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Original Research Paper

Kinetic comparison of two basic heterogenous catalysts obtained from sustainable resources for transesterification of waste cooking oil

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HIGHLIGHTS

➢DM water treatment precipitates as a novel catalyst for biodiesel production.

➢Reusability/stability of the new catalyst was higher than the calcinated waste mussel shells.

➢After five times of reusing the new catalyst, only 6.15% of CaO was extracted by methanol.

➢Reaction in presence of the new catalyst was faster than the calcinated mussel shells.

GRAPHICAL ABSTRACT
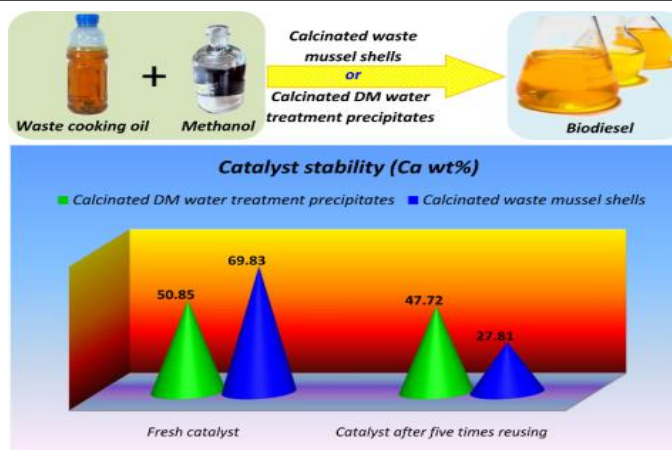
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ABSTRACT

Alkaline earth metal oxides are appropriate catalysts for biodiesel production and among them, CaO and MgO are known for possessing the best efficiency. In this study, catalysts synthesized from economical and sustainable resources were used for biodiesel production. More specifically, waste mussel shells and demineralized (DM) water treatment precipitates as calcium and magnesium carbonate sources, were converted into calcium and magnesium oxides at temperatures above 900 °C. Methanol and waste cooking oil were reacted in a 250 mL two-necked flask at 24:1 and 22.5:1 ratios in presence of 12 and 9.08 wt% of mussel shell-based and DM water treatment precipitates-based catalysts, respectively. The effects of temperature (328, 333, 338, 343 and 348 K) and time (1, 3, 5, 7 and 8 h) at a stirrer speed of 350 rpm on the conversion of the oil into biodiesel were investigated. The results obtained indicated a pseudo-first order kinetics for the transesterification reaction using both catalysts. The activation energies in the presence of the DM water treatment precipitates and mussel shell catalysts were measured at 77.09 and 79.83 kJ.mol⁻¹, respectively. Accordingly, the DM water treatment precipitates catalyst resulted in a faster reaction due to its lower activation energy value. Moreover, the catalysts were reused five times and the results obtained showed that the methanol-driven extraction of CaO contained in the DM water treatment precipitates catalyst was lower than the waste mussel shell catalyst proving the higher stability of the new heterogeneous catalyst i.e. the calcinated DM water treatment precipitates.
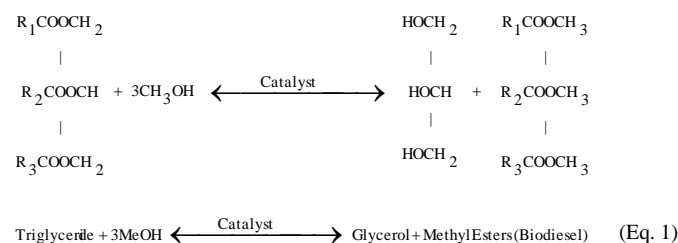
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1. Introduction

Due to the increasing demand for fuel and energy and limited fossil fuel resources, a great deal of attention has been paid to alternative renewable fuels (Liu et al., 2011; Rezaei et al. 2013). Biodiesel, also known as fatty acid methyl ester (FAME), is obtained through the transesterification reaction between oil and alcohol in the presence of a suitable catalyst (Kouzu et al., 2008; Yin et al., 2012). Biodiesel in comparison with the fossil-based diesel fuel, not only has higher lubricity, flash point, oxygen content and cetane number but also results in lower hazardous emissions when combusted because of its low sulfur content (Kouzu et al., 2008; Omar and Amin, 2011; Lin and Cheng, 2012; Yin et al., 2012). Biodiesel can be derived from vegetable oils, animal fats, and waste cooking oil (Endalew et al., 2011; Taufiq-Yap et al., 2011).

