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Kinetic Study and Simulation of Oleic Acid Esterification in Different Type of Reactors

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Abstract

Esterification reaction is most important reaction in biodiesel production. In this study, oleic acid was used as a suggested feedstock to study and simulate production of biodiesel. Batch esterification of oleic acid was carried out at operating conditions; temperature from 40 to 70 °C, ethanol to oleic acid molar ratio from 1/1 to 6/1, H_2SO_4 as the catalyst 1 and 5% wt of oleic acid, reaction time up to 180 min. The optimum conditions for the esterification reaction were molar ratio of ethanol/oleic acid 6/1, 5%wt H_2SO_4 relative to oleic acid, 70 °C, 90 min and conversion of oleic 0.92. The activation energy for the suggested model was 26625 J/mole for forward reaction and 42189 J/mole for equilibrium constant. The obtained results simulated to other types of reactors with different operating conditions using reactop cascade package. The conversion of oleic acid of simulation results at optimum operating conditions was 0.97 for isothermal batch and plug flow reactors, 0.67 for isothermal CSTR, while the conversions of oleic acid in the adiabatic mode were 0.82, 0.40, 0.74 for batch, CSTR, PFR reactors respectively.

Key word: Oleic acid, Esterification, Kinetic study, Simulation.

Introduction

Energy sources can be classified into three groups fossil, fissile, and renewable. The term fossil refers to an earlier geological age. Fossil fuels were formed many years ago and are not renewable. The fossil energy sources are petroleum, coal, bitumen, natural gas, oil shale, and tar sands. The main fissile energy sources are uranium and thorium [1].

One of the main and most important non-renewable energy sources is oil, the production rate of oil is expected to peak in the next few years therefore, the world needs an alternative and renewable energy source that are able to meet world energy needing [2].

The renewable energy sources such as biomass, hydro, wind, solar (thermal and photovoltaic), geothermal, marine, and hydrogen will play an important role in the future. It is predicted that in 2025, approximately half of the global energy supply will come from renewable energy, and electricity generation from renewable will be more than 80% of the total global electricity supply [3, 4].

Biomass can be converted into liquid and gaseous fuels through thermo-chemical and biological methods. Biofuel is a non-polluting, locally available, accessible, sustainable, and reliable fuel obtained from renewable sources [5]. Liquid biofuels fall into the following categories: (a) vegetable oils and biodiesels, (b) alcohols, and (c) bio-crude and synthetic oils [1].

Esterification is one of the most important reactions in chemical industry; and the relative reaction is usually conducted by using, in general, homogeneous acid catalysts [6].

Esterification reaction carried out between carboxylic acids (free fatty acids) and alcohols with the presence of an acid catalyst (such as sulfuric acid, orqanic sulfonic acid, and hydrochloric acid) to form ester and water (see equatin 1) [7].

$$\mathrm{RCOOH} + \mathrm{R'OH} \leftrightarrow \mathrm{RCOOR'} + \mathrm{H_2O} \quad \ldots(1)$$

FFA alcohol Ester Water

The present work, intend to produce ethyl ester (biodiesel) from the oleic acid by esterification process. The effects of reaction temperature, amount of catalyst, and the molar ratio alcohol/oil were considered. Also, the kinetic of oleic acid esterification were studied and the results were simulated to different type of reactors and operating conditions.

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. Sulfuric acid as an acid catalyst obtained from local markets, the purity of this acid is 98% (Sp.Gr. is 1.84) Aldrich.
4. Sodium hydroxide for titration (RIEDEL_DEHAEN AG SEELZE_HANNOVER Chem. rian, plozchen, DAB7, B.P.1968 M.Wt. 40).
5. Phenolphthalein (as indicator), Fluka.

Apparatus

The apparatus used in this study for esterification reaction is shown in Figure 1. The batch scale system consists of the followings:

1. Heat flat magnetic stirrer (Stuart (CB302)/USA.
2. Reflux Condenser (Germany).
3. Centrifuge **(**Griffin & George Loughborough/Britain**)**
4. Mercury thermometer from zero to 250 °C**.**
5. 3 Necks flask (500 ml).
6. Sensitive balance.

