

Kinetic study of Esterification of Adipic acid with Methanol over Amberlyst 15

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Abstract: Dimethyl adipate (DMA) is an important chemical which has been considered as environmentally benign (green) solvent used mostly as paint stripper and solvent. This paper represents the kinetic behaviour of esterification of adipic acid with methanol over Amberlyst 15 catalyst at reflux. Effect of various parameters such as temperature (313, 323, 333 K), alcohol to acid ratio (10:1, 15:1, 20:1) and catalyst loading (5%, 7%, 10%) were tested. Higher agitation speed was used in order to increase the contact of reactants with the catalyst. A pseudo-homogeneous model was employed to validate the experimental data and activation energy of the reaction was found to be 14.471 KJ/mol.

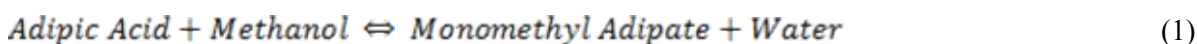
Keywords: Amberlyst 15, Activation energy, Dimethyl adipate, Esterification.

1. Introduction

Adipic acid, glutaric acid and succinic acid are dicarboxylic acids that are abundantly present in the waste streams of adipic acid manufacturing plants (caprolactam plants)^{1,2,3}. Though they had been incinerated in the past to avoid environmental contamination, recovery techniques have long been used in order to convert these chemicals into valuable products³. Esterification of dicarboxylic acids with alcohols to produce diesters is the most acceptable method for their conversion⁴. However, biological conversion of dicarboxylic acids has been lavishly studied⁵.

Dibasic Esters (DBE), also known as DMEs (dimethyl esters) are chemical compounds composed of a mixture of three dibasic esters namely: dimethyl adipate (DMA), dimethyl glutarate (DMG) and dimethyl succinate (DMS). DBE is used in a variety of solvent applications both as a standalone solvent and in formulations; however, it can be used as a chemical intermediate. It has been considered as green solvent to replace toxic and highly volatile solvents such as methylene chloride⁶. Also they have applications in coating industry to clean adhesives, polyurethane foams and unsaturated polyester resins⁷.

Dibasic esters are generally produced by catalytic esterification of dicarboxylic acids. Cation exchange resins have been used as efficient and eco-friendly catalysts in such esterification systems⁴. The esterification reaction of adipic acid with methanol is one of the main reactions in this scenario that includes a two steps cascade reversible reaction as follows:



Since it is an equilibrium reaction, several methods are available in order to shift the reaction towards formation of the desired product such as continuous water removal from the reaction mixture and using excess

of methanol^{8,4}. However, dimethyl adipate (DMA) and water may form an azeotropic mixture that makes the separation process a bit challenging⁹.

There have been a few recent studies in the literature for the same system that aim for efficient production of diesters. In all these investigations cation exchange resins have been considered as the catalyst^{8,9,10,11}. Chan et al. (2009) studied a continuous esterification process of adipic acid with methanol over acidic ion exchange resin (Amberlyst 35) catalyst. Experiments were performed in a packed column and kinetics of the reaction was evaluated at different conditions of feed mole ratio, catalyst loading and temperature. Kinetics of esterification of glutaric acid with methanol over Amberlyst 35 catalyst was also studied by Tsai et al. (2010) in a packed bed column. Hung et al. (2008) proposed a conceptual design for reactive distillation of adipic acid and glutaric acid with methanol over solid acid catalyst and reported a high purity of diester product. In this work, total annual cost is reported much higher than esterification of acetic acid because of excess use of methanol.

This paper represents the kinetic study of adipic acid esterification with methanol over Amberlyst-15 catalyst in a laboratory reactor setup. Experiments were performed for different conditions of temperature, feed mole ratio (alcohol/ acid) and catalyst loading. A pseudo-homogeneous model, called as YT model (Yadav and Thathagar, 2002), was employed to validate the experimental data⁴.

2. Experimental

2.1 Materials

High purity (99.9%) of methanol was used for all the experiments. Adipic acid was purchased from Sigma-Aldrich with 99 % purity and Amberlyst 15 dry from Rohm and Haas Company (USA) was utilized for the experiments. NaOH was obtained from s. d. fine chemicals, Mumbai, India.

2.2 Analysis

Analysis for the experiments was carried out with both titration and gas chromatography methods. Samples were titrated against 1 N alcoholic NaOH solution using phenolphthalein as the indicator to identify quantity of unreacted acid including adipic acid and monomethyl adipate if present. Gas chromatography analysis of the samples was performed to confirm the titration results using Carbowax AC-0.07 column with FID. Para-cymene was used as the internal standard and methanol as the solvent. Oven temperature was kept at 453 K.

