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Kinetics and Mass Transfer Study of Oleic Acid Esterification over Prepared Nanoporous HY zeolite

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Abstract

A mathematical model was proposed to study the microkinetics of esterification reaction of oleic acid with ethanol over prepared HY zeolite catalyst. The catalyst was prepared from Iraqi kaolin source and its properties were characterized by different techniques. The esterification was done under different temperature (40 to 70˚C) with 6:1 for molar ratio of ethanol to oleic acid and 5 % catalyst loading.

The microkinetics study was done over two period of time each period was examined individually to calculate the reaction rate constant and activation energy. The impact of the mass transfer resistance to the reactant was also investigated; two different studies have been accomplished to do this purpose.

The effect of the external mass transfer resistance was studied by exploring different stirring speed (400 to 800 rpm). The results show that, the oleic acid conversion increase with increasing the stirring speed until reached 600 rpm, after this rpm the conversion doesn't increase significantly, which mean that, the effect of external mass transfer resistance was eliminated. The activation energy for the first period is equal to 41.84 kJ/mol while in the second period is equal to 52.03 kJ/mol. The Thiele modulus calculation results show that there is no effect of mass transfer on the reaction inside the catalyst pores.

Key Words: Biodiesel, Microkinetics, Nanoporous, HY zeolite, Mass transfer, Oleic acid, Heterogeneous Catalyst, Thiele modulus

Introduction

Biodiesel can be defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats and alcohol with or without a catalyst [1-5]. Biodiesel can be produced by an efficient and commonly method called transesterification reaction from which vegetable oil reacted with suitable alcohol to produce biodiesel and glycerol, therefore this method called alcoholysis [6, 7].

Methanol is widely used as alcohol reactant which is mainly produced by oxidation processes of methane, a natural gas component, hence a non-renewable energy [8, 9]. Ethyl alcohol is also suitable to use in esterification or transesterification reactions to produce the biodiesel [4, 10-12].

Oils and fats such as waste cooking oils, non-edible oils (jatropha oil, for example), and various animals fats are promising raw materials for biodiesel production. Such materials are having large amount of free fatty acid (FFA) that causes undesired phenomena of the formation of soap as a by-product. Therefore, before transesterification reaction, free fatty acid must converted to fatty acid methyl or ethyl ester by esterification reaction [13]. Esterification reactions can be carried out by acid such as sulfuric acid or hydrochloric acid in case of using homogeneous acidic catalysts to produce alcoholic esters and water.

In spite of acid homogenous catalysts does not make the problems of forming soap as when used homogeneous base catalysts, but another problems may arise likes formation of high quantities of by-products beside corrosion problems, therefore, the using of solid acid catalysts (heterogeneous catalysts) are always recommended to overcome these problems in esterification process [14]. The solid acid catalysts have many advantages besides overcoming the defects of homogeneous acid catalysts in that it's simply recovery of catalyst with a filtration, higher activity, selectivity, longer usage and compatible with environment, the Reusability criterion of the heterogeneous catalysts make continuous mode i.e. fixed-bed very effective. Such continuous process can reduce product separation and purification costs, make it economically viable to compete with commercial petroleum-based diesel fuel [15]. Solid acid catalysts can carry out esterification reactions and transesterification reactions simultaneously [16, 17]. Many types of solid acid catalysts, such as zeolites [11, 12, 18], Amberlyst-15 [19], SO4/ZrO_2 [20] and Tin compounds [21] have been tested in biodiesel synthesis.

The kinetic mechanism for esterification reaction is complicated when heterogeneous catalysts are used. The rate determining step in carboxylic acid esterification can be any of the elementary reaction steps, including external mass transport in the bulk liquid, adsorption, desorption, and surface reactions. Therefore, heterogeneous kinetic models based on Langmuir-Hinshelwood (LHHW) and Eley-Rideal (ER) mechanism was applied for the esterification process [22].

Kinetics of heterogeneously catalyzed transesterification follows LHHW model when using solid catalysts containing Lewis acid/base sites [23], while ER mechanism was followed by solid base catalysts [24]. A solid catalyst that leached substantially into the reaction media cannot be considered heterogeneous as the reaction mechanism of such catalysts followed kinetic mechanisms similar to that of homogeneous transesterification [10, 25].

In this present work, a first-order kinetics model for esterification reaction of oleic acid with ethanol catalyzed by nanoporous HY zeolite will be proposed based on Langmuir-Hinshelwood model. The effect of external mass transfer resistance was investigated to select the optimum rpm that used for kinetic inspection. The overall reaction rate was assumed to follow a first-order expression with respect to oleic acid. The rate-limiting step will be also determined and the effective activation energy will be calculated based on the experimental data. Finally, the effect of internal mass transfer resistance to the reactant will also be investigated based on Thiele modulus calculations.

Experimental Work

Catalyst Preparation

Preparation of Zeolite from Iraqi Kaolin

The preparation of HY-kaolin was included two steps as conventional methods of preparation [26], the first step deals with the prepared of NaY zeolite as an intermediate step and the next step related to convert NaY to HY zeolite (HY-kaolin) using ion exchange technique.

