Int. J. Environ. Sci. Technol. (2013) 10:847–854
DOI 10.1007/s13762-012-0137-4

ORIGINAL PAPER

Utilization of constructional lime as heterogeneous catalyst in biodiesel production from waste frying oil

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Received: 24 January 2012 / Accepted: 2 August 2012 / Published online: 19 March 2013

Abstract Waste frying oil as valueless material which is disposed to environment can be used as a promising feedstock to produce biodiesel. In this study, constructional lime was used as alkaline heterogeneous catalyst for biodiesel production from virgin and waste frying oil. After determining the best activation temperature for the catalyst (600 °C), transesterification reactions were carried out at 65 °C, MeOH to oil molar ratio of 12:1, and 1 wt% of activated constructional lime under vigorous mixing for 5 h. Yield of reactions for virgin and waste frying oil (2.17 % free fatty acid) and pretreated waste frying oil (0.918 % free fatty acid) were 87, 93.9, and 94 %, respectively. Transesterification of virgin frying oil and pretreated waste frying oil were done at 65 °C, MeOH to oil molar ratio of 6:1, and 1 wt% of KOH as catalyst under vigorous mixing for 2 h, for comparison. Yield of the reaction was 98.6 and 95.1 %, respectively. Therefore, when constructional lime is used as catalyst pretreatment of waste oil is not necessary.

Keywords Fatty acid methyl ester · Lime · Solid base catalyst · Transesterification · Waste oil

Introduction

Fatty acid alkyl ester (FAAE) or biodiesel which is produced from renewable feed stocks such as vegetable oils and animal fats has gained great attention of many nations in recent decade. This bio-fuel is a sustainable alternative for decreasing fossil diesel, and will be very important in future (Janaun and Ellis 2010; Jacobson et al. 2008; Umdu et al. 2009; Zabeti et al. 2009a; Silva et al. 2010). Moreover, it has a lot of benefits rather than traditional diesel fuel. Some of them are as follow: environmental friendly emissions, biodegradable and renewable, non-toxic, better lubricity, no sulfur, and aromatic content, and it can be used in diesel engine without any change (Jacobson et al. 2008; Umdu et al. 2009; Leung et al. 2010; Li et al. 2009; Ghanei et al. 2011; Balat and Balat 2010). Furthermore, it is the only alternative fuel that passed the health effects testing requirements of the 1990 Clean Air Act Amendments (Jacobson et al. 2008).

Biodiesel is produced by alcoholysis (commonly methanolysis) of triglycerides (TGs) in the presence of appropriate catalyst. This reaction is called as transesterification. Figure 1 shows the scheme of the mentioned reaction (Leung et al. 2010; Ghanei et al. 2011; Veljković et al. 2009, Boz et al. 2009; Helwani et al. 2009). Since the cost of raw material has a major impact on final price of biodiesel, use of inexpensive feed stocks such as waste frying (WFO) and cooking oil (WCO) is recommended to reduce final price of biodiesel. The main problem of these type oils is high free fatty acid (FFA) content which makes some difficulties in process (Jacobson et al. 2008; Fraile et al.

Electronic supplementary material The online version of this article (doi:10.1007/s13762-012-0137-4) contains supplementary material, which is available to authorized users.

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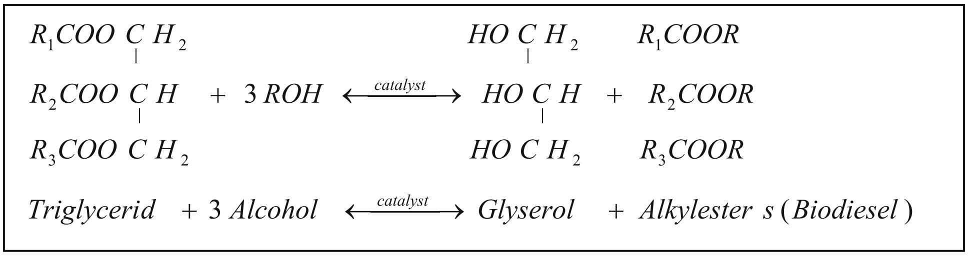

$$\begin{array}{llcll} R_1COO\,CH_2 & & & HO\,CH_2 & R_1COOR \\ R_2COO\,CH & +\ 3\,ROH & \xleftrightarrow{catalyst} & HO\,CH & +\ R_2COOR \\ R_3COO\,CH_2 & & & HO\,CH_2 & R_3COOR \\ Triglycerid & +\ 3\ Alcohol & \xleftrightarrow{catalyst} & Glyserol & +\ Alkylester\ s\,(Biodiesel) \end{array}$$