Transesterification reaction occurs between triglycerides and methanol leading to the production of FAME and glycerol as byproduct (Di Serio et al., 2008; Veljkovic et al., 2009; Endalew et al., 2011; Sharma et al., 2011; Taufiq-Yap et al., 2011). The typical reaction scheme for the transesterification is presented in the following equation (**Eq. 1**).

$$
\begin{array}{ccc}
R_1COOCH_2 & & HOCH_2 \quad R_1COOCH_3 \\
| & & | \qquad\qquad | \\
R_2COOCH + 3CH_3OH \xrightleftharpoons{\text{Catalyst}} & HOCH + R_2COOCH_3 \\
| & & | \qquad\qquad | \\
R_3COOCH_2 & & HOCH_2 \quad R_3COOCH_3
\end{array}
$$

$$
\text{Triglyceride} + 3\text{MeOH} \xrightleftharpoons{\text{Catalyst}} \text{Glycerol} + \text{Methyl Esters (Biodiesel)} \qquad \text{(Eq. 1)}
$$

Compared to homogenous catalysts, basic and acidic heterogeneous catalysts have the advantages of easy and cheap separation and regeneration (Birla et al., 2012; Gaikwad and Gogate, 2105). Overall, basic heterogeneous catalysts are preferred because of their higher activity compared to acidic ones (Endalew et al., 2011). Among the basic heterogeneous catalysts, calcium oxide (CaO) has attracted the most attention because of its high catalytic activity, regenerability/reusability, and that there are plenty of relatively inexpensive resources for its production (waste shells, egg shells, etc.). Moreover, CaO is not sensitive to small amounts of FFA and moisture, and is therefore, suitable for waste cooking oils (Veljkovic et al., 2009; Boey et al., 2011).

Regardless of the type of the catalyst used, establishing the reaction kinetics is necessary in order to obtain more in-depth information such as reactor configuration, reaction time and optimum process temperature. Veljkovic et al. (2009) studied the kinetics of sunflower oil transesterification with methanol over CaO as catalyst. They found out that during the first stage of the process, mass transfer of triglyceride controlled the reaction and in the latter stage, the chemical reaction became the rate determining factor (Veljkovic et al., 2009). In a different study, Dossin et al. (2006) investigated the kinetics of ethyl acetate methanolysis catalyzed by magnesium oxide (MgO) as heterogeneous catalyst. They used a three step 'Eley-Ridel' mechanism in liquid phase and reported that methanol adsorption was the rate determining step in that reaction (Dossin et al., 2006). Birla et al. (2012) reported a first order kinetics for the transesterification of waste cooking oil in the presence of snail shell as a heterogeneous base catalyst. They determined the activation energy of 79 kJ.mol^{-1} and the frequency factor of 2.98×10^{10} min^{-1} (Birla et al., 2012). Recently, Pukale et al. (2015) investigated the effect of ultrasound on kinetics of transesterification of waste cooking oil using heterogeneous solid catalyst. They reported an activation energy of 64.241 kJ.mol^{-1} in presence of K$_3$PO$_4$ catalyst. Moreover, they obtained a higher yield in the presence of ultrasound as compared to the conventional approach under similar conditions (Pukale et al., 2015).

