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Kinetics of Modified Zirconia-catalyzed Heterogeneous Esterification Reaction for Biodiesel Production

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Abstract: Biodiesel is one of the new possible substitutes of regular fuel for engines and is produced from different vegetable oils or animal fats. The main reaction involved is the transesterification of triglycerides into esters. The employment of low quality or waste raw materials has been considered to strongly improve the economic competitiveness of this biofuel with respect to the petroleum-derived diesel. In the case of waste raw materials characterized by a high content of Free Fatty Acids (FFAs), direct esterification of the FFAs is the primary route for producing biodiesel. The novel sustainable esterification process based on catalytic Reactive Distillation Column (RDC) has been proposed to overcome the shortcomings in the conventional process. A reliable kinetic model which would be applicable in a wide range of operating conditions is an important data for the RDC design. In the present study, kinetics of heterogeneous catalyzed direct fatty acid esterification was studied with a tungstated zirconia catalyst in a stirred batch reactor to synthesis biodiesel. The waste cooking oil with high content of FFAs was simulated by mixing pure oleic acid with refined palm oil. Ethanol was used in the experiments instead of methanol because it is less toxic and safer to handle. The effects of the main variables involved in the process such as reaction temperature, amount of catalyst, amount of triglyceride and the molar ratio of alcohol/free fatty acid were analyzed. The experimental data were interpreted with a second order, pseudo homogeneous kinetic model and a good agreement between experimental data and the model is obtained.

Key words: Kinetics, modified zirconia, esterification, biodiesel, kinetic modeling, reactive distillation

INTRODUCTION

The need for near and long-term sources of energy has motivated research on sustainable fuels, such as ethanol and biodiesel. Biodiesel (alkyl esters from vegetable oils or animal fats) is used as a substitute of the regular diesel. A great number of advantages are offered by biodiesel, namely, lower emission of CO due to a better combustion, a better lubricating effect on engines, non-sulfur emission and non-particulate matter pollutants (Knothe *et al.*, 2005; Srivastava and Prasad, 2000; Marchetti *et al.*, 2007; Vicente *et al.*, 2004).

Biodiesel is commonly synthesized using well established homogeneous alkali-catalysed transesterification methods. However, these processes are suitable only for feedstocks containing low concentrations of Free Fatty Acids (FFA), such as refined vegetable oils and refined animal fats. The fact that these edible-grade feedstocks are also in great demand for food production limits their utilization for the production of biodiesel. The employment of cheaper,

recycled feedstocks, such as yellow grease and inedible animal fats, improves the economic competitiveness of this biofuel with respect to the petroleum-derived diesel (Kulkarni and Dalai, 2006; Lotero *et al.*, 2005). These lower grade feedstocks can be converted to biodiesel using acid catalysed esterification process. It can be converted to biodiesel using alkali catalysed transesterification method if the lower grade feedstocks are pretreated in the esterification step to avoid saponification reactions during later transesterification.

Conversions for esterification reactions have long been known to be limited by a slow reaction rate and the existence of reversible reactions. Reactive distillation is an effective method that has considerable potential for carrying out equilibrium-limited liquid-phase reactions. It is a unit operation that combines chemical reaction and distillation within a single vessel, thereby reducing equipment and recycle costs.

To accelerate the reaction rate, catalysts are always employed in a liquid-phase esterification. Despite a strong catalytic effect, the use of homogeneous catalyst, such as

