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Liquid-liquid Equilibria (LLE) of the quaternary mixture (acetic acid + ethanol + ethyl acetate + water) arising out of esterification reaction: Optimization studies

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ABSTRACT

The kinetics of esterification of acetic acid with ethanol over a heterogeneous catalyst, Dowex 50wx8-400 catalyst (hydrogen ion based catalyst), was performed in an isothermal batch reactor. Influence of different operating parameters, such as, effect of temperature (40 to 70 °C), catalyst loading (0.6 g to 1.5 g), initial molar ratios of acetic acid and ethanol (1:1 to 1:4), were studied. Conversion as high as 83% have been obtained. The activation energy of esterification of acetic acid with ethanol using Dowex 50 Wx8-400 was found to be 30.02 kJ mol^{-1}. The experiment results of the esterification reactions were correlated with pseudo – homogeneous (PH) model. Furthermore, an activity-based kinetic model for quaternary system (Acetic acid + Ethanol + Ethyl acetate + Water) was developed and correlated using the UNIQUAC (universal quasi-chemical equation) and NRTL (Non random two liquid) model to compute the activity coefficients. Response surface methodology (RSM) was employed to investigate the non linear dependency of operating parameters on the obtained response (ethyl ester conversion).

1. Introduction

Esterification of acetic acid with alcohol had been widely studied, mainly because of its industrial uses [1–5]. Esters obtain from acetic acid, such as, ethyl acetate, propyl acetate etc., are important class of chemicals and industrial products, and are having applications in a variety of areas such as solvents, plasticizers, pharmaceuticals, paint, varnish, confectionary, perfumes and wine asphyxiate intermediates.

Ethyl acetate is synthesized by the different approaches, like, esterification of acetic acids with ethanol [6–9], esterification of ethylene with acetic acid in the presence of $H_4SiW_{12}O_{40}/SiO_2$ catalyst [10]. Popular and more widely used esters of acetic acid had been prepared by esterification with different alcohols such as n-propyl alcohol, isopropyl alcohol (2-propanol), n-butyl alcohol and isobutyl alcohol (2-butanol) [11]. Conversion of the esterification reactions was known to be limited by very slow reaction rate and the existence of reversible reactions. Due to this, various accelerators (catalysts) have been used to increase the reaction rate [12]. These accelerators include, homogeneous as well as heterogeneous catalysts, and have been extensively studied in the last few decades [13–16]. Homogeneous catalysts are more favoured owing to being economical and providing higher yield; though present time research is on heterogeneous catalysts, as ecological factors favour them. Various acidic materials have been investigated as heterogeneous catalysts for the esterification of carboxylic acids [17,18].

A sequential experimental design has been used to correlate the parameters of several kinetic models for the synthesis of isoamyl acetate catalyzed by Amberlite IR-120 (an ion exchange resin) [19]. Experiments were performed in the temperature range of 322–362 K. The authors correlated the experimental data with various kinetic models such as Langmuir–Hinshelwood–Hougen–Watson (LHHW), Eley rideal (ER) and pseudo – homogeneous (PH) model and found, LH and PH models are best fitted with experimental results. Second order UNIFAC and NRTL activity models were used for liquid phase non-ideality of reaction mixture. NRTL is found to be good as its comparison to the resin sorption phenomena.

Merchant et al. [20] presented the kinetics of the Amberlite IR 120-catalyzed esterification of ethanol with acetic acid, propanoic and pentanoic acid, respectively. An Eley Rideal mechanism (with the surface reaction between adsorbed ethanol and acid) was used to correlate the experimental results. The modified UNIFAC model was used to predict system non idealities. Bedard et al. [21] summarize the mechanism of acetic acid and ethanol esterification over zeolites. Four zeolite framework materials (H-BEA, H-FER, H-MFI, and H-MOR) were chosen to study the effects of zeolite pore size and connectivity on the kinetics and mechanism of esterification. Yagyu and coworkers [22] studied

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direct esterification of aqueous acetic acid with ethanol (molar ratio = 1:1) catalyzed by polystyrene-supported homogeneous sulfonic acids. Toluene was used as an additive to increase the ethyl acetate production from the aqueous phase. Toikka et al. [23] worked on the quaternary system acetic acid–ethanol–ethyl acetate–water and ternary subsystems acetic acid–ethyl acetate–water and ethanol–ethyl acetate–water system for solubility, critical states and liquid–liquid equilibrium (LLE) at 303.15 K and 313.15 K and 1 atmospheric pressure. Experimental LLE data were compared with the values calculated by UNIFAC and NRTL models. Orjuela et al., [24] studied the esterification of succinic acid, acetic acid and mixture of both acids with ethanol using Amberlyst 70 cation exchange resin as catalyst. Batch isothermal reactor was used to perform the reactions at different molar ratios (1:1–27:1), temperatures (343–393 K) and catalyst loading (1.0–9.3 wt% of the solution). Pseudo – homogeneous model for esterification kinetics and the NRTL based activity model have been used.