Preparation of Nay-Kaolin Zeolite

Iraqi kaolin clay was sieved to 75µ to ensure very fine powder and then mixed with 40 wt % sodium hydroxide solutions, using 1 kaolin /1.5 NaOH by weight, then, the mixture entered furnace at 1123 K for 3 hours to obtain fused kaolin. The fused kaolin was milled to convert it in powder form. 50 g of the prepared kaolin and 63 g of sodium silicate were dispersed in 500 ml of deionized water under constant stirring at 323 K for 1 h by electrical magnetic stirrer, Heat (Stuart (CB302) / USA). The slurry with pH approximately 13.3 was transferred to Teflon Bottle and entered an oven for ageing at 323 K for 24 h, under static conditions. The slurry was crystallized at 373 K for 48 h, after that, the crystalline slurry was filtered using Buchner Funnel with the aid of a vacuum pump and washed with deionized water until the pH arriving to 11.7. The crystalline mass in filter paper was entered again to the oven for drying at 373 K for 16 h; finally, in order to obtain a pure NaY zeolite, the dried powder was calcined at 773 K for 1 h.

Preparation of HY-Kaolin Zeolite

One hundred grams of prepared NaY zeolite was mixed with 600 ml of saturated aqueous solution of 1 M ammonium nitrate at 353 K for 4 h, placing in the 3 necks flask (1000 ml), which fitted with reflex condenser. The mixture was filtrated, washed with deionized water and finally dried at 373 K for 6 h, the product from this step called NH_4Y zeolite. 40 g of the prepare NH_4Y zeolite was mixed with 800 ml of 0.5 N Oxalic acid at room temperature for 8 h. The slurry was filtered, washed with deionized water and dried at 373 K; finally the dried zeolite was calcined at 823 K for 5 h.

Catalysts Characterizations

The crystallinity of the powder patterns for prepared HY zeolite was investigated using X-Ray diffraction (XRD) using diffraction angle 2θ (deg) between 4˚ and 50˚ with a 2θ step size of 0.026 and a step time of 50 sec with Cu Kα radiation (λ = 1.5406 A˚), the X-ray tube operated at 40 kV and 30 mA using fixed 1/4˚ anti-scatter slit. Nitrogen adsorption / desorption measurements were conducted using a Micromeritics ASAP 2020, pore analysis by N_2 physisorption at -196 ˚C. The sample were degassing for 12 h at 350˚C under vacuum pressure (less than 10^{-5} mbar) prior to analysis. BET-surface areas of the samples were calculated using the Brunauer–Emmett–Teller (BET) method in relative pressure range 0.05–0.35. The total pore volume is specified from the adsorption branch of the N_2 isotherm as the amount of liquid nitrogen adsorbed at $p/p_0 = 0.995$. Mesoporous mean diameters for prepared HY was calculated from the nitrogen sorption data using BET analysis (4 V/A). The hydrodynamic diameter zeolites was determined by dynamic light scattering (DLS) technique using zeta sizer (Malvern Instrument), Micropours structure was determined by scanning electron microscopy (SEM). The x-ray fluorescent (XRF) was applied to catalyst for chemical elemental analysis.

Experimental Setup

The esterification reaction of oleic acid in batch reactor was carried out in a laboratory scale reactor as shown in Figure 1. The apparatus used for the experiment consists of 500 ml three neck flat bottom glass flask and electrical heater with magnetic stirrer arrangement to achieve a perfect contact among the reactants.

One side neck of the reactor is plugged with air tight rubber stopper which holds the thermometer used to measure the reaction temperature. The other side neck is used to draw the sample oil and alcohol catalyst mixture. The water cooled condenser was inserted through the main neck of the reactor to recover the escaping ethanol which has a boiling point of 78 ˚C and vaporizes at the elevated temperature during the reaction. The condenser also helps in maintaining atmospheric pressure inside the reactor; water path was used in order to keep the temperature at the desired level

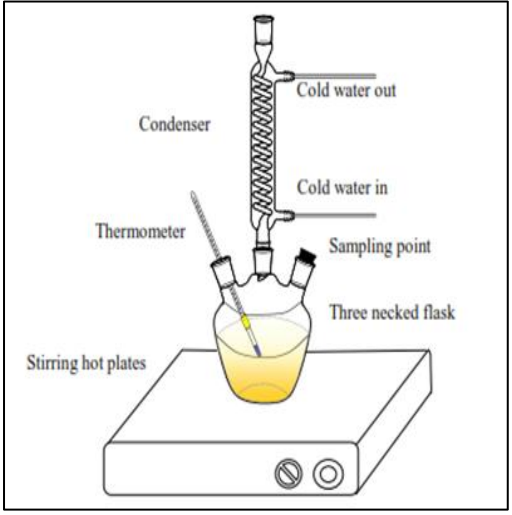

Fig. 1, schematic diagram of the batch reactor

The desired amount of catalyst (HY zeolite) before each experimental was dried at 130°C up to 2 h to eliminate any possible amount of water.