sulfuric acid, suffers from drawbacks (Malone and Doherty, 2000), such as the existence of side reactions with reactants/products, equipment corrosion and having to deal with acid-containing waste. Many solid acid catalysts have been investigated as potential replacements for mineral acids in esterification reactions are: tungsten oxides (Furuta *et al.*, 2004; Lopez *et al.*, 2005, 2007a, b), Sulfated Zirconia (SZ) (Kiss *et al.*, 2006; Ni and Meunier, 2007), Amberlyst 115, Lewatit GF 101, sulfonated saccharides (Takagaki *et al.*, 2006; Mo *et al.*, 2008), Nafion1 resins (Liu *et al.*, 2006; Lopez *et al.*, 2007a, b; Nijhuis *et al.*, 2002) and organosulfonic functionalized mesoporous silicas (Mbaraka *et al.*, 2003, 2006; Jackson *et al.*, 2006). However, the basic investigation of intrinsic reaction kinetics in the presence of an emerging heterogeneous catalyst is very limited for the esterification of fatty acid with alcohol. In the present study, the kinetic behaviour of the heterogeneously catalysed esterification of oleic acid with ethanol is studied in a stirred batch reactor using tungstated zirconia as a catalyst. Ethanol is used as alcohol instead of methanol since ethanol is safer to handle and if ethanol is employed, the final fuel product can be considered 100% natural and renewable. The experimental reaction rates obtained in this work were correlated by heterogeneous kinetic models. The developed rate expression would be applicable over a wide range of operating conditions and could be conveniently used for the design of a reactive distillation column.

MATERIALS AND METHODS

Commercially available tungstated zirconia (XZO1251) amorphous precursors were provided free of charge by Magnesium Electron, Inc. (MEI, Manchester, UK). The amorphous samples were dehydrated at 120°C for 1h and then calcined in a furnace at 400°C using flowing air. Oleic acid (99%) were purchased from Sigma-Aldrich while ethanol (99.5%) were purchased from Acros Organics.

The liquid phase reaction was carried out in a batch reactor. The oleic acid and the known amount of catalyst were placed in 500 mL batch reactor (round bottom flask) fitted with a reflux condenser. The reactor contents was heated to the reaction temperature in an oil bath and continuously stirred. The esterification was started by adding the pre-heated ethanol to this mixture. The reaction was carried in the temperature range of 303.15-323.15 K while the catalysts loading was varied from 0.5-1.5 g. Reaction temperature was controlled within an accuracy of ± 1 K using a thermocouple with digital temperature controller. The molar ratio of ethanol to oleic

acid was varied from 1 to 5 and the total reaction mixture volume was kept constant as 200 mL. All the experiments were repeated at least two times to check the reproducibility.

A 2 mL portion of the reaction mixture sample was withdrawn at each decided reaction time and titrated by 0.01 N NaOH aqueous solution using phenolphthalein as an indicator. Prior to titration, the solid catalyst was separated from the reaction mixture by centrifugation to limit further reaction and the sample was dissolved in ethanol. The amount of NaOH consumed was recorded and acidity was calculated using the following equation (Tesser *et al.*, 2005):

$$a = \frac{V1000M_w C}{W} \quad (1)$$

where, a is the acidity index; C the concentration measured by titration, mol L^{-1} ; W the weight of the sample, mg; M_w the molecular weight of the solution, g mol g^{-1} ; V the volume of solution employed for titration, mL.

The conversion of FFA, X_A was calculated using the following definition:

$$X_A = \frac{a_i - a_t}{a_i} \quad (2)$$

where, a_i is the initial acidity of the mixture and a_t is the acidity at a t time.

BATCH KINETICS RESULTS

Effect of the amount of catalyst: Figure 1 shows the effects of varying the amount of catalyst. The amount of catalyst was varied from 0.5 to 1.5 g at a temperature of 313.15 K, reactant molar ratio (ethanol to oleic acid) of 5:1 and stirrer speed of 300 rpm. The reaction was highly dependent on the amount of catalyst. The higher the amount of catalyst, the faster the rate at which reaction equilibrium was reached due to the increase in the total number of available active catalytic sites for the reaction. For heterogeneous catalysed reactions, it is not very practical to use more than 10% (w/w) catalyst loading and hence it can be concluded that the optimum catalyst loading based on the current findings was 1.5 g.