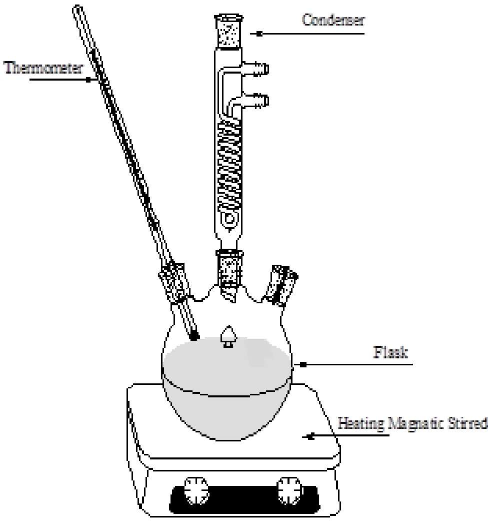

Fig. 1, Schematic diagram of the reactor

Esterification of Oleic Acid

The esterification reaction 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 constant temperature. The agitation was kept constant at 300rpm. This process was studied at different percent of ethanol/oil mole ratio of 1/1, 3/1, 6/1 sulfuric acid as a catalyst of 1 and 5 wt% relative to oleic acid, reaction time up to 180 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 mixer was agitated and preheated to the desired temperature and then H_2SO_4 was added. At each period of time (15 or 30 minutes), 5 ml from the mixture reaction was taken and 2 drops of phenolphthalein was added as indicator and titrated with 1 molarity of NaOH in order to obtain oleic acid conversion[8].

Results and Discussion

Effect of Operating Temperature and Time on the Oleic Acid Conversion

Figures 2 and 3 show the oleic acid conversion with reaction time at various temperatures and ethanol/oleic acid molar ratio 6/1 with 1 and 5 wt.% of H_2SO_4.

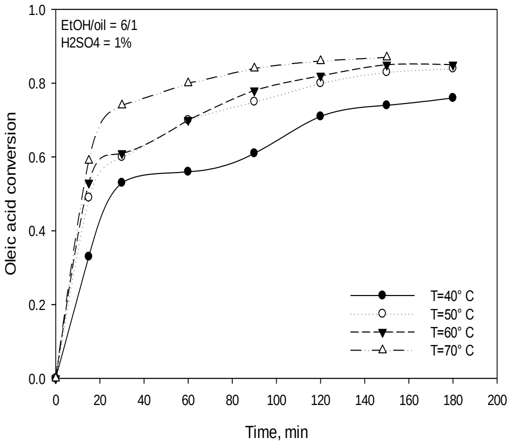

Fig. 2, effect of the reaction temperature on oleic acid conversion by esterification reaction, 6/1 ethanol/oil mol. ratio and 1 wt% H_2SO_4

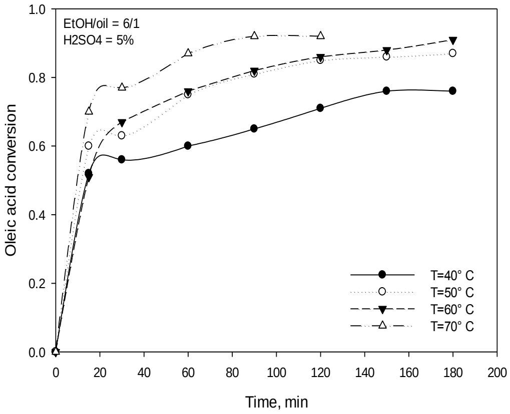

Fig. 3, effect of the reaction temperature on oleic acid conversion by esterification reaction, 6/1 ethanol/oil mol. ratio and 5 wt% H_2SO_4

As shown in the fig 2 the conversion of oleic acid at 6/1 ethanol/oleic mol. ratio and 1% H_2SO_4 was 0.87 at 70° C after 150 minutes and was 0.92 at 70° C after 90 minutes with 5% H_2SO_4, which is the highest conversion achieved in this study (as shown in Fig.3).