At the beginning, the reactor was kept in water bath and loaded with 50 ml (44.75 g) of oleic acid which was mixed with 6:1 ethanol to oil, preheated to desired temperature (40, 50, 60 or 70˚C) and then 5 wt. % prepared HY zeolite was added to the mixture.

Analytical Method

The mixtures of reactants which consist from the reactants and products were analyzed after each period of time (15 minutes), approximately 5 ml from the reaction mixture was withdrawn and centrifuged for 10 min to improve the separation of the phases and then certain amount from the top layer of product was taken and then added 2 drops of phenolphthalein as indicator and titrate with 0.1 molarity of KOH in order to evaluate the acid value (AV) as shown in the following equation; (Karnasuta et al.,2007)

$$AV = \frac{\text{ml of KOH} \times N \times 56}{\text{Weigth of Sample}} \qquad \dots (1)$$

From the acid value, the conversion of the oleic acid can be calculated for each amount of the catalyst as shown in the equation (2);

$$\text{converion} = \frac{AV_{to} - AV_t}{AV_{to}} \qquad \dots (2)$$

Where:

AV_{to} (acid value of the reaction product at time 0)

AV_t (acid value of the reaction product at time t)

Kinetic and Mass Transfer of Esterification of Oleic Acid

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

Differential method of analysis obtained data has been used to find suitable kinetic model for oleic acid esterification.

Assumptions for the Present Kinetic Model

In the present work, we focus on the kinetics model of reaction catalyzed by solid HY-kaolin, for single step. The stoichiometric equation of this reaction could be presented in equation (3):

$$OA + E \xleftrightarrow{Catalyst} P + W \qquad \ldots (3)$$

Where OA is oleic acid (simulated free fatty acid in sunflower oil), E is ethanol, P is fatty acid ethyl esters (FAEE) and W is water.

Generally, the heterogeneously-catalyzed esterification is a very complicated reaction involving a liquid-liquid-solid three-phase system where reactions occur on the surface of the solid catalyst. Therefore, the chemical reaction rate on the catalyst surface, the external and internal mass transfer rate of reactant and product molecules, the absorption rate of reactant molecules on active sites of the catalyst, and the desorption rate of products could impact the overall rate. One or more of these rates may be the limiting rate. Thus, the kinetics study of this liquid-liquid-solid system reaction in this present work will include not only developing the overall reaction rate expression but also identifying the rate-limiting step; some assumptions were made for developing the kinetics model:

1- The external mass transfer of ethanol and oleic through the bulk phase to the catalyst surface and the internal diffusion rate of ethanol toward active sites do not limit the overall reaction rate i.e. the mixing of the reaction system is perfect and small particle size.

2- Ethanol and oleic acid molecules are chemisorbed on active sites, and the adsorption follows the first-order Langmuir adsorption isotherm. Since an excess amount of ethanol is used and the adsorption of ethanol on HY-kaolin zeolite is quick, the fraction of surface covered by ethanol is assumed to be constant.

3- Esterification reaction occurs between neighboring chemisorbed ethanol molecules oleic acid molecules.

4- The overall esterification reaction on the catalyst surface follows pseudo-first order kinetics with respect to oleic acid and the reverse reaction can be neglected for the initial period of time before reaching the equilibrium reaction.

5- No temperature gradient exists through the catalyst pore channel due to the small reaction heat and nano sized catalyst particles.

6- The adsorption-desorption equilibrium of reaction products, FAEE (biodiesel) and water, is reached quickly and do not affect the overall rate.

Mathematical Kinetics Model

Based on the quasi-steady state assumption, the amount of adsorption of oleic acid (OA) molecules is equal to the sum of the amount of desorption and the amount of oleic acid consumed by chemical reaction on the surface.

According to assumption (2), (3), and (4) the reaction rate is described as:

$$-r_{OA} = -\frac{dC_{OA}}{dt} = k_s \theta_M C_{OA,s} \qquad \ldots (4)$$

Where C_{OA} is the oleic acid concentration in the bulk liquid phase, ks is the chemical reaction constant on the catalyst surface, and θ_M is the occupied fraction of active sites by ethanol, $C_{OA,s}$ is the concentration of oleic acid on the catalyst surface.