Effect of reaction temperature: Figure 2 presents the variation of oleic acid conversion at different reaction temperatures in the range of 303.15 to 323.15 K at a reactant molar ratio of 5:1, a stirrer speed of 300 rpm and the amount of catalyst of 1.5 g. The results showed that

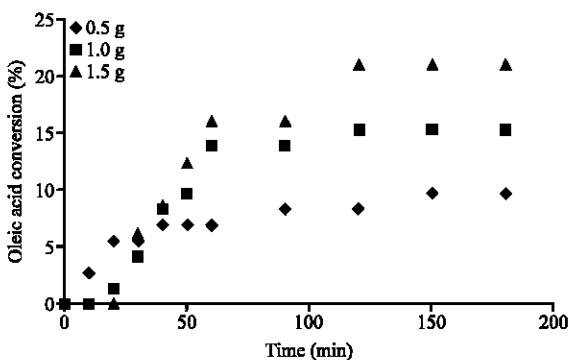


Fig. 1: Effect of different amount of catalyst

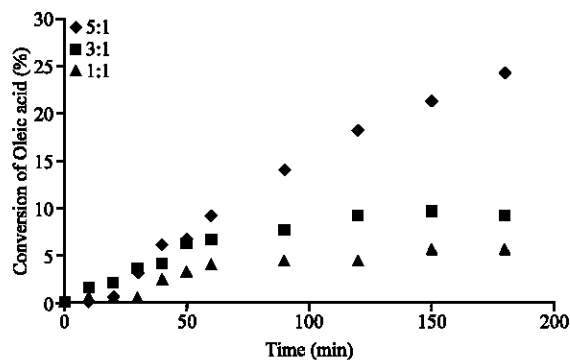


Fig. 3: Effect of different reactant molar ratio

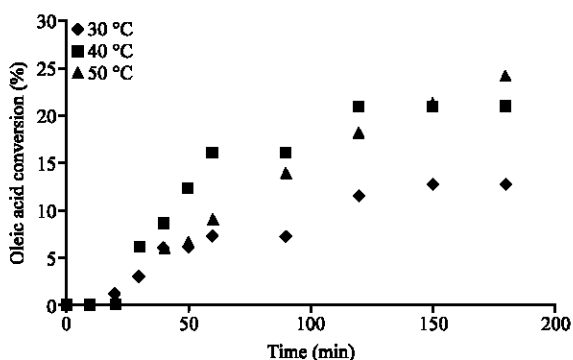


Fig. 2: Effect of different reaction temperature

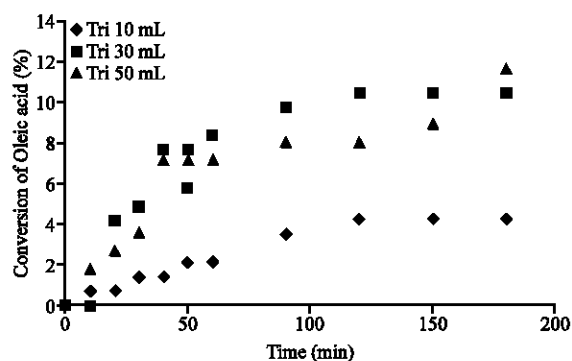


Fig. 4: Effect of different amount of triglycerides

the reaction was typically endothermic. The higher temperature yielded the greater conversion of oleic acid at a fixed contact time under otherwise identical conditions. The rate of oleic acid conversion increased with an increase in reaction temperature from 303.15 to 323.15 K because increasing the temperature accelerated the forward reaction. This result corroborates with those obtained by Trubiano *et al.* (2007) where the reaction of oleic acid and ethanol to produce ethyloleate was carried out using a commercial enzyme as catalyst.

Effect of reactant molar ratio (ethanol to oleic acid): The initial molar ratio of ethanol to oleic acid was varied from 1:1 to 5:1 at a temperature of 323.15 K, an amount of catalyst of 1.5 g and a stirrer speed of 300 rpm. The results are shown in Fig. 3. The equilibrium oleic acid conversion increased from about 5% at a reactant molar ratio of 1:1 to 25% at a reactant molar ratio of 5:1. Esterification of oleic acid with ethanol is an equilibrium-limited chemical reaction and because the position of equilibrium controls the amount of ester formed, the use of an excess of ethanol increases the conversion of oleic acid. When the reactant molar ratio was low, the reaction occurred faster but reached a lower final conversion as compared with the