Fig. 1 The scheme of transesterification of triglycerides (TGs)

2009; Sharma and Singh 2009; Sabudak and Yildiz 2010). Although strong and homogenous bases are able to accomplish the reaction over 98 %, very fast recovery of catalysts is much difficult and makes hazardous waste waters (Ghanei et al. 2011; Veljković et al. 2009; Kawashima et al. 2008; Silva et al. 2010). Moreover, when waste oils are used as feed, the catalyst is consumed to form soap instead of biodiesel due to the high FFA of used oil (Jacobson et al. 2008; Ghanei et al. 2011; Balat and Balat 2010). Hence, introducing new catalytic systems, especially heterogeneous catalysts, is necessary. Heterogeneous catalysts are separated from products easily and they can be used several time, and also prevent the formation of unwanted byproduct and waste waters (Li et al. 2009; Ghanei et al. 2011; Kawashima et al. 2008; Boz et al. 2009; Guo et al. 2010).

There are two main categories in heterogeneous catalysts that are applicable in transesterification process, acidic and basic solids. In the first group solid acids such as tungstophosphoric acid, zinc ethanoate, zinc stearate and transition metal oxides which have acidic characterization on alumina and silica as support were investigated, and zinc stearate on silica gel selected as the best one (Jacobson et al. 2008; Helwani et al. 2009; Sharma and Singh 2009). In the second group, further investigations have been performed due to good accessibility and high activity in moderate reaction conditions. Alkali earth metal oxide and methoxide and mixture of them, especially calcium oxide, are reported as active catalysts (Veljković et al. 2009; Kawashima et al. 2008; Sun et al. 2010; Liu et al. 2007; Wen et al. 2010; Liu et al. 2008a, 2008b; Zabeti et al. 2009b; Fraile et al. 2009; Guo et al. 2010). In most cases, laboratory grade or synthesized CaO, which is expensive, with or without support has been used as catalyst to transesterify the virgin edible oil to biodiesel, and high yield has been achieved (Liu et al. 2008b; Kouzu et al. 2008, 2009; Albuquerque et al. 2008). Recently, in order to prepare CaO from low expense and useless resources, use of waste materials such as egg shell, oyster shell, mud carb shell, and cockle shell has been reported by Chakraborty et al. (2010), Viriya-empikul et al. (2010), Nakatani et al. (2009) and Boey et al. (2009, 2011), respectively.

Lime as a constructional material is produced from heating of lime stone in the large traditional limekiln, in commercial scale. Calcium oxide is the predominant constituent of lime that absorbs water intensively and forms quicklime (calcium hydroxide). Thus, this inexpensive and abundant material can play the role of catalyst in transesterification of vegetable oils, with a minor pretreatment. Low price of constructional lime (CL) and WFO, and lack of sufficient information in this field encouraged us to perform this work. In the present study, transesterification of virgin and WFO in the presence of lime as catalyst have been investigated. In the first step, appropriate temperature for catalyst pretreatment process was determined. Then, transesterification of WFO with and without acid pretreatment were performed, and the products were evaluated. Finally, the results were compared to corresponding homogenous alkali catalyst process. The main steps of research were done during 2011 in Biodiesel Research laboratory of Islamic Azad University (Farahan branch), Farahan, Iran. Also some analytical services were received from Isfahan University, Isfahan, Mahidasht agro-industry, Kermanshah, and NPC-RT co., Tehran, Iran.

Materials and methods

Waste frying oil was collected from local restaurant. Virgin frying oil (VFO) with the brand name of “Varamin” was supplied by the mentioned restaurant. Constructional lime was supplied from construction workshop in campus. The reagents used during synthesis and purification procedures were: methanol 99.9 % (chromatography grade, Merck), potassium hydroxide (KOH) 85 % pellets (GR for analysis, Merck), hydrochloric acid 37 % (GR for analysis, Merk), n-Hexane 95 % (extra pure, Merk), and some other chemicals were purchased from country company. Methyl laurate (methyl dodecanoate) ≥99.7 % were supplied from Sigma as standard for GC analysis.