The cost of raw material typically accounts for about 70–80 % of the total cost of biodiesel production. Therefore, there is a need to develop technologies for producing biodiesel from non-edible and waste oil resources using highly efficient catalysts (Gole and Gogate, 2012a; Maddikeri et al., 2012; Gaikwad and Gogate, 2105). On such basis, the present study was set to reduce the cost of biodiesel production from waste cooking oil using CaO and MgO catalysts generated from inexpensive resources. More specifically, waste mussel shells containing lots of calcium carbonate was converted into CaO by calcination at 1050 °C as elaborated in our previous study (Rezaei et al., 2013). Moreover, a novel catalyst was also prepared herein by conversion of DM water treatment precipitates into CaO/MgO by calcination at different temperature values. Both catalysts were then compared by taking into account the effects of temperature (328, 333, 338, 343 and 348 K) and time (1, 3, 5, 7 and 8 h) at a stirrer speed of 350 rpm on the conversion of the oil into biodiesel. Finally, the reusability/stability of the new catalyst was compared with that of the calcinated waste mussel shells by re-using for five times.

2. Materials and methods

2.1. Materials

Waste cooking oil obtained from a local restaurant and methanol 99.5 % (Merck, Germany) were used in this study for esterification and transesterification reactions. Sulfuric acid 97 % (Merck, Germany) was used as catalyst in the esterification reaction. Potassium hydroxide 85 % (Merck, Germany) was used for determination of acidic number. Waste mussel shell and DM water treatment precipitates were used as the source for generating the catalysts used in the transesterification reaction. *n*-hexane 95 % (Merck, Germany) and methyl laurate (methyl dodecanoate) >99.7 % supplied by Sigma Aldrich were used in the gas chromatography (GC) analyses for determining the produced biodiesel purity.

2.2. Catalysts preparation and characterization

Mussel shell and DM water treatment precipitates were ground by a mortar. Obtained powders were sieved to separate micro-particles (125-250 μm), and were then dried at 110 °C for 18 h. Finally waste mussel shell powder was calcinated at 1050 °C accordingly to our previous findings (Rezaei et al., 2013) and DM water treatment precipitates powder was calcinated at different temperatures of 800, 900 and 1000 °C for 2 h to determine the optimal temperature value leading to the highest conversion of calcium and magnesium carbonates into CaO/MgO catalyst.

The crystalline phases of the DM water treatment precipitates calcinated at different temperature values were characterized by X-ray diffraction analysis (XRD). XRD analysis was performed through Cu Ka radiation. The data showing the intensity was plotted in a chart based on 2-Theta in a range of 10–80° with a step of 0.06°. X-ray florescence (XRF) (Spectro Xepor 03 plus) analysis was applied to determine the chemical elements composition of the catalyst after the 2 h calcination.

2.3. Esterification reaction

Since the acidic number of the waste cooking oil was measured at 2 mg KOH/g oil, an esterification stage was carried out to achieve an acidic number below 1 mg KOH/g (Gole and Gogate, 2012b). Esterification reaction was performed with 5 wt% H$_2$SO$_4$ as catalyst, with a methanol to oil molar ratio of 18:1 at 65 °C for 5 h, as previously described by Encinar et al. (2011). After the esterification, the acidic number of the waste cooking oil decreased to 0.49 mg KOH/g oil.

2.4. Transesterification reaction procedure

Transesterification reaction was conducted in a 250 mL two necked flask equipped with a thermometer and a condenser. The mixture of waste cooking oil, methanol and catalyst was mixed using a stirrer at 350 rpm. Optimal values of methanol to oil molar ratio and catalyst concentration were obtained from our previous studies (Rezaei et al., 2013; Davoodbeygi, 2013). To determine the kinetics, the mentioned reaction was carried out at different reaction temperatures of 328, 333, 338, 343, 348 K and different reaction times of 1, 3, 5, 7 and 8 h. After the reaction, the catalyst was first separated by centrifugation and then, glycerol and the produced biodiesel were separated using a separation funnel. For increasing the purity of the produced biodiesel, the product was washed several times with water (90 °C). Finally, the produced biodiesel was dried in the oven at 110 °C for 2 h.

