

Soybean Oil Transesterification Reactions in the Presence of Mussel Shell: Pseudo-First Order Kinetics

Mohadesi, Majid*⁺

*Chemical Engineering Department, Faculty of Energy, Kermanshah University of Technology,
Kermanshah, I.R. IRAN*

Moradi, Gholamreza; Davvodbeygi, Yeganeh; Hosseini, Shokoufeh

*Catalyst Research Center, Faculty of Chemical and Petroleum Engineering, Razi University,
Kermanshah, I.R. IRAN*

ABSTRACT: Calcium oxide is one of the appropriate catalysts for biodiesel production. In this study, cheap and compatible with environment catalyst has been used. Mussel shell of Persian Gulf coast is one of the sources of calcium carbonate that is converted to calcium oxide at calcination temperature up to 950 °C. Transesterification reaction was carried out at optimum condition of our previous study (calcination temperature of 1050 °C, methanol to oil ratio of 24:1 and catalyst to oil ratio of to 12 wt.%) in a 250mL two-necked flask. In this study, the effects of stirrer speed (250 and 350rpm), the reaction temperature (328.15, 333.15, and 338.15K) and reaction time (1, 3, 5, 7 and 8h) on the methyl ester conversion were investigated. The methyl ester conversion, in stirrer speed of 250rpm, reaction temperatures of 328.15 and 333.15K and reaction times of less than 5h is too low. But at the reaction temperature of 338.15K (near to methanol boiling point), the mixing is increased slightly and the reaction occurs at a higher rate and the methyl ester conversion is increased. These results indicate that diffusion has a significant role in the methyl ester conversion rate in the heterogeneously catalyzed reaction. In stirrer speed of 350rpm, the diffusion problem has been solved somewhat and the reaction in the catalyst surface is the controller of the overall reaction rate. In this stirrer speed (350rpm) the methyl ester conversion versus time in all temperature shows pseudo-first-order kinetics. Firstly, the rate was determined at the various temperatures and then the activation energy for the transesterification reaction of soybean oil with methanol was obtained in the presence of mussel shell as the catalyst. Results demonstrate the high precision of the pseudo-first-order kinetics model regard to methyl esters concentration.

KEYWORDS: Biodiesel; Kinetics; Heterogeneous catalyst; Mussel shell; Transesterification.

* To whom correspondence should be addressed.

+ E-mail: m.mohadesi@gmail.com ; m.mohadesi@kut.ac.ir
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INTRODUCTION

Nowadays, due to the concerns of energy consumption and global warming, bio-based fuels such as biodiesel have been in focus. Biodiesel is a nontoxic and renewable fuel that has found favor because of the properties such as good lubricant properties, high cetane number, lack of aromatics, and lower sulfur emissions [1-3]. But biodiesel fuel is about 1.5 times more expensive than diesel fuel. Another biodiesel disadvantage is that it can harm rubber hoses in some engines. As Biodiesel cleans the dirt from the engine, this dirt can then get collected in the fuel filter, thus clogging it [4].

The most common method for biodiesel production is transesterification of vegetable oils or animal fats with alcohol (methanol or ethanol) in the presence of catalyst [5, 6]. Glycerol is the by-product in the transesterification that can be applied in many applications for instants food, cosmetic and pharmaceutical industries [7]. Conventionally, biodiesel is produced using a homogenous catalyst like alkaline catalysts NaOH or KOH. The advantages of these catalysts are biodiesel production in the short time (about 1 h) and the reaction occurs under mild conditions, but this process requires some stages for separation of catalyst and products purification that results in economic and environmental issues [8-11]. As these problems in the approach of using homogenous catalysts, heterogeneous catalysts have been suggested. Heterogeneous catalysts have the advantages of simpler and cheaper processes and the catalyst can also be reused several times. The main problem of these catalysts is the lower reaction rate that can be overcome by increasing the reaction temperature, pressure, and alcohol to oil ratios [12].