Catalyst pretreatment

Excess amount of lime was charged in a crucible and it was put in electrical furnace. The furnace was warmed up to the assigned temperature and this condition was kept for 4 h. Then, activated catalyst was cooled to 150 °C, naturally. At this time, appropriate amount of catalyst was weighed and transferred to reactor, immediately.

Catalyst characterization

The X-ray diffraction (XRD) patterns of the CL as catalyst at different preheating temperature were recorded on a Bruker D8 Advance X-Ray Diffractometer equipped with a graphite monochromator, copper radiation, and scintillation counter (detector) in the range of $2\theta = 5–80°$. The surface area and pore size of the 600 °C preheated CL were measured by N_2 adsorption/desorption using a Quantachrome NOVA Automated Gas Sorption System (Quantachrome Instruments). Before N_2 adsorption/desorption measurement, the catalyst was heated under nitrogen flow at 573 K overnight in a Quantachrome Flow Degasser to desorb any impurities that might have adsorbed on the solid during exposure to air.

Waste frying oil pretreatment

Collected WFO was too much dark and also it contained solid particles. Thus, it was heated up to melt solid portion of oil, and then WFO was filtered under vacuum to separate solid impurity. The filtered oil was heated up to 110 °C and retained these condition for 15 min, to evaporate the water (Sabudak and Yildiz 2010).

Soap and acid value

Soap index or value is defined as mg of KOH consumed for saponification of 1 g of oil. This index was determined for the virgin and WFO according to Cd 3b-76 AOCS official methods (1998). Soap value is necessary to determine average molecular weight of oil.

Acid index or value is defined as mg of KOH consumed to neutralize the free fatty acids which exist in 1 g of oil. Acid value was determined for the WFO and intermediate products according to Ca 5a-40 AOCS official methods (1998).

Acid processing (pretreatment) of waste frying oil

In order to reduce the acid value, esterification of WFO was carried out in a 500 ml three neck flat bottom flask that it was placed on a hot plate magnetic stirrer, and it was equipped with a condenser and thermometer. The reactor was charged by 250 g of oil, initially and then heated up to 65 °C. Next, concentrated hydrochloric acid (2 % based on oil weight) was dissolved in methanol (methanol/oil molar ratio was 6), and then the solution was added to reactor and reaction. This reaction was continued for 6 h under vigorous mixing and temperature controlling. After the mentioned reaction time, the flask was cooled and reaction mixture was transferred to separator funnel. After enough settling, the residual methanol was separated from oil layer. The product was washed with hot distilled water to remove remained catalyst. Washing was continued until drainage pH became same as distilled water. Then the product was heated up to 110 °C for about 15 min to eliminate residual water and methanol.

Biodiesel synthesis

Transesterification of virgin and WFO was carried out in a 250 ml three neck flat bottom flask that it was equipped with a condensation system and thermometer. The reactor was placed on a hot plate magnetic stirrer. Operational conditions were as follows: atmospheric pressure; weight of catalyst: 1 % based on initial oil weight; methanol/oil molar ratio: 12; reaction temperature, 65 °C; under vigorous mixing that was made by magnet stirrer and reaction times were 1, 2, and 5 h. The reactor was charged by 100 g of oil initially, and heated up to the reaction temperature. Then, mentioned amount of catalyst was poured on oil. Finally, the methanol was added to reactor and reaction was started. In the case of homogenous alkali catalyst, KOH pellet was dissolved in methanol. After the mentioned reaction time, the flask was cooled immediately and reaction mixture was separated, and the produced biodiesel was washed with hot distilled water and dehydrated same as previous section.

Determination of catalyst pretreatment temperature

Transesterification of VFO was carried according to Sect. "Biodiesel synthesis". Operational conditions were as follows: atmospheric pressure; weight of catalyst: 5 % based on initial oil weight; methanol/oil molar ratio: 12; reaction temperature, 65 °C; under vigorous mixing that was made by magnet stirrer and reaction time was 5 h. Different temperature was set for catalyst pretreatment process, without pretreatment 200, 400, 600, 800, and 1000° were examined.