operating conditions under higher molar ratio. In the latter case, the final conversion was higher, but the initial reaction rate was slow. This non-common behavior is due to the dissolution versus kinetics effect. For short times, when the amount of ethanol is high, the dissolution effect of ethanol is stronger than the kinetics effect, producing a smaller reaction rate. However, as time continues, the reaction continues to take place and the high concentration of alcohol produces the higher final conversion but required a longer reaction time. Contrarily, when small amounts of ethanol are used, the dissolution effect is less intense, but also, because the concentration is lower, the final conversion achieved is smaller.

Effect of the amount of triglycerides (TGs): The amount of triglycerides (TGs) was varied from 10 to 30 mL at a temperature of 323.15 K, an amount of catalyst of 1.5 g, a reactant molar ratio of 5:1 and a stirrer speed of 300 rpm. The results are shown in Fig. 4. Under the reaction conditions that have been tested, the transesterification reaction of TGs takes place simultaneously with the esterification reaction. The amount of ester produced comes in a large part from the free fatty acids and in a smaller amount from the TGs. When the amount of TGs

increased from 10 to 30 mL, the oleic acid conversion increased because of the increasing in the amount of free fatty acid contained in the refined palm oil that used to model the mixture of TGs and acid. Nevertheless, the initial reaction rate and the oleic acid conversion decreased as the amount of triglycerides increased to 50 mL. The selectivity of the catalyst to the esterification was apparently affected by the transesterification as the amount the TGs was substantial.

Kinetic modeling: The esterification reaction between oleic acid and ethanol can be represented in the following schematic form:



The kinetics of esterification reaction can be expressed using a simple pseudohomogeneous model or more complex models based on the Langmuir Hinshelwood Hougen Watson mechanism (LHHW) or the Eley-Rideal (ER) mechanism (Lee *et al.*, 2000; Gangadwala *et al.*, 2003; Saha and Sharma, 1997; Saha and Streat, 1999) in the absence of any intraparticle diffusional limitation. Pseudohomogeneous first and second order models are applicable to many heterogeneously catalysed reactions. These models are applicable for highly polar reaction medium.

For the modeling of the experimental runs in the present study, a pseudo-homogeneous second-order equilibrium model has been used with an expression of the reaction rate as follows:

$$-r_A = k(C_A C_B - \frac{C_C C_D}{K_e}) \quad (4)$$

where, $-r_A$ denotes the reaction rate of oleic acid, C_A denotes the concentration of oleic acid; C_B denotes the concentration of ethanol; C_C and C_D are the concentrations of ethyl oleate and water, respectively, formed during the reaction and k and K_e are the kinetic constants for the forward reaction and equilibrium constant, respectively.

Reaction rates were calculated by the differential methods as proposed by Cunill *et al.* (2000). In the case of this heterogeneously catalysed reaction, the equation as below was used:

$$-r_A W = N_{A0} \frac{dX_A}{dt} \quad (5)$$

where, W is the weight of the catalyst, N_{A0} is the initial number of moles of oleic acid, X_A is the conversion of oleic acid and t is the time of the reaction.

The determination of the kinetic parameters appearing in Eq. 4, kinetic constant k and equilibrium constant K_e , was performed by a nonlinear regression program that iteratively adjusts these parameters until a predefined criterion was satisfied. In our case, the criterion is the minimization of the Sum of Residual Squares (SRS) between the experimental and calculated reaction rates using the equation:

$$SRS = \sum (r_{exp} - r_{calc})^2 \quad (6)$$

where SRS is the minimum sum of residual squares resulting in the fitting procedure and r is the reaction rate. The subscripts *exp* and *calc* denote experimental and calculated values, respectively.

The values of the parameters obtained at each temperature have then been correlated by means of the usual Arrhenius-type plot, allowing an evaluation of the activation energy and of the heat of the reaction. The obtained results are reported in Table 1.

