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Kinetics of esterification of methanol and acetic acid with mineral homogeneous acid catalyst

Mallaiah Mekala *, Venkat Reddy Goli

Department of Chemical Engineering, National Institute of Technology, Warangal 506004, India

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ABSTRACT

In this work, esterification of acetic acid and methanol to synthesize methyl acetate in a batch stirred reactor is studied in the temperature range of 305.15–333.15 K. Sulfuric acid is used as the homogeneous catalyst with concentrations ranging from 0.0633 mol·L^{-1} to 0.3268 mol·L^{-1}. The feed molar ratio of acetic acid to methanol is varied from 1:1 to 1:4. The influences of temperature, catalyst concentration and reactant concentration on the reaction rate are investigated. A second order kinetic rate equation is used to correlate the experimental data. The forward and backward reaction rate constants and activation energies are determined from the Arrhenius plot. The developed kinetic model is compared with the models in literature. The developed kinetic equation is useful for the simulation of reactive distillation column for the synthesis of methyl acetate.

1. Introduction

Carboxylic acid esters constitute major components of numerous natural products and synthetic compounds. They are widely used as softeners, emulsifiers, dispersants, detergents, surfactants, solvents and biodiesel fuels. Several synthetic routes are available to obtain carboxylic acid esters. A comprehensive review of ester synthesis route is available [1].

The kinetics of esterification reaction between acetic acid and methanol in alcoholic and non-hydroxylic media was investigated earlier by Rolfe and Hinsshelwood [2]. They proposed a kinetic model based on the theory of molecular statistics of esterification reaction by using hydrochloric acid as the catalyst. The kinetics of esterification of acetic acid with methanol using a homogeneous hydrogen iodide catalyst was investigated by Ronnback *et al.* [3], where the protonation of carboxylic acid was considered as the rate-initiating step in the reaction mechanism. They observed that hydrogen iodide was esterified by methanol and produced methyl iodide as a by-product. Hilton and Smith [4] found that the kinetics of acid catalyzed esterification of *n*-aliphatic acid with methanol is influenced by the length of carbon chains with different buffer solutions.

Agreda *et al.* [5] proposed a rate expression for esterification reaction using homogeneous sulfuric acid as a catalyst while carrying out the reaction in a reactive distillation unit. The kinetic model shows nonlinear dependence on the catalyst concentration without the kinetic parameters reported. Engell and Fernholz [6] and Kruel *et al.* [7] modified the kinetic model proposed by Agreda *et al.* [5] for the esterification reaction using heterogeneous sulfonic ion exchange resin as the catalyst. Liu *et al.* [8] developed a rate expression for the esterification reaction of methanol with acetic acid using homogeneous sulfuric acid catalyst, presenting a linear kinetics on catalyst concentration. Elgue *et al.* [9] also proposed a linear kinetics on catalyst concentration and applied it for intensification of methyl acetate production in a continuous reactor. The catalytic esterification reaction between methanol and acetic acid for the synthesis of methyl acetate with Amberlyst-15 (dry) as heterogeneous catalyst was studied by Ismail *et al.* [10] in the temperature range of 318–338 K. The similarities and differences between heterogeneous and homogeneous catalyzed esterification reactions of acetic acid with methanol were described by Liu *et al.* [11]. They presented the kinetics using a commercial nafion/silica nano composite catalyst (SAC-13) and H_2SO_4 separately, reported that heterogeneous and homogeneous catalysts show similar reaction inhibition by water formation, and suggested a common reaction mode based on Bronsted acid sites.

The kinetics of reversible liquid-phase esterification of acetic acid with methanol using sulfuric acid catalyst in an isothermal batch reactor was investigated by Ganesh *et al.* [12]. They observed that the rate constant is influenced by the concentration of catalyst and the reaction rate increases with the catalyst concentration. They also observed that the catalyst activity is slightly inhibited by the formation of water in the reaction mixture. The reaction kinetics and chemical equilibrium of the reversible catalytic esterification of acetic acid with methanol were investigated by Popken *et al.* [13]. The reaction was catalyzed homogeneously by acetic acid itself and heterogeneously by an acidic ion-exchange resin.

Without catalyst it requires very long time to reach equilibrium [13]. Although acetic acid itself may act as a catalyst, its activity for reaction is

* Corresponding author.
E-mail address: mmyadav2001@gmail.com (M. Mekala).

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very low due to its weak acidic nature. The addition of catalyst improves the acidic nature of the reaction mixture by providing more H^+ ions for the reaction. Homogeneous catalysts such as hydrochloric acid, hydrogen iodide, hydrogen bromide and sulfuric acid have been used for the esterification reaction between acetic acid and methanol. It is reported that sulfuric acid is a better catalyst due to its greater density of acid sites per gram and it can prevent the side reactions [11]. It is more effective than the heterogeneous catalyst for the esterification reaction, so it is selected for the present study.

Although a large number of studies are available in literature, some uncertainties remain in the reported kinetic models. In the present paper, the esterification reaction of acetic acid with methanol to produce methyl acetate using homogeneous sulfuric acid catalyst is studied at different temperatures, catalyst concentrations and feed molar ratios. The kinetic models based on concentration as well as activity are developed and the model predictions are compared with experimental data. The model predictions are also compared with the models in literature.

2. Experimental

2.1. Chemicals

Acetic acid (99.95%, by mass), methanol (99%, by mass), and sulfuric acid (98%, by mass) were purchased from SD Fine Chemicals Ltd. (Mumbai, India) and used without any further purification.