Biodiesel characterization

The composition and quantity of fatty acid methyl ester (FAME) in biodiesel was determined using a HP 6890 gas chromatograph with a flame ionization detector FID. The capillary column was a BPX-70 high polar column with a length of 120 m, a film thickness of 0.25 μm, and an internal diameter of 0.25 mm. Nitrogen was used as carrier gas and also as an auxiliary gas for the FID. One microliter of sample was injected using a 6890 Agilent Series Injector. Lauric acid methyl ester (methyl laurate) was added as a reference into the crude biodiesel, and the samples were analyzed by the above mentioned GC. The analysis of biodiesel for each sample was carried out according to Wang et al. (2006).

$$\text{FAME wt\%} = \left(\frac{\text{area of all FAME}}{\text{area of reference}} \times \frac{\text{weight of reference}}{\text{weight of Biodiesel sample}} \times \frac{f_{\text{FAME}}}{f_r}\right) \times 100 \qquad (1)$$

where f is correction factor for transforming area % to wt%, and it can be obtained from calibration.

Physical properties measurement

Specific gravity is defined as ratio of density (weight of unit volume) to density of pure water in 60 °F. This property was measured by standard E100 hydrometer in 60 °F bath according to ASTM 1298 (Ghanei et al. 2011). The ability of a material to flow is named as viscosity. ASTM D 445 provides a method for obtaining the kinematic viscosity and the calculation method to determine the dynamic viscosity (Fernando et al. 2007). Cannon glass capillary kinematic viscometer was used for determination of viscosity of all biodiesel samples. The temperature in which the first crystalline particles are formed is the cloud point. It is the starting point to freezing. Cloud point of the samples was measured according to ASTM 2500. E1 thermometer was used and cold bath was made by use of ethanol and solid carbon dioxide. The temperature un which the first droplet of solid sample can flow is defined as pour point. It is the starting point to melting. This property was measured for the samples according to ASTM D97. E1 thermometer was used and cold bath was made by use of ethanol and solid carbon dioxide. Flash point temperature is the minimum temperature at which vapor pressure of the hydrocarbon is sufficient to produce the vapor needed for spontaneous ignition of the fuel with air in the presence of an external source, i.e., spark or flame. A Pensky-Martens closed-cup tester of fuel oils (ASTM 1994a) was used to determine this property according to ASTM D 93 (Fernando et al. 2007).

Results and discussion

Catalyst characterization

The surface area and pore size data for preheated CL at 600 °C as desired catalyst were measured according to Sect. "Catalyst characterization", and the results are presented in Table 1. Depending on reported results, surface area and pore volume of the mentioned catalyst is inadequate. Therefore, more researches are necessary to enhance the surface area and pore volume through use of better structure or use of support. Medium pore diameter put this catalyst in mesoporous category. However, due to low porosity, it is not important.

Figure 2 shows XRD patterns for CL with different preheating temperatures. According to XRD graph, CL is composed of calcium carbonate (~80 %) and calcium hydroxide (~20 %), when no preheating was considered. Majority of calcium carbonate phase is in the form of calcite (~90 %) and remained part is in aragonite form

Table 1 Surface area data for desired catalyst

Catalyst name	BET surface area (m^2/g)	BJH surface area (m^2/g)	BJH pore volume (cm^3/g)	BJH pore diameter (Å)
Preheated lime at 600 °C	6.064	6.921	3.792e−2	25.3