Many heterogeneous catalysts were applied for the transesterification reaction in the literature, for example, calcium carbonate, sulfated zirconia, zeolites, alumina loaded with alkaline metal salts, calcium oxide loaded with lithium ion and etc [3, 13-18]. Among the heterogeneous catalysts, calcium oxide was found as the potential one due to properties such as low cost, low alcohol solubility, high basic strength, non-corrosive, environmentally friendly and has a tolerance of moisture and free fatty acids [5, 10, 19]. On the other hand, several studies showed substantial alcohol solubility, notable moisture adsorption, as well as deactivation due to glycerol as a side reactions' product adsorption [20].

Calcium oxide can be derived from the waste resource

like shells of oysters, chicken eggs shell, mud crab, waste mollusk and mussel [19, 21-25]. There are few investigations about the kinetics of transesterification catalyzed by heterogeneous base catalysts [26-31]. *Dossin et al.* investigated the kinetics of ethyl acetate methanolysis catalyzed by magnesium oxide as a heterogeneous catalyst. They used a three-step 'Eley-Rideal' mechanism in the liquid phase and reported that methanol adsorption is the rate-determining step in this reaction [26]. *Veljkovic et al.* studied the kinetics of sunflower oil transesterification with methanol over CaO as a catalyst. They found that in the initial period of process mass transfer of triglyceride controlled the reaction and in the latter period, the chemical reaction becomes the rate-determining step [27]. *Birla et al.* reported first-order kinetics for the transesterification of waste frying oil in the presence of snail shell as a heterogeneous base catalyst. They determined the activation energy of 79 kJ/mol and the frequency factor of $2.98 \times 10^{10} \text{ min}^{-1}$ [28].

Likozar and Levec developed an overall model, based on the fatty acid composition of species, acknowledging mixing, mass transfer, and a single set of kinetic parameters for an appropriate process sensitivity analysis, monitoring, regulation, optimization, or intensification, regardless of process conditions and resource origin [29]. In another study, they present a model for the transesterification of different oils and alcohols, based on the fatty acid composition of triglycerides, diglycerides, and monoglycerides, and) (biodiesel), acknowledging chemical equilibrium, reaction kinetics and mass transfer [30]. Their models can be used in batch and continuous reactors for different vegetable or non-edible oils. Recently, *Likozar et al.* studied the chemical equilibrium, reaction kinetics and mass transfer for the transesterification of oil to biodiesel in a continuous tubular reactor with static mixers at several conditions [31].

In this work, the kinetics model for the transesterification of soybean oil with methanol catalyzed by waste mussel shell catalyst collected in of Persian Gulf coast was investigated. The reaction was done at optimal conditions of our previous study [25] (calcination temperature of 1050 °C, catalyst concentration of 12 wt. % and methanol to oil molar ratio of 24). The concentration of methyl esters was measured and a kinetic model was presented based on it. Although the tri-step reaction of transesterification produces other products, in this study due

Table 1: Composition of soybean oil of Nazgol Company

Fatty acid name	Composition, wt. %
Lauric	0.1
Myristic	0.1
Palmitic	10.2
Stearic	3.7
Oleic	22.8
Linoleic	53.7
Linolenic	8.6

to the limitation of available data, a model was presented based on methyl esters conversion. Also due to small changes in methanol amount, its concentration has been concerned constant during the reaction. The reaction rate constants were determined at different temperatures. Then the activation energy was obtained from experimental data.

EXPERIMENTAL SECTION

Materials

In this study soybean oil manufactured in Nazgol Oil Company (Iran, Kermanshah) and methanol 99.5 % (for synthesis, Merck) have been used for the transesterification reaction. The detailed composition of soybean oil used in this study is given in Table 1. Mussel shell of Persian Gulf coast has been applied as the catalyst. Also, *n*-hexane 95 % (extra pure, Merck), methyl laurate (methyl dodecanoate) >99.7 produced at Sigma and standard for using in Gas Chromatography (GC) column have been employed in this work.

Preparation mussel shell as a catalyst

First, mussel shell was milled by mortar and then fine particles (125-250 micron) were sieved and then particles were calcined in a furnace at the temperature of 1050 °C for 2 h. This procedure was optimized in Rezaei *et al.* [25] study.

