Kinetic Study and Simulation of Oleic Acid Esterification over Prepared NaY Zeolite Catalyst

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Abstract

Esterification considers the most important reaction in biodiesel production. In this study, oleic acid was used as a suggested feedstock in order to study and simulate production of biodiesel. The batch esterification reaction of oleic acid was carried out at various operating conditions; temperature from 40 to 70 °C, ethanol to oleic acid molar ratio from 3/1 and 6/1 and a reaction time up to 180 min.

The catalyst used was prepared NaY zeolite, which is added to the reaction mixture as 2, 5 and 10 wt.% of oleic acid.

The results show that the optimum conditions, gives 0.81 conversion of oleic acid, were 6/1 molar ratio of ethanol/oleic acid, 5 wt.% NaY relative to initial oleic acid, 70°C and 60 minutes. The activation energy of the suggested model was 42692 J/mole for forward reaction and 17218 J/mole for backward reaction.

Key Word: Oleic acid, Esterification, Kinetic study, Simulation, heterogeneous catalyst, zeolite.

Introduction

One of the most promising sources is biodiesel, an alternative diesel fuel derived from renewable sources with high quality, which allows the substitution of fossil diesel oil without engine modifications [1-3]. Biodiesel shows a favorable combustion emission profile, producing much less carbon monoxide, sulfur dioxide and unburned hydrocarbons than petroleum-based diesel fuel [4, 5].

Biodiesel can be chemically defined as a fuel composed of mono-alkyl esters of long chain fatty acids derived from renewable sources, such as vegetable oils and animal fats [6]. Several vegetable oil varieties such as canola, palm, palm kernel, sunflower and coconut oil have been studied as feedstock for biodiesel production [7].

Most of the commercial production of biodiesel worldwide uses homogeneous catalysts, which are corrosive and non-reusable and produces waste that needs to be neutralized, hence, increasing the overall costs and leads to an environmental concerns [8].

The choice of the fats or oils to be used in producing biodiesel depends on the process and raw material cost and impurities. Low quality oil contains high levels of free fatty acid (FFA) and water. When FFA is present in the feedstock, it reacts with the homogeneous base catalysts and may deactivate the catalyst and form unwanted soap by-products. In

addition, the present of water in the reaction mixture also leads to the deactivation of homogeneous catalysts. Ma and Hanna [9], reported that water should be kept below 0.06 % and FFA should be kept below 0.5 wt. % to get the best conversions. The removal of homogeneous catalysts is technically difficult and large amount of wastewater is produced during the process and needs to be treated via neutralization process [10, 11].

Abbas and Abbas [12] studied the esterification reaction of oleic acid with ethanol at present of water. The best conditions for the esterification reaction were 6/1 molar ratio of ethanol/oleic acid, 5 wt. % H_2SO_4 relative to oleic acid, 70 °C, 90 min and conversion of oleic 0.92 the activation energy for suggested model were 26625 J/mole for forward reaction and 42189 J/mole for equilibrium constant.

In order to reduce the production cost of biodiesel, some researchers conducted research by using a solid catalyst [13]. Biodiesel production using solid catalysts has an economic benefit in terms of cheaper production costs because of the reusable nature of the catalyst and the possibility to be used in low quality feedstock [14], and offer the possibility of carrying out both trans-esterification and esterification simultaneously [15].

Another advantage of a heterogeneous catalyst is that the catalyst is easily separated from the reactants and products. Reduction of the biodiesel production cost can be achieved if a heterogeneous catalyst is used. Heterogeneous catalyst offers easier production process, improve product quality and also reduce corrosion and toxicity problems. Furthermore, it can be used for low quality feedstock, which contains high FFA [16].

Additional benefit with solid based catalyst is the lesser consumption of catalyst. As per studies, for production of 8000 tons of biodiesel, 88 tons of sodium hydroxide may be required [17], while only 5.7 tons of solid supported MgO are sufficient for production of 100,000 tons of biodiesel [18].