According to the proposed reaction mechanism, the adsorption of OA is the rate-limiting step. Then the net rate of OA adsorption-desorption is equal to the reaction rate on the catalyst surface:

$$r_{ads-des} = k_{ads}\,(1-\sum\theta)C_{OA} - k_{des}\,C_{OA,s} = -r_{OA} = -\frac{dC_{OA}}{dt} = k_s\theta_M C_{OS,s} \quad \ldots (5)$$

Where $r_{ads\text{-}des}$ is the net rate of OA adsorption-desorption, k_{ads} and k_{des} are adsorption and desorption rate constants, respectively, $\sum\theta$ is the total fraction covered by all species in the liquid mixture, Rearrange Eq. (5) to get the non measurable $C_{OA,s}$ in terms of measurable C_{OA}:

$$C_{OA,s} = \frac{kads\ K_{ads}(1-\sum\theta)}{K_{des}+K_s\theta_M}\,C_{OA} \quad \ldots (6)$$

Substitution of Eq. (6) into Eq. (4) results in:

$$-r_{OA} = -\frac{dC_{OA}}{dt} = (k_s\theta_M)\,\frac{K_{ads}\,(1-\sum\theta)}{K_{des}+K_s\theta_M}\,.\,C_{OA} \quad \ldots (7)$$

Assuming;

$$k_{eff} = (k_s\,\theta_M)\,\frac{K_{ads}(1-\sum\theta)}{K_{des}+K_s\,\theta_M} \quad \ldots (8)$$

Eq. (7) becomes:

$$-r_{OA} = -\frac{dC_{OA}}{dt} = k_{eff}\,C_{OA} \quad \ldots (9)$$

Where k_{eff} is the effective rate constant reflecting both the chemical reaction and adsorption-desorption resistance on the surface. In a batch reactor, C_{OA} can be expressed in terms of the conversion of oleic acid x_{OA}:

$$C_{OA} = C_{OAi}\,(1-x_{OA}) \quad \ldots (10)$$

Where, C_{OAi} is the initial concentration of OA. Then Eq. (9) becomes:

$$\frac{dx_{OA}}{dt} = k_{eff}\,(1-x_{OA}) \quad \ldots (11)$$

The integration of Eq. (11) between 0 and any time versus zero conversion and conversion, gives:

$$-\ln(1-x_{OA}) = k_{eff}t + C \quad \ldots (12)$$

Result and Discussion

Characterization of Synthesized Catalysts

The crystallinity of the prepared HY zeolite was investigated by using XRD technique as shown in figure 2.

From figure 2, the diffraction pattern of the prepared HY zeolite is approximately comparable with the standard faujasite zeolite (FAU) type Y according to the Commission of the International Zeolite Association (IZA) [27], since the highest peak at intercept (1, 1, 1) of the standard is 6.33 [28], which is nearly to the highest peak of the prepared zeolite which was equal to 6.34.

The BET surface of the prepared HY zeolite was 389.55 m^2/g while the pore volume and pore size of the prepared HY zeolite were equal to 0.853 cm^3/ g and 12.341 nm, respectively.

The average particle size of the prepared HY zeolite was equal to 1435 nm according to Dynamic Light Scattering (DLS) technique.

The chemical composition for the prepared catalysts was analyzed using X-ray fluoresce (XRF), as shown in table 1.

The molar ratio (Si/Al) for the prepared HY zeolite was equal to 3.1; these results were in a good agreement with the results that obtained Abbas and Abbas [11, 12].

The surface structure (morphology) and also general view of the particle size distribution of the prepared and commercial HY zeolite can be explored by using scanning electron microscopy (SEM) image, therefore, figure 3 represents the images of prepared HY zeolite at magnification of 1000 degree.

The particle shape of the prepared HY zeolite as spherical particle and the increase in particle volume due to the large amount of the impurities that made particles had the agglomeration tendency as shown in figure 3.

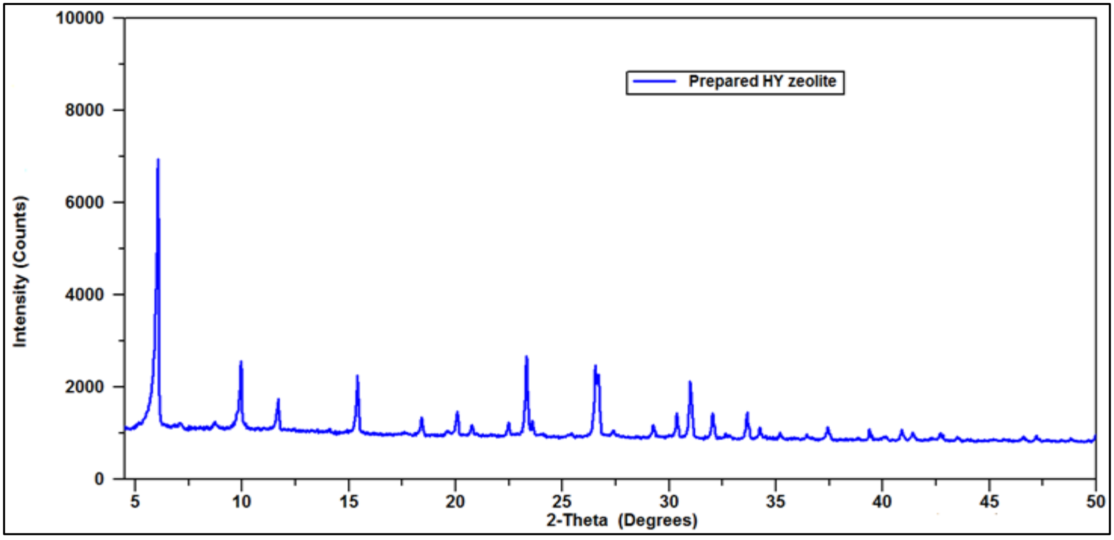

Fig. 2, XRD patterns for the prepared HY zeolite

Table 1, the chemical composition of the of prepared HY zeolite

Oxides, wt. %	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	MgO	K_2O	CaO	P_2O_5	L.O.I
HY Zeolite	15.92	58.11	3.191	5.147	1.222	0.067	4.112	0.6448	11.587

