh, re-used and calcined catalyst for the transesterification reaction of refined cottonseed oil at 200 °C with methanol to oil molar ratio equal to 6 to 1 and 1 wt.% catalyst.

sion of triglycerides to biodiesel was achieved while the free fatty acids content decreased considerably to 1 wt.% when a high acidity cottonseed oil used. When the AFF was used as oil raw material a conversion of 99% was also achieved for triglycerides within 3 h. These extreme experiments assign the Mg–Al–CO₃ catalyst the advantage of catalysing both esterification and transesterification reactions, without negative effects stemming from the presence of either the FFAs or the water. In contrast, the activity of most catalysts referred in literature was significantly affected by the presence of FFAs and/or water in the feed oils like ETS-10 catalysts (Suppes et al., 2004) the activity of which was quenched when a high FFAs (27%) vegetable oil feedstock was used.

5. Conclusion

The hydrotalcite Mg–Al–CO₃ system used in this study is an effective catalyst for transesterification of vegetable oils and fats. More importantly, it was proved that this catalyst is very active up to 210 °C when feeds with high FFA and water content were processed. The deactivation observed in the first cycle of operation of the non-calcined form of the catalytic system is attributed to the thermal treatment during reaction as the catalyst activity during the second cycle of operation was identical with that of the calcined form. High diglycerides and monoglycerides content in the product due to equilibrium reactions can be considerably reduced with removal of the glycerin phase and further reaction of the oil phase with fresh reactants. This catalytic system appears very attractive for industrial application because it can be applied in a wide range of feeds with high FFA and water content while FFAs appear to enhance the reaction rates acting as catalysts but they are also consumed through esterification reactions to produce esters.

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References

Al-Widyan, M.I., Al-Shyoukh, A.O., 2002. Experimental evaluation of the transesterification of waste palm oil into biodiesel. *Bioresource Technology* 85, 253–256.

- Anastopoulos, G., Lois, E., Zannikos, F., Kalligeros, S., Teas, C., 2001. Influence of fatty acid methyl esters from hydroxylated vegetable oils on diesel fuel lubricity. *Tribology International* 34, 749–755.
- Cantrell, D.G., Gillie, L.J., Lee, A.F., Wilson, K., 2005. Structure-reactivity correlations in MgAl hydrotalcite catalysts for biodiesel synthesis. *Applied Catalysis A: General* 287, 183–190.
- Cavani, F., Trifirb, F., Vaccari, A., 1991. Hydrotalcite-type anionic clays: preparation, properties and applications. *Catalysis Today* 11, 173–301.
- Di Serio, M., Ledda, M., Cozzolino, M., Minutillo, G., Tesser, R., Santacesaria, E., 2006. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. *Industrial & Engineering Chemistry Research* 45, 3009–3014.
- Diasakou, M., Louloudi, A., Papayannakos, N., 1998. Kinetics of the non-catalytic transesterification of soybean oil. *Fuel* 77, 1297–1302.
- Fukuda, H., Kondo, A., Noda, H., 2001. Biodiesel fuel production by transesterification of oils. *Journal of Bioscience and Bioengineering* 92, 405–416.
- Goodrum, J.W., Geller, D.P., 2005. Influence of aceto acetic esters and dicarboxylic acid esters on diesel fuel lubricity. *Bioresource Technology* 96, 851–855.
- Kim, H.J., Kang, B.S., Kim, M.J., Park, Y.M., Kim, D.K., Lee, J.S., Lee, K.Y., 2004. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis Today*, 315–320.
- Knothe, G., Sharp, C.A., Ryan, T.W., 2006. Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine. *Energy & Fuels* 20, 403–408.
- Lotero, E., Liu, Y., Lopez, D.E., Suwannakarn, K., Bruce, D.A., Goodwin, J.G., 2005. Synthesis of biodiesel via acid catalysis. *Industrial & Engineering Chemistry Research* 44, 5353–5363.
- Ma, F., Hanna, M.A., 1999. Biodiesel production: a review. *Bioresource Technology* 70, 1–15.
- Meher, L.C., Sagar, D.V., Naik, S.N., 2006. Technical aspects of biodiesel production by transesterification: a review. *Renewable and Sustainable Energy Reviews* 10, 248–268.
- Nabi, N., Akhter, S., Shahadat, M.Z., 2006. Improvement of engine emissions with conventional diesel fuel and diesel–biodiesel blends. *Bioresource Technology* 97, 372–378.
- Plank, C., Lorbeer, E., 1995. Simultaneous determination of glycerol, and mono-, di- and tri-glycerides in vegetable oil methyl esters by capillary gas chromatography. *Journal of Chromatography A* 697, 461–468.
- Reichle, W.T., 1985. Catalytic reactions by thermally activated, synthetic, anionic clay minerals. *Journal of Catalysis* 94, 547–557.
- Schumacher, L.G., Borgelt, S.C., Fosseen, D., Goetz, W., Hires, W.G., 1996. Heavy-duty engine exhaust emission tests using methyl ester soybean oil/diesel fuel blends. *Bioresource Technology* 57, 31–36.
- Siano, D., Nastasi, M., Santacesaria, E., Di Serio, M., Tesser, R., Minutillo, G., Ledda, M., Tenore, T., 2006. International Patent Application No. WO 2006/050925.
- Srivastava, A., Prasad, R., 2000. Triglycerides-based diesel fuels. *Renewable and Sustainable Energy Reviews* 4, 111–133.
- Suppes, G.J., Dasari, M.A., Daskocil, E.J., Mankidy, P.J., Goff, M.J., 2004. Transesterification of soybean oil with zeolite and metal catalysts. *Applied Catalysis A: General* 257, 213–223.
- Wenlei, Xie, Hong, Peng, Ligong, Chen, 2006. Calcined Mg–Al hydrotalcites as solid base catalysts for methanolysis of soybean oil. *Journal of Molecular Catalysis A: Chemical* 246, 24–32.