The present work, will intend to produce an ethyl ester (biodiesel) from the oleic acid by the esterification process by using NaY zeolite as a catalyst. The effects of reaction temperature, catalyst load, and the molar ratio alcohol/oil were considered. Also, the kinetics of oleic acid esterification were studied and the results were simulated, using *ReactOp* simulation package.

Experimental Work
Materials
1. Oleic acid, obtained from local markets. The specific gravity of the oleic acid is 0.895, BDH Chemicals Ltd.
2. Ethyl alcohol obtained from local markets with specific gravity is 0.7692 (88 to 90 wt. %).
3. The kaolin clay is available locally in Al-Dewekhala quarry in Al-Enbar region, it was supplied from state company of Geological Surveying and Mining.
4. Sodium hydroxide (RIEDELDEHAEN AG SEELZEHANNOVER Chem. rian, plozchen, DAB7, B.P.1968 M.Wt. 40).
5. Sodium silicate (Na_4SiO_4) was supplied by (BDH Limited pool England).
6. Phenolphthalein (as indicator), Fluka.

Catalyst Preparation
Kaolin was mixed with 40 wt. % of sodium hydroxide solution using kaolin / NaOH = 1/1.5 g/g and fused at

850°C for 3 h. 50 g of fused kaolin and 63 g of sodium silicate were placed in 500 ml of deionized water under constant stirring at 50°C for 1 hour, then the slurry with pH 13.3 was placed in a glass jar and subjected to ageing at 50°C for 24 h. The produced slurry was crystallized at 100 °C for 48 h. The crystalline mass repeatedly washed with water until the pH arriving 11.7, then the crystalline mass was dried at 100 °C for 16 h.

All prepared NaY zeolite catalyst characterization was done in the State Company of Geological Survey and Mining – Iraqi Ministry of Industry and Minerals.

Apparatus

The apparatus used in this study for esterification reaction is shown in Figure 1. The batch scale system consists of the followings:
1. 3 Necks flask (500 ml).
2. Heat flat magnetic stirrer (Stuart (CB302) /USA.
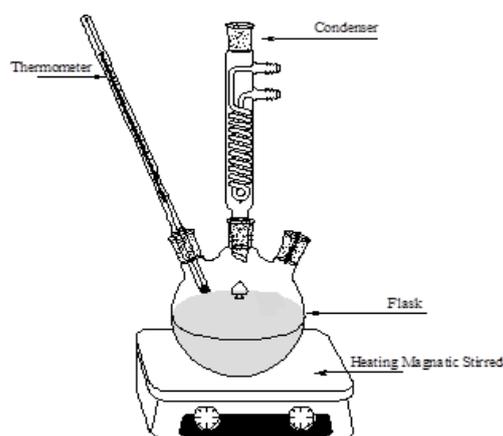3. Reflux Condenser (Germany).
4. Mercury thermometer from zero to 250 °C.

Fig. 1, Schematic diagram of the reactor

Esterification of Oleic Acid

The esterification reaction was carried out between acid and free fatty acid (FFA) to produce ester (biodiesel) and water. The system was maintained at atmospheric pressure and experiments were carried out at a constant temperature. The agitation was kept constant at 300 rpm. This process was studied at different percent of ethanol/oil mole ratio of 3/1 and6/1. Prepared NaY zeolite as a catalyst of 2, 5 and 10 wt. % relative to oleic acid, reaction time up to 150 minutes and at different temperatures 40 to 70°C.

The esterification reactor was loaded with 15 ml (13.43 g) of oleic acid, and the desired amount of ethanol. The mixture was agitated and preheated to the desired temperature and then NaY zeolite was added. At each period of time, 5 ml from the mixture reaction was taken and centrifuged (by Griffin and George Lough borough/Britain - Centrifuge) for 10 min to improve the separation of the phases and 2 drops of phenolphthalein was added as indicator and titrated with 1 molarity of NaOH in order to obtain oleic acid conversion.