L.O.I …loss on ignition

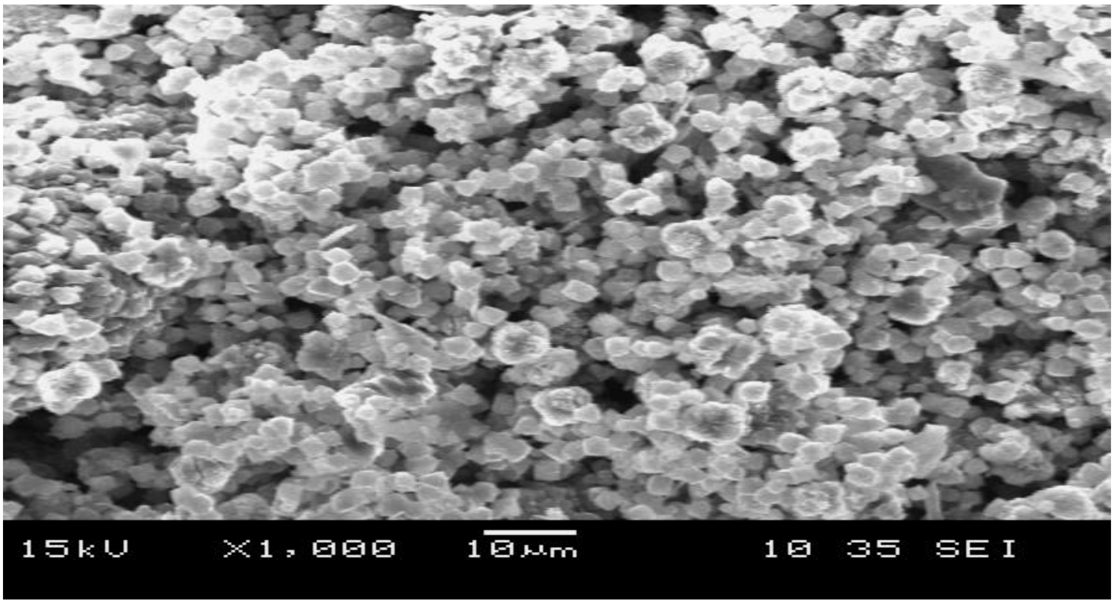

Fig. 3, Scanning Electron microscopy for prepared HY zeolite

Effect of the External Mass Transfer Resistance on Esterification Reaction

In order to study the effect of external mass transfer resistance to the oleic acid, different stirring speed (i.e. different rpm) were utilized for this purpose, figure 4 shown the relationship between oleic acid conversion with rpm at different temperature 40, 50, 60 and 70 ˚C with 6:1 molar ratio of ethanol to oleic and 5 wt. % of prepared HY zeolite loading with respect to oleic acid for one hour.

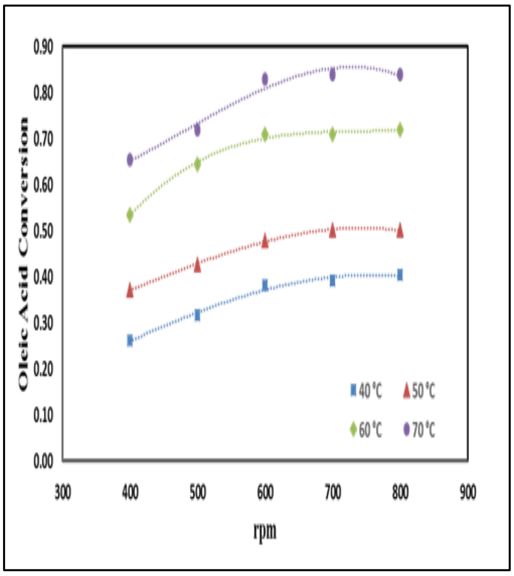

Fig. 4, the effect of the stirring speed on the esterification reaction of oleic acid

The oleic conversion increase with increasing temperature and also the conversion increases with increasing stirring speeds until reach to 600 rpm, over these speeds (700 and 800 rpm), there is no significant increase in oleic acid conversion, so that, it can be considered the optimum stirring speed of the reactant is equal to 600 rpm by which the external mass transfer resistance can be neglected, this value of rpm agreed with many researchers outcomes [29, 30].