2.3 Apparatus and procedure

Esterification reaction of adipic acid with methanol was carried out in a three necked glass reactor and the volume of the reaction mixture was kept the constant value of $1.5 \times 10^{-4} \text{ m}^3$ for all experiments. The reactor was equipped with a stirrer kept at the constant speed of 13 rps for all the runs in order to attain the highest conversion (Yadav and Thathagar, 2002). A reflux condenser was used to prevent loss of volatile components. Initial concentration of adipic acid considered to be 2.18 mol/lit for all experiments. A mixture of adipic acid and methanol with a pre-specified mole ratio, which was prepared gravitationally, was charged into the reactor. The catalyst was kept in a vacuum heater for 3 hours with the temperature of 383 K before adding to the reactor. After the desired temperature was attained, at constant stirring, a known amount of catalyst was added to the reactor and zero time of reaction was recorded. Temperature variation of the reaction was controlled within $\pm 0.5 \text{ K}$. A total of 6 hours run for each experiment were considered with samples taken out for analysis at regular intervals.

3. Results and Discussions

3.1 Kinetic modeling

Different models such as pseudo-homogeneous (PH) model, Langmuir-Hinshelwood (LHW) model and Eley-Rideal (ER) model have been proposed for liquid phase reactions that are catalyzed by ion exchange resin catalysts without any diffusion constraints (Chakrabati and Sharma, 1993). In order to model this reaction system the Yadav and Thathagar (2002) model is considered which was proposed for esterification of maleic

acid with ethanol over cation-exchange resin catalyst. In this model the first reaction step is assumed to be very fast that makes the second step the rate controlling one. Considering the two step following reaction:



The monoester (C) is in equilibrium with the diester (E) and methanol (B) at any time as a result of the fast first step reaction. Hence the concentration of monoester can be represented as:

$$C_C = K_1 \frac{C_A C_B}{C_D} \quad (4)$$

Where, K_1 is the equilibrium rate constant. Also the concentration of the components with respect to conversion is given as:

$$C_A = C_{A0}(1 - X_A) \quad (5)$$

$$C_B = C_{A0}(M - 2X_A) \quad (6)$$

$$C_E = C_{A0}X_A \quad (7)$$

$$C_D = 2C_{A0}X_A \quad (8)$$

The rate of formation of dimethyl adipate is given as:

$$\frac{dC_E}{dt} = wk_3K_1C_C C_B - wk_4C_E C_D \quad (9)$$

Let $k_3K_1=K$ that is the forward reaction rate constant. By substituting Eq. (4) in above we get:

$$\frac{dC_E}{dt} = wK \frac{C_A C_B^2}{C_D} - wk_4C_E C_D \quad (10)$$

Eq. (10) can be represented in terms of conversion:

$$\frac{dX_E}{dt} = KC_{A0} \left[\frac{(1 - X_A)(M - 2X_A)^2}{2X_A} - 2X_A^2 \frac{k_4}{K} \right] \quad (11)$$

Methanol was introduced into the system in high excess. Hence the backward reaction is not very considerable and is neglected.

$$\frac{dX_E}{dt} = KC_{A0} \left[\frac{(1 - X_A)(M - 2X_A)^2}{2X_A} \right] \quad (12)$$

By integrating Eq. (12) and considering that M value is neither 1 nor 2 then we have:

$$\begin{aligned} & \frac{2}{(M-2)} \left[\frac{1}{(M-2)} \ln \left\{ \frac{M}{(M-2X_A)} \right\} - \frac{1}{(M-2)} \ln(1-X_A) - \frac{2X_A}{(M-2X_A)} \right] \\ & = wKC_{A0}t = k_1t \end{aligned} \quad (13)$$

3.2 Effect of temperature

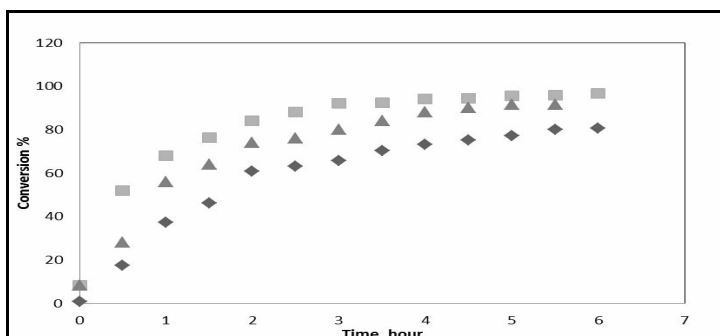


Figure 1: Effect of temperature. Catalyst loading: 7% w/w. mole ratio of alcohol/acid=20. ■, 333 K; ▲, 323 K; ◆, 313 K.