2.5. FAME analysis

FAME characterization was carried out by a HP 6890 gas chromatograph with a flame ionization detector (FID). The capillary column was a BPX-70 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 the carrier gas and also as an auxiliary gas for FID. 1 μL of the sample was injected by a 6890 Agilent Series Injector. The inlet temperature was at 50 °C, which was heated up to 230 °C. Methyl laurate (C12:0) was added as an internal reference into each biodiesel sample prior to GC analysis to determine biodiesel purity using the following equations (**Eqs. 2 and 3**) as described by Rezaei et al. (2013).

$$\text{Purity}(\%) = \frac{\text{area of all FAME}}{\text{area of reference}} \times \frac{\text{weight of reference}}{\text{weight of biodiesel sample}} \times 100 \qquad (\text{Eq. 2})$$

$$\text{Conversion}(\%) = \frac{\text{area of all FAME}}{\text{area of reference}} \times \frac{\text{weight of reference}}{\text{weight of biodiesel sample}} \times \frac{\text{weight of biodiesel produced}}{\text{weight of oil used}} \times 100$$
$$(\text{Eq. 3})$$

2.6. Kinetics of process

The effects of temperature and time were investigated to determine the reaction kinetics. Since the amounts of catalysts used were enough to convert the oil into FAME, thus, the reverse reactions could be ignored. Moreover, the changes in catalysts concentration changes during the reaction could also be overlooked (Zhang et al., 2010). Assuming that the transesterification reaction is carried out in one step, transesterification reaction rate can be calculated through the following equation (**Eq. 4**) (Vujicic et al., 2010):

$$-r_{TG} = -\frac{d[TG]}{dt} = \frac{d[ME]}{dt} = k'.[TG].[ROH]^3 \qquad (\text{Eq. 4})$$

Where r_{TG} represents the rate at which triglycerides are used, [TG], [ME] and [ROH] are triglyceride, methyl ester and methanol concentrations, respectively, and k' is the reaction constant. Because of the high methanol to oil molar ratio, methanol concentration changes during the reaction can be neglected and the reaction can be considered as a pseudo-first order reaction (Freedman et al., 1984; Zhang et al., 2010; Singh and Fernando, 2007). Therefore, the reaction rate could be expressed as follows (**Eq. 5**):

$$-r_{TG} = -\frac{d[TG]}{dt} = k.[TG] \qquad (\text{Eq. 5})$$

In which k is the reaction constant which is equal to $k'.[ROH]^3$ (**Eq. 6**).

$$-\ln(1 - X_{ME}) = k.t \qquad (\text{Eq. 6})$$

Where X_{ME} is the methyl ester conversion.

2.7. Activation energy determination

Arrhenius equation establishes a relation between reaction rate constant (K), temperature (T) and activation energy (E_a) as follows (**Eq. 7**):

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \qquad (\text{Eq. 7})$$

Where k_0 and R are the frequency factor and universal gas constant, respectively. This equation could be rewritten as follows (**Eq. 8**):

$$\ln(k) = -\frac{E_a}{RT} + \ln(k_0) \qquad (\text{Eq. 8})$$

By plotting the diagram of ln (k) vs. 1/T, the slope is equal to -E_a/R and the intercept will be ln (k_0).

2.8. Reusability of catalyst

DM water treatment precipitates catalyst obtained under optimal conditions was re-used for five times. Before each reusing, catalyst was washed by methanol and the residual methanol was vaporized, by heating on a stirrer at 90 °C (100 rpm). XRF analysis was used to compare the major available elements in the catalyst re-used for five times and the fresh catalyst.