The oleic acid conversion increased with increasing temperature. Increasing the temperature may causes increase of molecule activity, which means that more molecules have more energy, thus, the possibility of molecule to react increased.

These results are in a good agreement with the results of the production of fatty acid ethyl ester (FAEE) from oleic acid (FAA) with short-chain alcohols (ethanol, propanol and butanol) under ultrasonic irradiation reported by Hanh et al. [9] The higher conversion for the esterification process was 0.92 at the reaction temperature 60° C and 3/1 mol. ratio of ethanol to oleic acid with 5% H_2SO_4 after 2 hours irradiation.

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

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

Figures 4 and 5 show the conversion of oleic acid with reaction time at various ethanol/oleic acid molar ratios using 1 and 5 wt. % H_2SO_4 (as catalyst) at 70 °C.

It can be observed that the oleic acid conversion increased from 0.61 at a molar ratio of 1/1 to 0.87 at a molar ratio of 6/1 after 180 min using 1 wt% of H_2SO_4 at 70°C (Fig. 4). By using 5 wt% H_2SO_4 at 70°C, the oleic acid conversion increased from 0.87 at 1/1 of ethanol/oil mol. ratio after 180 min to 0.92 at 6/1 ethanol/oil mol. ratio after 90 min, which is the highest conversion achieved in this study (in Fig.5).

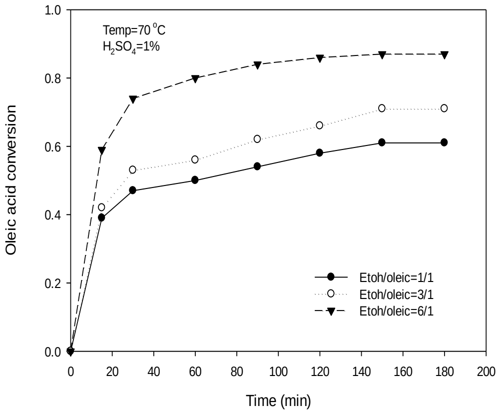

Fig. 4, effect of the ethyl alcohol/oleic mol. ratio on oleic acid conversion by esterification reaction, at the temperature 70° C and 1 wt% H_2SO_4

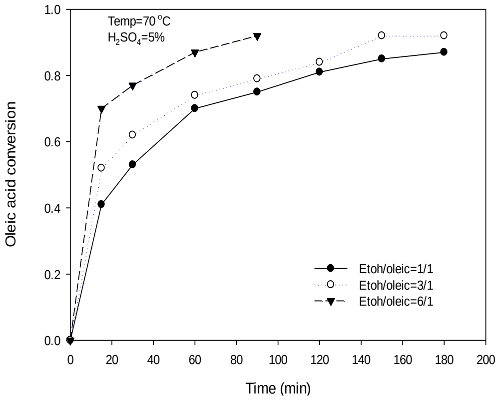

Fig. 5, effect of the ethyl alcohol/oleic mol. ratio on oleic acid conversion by esterification reaction, at the temperature 70° C and 5 wt% H_2SO_4

Increasing in ethanol/oleic mol. ratio causes increasing 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 [10].

These results are a good agreement with those obtained by Marchetti and Errazu [11], the highest conversion of FFA was 0.96 at the reaction conditions molar ratio of ethanol to acid oil was 6.126, reaction temperature 55° C, reaction time 240 min and 2.261 wt% H_2SO_4.

Effect of Catalyst Amount on the Oleic Acid Conversion

The amount of catalyst affect on the oleic acid conversion is given in Fig.6. It shows the relationships between the oleic acid conversion and time at various catalyst concentrations with ethanol/oleic acid molar ratio 6/1 and 70°C. The oleic acid conversion increased with increasing the catalyst concentration.