Results and Discussion
Catalyst Characterization by X-ray Diffraction

The comparison between lattice spacing by X-ray diffraction (via XRD-7000 diffractometer) shows that the prepared NaY zeolite is approximately comparable with the standard. As shown in figure 2.
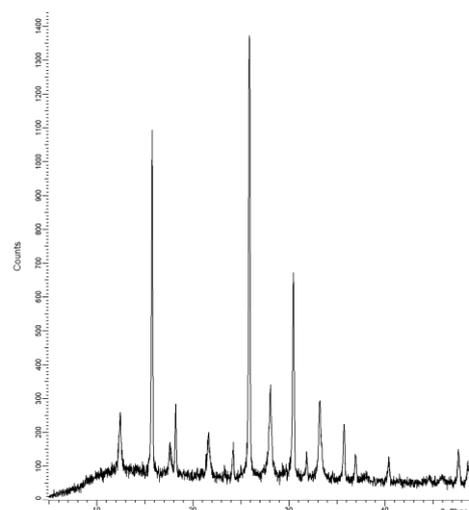

Fig. 2, X-ray diffraction of the prepared NaY zeolite

The Na_2O content of prepared NaY zeolite was analyzed and it was 12.26 wt. %. The surface area, measured by BET method, of prepared catalyst was equal to 330 m^2/g. While, the pore volume was equal to 0.35 cm^3/g.

Effect of Operating Temperature and Time on the Oleic Acid Conversion

Figure 3 shows the oleic acid conversion with reaction time at various temperatures and ethanol/oleic acid molar ratio 6/1 with 5 wt.% of NaY zeolite.
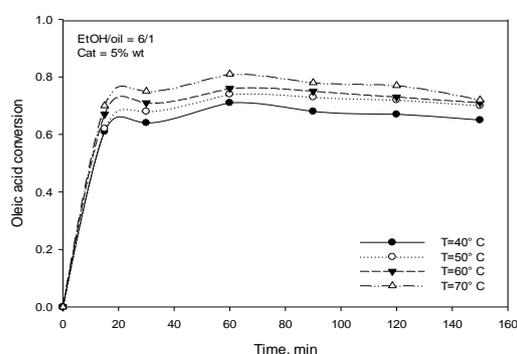

Fig. 3, Effect of the reaction time on oleic acid conversion by the esterification reaction at different temperature, 6/1: ethanol/oil molar ratio and 5 wt. % NaY

As shown in the figure 3, the conversion of oleic acid at 6/1 ethanol/oleic molar ratio and 5wt. % NaY was 0.8 after 60 minutes and was 0.72 after 150 minutes with the same condition.

At the beginning of the reaction the oleic acid conversion increased with temperature. According to the collusion theory [19], which is the famous theory described the chemical reaction, increasing in reaction temperature may causes an increase in molecule activity, which means that more molecules have more energy to react, and reduction in viscosity of reaction mixture (i.e. remarkable increasing of diffusivity). Thus, increasing of temperature increases the possibility of the molecule to diffuse

through the catalyst pores, reach to the active site of catalyst and react. But after 60 minutes the oleic acid conversion decreased because the water molecules may be clump in the pores of catalyst, due to the hydrophilic property of the zeolite [20], and that will increase the backward reaction.

Effect of Ethyl Alcohol/Oil Molar Ratio on the Oleic Acid Conversion

The molar ratio of ethanol to oleic acid is one of the most important variables that affects the conversion of oleic acid. The experiments of esterification reaction of oleic acid with ethanol were carried out under various ethanol/oil molar ratios (3/1 and 6/1).

Figure 4 shows the conversion of oleic acid with reaction time at various ethanol/oleic acid molar ratio using 5 wt. % NaY (as catalyst) at 70°C.
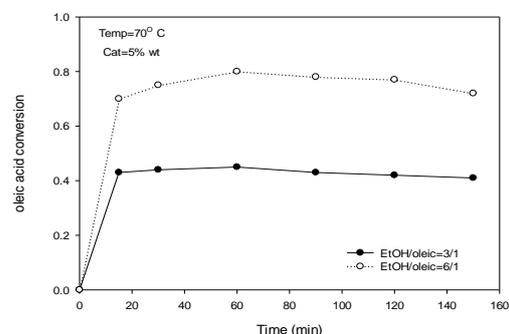

Fig. 4, Effect of reaction time on oleic acid conversion by esterification reaction at different ethyl alcohol/oleic molar ratio, at the temperature 70° C and 5 wt.% NaY

It can be observed that the oleic acid conversion increased from 0.45 at molar ratio of 3/1 to 0.81 at a molar ratio of 6/1 after 60 min using 5 wt. % of NaY at 70°C (Fig. 4).