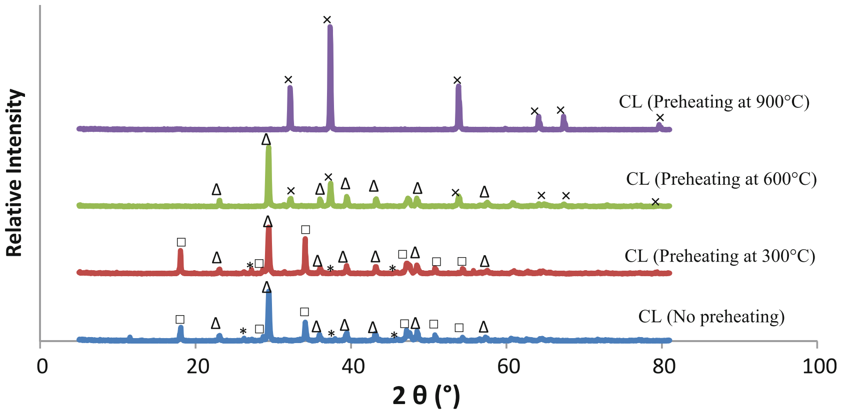

Fig. 2 XRD patterns for constructive lime at different preheating temperature

(~10 %). In this step, no CaO phase has been detected. When preheating process was performed in 300 °C no important change was observed. Calcium carbonate (aragonite) and calcium hydroxide peaks completely disappeared, after preheating process at 600 °C, and instead of them, calcium oxide peaks were appeared. Preheating at higher temperature conduced to transform all of compounds to CaO form. Since the active component in transesterification of TGs is calcium oxide, CL without heat pretreatment cannot catalyze the reaction. Therefore, pretreatment should be done, at least, at 600 °C to regenerate the CaO that it is transformed to $Ca(OH)_2$ during storage time, due to water absorption. At this step, unconverted $CaCO_3$ play the role of support in catalyst. If it is necessary to convert all of constituents to CaO, preheating at 900 °C is suitable (Liu et al. 2008a; Kouzu et al. 2008).

Optimizing the catalyst pretreatment temperature

Six similar reactions were performed according to Sect. "Determination of catalyst pretreatment temperature" at different pretreatment conditions. Particle size for lime was between 180 and 250 µm. After completion of each reaction, weight percent of fatty acid methyl ester (biodiesel) for all samples were determined according to Sect. "Biodiesel characterization". Purity of biodiesel or weight percent of fatty acid methyl ester in reaction product as function of pretreatment condition (temperature) has been presented in Fig. 3. It is obvious that when no pretreatment was used and when the temperature was less than 400 °C, the conversion of triglyceride is poor. In fact, no reaction has happened. However, when pretreatment temperature was increased to 400 °C, the catalyst was activated, fairly, and moderate conversion was seen. When, the temperature was elevated to 600 °C and more, concentration of biodiesel in product increased, intensively. Although all temperatures higher than 600 °C are suitable for catalyst activation, influence of temperature on biodiesel purity is negligible. On the other hand, mechanical strength of catalyst was decreased when pretreatment temperature was above 600 °C and it caused purification step more difficult. Therefore, 600 °C was selected as best pretreatment temperature for all of this work. According to XRD results, preheated CL at 600 °C contains around 30 % CaO, and the above result shows more CaO in reaction medium is excess and it does not influence on yield.

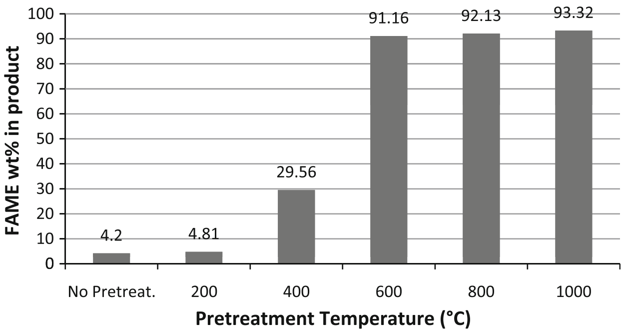

Fig. 3 Biodiesel concentration in reaction product at different pretreatment temperature

Acid processing of waste frying oil

At first, WFO was so much dirty, had bad smelling, and the color was dark brown. After pretreatment (Sect. "Waste frying oil pretreatment"), some characterization tests including soap index and acid value were done. Composition and the other data for WFO were given in Table 2. Free fatty acid weight percent for WFO before esterification was 2.17 %, which is more than acceptable value (0.5 %) for base-catalyzed transesterification. Also, this amount of FFA in feed forms soap in product, if homogenous alkali catalyst will be used. In order to reduce the FFA content of feed, acid catalyzed esterification was performed according to Sect. "Soap and acid value", and after 2, 4, 6 h the FFA% was 1.04, 1, and 0.918 %, respectively. Figure 4 shows the changes of free fatty acid percentage during esterification reaction. From Fig. 4, it is clear that only 2 h acid processing was sufficient. After 2 h, no significant change in FFA% was occurred. However, after 6 h the reaction mixture with FFA% equal to 0.918 % is subjected to alkali catalyzed process. In this