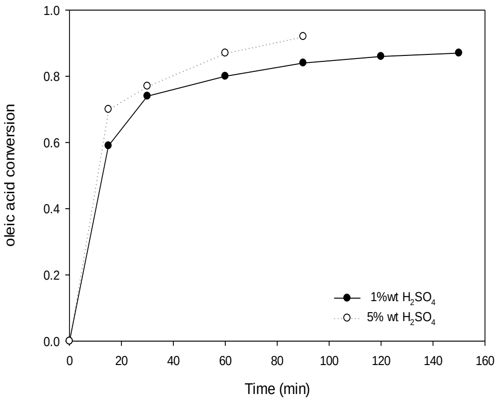

Fig. 6, effect of the amount of catalyst concentration (H_2SO_4) on oleic acid conversion by esterification reaction, at the temperature 70° C and 6/1 ethanol /oleic molar ratio

The reaction rate of esterification is directly proportional to the amount of a catalyst, so the catalyst is used to enhance the reaction rate and conversion. The amount of sulfuric acid employed as a catalyst is related to the formation of H^+ that catalyzes the reaction.

Kinetic of Oleic Acid Esterification

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

The data obtained by Differential method of analysis obtained data has been used to find 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 power 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. 2 to 6).

$$C_{18}H_{34}O_2 + C_2H_6O \leftrightarrow C_{20}H_{38}O_2 + H_2O \quad ...(2)$$

$$-r_A = k_1 C_A^{n1} C_B^{m1} - k_2 C_C^{n2} C_D^{m2} \quad ...(3)$$

$$K_{eq=} k_1/k_2 \quad ...(4)$$

$$K_{eq} = C_{Ce}^{n2} C_{De}^{m2} / C_{Ae}^{n1} C_{Be}^{m1} \quad ...(5)$$

$$-r_A = k_1 C_A^{n1} C_B^{m1} - (\frac{k_1}{K_{eq}}) C_C^{n2} C_D^{m2} \quad ...(6)$$

Where:

k = rate coefficient of reaction.

1= forward reaction, 2= backward reaction, n and m are the reaction orders.

K_{eq} = equilibrium constant.

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.

According to Arrhenius law [12] a plot of Ln k vs. 1/T gives a straight line, with slope for E/R to find activation energy for forward reaction and equilibrium reaction (figs.7 and 8).

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

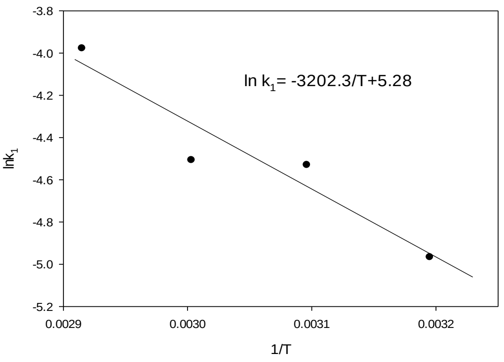

Fig. 7, show the linear plot of ln k vs. 1/T resulting from the esterification of oleic acid for forward reaction

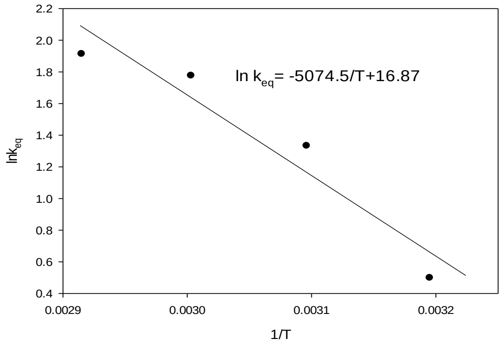

Fig. 8, show the linear plot of ln k_{eq} vs. 1/T resulting from the esterification of oleic acid for equilibrium reaction

Table 1, Constant values of the esterification reaction kinetic model

Constant value	Esterification reaction
$k_{\circ e}$	$2.1*10^7$
E_{eq} (J/mole)	42189
k_{o1}	196.3
E_1 (J/mole)	26625
n_1	1.25
m_1	0.5
n_2	1
m_2	0.5

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 fig.9.