The mechanism of an esterification reaction between a triglyceride and alcohol involves one mole of triglyceride for one mole of alcohol. The stoichiometric ratio is not used and an excess of alcohol is mandatory

to reach good conversion. Usually, the molar ratio 6:1 is allowed to shift the equilibrium towards the formation of the product and enable to reach better conversion [21, 22].

Increasing in ethanol/oleic mol. ratio in the range up to 6/1 causes increased in the conversion in oleic acid, because the esterification of oleic acid with ethanol is an equilibrium-limited chemical reaction and the position of equilibrium controls the amount of ester formed [23]. Also, the increasing can be explained by the emulsion system changes from the dispersion of ethanol into oleic acid towards the dispersion of oleic acid into ethanol. This transformation results cause an increase in the interfacial area up to a point above which the interfacial area starts to decrease as the cavitations in ethanol phase is much easier than in oleic acid phase due to viscosity difference [24].

Effect of Catalyst Amount on the Oleic Acid Conversion

The catalyst load effect on the oleic acid conversion is given in figure 5. The oleic acid conversion increased with increasing the catalyst load (from 2 to 5 wt. %). The reaction rate of esterification is directly proportional to the amount of a catalyst, due to the increase of active site numbers, so the catalyst is used to enhance the reaction rate and conversion.
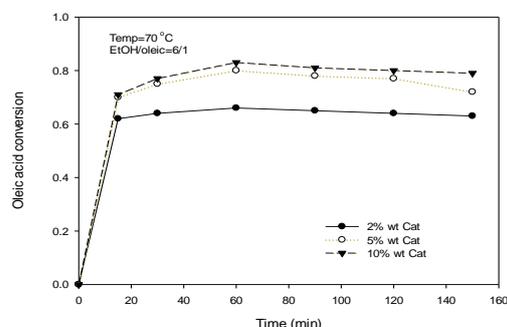

Fig. 5, Effect of the reaction time on oleic acid conversion by esterification reaction at different catalyst load (NaY), temperature 70 $^{\circ}$C and 6/1: ethanol /oleic molar ratio

At catalyst weight present more than 5 wt. % the effect of catalyst load did not show any remarkable effect on oleic acid conversion, may be due to increasing the surface area of zeolite catalyst that causes more accumulation of water in the pores as a result of the hydrophilic action of the zeolite [25]. This accumulation of water increasing backward reaction (Eq. 1).

Catalyst Reuse

The solid catalyst needs to be regenerated when they have been used for a period of time in order to have good performance. Stopping the reaction and regeneration the catalyst is an expensive non-conventional operation [26].

The NaY catalyst was reused after drying it at 100°C for 24 hours (without regeneration). The conversion decreased from 0.81 (for fresh catalyst) to 0.56 (for reused catalyst), as shown in Fig.6.
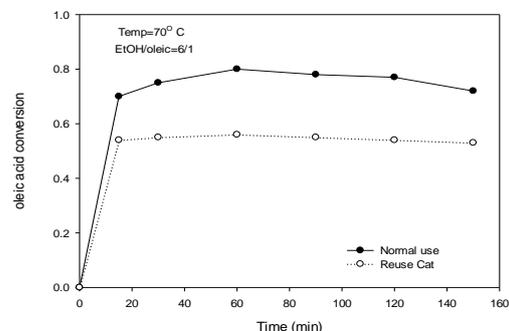

Fig. 6, Effect of the reaction time on oleic acid conversion by the esterification reaction using fresh and reuse NaY at the temperature 70° C and 6/1: ethanol /oleic molar ratio

Kinetic of Oleic Acid Esterification

Kinetic obtained from laboratory unit are usually played an important role in modeling and scale up designs for new biodiesel production units.