3. Results and discussion

3.1. Catalyst preparation and characterization

As illustrated in **Figure 1**, the DM water treatment precipitates catalyst at calcination temperature of 800 °C showed the peaks related to $CaCO_3$, CaO, and MgO. Apparently, at this temperature $MgCO_3$ must have been converted into MgO completely because no peak associated with $MgCO_3$ was observed. At calcination temperatures above 900 °C, the major peaks were related to CaO and MgO only, which indicated full conversion of $CaCO_3$ and $MgCO_3$ to CaO and MgO, respectively. Since the change of calcination temperature from 900 to 1000 °C did not lead to any further favorable changes, therefore, it could be concluded that the optimum calcination temperature for the production of the DM water treatment precipitates catalyst was 900 °C.
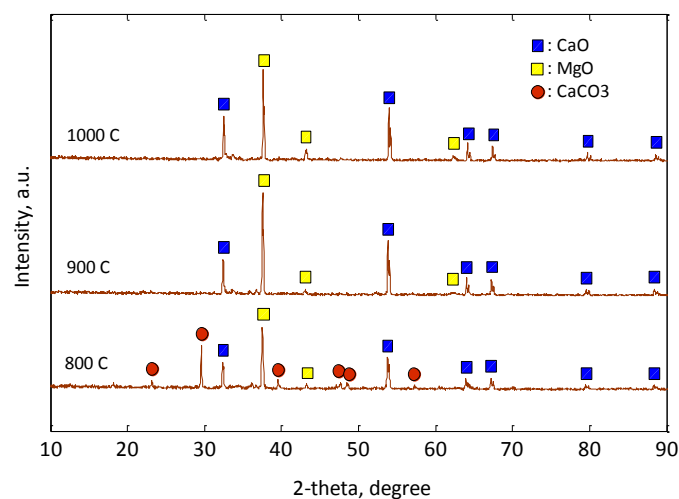

Fig.1. The XRD patterns of the DM water treatment precipitates catalyst calcined at 800, 900 and 1000 °C.

The results of the XRF analysis on the fresh catalyst and the catalyst after five times of reusing in the transesterification reaction are presented in **Table 1**. As seen, about 60 wt% of the fresh calcined DM water treatment precipitates catalyst composed of two elements of Ca (50.85 wt%) and Mg

(9.34 wt%), which are in existence with CaO and MgO molecules, respectively. The results of the XRF analysis of the calcinated waste mussel shell are also presented in the same table (Rezaei et al., 2013).

Table 1.
The weight percentages of the major elements in the fresh and five-time used DM water treatment precipitates catalyst based on the XRF analysis.

Catalyst type	Element	Fresh catalyst	Catalyst after 5 times of reusing	Reference
Calcinated DM water treatment precipitates	Ca, wt%	50.85	47.72	Present study
	Mg, wt%	9.34	9.52	
Calcinated waste mussel shells	Ca, wt%	69.83	27.81	Rezaei et al. (2013)

The major concern pertaining to heterogeneous catalysts used in the Transesterification reaction is that the active part of the catalyst e.g. CaO is extracted by methanol. This in turn reduces the stability/reusability of the catalyst in the subsequent reactions. According to the XRF analysis results, 60.17% of the CaO contained in the calcinated waste mussel shells catalyst was extracted by methanol after five times of reusing in transesterification reaction (Rezaei et al., 2013), while only 6.15% of the CaO contained in the calcinated DM water treatment precipitates catalyst was extracted after five times of reusing. Therefore, the latter resulted in significantly higher biodiesel conversion (data not shown).

3.2. Temperature and time effect

According to our previous study (Davoodbeygi, 2013) at stirring speeds lower than 350 rpm, diffusion problem was the rate-limiting step; while high stirring speeds led to saponification. So, the stirrer speed of 350 rpm was considered for all experiments in the present study. **Table 2** shows conversion (%) of oil into FAME and different times internals and temperatures (i.e. 328, 333, 338, 343 and 348 K) using waste mussel shell and DM water treatment precipitates catalysts. As presented in the table, at all the investigated temperatures, the trends observed for FAME production over time using both catalysts were similar. With increasing the temperature from 328 to 343 K, the conversion rate was improved from 28 and 30% to 78 and 82% using the DM water treatment precipitates and the waste mussel shell catalysts, respectively. Similar trend was also reported by Pukale et al. (2015). Such an increase in biodiesel yield by increasing reaction temperature could be attributed to the enhanced solubility of methanol in oil phase as a result of temperature increase. Further increasing of the temperature had no significant effect on biodiesel yield.