Effect of temperature on rate of esterification reaction of adipic acid and methanol was obtained at 313, 323 and 333 K, considering the constant values for feed mole ratio (acid to alcohol) of 20 and catalyst loading of 7% w/w. The conversion of adipic acid, also the forward reaction rate, were found to increase by rising temperature as a result of higher kinetic energy of the molecules and more number of collisions as shown in the Fig. 1.

Temperature effect study is essential in order to calculate activation energy of the reaction. In the Fig.2 the LHS of the Eq. (13) was plotted against time which shows that the YT model is suitable to represent the experimental data at different temperatures. Slope of each line represents the value of K_1 from which K value is calculated that is the reaction rate constant. The reaction rate constant (K) obtained from the YT graph was used to calculate the activation energy in the Arrhenius plot (Fig. 3). The activation energy was found 14.471 KJ/mol.

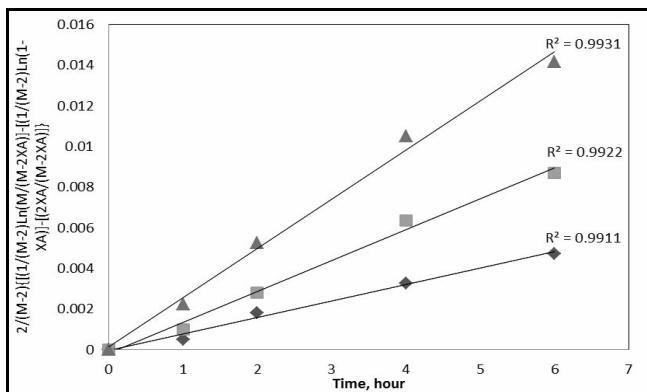


Figure 2: Kinetic plots for effect of temperature. Catalyst loading: 7% w/w. ratio of alcohol/acid=20 ; ♦, 313 K; ■, 323 K; ▲, 333 K.

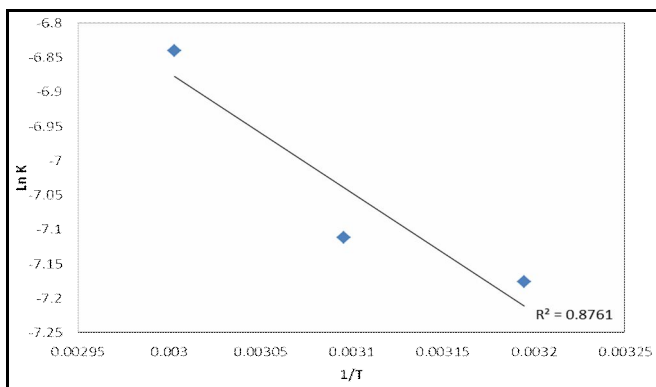


Figure 3: Arrhenius plot of $\ln k$ vs. $1/T$. Catalyst loading: 7% w/w. ratio of alcohol/acid=20.

3.3 Effect of catalyst loading

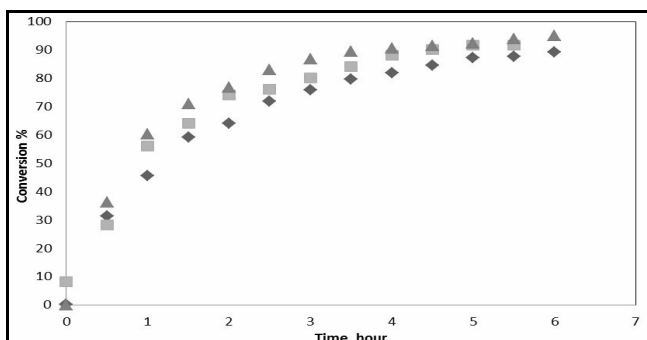


Figure 4: Effect of catalyst loading. Temperature: 323 K. mole ratio of alcohol to acid=20. ♦,5%; ■,7%; ▲,10% w/w.

The experiments were conducted for catalyst loadings of 5%, 7% and 10% of total weight of the reactants, considering constant values of feed mole ratio of 20 at 323 K. It was found that a significant raise in conversion was achieved by rising catalyst amount which in turn increased the reaction rate (Fig. 4). This is because more active sites of the catalyst are available for the reaction.

The LHS of the Eq. (13) was plotted against time (Fig. 5) signifying that the YT model fits the experimental data well. K values obtained from the YT plot were higher at higher catalyst loading showing higher reaction rate.