Catalyst characterization

Mussel shell catalyst was characterized by X-Ray Diffraction (XRD) (X'Pert PRO) and X-Ray Fluorescence (XRF) (Spectro Xepor 03 plus). XRD analyze was carried out by Cu K α diffraction. The data that show intensity is plotted in the chart based on 2 θ in a range of 10-80° with a step of 0.06°.

Reaction procedure

Transesterification reaction was conducted in a 250 mL two-necked flask. The mixture of soybean oil, methanol (methanol to oil molar ratio 24:1) and 12 wt. % mussel shell catalyst (previous study optimal condition [25]), was mixed within 250 and 350 rpm stirrer speed. To determine the kinetics, mentioned reaction was carried out at reaction temperatures of 328.15, 333.15, 338.15 K and reaction times of 1, 3, 5, 7, 8 h. After the reaction, first, the catalyst was separated by centrifugation and then glycerol and produced biodiesel were separated within a separation funnel. For increasing produced biodiesel purity, it was washed several times by water with the temperature of 90 °C. Finally, to remove the residual water, it was placed in the oven with a temperature of 110 °C for 2 h.

Gas chromatography analysis

Fatty Acid Methyl Ester (FAME) characterization in biodiesel, samples were 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 μ m and an internal diameter of 0.25 mm. Nitrogen was used as the carrier gas and also as an auxiliary gas for FID. One μ L of the sample was injected by a 6890 Agilent Series Injector. The inlet temperature of the sample into injector was 50 °C, which was heated up to 230 °C. Methyl laurate (C12:0) was added as a reference into the biodiesel and the samples were analyzed by GC that was mentioned above. The weight percentage of FAME or biodiesel purity was calculated using Equation (1):

$$\text{Purity(\%)} = \frac{\text{area of all FAME}}{\text{area of reference}} \times 100 \quad (1)$$

$$\frac{\text{weight of reference}}{\text{weight of biodiesel sample}} \times 100$$

Also, the produced biodiesel conversion was defined using equation (2):

$$\text{Conversion(\%)} = \text{Purity} \times \frac{\text{weight of produced biodiesel}}{\text{weight of used oil}} \quad (2)$$

RESULTS AND DISCUSSION

Catalyst characterization

Fig. 1 shows XRD pattern of uncalcined mussel shell and calcined one at the temperatures of 550, 750, 950,

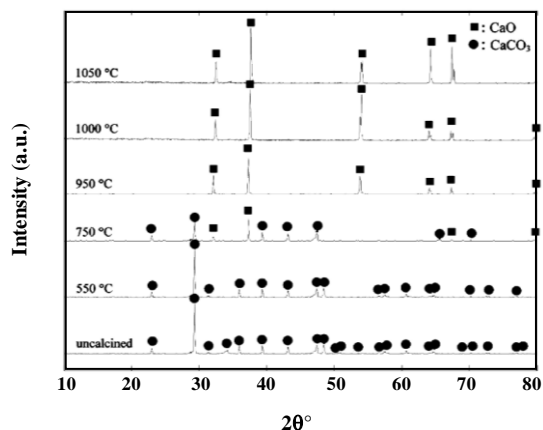


Fig. 1: The uncalcined and calcined XRD patterns in 550, 750, 950, 1000 and 1050 °C [25].

1000, 1050 °C during 2 h. At lower temperatures, more percentage of the catalyst is in the form of CaCO_3 . At temperatures higher than 950 °C, CaCO_3 has been converted to CaO . By increasing the temperature from 950 °C to 1000 and 1050 °C the extent of the peaks becomes high that shows the crystals in mussel shell get finer. In the previous study [25] it was found that the temperature of 1050 °C is the most appropriate temperature for mussel shell catalyst calcination (in this temperature the conversion of produced biodiesel was maximized). Also, XRF results showed that the amount of Ca in mussel shell calcined at 1050 °C was 97.77 % [25].