2.2. Experimental setup

The esterification reaction was carried out in a 500 ml three neck round-bottom flask placed in a heating rota mantle, which contains a heating knob and a speed control knob. The rota-mantle was maintained at constant temperature by adjusting the heating knob. The minimum stirring speed was maintained at 240rpm for uniform mixing of catalyst in the reaction mixture using the speed control knob. A glass thermometer inserted into the reactor was used to measure the reaction mixture temperature inside the flask. A spiral condenser was connected vertically to the reaction flask to reduce the vapor losses from the reactor.

2.3. Experimental procedure

In the experiment, equimolar quantities of methanol (32 g) and acetic acid (60 g) were charged to the reactor. The desired amount or concentration of sulfuric acid was added to initiate the reaction. When the reaction mixture reached the desired reaction temperature, the time was noted. The samples were withdrawn at regular intervals of time and analyzed for the acetic acid concentration. The reaction was carried out for sufficient time to reach equilibrium conversion or without further decrease in acetic acid concentration.

2.4. Analysis

The acetic acid concentration was determined by titration of reaction mixture sample with standard solution of NaOH using phenolphthalein as the indicator. To prepare the standard solution of NaOH, pure water was obtained from an ultra-pure water purifier system (Millipore-Synergy UV system) with a resistance of 18.2 MΩ.

3. Results and Discussion

The present esterification reaction with homogeneous catalyst is investigated at 1:1 mole ratio of acetic acid to methanol, with the temperature varied from 305.15 to 333.15 K and the catalyst concentration varied from 0.0633 mol·L^{-1} to 0.3268 mol·L^{-1}.

3.1. Effect of different factors on the reaction

3.1.1. Effect of temperature

The experimental results for conversion of acetic acid at different temperatures with fixed catalyst concentration (0.1288 mol·L^{-1}) are shown in Fig. 1. The rate of conversion of acetic acid increases with temperature. At the lowest temperature (305.15 K), the reaction reaches equilibrium after 400 min and at higher temperature, and the time required for the reaction to reach equilibrium reduces drastically. At 333.15 K the time needed is only 100 min. The higher the reaction temperature, the shorter the time required to reach equilibrium. At equilibrium, the acetic conversion is 0.69 or 69%.

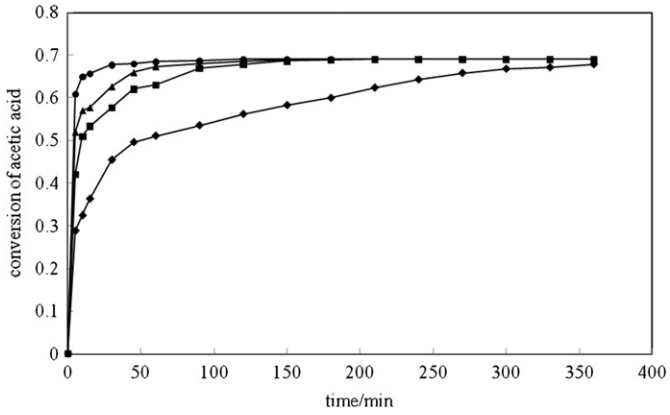

Fig. 1. Effect of temperature on reaction kinetics at 0.1288 mol·L^{-1} catalyst concentration. ♦ 305.15 K; ■ 313.15 K; ▲ 323.15 K; ● 333.15 K.

3.1.2. Effect of catalyst concentration

Fig. 2 shows the effect of catalyst concentration on the conversion of acetic acid at a fixed temperature of 323.15 K. As the catalyst concentration increases the reaction reaches equilibrium faster. At 0.3268 mol·L^{-1} catalyst concentration the reaction takes about 70 min to reach equilibrium whereas at 0.0633 mol·L^{-1} it only takes about 150 min. The effect of catalyst concentration on the acetic acid conversion is similar to that of the effect of temperature.

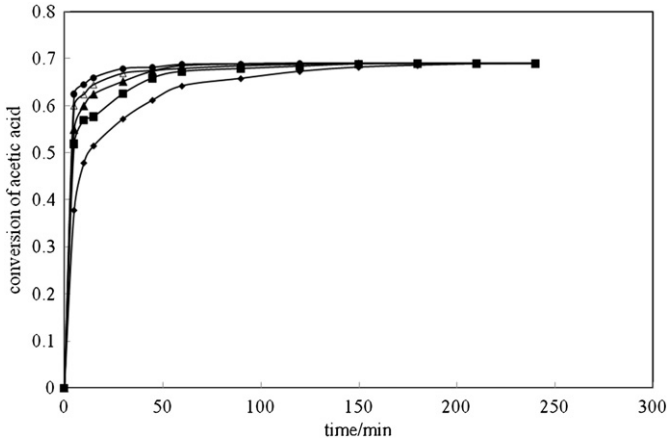

Fig. 2. Effect of catalyst concentration on reaction kinetics at 323.15 K. ♦ 0.0633 mol·L^{-1}; ■ 0.1288 mol·L^{-1}; ▲ 0.1923 mol·L^{-1}; △ 0.2576 mol·L^{-1}; ● 0.3268 mol·L^{-1}.

3.1.3. Effect of initial reactant mole ratio

Fig. 3 shows the effect of initial molar ratio of acetic acid to methanol on the acetic acid conversion at fixed catalyst concentration of 0.1288 mol·L^{-1} and reaction temperature of 333.15 K. The equilibrium