Figure 5 shows the Arrhenius-Van't Hoff plot. The obtained value of the apparent activation energy, 51.9 J mol^{-1} is roughly in agreement with the value obtained by Berriouis *et al.* (2007) of $40\text{-}50 \text{ kJ mol}^{-1}$, related to the esterification of free fatty acid in the sunflower oil with methanol using sulfuric acid as catalyst. The results related to the equilibrium constant show that the reaction is characterized by a endothermicity of 87.6 kJ mol^{-1} , because an increase of the equilibrium constant with the temperature has been observed. This result is in agreement with the literature work of Tesser *et al.* (2005).

Finally, the goodness-of-fit of the experimental data to the proposed model was assessed by comparing the

Table 1: Kinetic parameters

Parameter	Pre-exponential factor ($\text{L}^2/\text{mol}\cdot\text{g}\cdot\text{min}$)	Activation energy/Heat of reaction (kJ mol^{-1})
k	1.5×10^{10}	51.9
K_e	6.0×10^{12}	87.6

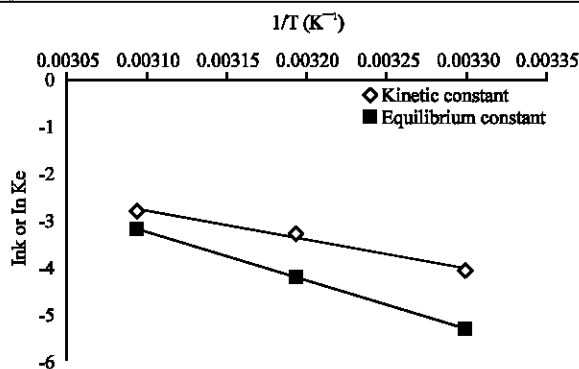


Fig. 5: Arrhenius-Van't Hoff plot

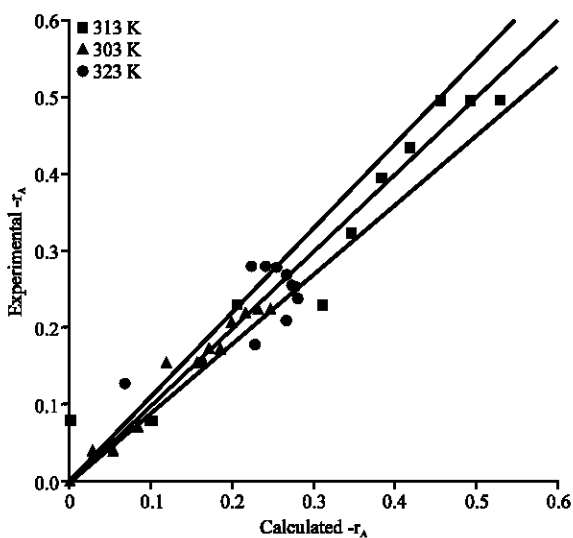


Fig. 6: Comparison of the experimental reaction rate and that predicted by Eq. 4

experimental reaction rate with the theoretical prediction at a reactant molar ratio of 5:1, a stirrer speed of 300 rpm and the amount of catalyst of 1.5 g. Figure 6 shows that three-fourths of the experimental data were reproduced with errors not greater than 10%.

CONCLUSIONS

The kinetic behaviour for the esterification of oleic acid with ethanol in the temperature ranging between 303 and 323 K, at the amount of catalyst of 0.5 to 1.5 g, at reactant molar ratios of 1:1 to 5:1 and at the amount of TGs of 10 to 30 mL was investigated experimentally in a stirred batch reactor using tungstated zirconia catalyst. The optimum condition for synthesising ethyl oleate has been delineated. The equilibrium conversion of oleic acid was found to increase with an increase in temperature and also it increases appreciably with an excess of ethanol in the reacting system. Kinetic parameters of a pseudo-homogeneous second order model have been determined by nonlinear regression on the experimental free-acidity data collected in different runs performed in a batch reactor. A satisfactory agreement between the model and the experiments has been obtained. The kinetic data for the esterification of oleic acid with ethanol would be useful for the simulation and design of a reactive distillation column for the production of biodiesel.

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