The data obtained by differential method of analysis has been used to find a favorable kinetic model for oleic acid esterification.

The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative -r_A, and testing the goodness of fit of the equation with experiment.

The conversion of oleic acid (x) fitted by the third order polynomial degree formula according to the time at certain temperature, and then finding the rate coefficients (k_1 and k_2) as well as the orders of the reactants and products materials (n_1, m_1, n_2 and m_2) using least squares method for the suggested reaction kinetics equation (Eqs. 1 to 5).

$$C_{18}H_{34}O_2 + C_2H_6O \leftrightarrow C_{20}H_{38}O_2 + H_2O \ldots (1)$$
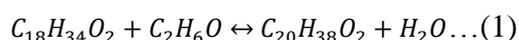
$$-r_A = k_1 C_A^{n1} C_B^{m1} - k_2 C_C^{n2} C_D^{m2} \quad \ldots(2)$$

$$K_{eq=}k_1/k_2 \qquad \ldots(3)$$

$$K_{eq} = C_{Ce}^{n2} C_{De}^{m2}/C_{Ae}^{n1} C_{Be}^{m1} \qquad \ldots(4)$$

$$-r_A = k_1 C_A^{n1} C_B^{m1} - (\frac{k_1}{K_{eq}}) C_C^{n2} C_D^{m2} \qquad \ldots(5)$$

The Arrhenius law [19]:

$$k = k_o e^{\left(\frac{-E}{RT}\right)} \qquad \ldots(6)$$

A plot of ln k vs. 1/T of Eq. 6 gives a straight line, with slope for -E/R to find activation energy for forward reaction and backward reaction (Figs. 7 and 8).

The values of constants in the esterification reaction of oleic acid are summarized in Table 1.

The obtained values of rate coefficients, equilibrium constant, orders of reactants and products materials, heat of reactions and activation energy were used to simulate the results.

Predicted values calculated from empirical model and experimental data are shown in figure 9.

Statistical analysis of the experimental data shows that the solution of the model (Eq. 5) is proportional with the experimental results. The statistical analyses are summarized in Table 2.
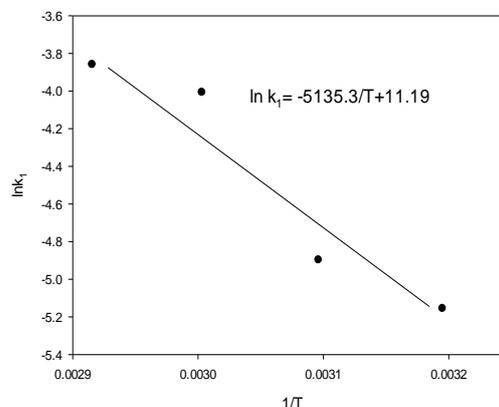

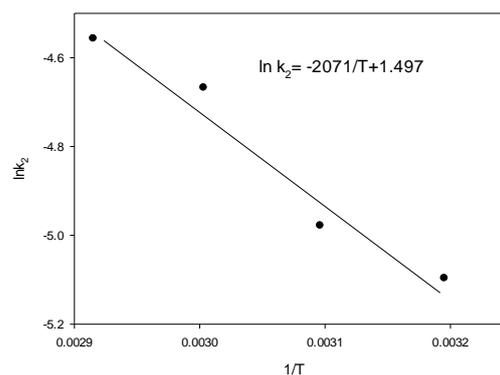Fig. 7, Plot of ln k_1 vs. 1/T resulting from the esterification of oleic acid for forward reaction

Fig. 8, Plot of ln k_2 vs. 1/T resulting from the esterification of oleic acid for backward reaction