Variables effect on the conversion

Fig. 2-a shows the amount of methyl ester conversion versus time at 328.15, 333.15 and 338.15 K in the stirrer speed of 250 rpm. In a temperature of 328.15 K up to 5 h, methyl ester conversion is so low about 0.05. Also at a temperature of 333.15 K up to the fifth hour of reaction, the methyl ester conversion reaches to 0.15. But at a temperature of 338.15 K the reaction carried out with higher speed relatively, such that after 5 h the methyl ester conversion is about 0.62. Also, the methyl ester conversion after 8 h at a temperature of 328.15, 333.15 and 338.15 K is about 0.73, 0.85 and 0.88 respectively. As seen at a temperature of 338.15 K the methyl ester conversion rate is much more than lower temperatures. At a temperature of 338.15 K that is methanol boiling point, the mixing speed has been increased relative to lower temperature. This subject leads to increasing the methyl

ester conversion rate. So in the stirrer speed of 250 rpm, a diffusion problem is the overall reaction rate controller and specific mechanism cannot be presented for that. Fig. 2-b shows methyl ester conversion during the time at temperatures of 328.15, 333.15 and 338.15 K within stirrer speed of 350 rpm. As clear in this figure (Fig. 2), in three temperatures amount of methyl ester conversion over time has the same procedure.

The methyl ester conversion at a temperature of 328.15, 333.15 and 338.15 K after 8 h is about 0.82, 0.87 and 0.90, respectively. According to Fig. 2-b, at stirring of 350 rpm the limitation of mass transfer is greatly reduced.

Reaction kinetics determination

Effects of temperature and time have been investigated for the reaction kinetics determination. Amount of used catalyst is enough that oil can react with methanol and converted to fatty acids methyl esters. Thus, the reverse reaction is negligible, and also can connive of the catalyst concentration changes during the reaction [32].

Assuming transesterification reaction is done in one step, the transesterification reaction rate can be written by Equation (3) [33]:

$$-r_a = \frac{d[\text{TG}]}{dt} = k'[\text{TG}] \cdot [\text{ROH}]^3 \quad (3)$$

In which $[\text{TG}]$ and $[\text{ROH}]$ are triglyceride and methanol concentration, respectively, and k' is the reaction constant. Because of 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 [32, 34, 35]. Finally, the reaction rate is expressed as follows:

$$-r_a = \frac{d[\text{TG}]}{dt} = k[\text{TG}] \quad (4)$$

In which k is the reaction constant that is equal to $k'[\text{ROH}]^3$. Assuming that triglyceride concentration in the initial moment ($t=0$) equal to $[\text{TG}_0]$ and integration from Equation (4):

$$\ln[\text{TG}_0] - \ln[\text{TG}] = kt \quad (5)$$

And from mass balance Equation (6) as follows:

$$X_{\text{ME}} = 1 - \frac{[\text{TG}]}{[\text{TG}_0]} \quad (6)$$

Table 2: Constant rate of transesterification at different temperatures

T, K	k, h ⁻¹	R ²
328.15	0.219	0.9896
333.15	0.248	0.9897
338.15	0.271	0.9876

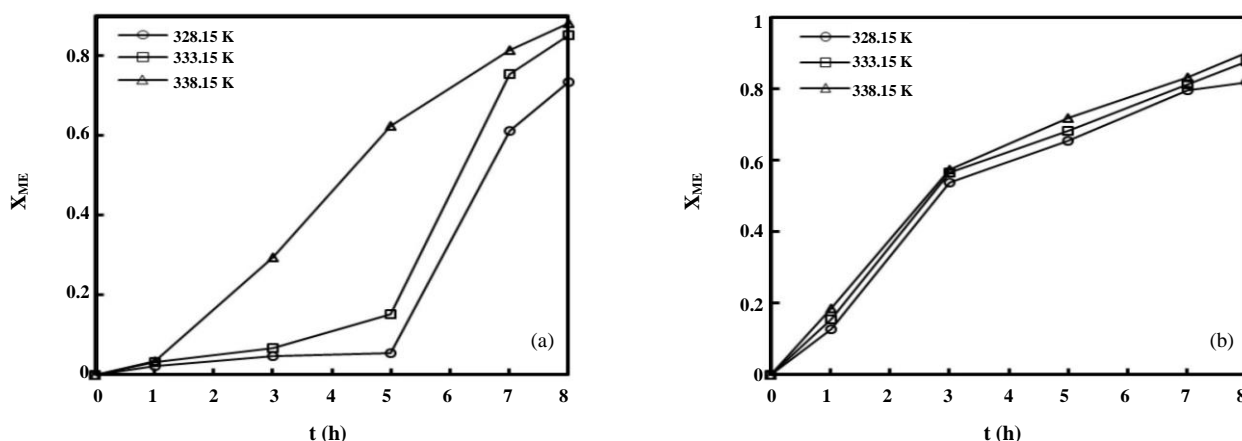


Fig. 2: Methyl ester conversion at different temperatures and times, a) stirrer speed of 250 rpm and b) stirrer speed of 350 rpm.

And:

$$[TG] = [TG_0](1 - X_{ME}) \quad (7)$$

Where X_{ME} is the methyl ester conversion and with the placement of Equation (7) in (5):

$$-\ln(1 - X_{ME}) = kt \quad (8)$$

Arrhenius equation establishes a relation between reaction rate constant (k), temperature (T) and activation energy (E_a) as follows:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

In this relation, k_0 and R are frequency factor and universal gas constant, respectively. This equation could be rewritten as:

$$\ln k = \frac{E_a}{RT} + \ln k_0 \quad (10)$$

By plotting the diagram of $\ln k$ versus $\frac{1}{T}$ the slope is equal to $-\frac{E_a}{R}$ and the intercept will be $\ln k_0$.

Kinetics of transesterification reaction of soybean oil with methanol in the presence of mussel shell as a catalyst at the temperatures of 328.15, 333.15 and 338.15 K within the stirrer speed of 350 rpm was investigated (methanol to oil molar ratio of 24:1 and catalyst to oil of 12 wt. % are according to the previous study [25]). The amount of methyl ester conversion at various temperature is shown in Fig. 2-b. The exponential procedure of methyl ester conversion versus time at different temperatures is indicating first-order kinetics for the transesterification reaction. By fitting the experimental data via temperatures in the equation (8) a good relation between $-\ln(1-X_{ME})$ and T is obtained. These results for the temperature of 328.15, 333.15 and 338.15 K are observable in Figs. 3-a, 3-b, and 3-c, respectively. Also, the values of k and the amount of R^2 for each temperature are given in Table 2.

According to reaction constant variation with temperature, the transesterification reaction activation energy is obtained by fitting $\ln k$ data versus $\frac{1}{T}$ with high accuracy (using equation (10)) as can be observed in Fig. 4. The resulted relation is as $\ln k = (-2365.9/T) + 5.6963$ by $R^2 = 0.9923$. So for the transesterification reaction,