Table 2 Composition and some characterization data of waste frying oil

Characterization	WFO
Free fatty acid (wt%)	2.17
Saponification index (mg KOH/g oil)	207.67
Mean molecular weight (g/mol)	810.416
Fatty acid composition	(wt%)
Lauric (C12:0)	0.35
Myristic (C14:0)	0.85
Palmitic (C16:0)	30.14
Palmitoleic (C16:1)	3.15
Stearic (C18:0)	5.65
Oleic (C18:1)	41.21
Linoleic (C18:2)	17.54
Linolenic (C18:3)	0.75
Arachidic (C20:0)	–
Eicosenoic (C20:1)	–
Behenic (C22:0)	0.35
Erucic (C22:1)	–

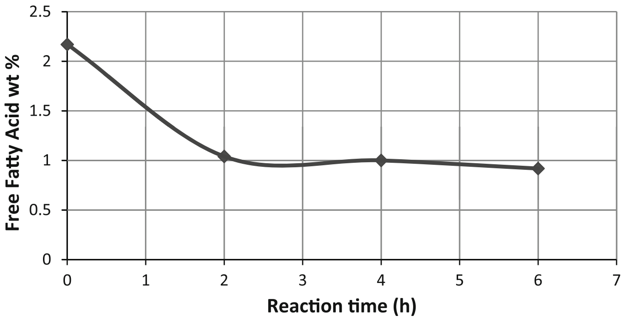

Fig. 4 Variation of free fatty acid content during acid catalyzed esterification

Fig. 5 Variation of biodiesel concentration during acid processing step

stage, transesterification of oil is performed parallel to esterification. The progress of biodiesel generation was measured according to Sect. "Biodiesel characterization" and presented in Fig. 5. As depicted in this figure esterification and transesterification of FFA and TGs are performed slowly (Wang et al. 2006; Zhang et al. 2003), in which after 6 h the methyl ester weight percent was 29.4 %. Depending on Fig. 3, only in the first 2 h of reaction esterification is significant, and afterward, biodiesel production is due to acidic transesterification.

Biodiesel synthesis

Alkali catalyzed biodiesel synthesis was performed at same operating condition according to Sect. "Biodiesel synthesis" for VFO, WFO, and acid processed waste frying oil (WFO6) with CL as heterogeneous catalyst, and KOH as good homogenous catalyst. The obtained results (FAME wt% in product) are given in Table 3. Figure 6 shows reaction progress for VFO and WFO6 in transesterification to biodiesel which is catalyzed by KOH (homogenous catalyst). Similarly, Fig. 7 shows reaction progress for VFO, WFO, and WFO6 in biodiesel production process in the presence of CL as heterogeneous catalyst. In case of WFO transesterification with KOH, reaction was impossible.

Table 3 FAME wt% in product for all reactions versus reaction time

Reaction time (h)	VFO (CL)	WFO (CL)	WFO6 (CL)	VFO (KOH)	WFO6 (KOH)
0	0	0	29.4	0	29.4
1	43.1	72.3	86.4	90.8	91.2
2	67	92.04	93.5	98.6	95.1
5	87	93.9	94	–	–

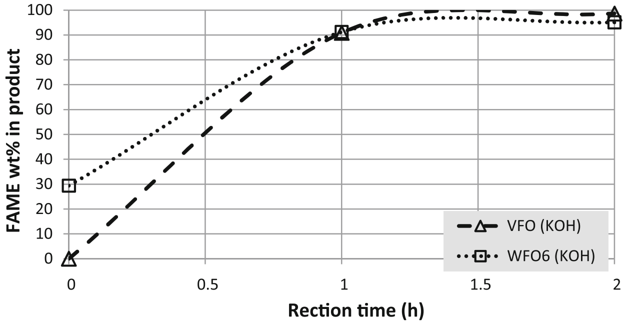

Fig. 6 Variation of FAME concentration during biodiesel production in presence of KOH as homogenous catalyst