Effect of Reaction Temperature on Oleic Acid Conversion

The reaction temperature is key factor for the kinetics of reactions because reaction rates are the temperature-dependent functions according Arrhenius's law. Esterification of oleic acid with ethanol takes place in the liquid phase, hence the reaction temperature should not be above the boiling point of ethanol (the boiling point of ethanol is 78 ˚C at atmospheric pressure). Figure 5 shows the oleic acid conversion with time at different temperatures: 40, 50, 60 and 70˚C for two hours, using 6:1 ethanol/oil molar ratios and 5wt. % of prepared HY zeolite with respect to oleic acid, these two values were selected as an optimum conditions since many researchers suggested these values [11, 14].

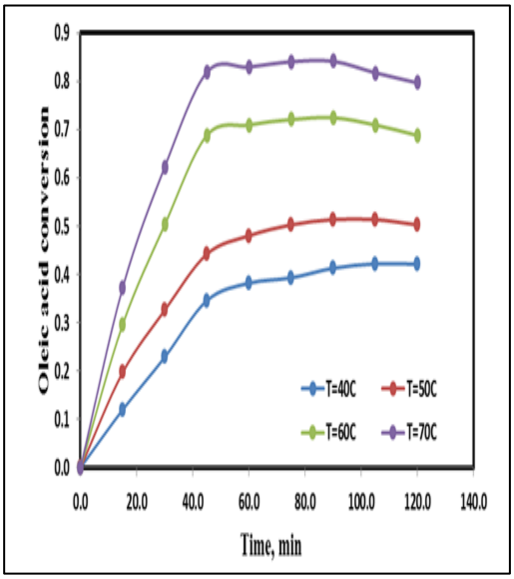

Fig. 5, Effect of reaction temperature on oleic acid conversion

The conversion of oleic acid increase with increasing temperature, for instance, the conversion of oleic acid at 40˚C is about 41% after 90 minutes, while the conversion of oleic acid at 70˚C is about 84% at same time, and these results are expected since the increase in temperature leads to increase in molecular activity (i.e. more molecules have energy to overcome the energy barrier of the reaction and react easily [31, 32].

Another reason may arises here, when temperature increase the viscosity of the reactants decrease, that’s means, the diffusion of the molecule is increased through the pores of the catalyst and as a results the reaction would be taken place rapidly at the active site of the catalyst for the first 45 minutes for all range of temperatures as shown in figure 5, after that, the conversion increase slightly until reach 90 minutes, finally, after 90 minutes, the conversion of oleic acid decreases due to deactivation of the HY-shale zeolite, and this deactivation attributed to clumping of water molecules inside the pores of the catalyst according to the hydrophilic property of the zeolite, consequently, the reverse reaction is increased and the conversion is decreased [33].

The maximum conversion at 70˚C was achieved after 90 minutes (i.e. the reaction reaches the equilibrium), while the maximum conversion at 40˚C was achieved after 120 minutes, it can be explained as the same reason above, since the reaction was very rapid at 70˚C, the catalyst deactivate early, while at 40˚C, the reaction was very slow that delay the deactivation of catalyst.

Effective rate constants and effective active energies

Effective rate constant (k_{eff}) can be obtained from the slop of plotting [–ln (1- x_{OA})] versus time (t) at different temperatures according to the equation (12). Figures 6 represent the oleic acid conversion for the period 0 to 45 min while this equation is not applicable for the period 45 to 90 min, therefore, using [x_{OA}/1-x_{OA}] instead of [–ln (1-x_{OA})] versus time which represent the second order with respect to oleic acid as shown in figure 7, with using the optimum conditions (5 wt % catalyst loading with respect to oleic acid, 6:1 ethanol/oil molar ratio and 600 rpm). The obtained effective reaction constants are listed in Table 2.

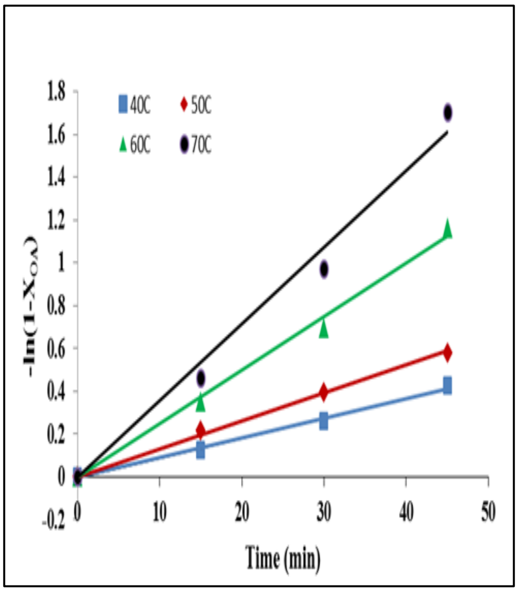

Fig.6, Reaction time (t) versus –ln (1-X_{OA}) plot for prepared HY zeolite in 0-45 min.