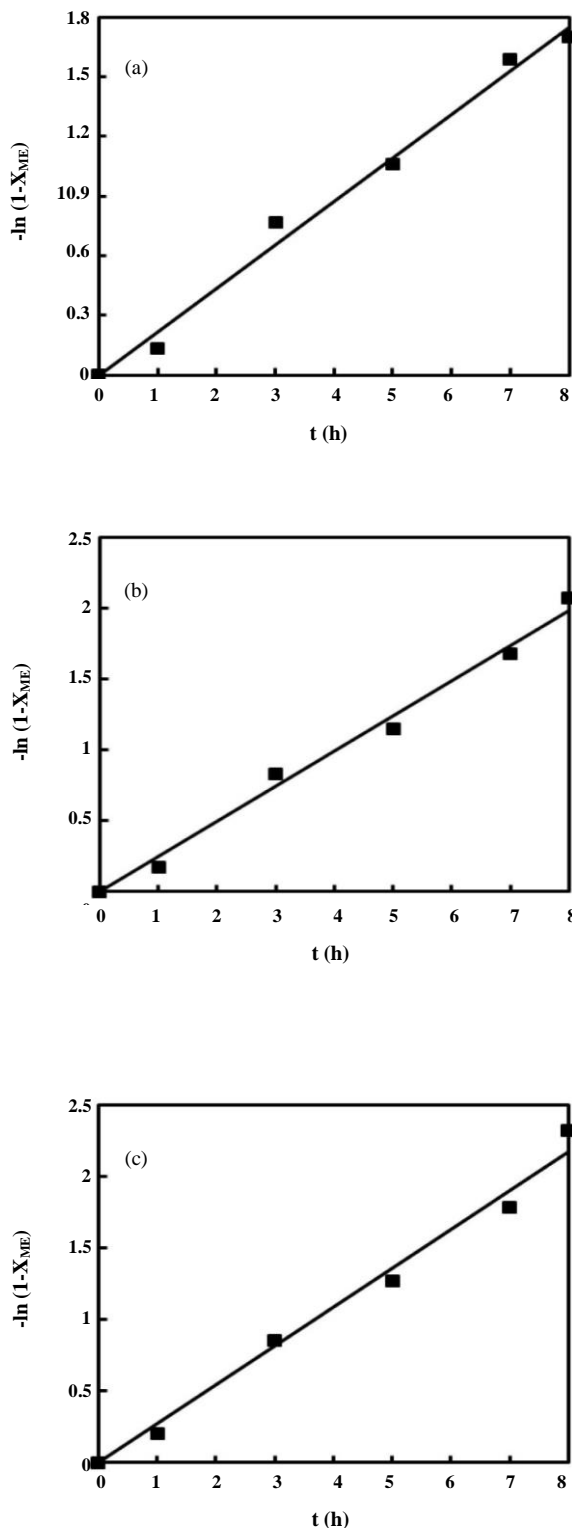


Fig. 3: Plot of $-\ln(1-X_{ME})$ via t at different temperatures, a) 328.15 K, b) 333.15 K and c) 338.15 K.

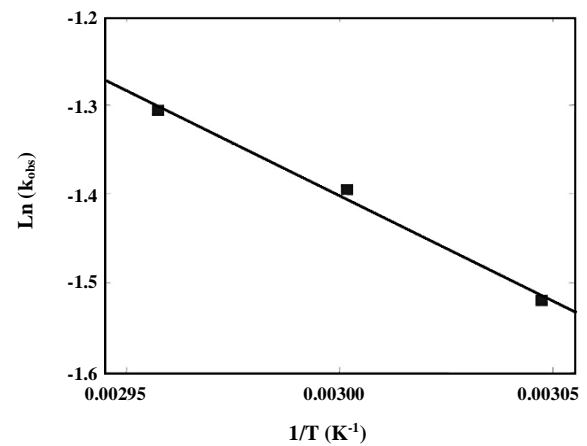


Fig. 4: Plot of $\ln k$ via $1/T$ for transesterification reaction.

the activation energy and frequency factor are equal to 19.67 kJ/mol and 297.76 h^{-1} , respectively.

Accordance of rate constant data versus temperature the reaction rate constant was obtained as $k = 297.76 \exp(-2365.9/T)$. By placing this relation in the Equation (8) and simplification:

$$X_{ME} = 1 - \exp\left(-297.76 \exp\left(\frac{2365.9}{T}\right)t\right) \quad (11)$$

Equation (11) shows the methyl ester conversion as a function of temperature in K and time in h. The methyl ester conversion in different times is plotted using equation (11) and also its experimental data at temperatures of 328.15, 333.15 and 338.15 K in Figs. 5-a, 5-b, and 5-c, respectively.