Table 2.
Conversion (%) of oil into FAME at different times and temperatures.

Time (h) \ t (K)	328	333	338	343	348
Waste mussel shell catalyst					
1	8	14	21	25	27
3	18	26	48	56	58
5	23	34	60	66	71
7	27	44	67	78	81
8	30	46	73	82	83
DM water treatment precipitates catalyst					
1	8	16	26	26	27
3	15	27	45	57	59
5	20	38	52	67	69
7	28	48	65	78	79
8	32	51	72	83	84

3.3. Reaction kinetics determination

The kinetics of transesterification reaction of waste cooking oil with methanol in the presence of the waste mussel shell catalyst (12 wt%) and DM water treatment precipitates catalyst (9.08 wt%) at the temperatures of 328, 333, 338, 343 and 348 K under the stirring speed of 350 rpm (methanol to oil molar ratio of 24:1 and 22.5:1, respectively) were investigated in the present study. The exponential trend of methyl ester conversion changes *vs.* time at different temperatures indicated a pseudo-first order kinetics for the transesterification reaction. By fitting the experimental data *via* temperatures in the Equation 6, a good relationship between $-\ln(1- X_{ME})$ and T was obtained. These results for the mussel shell and DM water treatment precipitates catalysts at the temperatures of 328, 333, 338, 343 and 348 K are presented in **Figure 2a** and **b**, respectively. Also the K and R^2 values for each temperature are presented in **Table 3**. As seen in **Figure 2** and **Table 3**, the kinetic rate constant increased with increasing the temperature. Also at high temperature values, the difference between the rate constants was low.
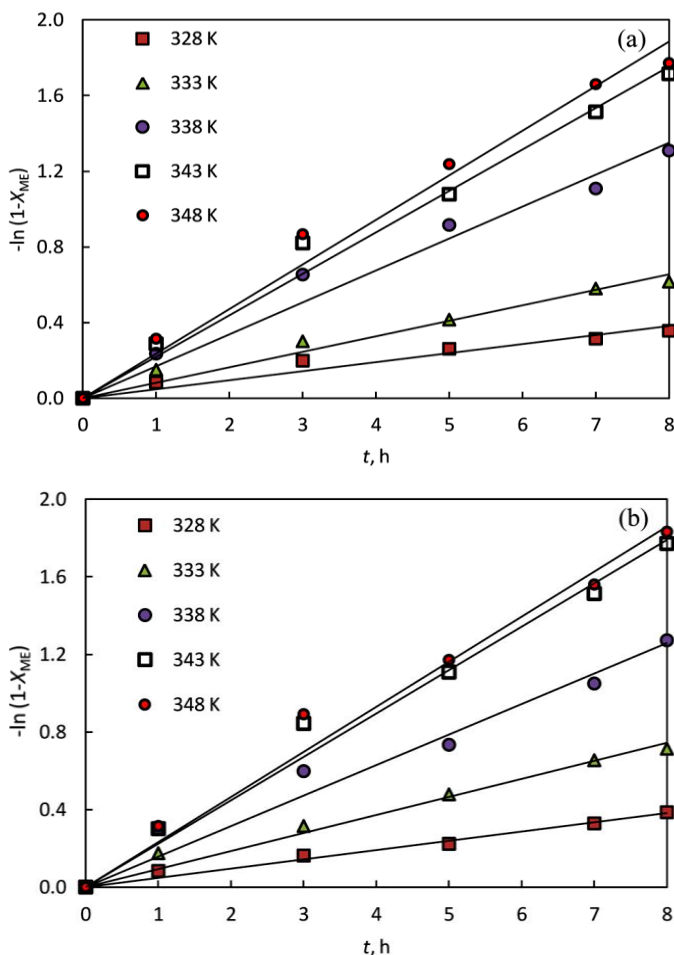

Fig.2. Plot of $-\ln(1 - X_{ME})$ via t at different temperatures, a) mussel shell, b) DM water treatment precipitates

Considering the reaction constant variations *via* temperature, and as shown in **Figure 3**, the transesterification reaction activation energy was obtained through fitting ln (k) data *vs.* $1/T$ with a high accuracy (using **Eq. 8**). For the transesterification reaction in the presence of the waste mussel shell and DM water treatment precipitates catalysts, the activation energy (E_a) were equal to 79.83 and 77.09 kJ.mol^{-1}, respectively.