According to Table 3 and Figs. 6 and 7, in the case of homogeneous catalyst (KOH), the reaction rate was faster than heterogeneous catalyst (CL) and after 2 h the reaction was nearly completed. Also, it is obvious that most of oil conversion has occurred before 1 h (Ghanei et al. 2011). In Fig. 6, it seems that FAME concentration for WFO6 is more than VFO in first half of reaction, but in second half it is vice versa and moreover, the differences between them are little. This event is due to initial level of FAME which is produced in acid processing of WFO. This phenomenon is also seen for heterogeneous catalyst (Fig. 7), but final concentrations of FAME in products are same for both WFO6 and WFO. It means in case of heterogeneous catalyst no acid processing is necessary. Therefore, elimination of this step which includes separate reactor and lots of hazardous waste waters and corrosion problems helps to

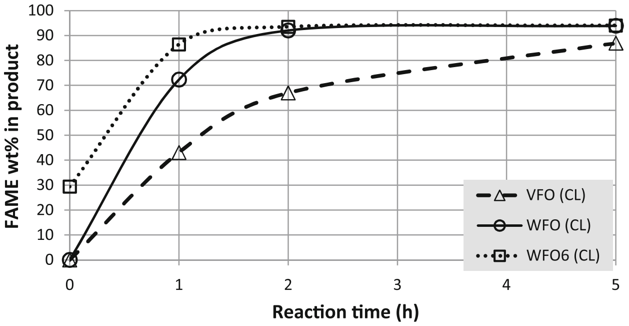

Fig. 7 Variation of FAME concentration during biodiesel production in presence of constructive lime as heterogeneous catalyst

Table 4 Physical properties for produced biodiesel

Property	VFO (CL)	WFO (CL)	WFO6 (CL)	VFO (KOH)	WFO6 (KOH)
FAME (wt%)	87	93.9	94	98.6	95.1
Specific gravity	0.891	0.881	0.880	0.877	0.881
Flash point (K)	449	441	439	435	436
Cloud point (K)	291	281	282	283	281
Pour point (K)	285	276	276	279	279
Viscosity (cP)	5.08	4.40	4.24	4.08	4.31

simplify the process, well. Otherwise, for homogeneous catalyst biodiesel production in the presence of high free fatty acid content is impossible. In comparison between Figs. 6 and 7 two things are obvious. First, when CL is used as heterogeneous catalyst the needed reaction time to complete is around two times that of homogeneous catalyst (KOH). Second, for VFO there is remarkable difference in progress of reaction with two types of catalysts.

Table 4 summarizes some important physical properties of various biodiesels which were produced in present study. According to Table 4, for all produced biodiesel except VFO (CL) have good physical properties as diesel fuel. Also, there is no considerable quality difference among products. It means in view point of physical properties, CL can be used as good catalyst to produce high quality biodiesel from waste oils as well as homogeneous catalysts.

Conclusion

Constructional lime as alkaline solid was utilized as heterogeneous catalyst for transesterification of virgin and WFO. At first, activation temperature (preheating temperature) was determined and then the desired catalyst was examined for mentioned purposes. Following points were concluded:

- Activation of CL as catalyst is necessary, due to regenerate CaO phase. Temperature of 600 °C is sufficient for desired conversion, and higher temperature increases amount of CaO in reaction medium without considerable influence on yield.
- No acid pretreatment for WFO with 2.17 wt% FFA is needed, and 93.9 % conversion was obtained after 5 h with 1 wt% preheated CL at 600 °C and methanol to oil molar ratio equal 12. Because this result is similar when 6 h acid processing was used (94 %) and no significant soap formation was observed.
- In comparison between KOH and CL, KOH has high activity and completes the reaction very fast; but it is not suitable for WFO, and acid processing is essential. On the other hand, the result of CL is very close to KOH.

In order to increase ester content of product to meet the EN 14214 specification, some approaches are proposed as follow: Enhancement of catalyst characteristics e.g., surface area and pore diameter. Use of higher amount of methanol and/or catalyst. Use of co solvent to dilute the oil for better diffusion, and break the inter phase mass transfer resistance. Use of advanced purification technique to purify the product.

Acknowledgments The authors acknowledge the analytical support of Mahidasht agro-industry co. (Nazgol).

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