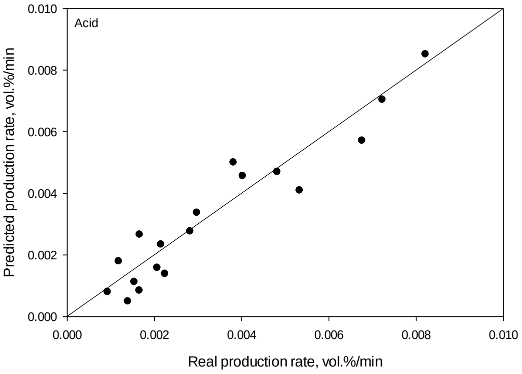

Fig. 9, Experimental and predicted values of apparent rate constant by using suggested model of esterification of oleic acid with 6/1 ethanol/oleic molar ratio, 5% H_2SO_4 as catalyst and temperature range from 40 to 70 ° C

Statistical analysis of the experimental data shows that the solution of the model (eq. 6) is proportional with the experimental data. The distribution of the experimental data around the model solution of esterification (correlation coefficient (R)) is about 0.9061, standard deviation (S) is $6.9*10^{-3}$, and average relative error is 1.34% in 95 % confidence level, as summarized in Table 2.

Table 2, statistical analysis of the model

statistical analysis	Esterification reaction
Correlation coefficient (R)	0.9061
Standard deviation (S)	$6.9 * 10^{-3}$
Average relative error	1.34%
Confidence level	95%

Simulation Results

Simulation for the behavior of batch, plug and mixed flow reactors in different operating modes (adiabatic and isothermal) was carried out at optimum conditions (70 °C, 6/1 ethanol/oleic mol ratio, 5% H_2SO_4 as catalyst) and the previously obtained results of kinetic models (Table 1) by using reactop cascade package to predict best reaction time.

Fig. 10 shows the reactants and products moles with reaction time for simulated and experimental results. At the beginning of reaction the system has only liquid phase of reactant (oleic acid and ethanol with 12% water content). As time proceeds, reactant consumed, while water and ester formed. At the simulated results, the reactants consumed and products formed faster than the experimental results (as shown in Table 3).

From this Table 3, simulated results are always higher than the experimental results which could be attributed to the effect of side reactions, which cause consumption of oleic acid to form undesirable products, such as water that reduced the formation of ester [8].

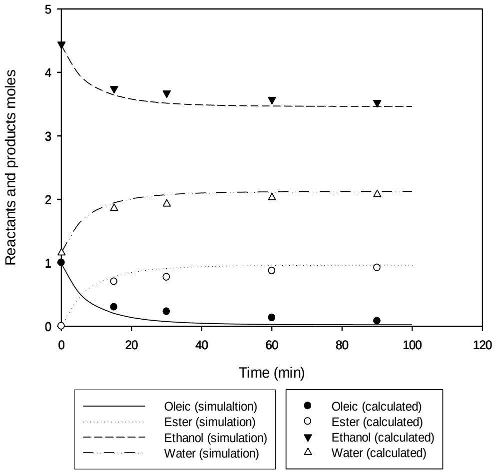

Fig. 10, show the reactants and products moles in experimental and simulation isothermal batch reactor with reaction time at best operating conditions

Figs. 11 and 12 show the oleic acid conversion with reaction time in batch, PFR and CSTR operating in isothermal and adiabatic mode, respectively.

The oleic acid conversion in isothermal batch and plug flow reactors were 0.97 after 90 min from the reaction, whereas the conversion in mixed flow reactor reached highest conversion 0.63 after 33 min and then the conversion dropped (fig. 11).

Fig. 12 shows the oleic acid conversion with time in batch, PFR and CSTR in adiabatic mode. The conversion of oleic acid were 0.84 and 0.75 after 90 min in a batch reactor and plug flow reactor, while the conversion in CSTR was 0.40 after 40 min and then dropped.