Table 3.
Transesterification reaction constant rate at different temperatures.

T (K)	K, h^{-1}	R^2
Mussel shell catalyst		
328	0.0476	0.94
333	0.0819	0.97
338	0.1690	0.97
343	0.2193	0.98
348	0.2359	0.98
DM water treatment precipitates catalyst		
328	0.0478	0.98
333	0.0932	0.98
338	0.1574	0.96
343	0.2240	0.98
348	0.2326	0.98

Usually, the activation energy for the transesterification of oil using base catalysts is in the range of 33.6–84 kJ.mol^{-1} (Freedman et al., 1986). The lower activation energy of the transesterification in the presence DM water treatment precipitates catalyst could be ascribed to the presence of the MgO molecules. This resulted in a faster reaction and therefore, it could be concluded that the DM water treatment precipitates catalyst would be more efficient for transesterification reaction. Moreover, the frequency factor (k_0) for the reactions catalyzed by waste mussel shell and DM water treatment precipitates catalysts were found to be at 2.81×10^{11} and 1.08×10^{11} h^{-1}, respectively.

3.4. Kinetics model accuracy

However The rate constants in the presence of the waste mussel shell and DM water treatment precipitates catalysts were obtained as

$$k = 2.81 \times 10^{+11} \exp\left(-\frac{96018}{T}\right) \quad \text{and} \quad k = 1.08 \times 10^{+11} \exp\left(-\frac{92728}{T}\right),$$

respectively. By placing these into the Equation 6 and after simplification, the methyl ester conversion in the presence of the catalysts as a function of temperature (K) and time (h), could be achieved as follows (**Eqs. 9** and **10**):

$$X_{ME,\text{mussel shell}} = 1 - \exp\left(-2.81 \times 10^{+11} \exp\left(-\frac{96018}{T}\right).t\right) \quad \text{(Eq. 9)}$$

$$X_{ME,\text{DM water unit precipitation}} = 1 - \exp\left(-1.08 \times 10^{+11} \exp\left(-\frac{92728}{T}\right).t\right)$$

$$\text{(Eq. 10)}$$

The Equations 9 and 10 were in a good agreement with the experimental data and their mean relative errors (MRE) with the experimental data were measured at 12.33 and 11.68 %, respectively.

4. Conclusions

Using economical and environment-friendly waste-oriented materials would play an important role in economizing and consequently expanding biodiesel production and use all around the world. In this study, DM water treatment precipitates were used as basic heterogeneous catalysts for producing biodiesel from waste cooking oil and methanol and was compared to the catalyst obtained through calcination of waste mussel shells (Rezaei et al., 2013). Since the variations in the methyl ester conversion were exponential at all the studied temperature values, therefore, a pseudo-first order kinetics for the transesterification reaction using both catalysts was considered. The activation energies in the presence of the calcinated DM water treatment precipitates and waste mussel shell catalysts were measured at 77.09 and 79.83 kJ.mol^{-1}, respectively. Hence, the DM water treatment

precipitates catalyst resulted in a faster reaction and could be a better option for industrial biodiesel production. Moreover, the DM water treatment precipitates catalyst had a higher efficiency through five times of reusing and just a small portion (6.15%) of the CaO was extracted by methanol while the loss reported for the calcinated waste mussel shell catalyst stood at 60.17% (Rezaei et al., 2013). Thus, the significantly less methanol-driven extraction rate of CaO from the DM water treatment precipitates marks it as an economical and stable heterogeneous catalyst for biodiesel production from waste cooking oil.

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