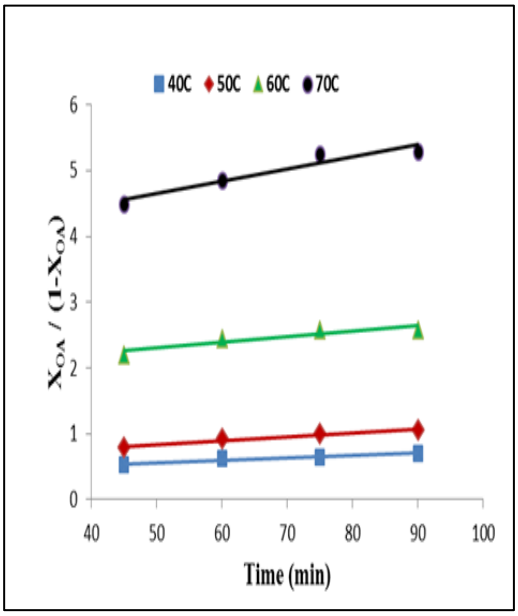

Fig. 7, Reaction time versus x_{OA}/1-x_{OA} plot for prepared HY zeolite in 45-90 min.

Table 2, Effective reaction constants for prepared HY zeolite

Temperature	k_{eff} (min^{-1})	
	0 to 45 min	45 to 75 min
40°C	0.009	0.003
50°C	0.013	0.005
60°C	0.024	0.008
70°C	0.035	0.018

The activation energy can be evaluated from the reaction rate constant according to the Arrhenius's equation (Eq. 13) [31, 32].

$$k_{eff} = A_0 e^{\frac{-Ea}{RT}} \qquad \dots (13)$$

Where:
A_0: is pre-exponential factor
Ea: is the activation energy of the reaction.

The activation energy and pre-exponential factor can be calculated by converting Arrhenius's equation to linear form for a particular range of temperatures, therefore, by taking ln (natural log) to the equation 13 leading to:

$$\mathrm{Lnk} = \ln A_0 - \frac{E_a}{R}\frac{1}{T} \qquad \dots (14)$$

For various temperatures (T) and various reaction rate constant (K_{eff}) data as shown in table 3, a plot of ln k versus 1/T yields a straight line and the slop of the line is $-E_a/R$. Figure 8 show the plots of ln k_{eff} versus 1/T for prepared HY zeolite in 0-45min and 45-90 min respectively. The pre-exponential factors and effective activation energies obtained from Equation 14 are listed in Table 4. The effective activation energies in 0-45 min and 45-90 min are 41.84 KJ/mol and 52.03 KJ/mol, respectively, the chemical reaction step seems more temperature-sensitive than oleic acid-adsorption step, since the activation energy in the second period is larger than the first period; the value of activation energy shows a good agreement with the value of activation energy obtaining from [34].

Table 3, values of 1/T versus lnk for different time (0 to 45 and 45 to 90 min)

Temperature			0 - 45 min		45 – 90 min	
T (C)	T (K)	1/T	k	ln k	k	ln k
40	313.15	0.003193	0.009	-4.71053	0.003	-5.809143
50	323.15	0.003095	0.012	-4.42285	0.005	-5.2983174
60	333.15	0.003002	0.024	-3.7297	0.008	-4.8283137
70	343.15	0.002914	0.035	-3.35241	0.018	-4.0173835

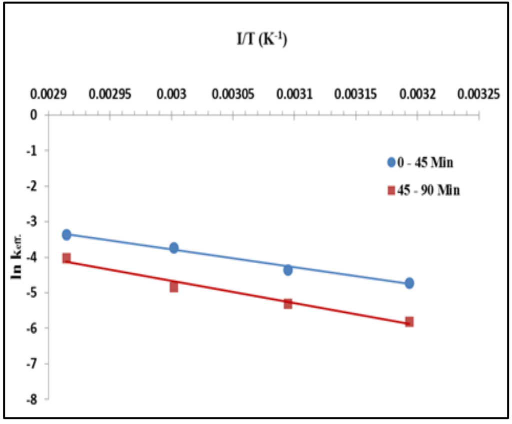

Fig. 8, Plot ln k_{eff} versus 1/T for HY-kaolin

Table 4, Effective activation energies, pre-exponential factors for different times

Time (min)	E_a (kJ/mol)	A_0 (min^{-1})
0-45	41.84	82454.34
45-90	52.03	1329083.28