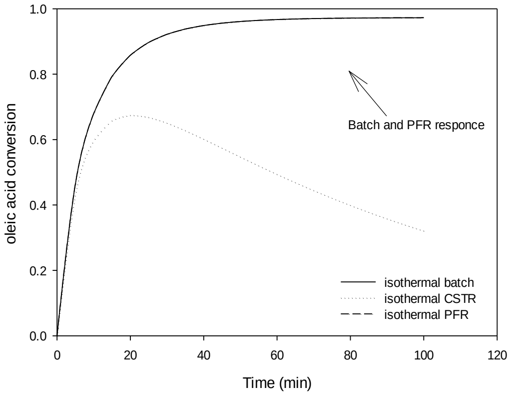

Fig. 11, shows oleic acid conversion with time in batch, PFR and CSTR reactors in isothermal mode at the best operating conditions

However, it is obvious that batch and PFR is substantially better than the CSTR for obtaining high conversions in both isothermal and adiabatic mode

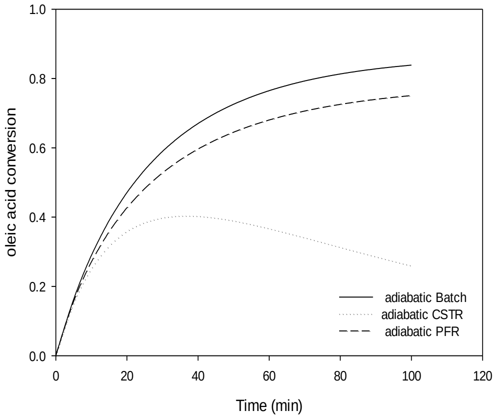

Fig. 12, shows the oleic acid conversion with time in batch, PFR and CSTR reactors in adiabatic mode at the best operating conditions

Table 4 shows numerically the highest and best conversion in simulation and experimental results at different types of reactors (from figures 10 to 12).

Table 3, higher results at the best conditions from experimental and simulated results

Experimental results					Simulation results				
Time	Moles of reactants and products				Time	Moles of reactants and products			
	oleic	Ethanol	Ester	Water		Oleic	Ethanol	Ester	Water
0	1	4.44	0	1.15	0	1	4.44	0	1.15
15	0.3	3.74	0.7	1.85	15	0.22	3.64	0.79	1.94
30	0.23	3.67	0.77	1.92	30	0.08	3.51	0.92	2.07
60	0.13	3.57	0.87	2.02	60	0.03	3.47	0.96	2.12
90	0.08	3.52	0.92	2.07	90	0.02	3.46	0.97	2.12

Table 4, highest conversion in simulation and experimental at operating conditions (T=70 °C, ethanol/oleic molar ratio=6/1, H_2SO_4 =5%wt)

Reactor type	Operating mode	Time (min)	conversion	Note
Batch	isothermal	90	0.92	Experimental
Batch	Isothermal	90	0.97	Simulation
Batch	Adiabatic	90	0.82	Simulation
CSTR	Isothermal	20	0.67	Simulation
CSTR	Adiabatic	40	0.40	Simulation
PFR	Isothermal	90	0.97	Simulation
PFR	Adiabatic	90	0.74	Simulation

Conclusion

1. The maximum conversion of oleic acid was 0.92 at 6/1 of ethanol/oleic acid mol. ratio after 90 minutes, 70° C and 5% H_2SO_4.
2. Increasing the ethanol/oleic acid molar ratio from 1 to 6 increases the conversion of oleic acid.
3. The activation energies for the suggested kinetic model were 26625

J/mole for the forward reaction and were 42189 J/mole for equilibrium constant.

4. The conversion of oleic acid in the simulated model in batch and plug flow reactors is higher than the conversion in CSTR reactor in each isothermal and adiabatic mode.

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

K_{eq} = equilibrium constant.

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_{eq} = activation energy for equilibrium reaction (J/mole)

k_o =frequency factor ($(mol)^{-0.74}$/minute) for forward reaction

k_{oe} = frequency factor for equilibrium reaction

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