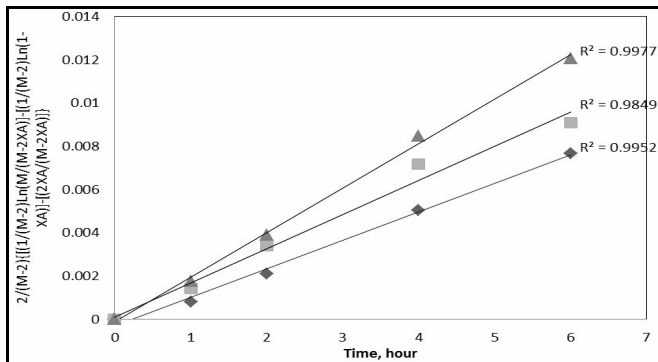


Figure 5: Kinetic plots for effect of catalyst loading. Temperature: 323 K. mole ratio of alcohol to acid=20. ♦,5%; ■,7%; ▲,10% w/w.

3.4 Effect of feed mole ratio

Esterification of adipic acid with methanol is an equilibrium reaction in which by using excess of methanol the equilibrium shifts towards formation of ester. Additionally, due to high boiling range between adipic acid and methanol, usually excess of methanol is preferred. Alcohol to acid ratios of 10, 15 and 20 were tested. The ratio of 15 gave the highest conversion at catalyst loading of 7% and 323 K. Beyond 15 there was no considerable change in conversion. Also ratio of 20 is very close to that of 15 that's why the latter is considered as the optimum ratio.

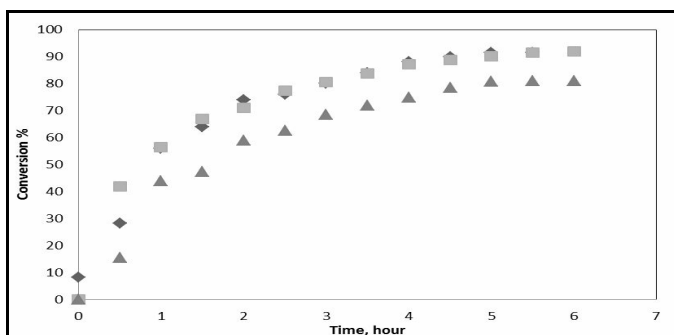


Figure 6: Effect of feed mole ratio (alcohol/acid). Temperature: 323 K. Catalyst loading: 7% w/w. Alcohol to acid ratio: ▲, 10; ■, 15; ♦, 20.

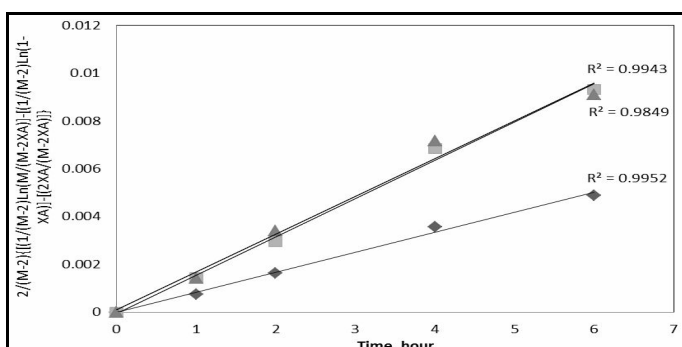


Figure 7: Kinetic plots for effect of feed mole ratio. Temperature: 323 K. catalyst loading: 7%. Alcohol to acid ratio: ♦, 10; ■, 15; ▲, 20.

4. Conclusion

Kinetic study of esterification of adipic acid with methanol was performed in a laboratory reactor using Amberlyst 15 as the catalyst. It was observed that a rise in temperature, alcohol to acid ratio and catalyst loading increased the acid conversion and rate of the reaction. However, alcohol to acid ratio of more than 15 does not introduce any significant rise in conversion. The Yadav and Thathagar model (YT model) was used to represent the experimental data and the activation energy was found to be 14.471 KJ/mol.

Nomenclature

A	Reactant A, adipic acid
B	Reactant B, methanol
C_A	Concentration of A, kmol/m ³
C_B	Concentration of B, kmol/m ³
C_C	Concentration of C, kmol/m ³
C_D	Concentration of D, kmol/m ³
C_E	Concentration of D, kmol/m ³
C_{A0}	Initial concentration of adipic acid, kmol/m ³
K_1	Rate constant, m ³ kmol ⁻¹ kg ⁻¹ S ⁻¹
M	Mole ratio of C_{B0} to C_{A0}
T	Time, hour
W	Catalyst loading, kg m ⁻³
X_A	Fractional conversion of A

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