Effect of Internal Mass Transfer

The esterification of oleic acid with ethanol catalyzed by solid acid contained three phases: liquids oil, ethanol phases and solid catalyst. Consequently interphase mass transfer is playing a crucial role in the reaction rate so that, the intraparticle diffusion might be the limiting step for a number of reactions, especially when the reactions taken place over microporous catalysts [35, 36]. Thiele modulus (M_T) is the dimensionless parameter widely used to estimate quantitatively the effect internal mass transfer on the reaction rate [32]:

$$M_T = L\sqrt{\frac{(n+1)K_{eff}\,C_{OA}^{n-1}}{2D_{eff}}} \quad \dots (15)$$

And,

$$D_{eff} = \frac{D_{AB}\,\epsilon_p}{\tau_p} \quad \dots (16)$$

Where:
n: order of the reaction
L: characteristic length of the catalyst particles (cm) = $L = \frac{R}{3}$, for sphere
K_{eff}: pseudo first order effective rate constant for the reaction (s^{-1})
D_{eff}: Effective diffusivity coefficient of the limiting reactant into the catalysts pores ($cm^2.s^{-1}$)
D_{AB}: molecular diffusion coefficient of the limiting reactant ($cm^2.s^{-1}$).
$\boldsymbol{\epsilon}_p$: porosity of the catalyst particles
$\boldsymbol{\tau}_p$: tortuosity of the catalyst pores

The prepared HY zeolite catalyst can be assumed spherical particles as seen in SEM technique (i.e. equation 19 is applicable) with the diameter of 1.435µm as evaluated from the DLS technique.

For different materials, $\boldsymbol{\epsilon}_p$ are usually in the range of 0.3 – 0.8, and the $\boldsymbol{\tau}_p$ from 1.4–12, (Veljkovic et al., 2009).

The value of the tortuosity ($\boldsymbol{\tau}_p$) that chosen is equal to 4, since many researchers in the literature chooses this value for zeolite type Y [36, 38].

The porosity of the catalyst ($\boldsymbol{\epsilon}_p$) can be defined as the void fraction using equation (17) [31].

$$\epsilon_p = \frac{\text{void volume of catalyst particle } (cm^3)}{\text{total volume of catalyst particle } (cm^3)} \dots (17)$$

The bulk density of the HY-kaolin was experimentally calculated and it was equal to 0.472 g/cm^3 and also the pore volume was evaluated by PJH method and it was equal to 0.853 cm^3/g, after substitution these values in equation (17), the value of the HY-kaolin porosity was equal to 0.403

The molecular diffusion coefficient of the oleic acid in ethanol (D_{AB}) can be calculated by using Wilke-Chang estimation method as shown in the relation [39];

$$D^{\circ}_{AB} = \frac{7.4 \times 10^{-8} \times (\Phi\, M_B)^{0.5} \times T}{\eta_B \times V_A^{0.6}} \quad \dots (18)$$

Where
The subscript A= oleic acid & B= ethanol
D°_{AB} = mutual diffusion coefficient of solute A in solvent B, cm^2/s
M_B = molecular weight of solvent B, g/mol
T = temperature, K
η_B = viscosity of solvent B, cp
V_A = molar volume of solute A at its normal boiling temperature, cm^3/mol
Φ = association factor of solvent B, dimensionless

Wilke and Chang [39] recommend that Φ be chosen as 2.6 if the solvent is water, 1.9 if it is methanol, 1.5 it is ethanol, and 1.0 if it is unassociated. The molar volume (V_A) of the solute (oleic acid) can be calculated in terms of critical volume (V_C) by using Tyn and Calus method as shown in the following equation;

$$V_A = 0.285 \times V_C^{1.048} \quad \dots (19)$$

The value critical volume (V_C) of oleic acid is 1152 cm^3/mol [40], so that the value of molar volume (V_A) of oleic acid is equal to 460.52 cm^3/mol.

Table (5), shows all values of molecular diffusion coefficient (D_{AB}) and also effective diffusion coefficient (D_{eff}) in cm^2/s at different temperatures.

The calculated Thiele modulus values at different reaction temperature are listed in Table (6).

The calculated effective diffusivity coefficients values range from 6.162 x 10^{-11} to 1.101 x 10^{-10} form 40 to 70 ˚C and these values are in agreement with Bobok et al. [38].

The values of Thiele modulus (MT) are less than 0.4, so this indication that the effect of internal mass transfer on the overall reaction rate can be neglected and these results could be attributed to the small particle size that made pore diffusion resistance very small. Finally, these results confirm the assumption (1).

Table 5, diffusivity coefficient calculation for prepared HY zeolite

Temp. (T)	Viscosity of ethanol (η_B)	D°_{AB}	D_{eff}
313	0.794	6.11565 E-06	6.16151 E-07
323	0.670	7.47905 E-06	7.53514 E-07
333	0.570	9.06333 E-06	9.13131 E-07
343	0.487	1.09266 E-05	1.10085 E-06

Table 6, Thiele modulus for prepared HY zeolite

Temp.	Diffusion Coefficient ($D_{eff.}$, m^2/s)	0 – 45 min	MT	45 – 90 min	$MT = \frac{R}{3} \times \sqrt{\frac{3 * K_{eff}}{2 * D_{eff}}}$
		K_{eff}		K_{eff}	
40˚C	6.16151E-11	0.009	0.002891	0.003	0.002043917
50˚C	7.53514E-11	0.013	0.003141	0.005	0.002386084
60˚C	9.13131E-11	0.024	0.003877	0.008	0.002741731
70˚C	1.10085E-10	0.035	0.004265	0.018	0.003745572

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