CONCLUSIONS

Using cheap and environment-friendly waste materials is so useful for biodiesel production. In this study mussel shell of Persian Gulf coast has been used as a catalyst of biodiesel production from soybean oil and methanol. XRD results show that the uncalcined mussel shell contains $CaCO_3$ and in the calcination temperature up to 950 °C it is converted to CaO . So mussel shell is an appropriate catalyst for this process. In this study in the stirrer speed (250, 350 rpm), reaction temperature (328.15, 333.15 and 338.15 K) and reaction time (1, 3, 5, 7, 8 h) at the previous study optimal condition has been investigated. Results demonstrated that in the stirrer speed of 250 rpm the controller step in the rate

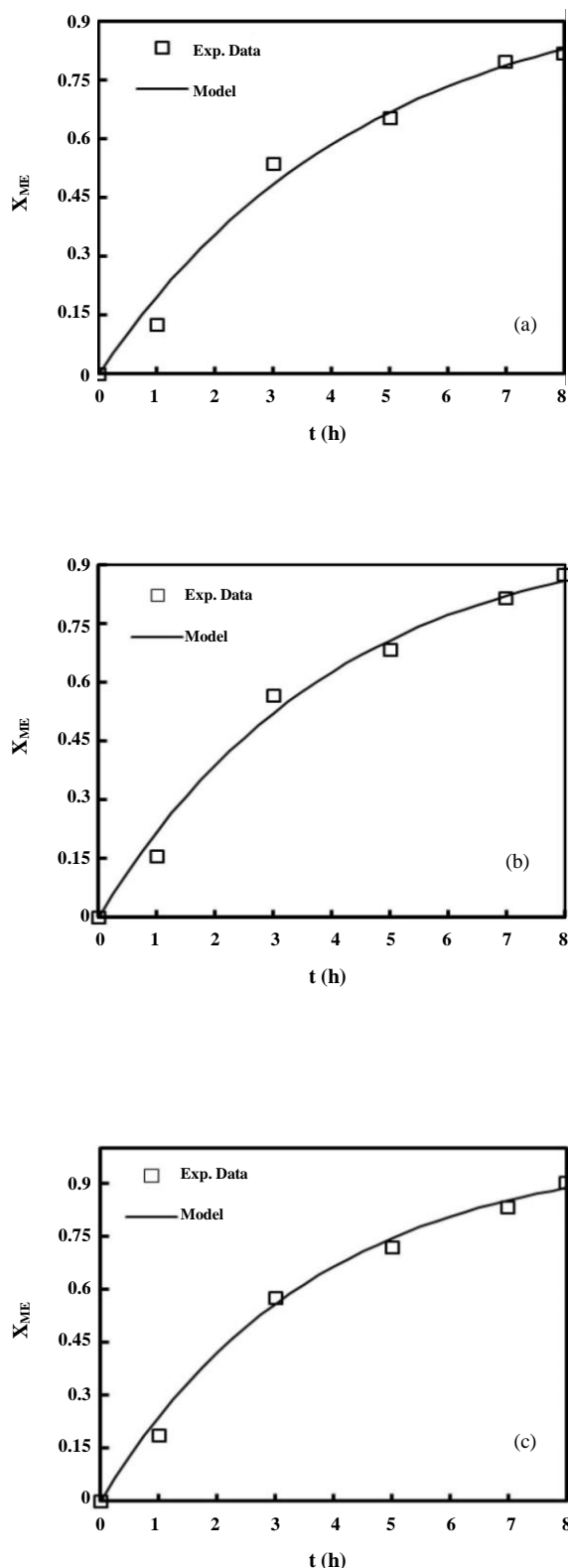


Fig. 5: Comparison of kinetics model with experimental data.

the mechanism is the diffusion of the particles into the catalyst. The clear reason for this speech is that at a temperature of 338.15 K that is almost methanol boiling point, the amount of mixing increasing and methyl ester conversion is so higher than two temperatures of 328.15 and 333.15 K. To overcome this problem, mixing speed can be as high as possible. Problems have been solved by setting the mixer speed at 350 rpm and the methyl ester conversion changes in all of the temperature are exponentially so a first order mechanism has been considered for the transesterification reaction. Results indicate the high accuracy of the selected pseudo-first order kinetics for the transesterification reaction of soybean oil with methanol in the presence of mussel shell as a catalyst.

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