Table 1, Constant values of the esterification reaction kinetic model

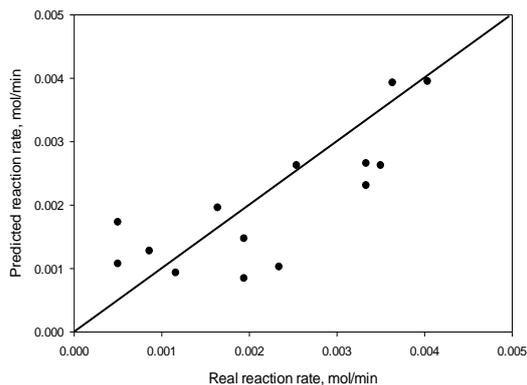| Constant	Value
k_{o1}	72402
E_1(J/mole)	42692
k_{o2}	4.5
E_2(J/mole)	17218
n_1	1
m_1	1
n_2	1.2
m_2	1
k_{oeq}	16089.3
E_{eq}(J/mole)	25474

Fig. 9, Real and predicted values of reaction rate by using suggested model of esterification of oleic acid with 6/1: ethanol/oleic molar ratio, 5% NaY as catalyst and temperature range from 40 to 70 ° C

Table 2, Statistical analysis of the model

Statistical analysis	Value
Standard error	$7.6*10^{-4}$
Average relative error, %	1.53
Standard deviation (S)	$6.5*10^{-4}$
Variance	$4.3*10^{-7}$
Confidence level	0.95

Simulation Results

Simulation for the behavior of batch and plug flow reactors in different operating modes (adiabatic and isothermal) was carried out at the best conditions. These selected conditions were 70°C (high temperature gives higher conversion), 60 minutes reaction time 6/1 ethanol/oleic molar ratio, 5 wt. % of NaY as catalyst. The simulation results are reported in Table 3.

As reported, simulated results of the isothermal operating mode are approximately identical to the experimental results.

The simulated results of the adiabatic operating mode show decreasing in oleic acid conversion, this lowering is due to the temperature decreasing of the reaction mixture through the endothermic reaction of esterification (ΔH_r =145.19 kJ/mol).

Table 3, Highest conversion results at the best conditions from experimental and simulated results of isothermal and adiabatic operation at 60 minutes reaction time

Reactor/operating mode	Conversion	$C_{18}H_{34}O_2$, kmol/m^3	C_2H_6O, kmol/m^3	$C_{20}H_{38}O_2$, kmol/m^3	H_2O, kmol/m^3
Initial values	0	1.00	4.44	0.00	1.25
Plug or batch/ isothermal	0.80	0.20	3.64	0.79	2.05
Experimental batch/ isothermal	0.81	0.19	3.63	0.81	1.96
Plug or batch/ adiabatic	0.76	0.24	3.68	0.76	1.91

Conclusion

1. The maximum conversion of oleic acid was 0.81 at 6/1 of ethanol/oleic acid molar ratio after 60 minutes, 70° C and 5% NaY.
2. Increasing the ethanol/oleic acid molar ratio from 3 to 6 increases the conversion of oleic acid.
3. The activation energies for the suggested kinetic model were 42692J/mole for the forward reaction and 17218 J/mole for the backward reaction.
4. The simulation results for isothermal batch and plug flow reactors show no remarkable differences from the experimental results.
5. Adiabatic operating mode results show lower conversion by 5% than isothermal operating mode results.

Nomenclatures

$-r_A$ = dx/dt reaction rate of oleic acid
A = oleic acid, B= ethanol, C= ester, D= water
k = rate coefficient of reaction.
1= forward reaction, 2= backward reaction, n and m are the reaction orders.
n_1 for oleic , m_1 for ethanol, n_2 for ester, m_2 for water.

C_A, C_B, C_C, C_D = reactants and products moles at any time.

C_{Ae}, C_{Be}, C_{Ce}, C_{De} = reactants and products moles at equilibrium time.

E_1 = activation energy for forward reaction (J/mole)

E_2 = activation energy for backward reaction (J/mole)

k_{o1}=frequency factor ((mol)$^{-2.2}$/minute) for forward reaction

k_{o2} = frequency factor for backward reaction ((mol)$^{-2.0}$/minute)

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