Through extensive analysis of literatures, it can be seen that none of the work was found on UNIQUAC modelling of a quaternary system of acetic acid + Ethanol + Ethyl Acetate + Water, so the objective of this study is to investigate the kinetic behaviour of the esterification of acetic acid with ethanol by using an isothermal batch reactor with acidic ion-exchange resin Dowex 50wx8-400 catalyst under isothermal conditions (313 to 343 K). The kinetic data obtained from this study were correlated with Pseudo homogeneous (PH) model. In the data correlation, a correlative solution model, the UNIQUAC and NRTL were employed to calculate the activity coefficients of each constituent [25,26]. An effort is made in this study using the response surface method (RSM) to obtain the dependency of operating parameters on the conversion obtained. The advantage of the response surface method is that it can consider the variability of the parameters influencing the conversion predictions. The developing relationship is also useful for reliability analysis.

2. Experimental

2.1. Materials

Ethyl acetate and acetic acid were obtained from Loba Chemicals, Mumbai, India Ltd. with a purity of 99%. Ethanol of 99.9% purity was obtained from MOLYCHEM, Mumbai, India. The purities of the chemicals were checked by gas chromatography (GC) and they were used without further purification.

The strongly acidic ion-exchange resin, Dowex 50wx8-400, supplied by Sigma Aldrich, USA was used as catalyst. The resin was washed several times with distilled water before use and dried at 353 K until the mass remained constant.

2.2. Apparatus and procedure

The esterification reaction was carried out in a round bottom glass flask (1000 ml) fitted with a water-cooled condenser in the temperature region of 313–343 K. The temperature was maintained using a thermostat. In a typical experiment, equimolar quantities of acetic acid (200 ml) and ethanol (204 ml) were introduced directly into the flask along with the Dowex 50Wx8-400 catalyst. Samples were drawn after the temperature is stabilized at close intervals of time and were analyzed by the Gas Chromatography for the determination of acetic acid concentration. The reaction is continued for 7 h. After the reaction was completed, the reactor contents were cooled, weighed, and analyzed. The first set of experiments was performed at different temperatures 313, 323, 333 and 343 K with 0.6 g catalyst concentration to determine the kinetic parameters. The next set of experiments was conducted at optimum temperature (333 K) with varying catalyst concentrations of 0.6 g, 0.9 g, 1.2 g and 1.5 g, to find the effect of the catalyst concentration on the kinetics. The final set of experiments was conducted at different molar ratios (1:1, 1:2, 1:3 and 1:4) with an optimum catalyst concentration (0.6 g) and temperature (333 K).

2.3. Analysis

After reaching phase equilibrium, samples were taken from reactor with a 1 μl chromatographic syringe ("Hamilton", USA) and analyzed by GC. A gas chromatograph (NUCON GC 5700 India) with thermal conductivity detector (TCD) and packed column Porapak (1 m long and 0.003 m i.d.), using packed column at oven temperature of 453 K, an injector temperature of 423 K and detector temperature of 453 K was used. Hydrogen with a flow rate of 45 ml/min was used as a carrier gas.

3. Results and discussions

3.1. Effect of different reaction factors

3.1.1. Effect of reaction temperature

Temperature has strong influence on the reaction rate in the esterification of acid and alcohol. In this work Dowex -50WX-400 ion exchange resin was used as a catalyst. The experimental results obtained at different temperatures with the fixed catalyst concentration (0.6 g) are depicted in Fig. 1. Beyond 3.5 h, conversion is observed to become linear at all the temperatures. At the reaction time of 420 min, conversion increased 49% to 72%, as the temperature was raised from 313 to 343 K. M.-H. Zhu et al. [27] was found the conversion of 77.1% in 85 °C at 8 h experimental runs using homogeneous catalyst, respectively. Hansnoglu et al. [28] used the same reaction medium as, acetic acid and ethanol for the esterification and obtained the conversion of 45% to 62.3% in temperature range of about 50 °C to 70 °C in the presence of Amberlyst 15 catalyst. Izci and Badur [12] prepared the batch reactor system for the esterification of acetic acid with isobutanol using Dowex 50wx2 catalyst and found the maximum conversion of 68% in 74 °C at 10 h of reaction. However, the conversion in the range of 333 K to 343 K is not substantial. Two aspects have been taken into account about the acceleration of rate with rise in temperature on the reaction. Higher temperature leads to attainment of equilibrium conversion in lesser time [29,30]. Secondly, increasing temperature increases the diffusion rate, which is the rate limiting step as stated by the principle of "adsorption- diffusion- desorption" [31].

3.1.2. Effect of catalyst loading

Catalyst loading being one of the alternative parameter in esterification reaction, also influences the reaction rate. As can be seen from Fig. 2, the ester conversion is 69.6% for 0.6 g catalyst and increases to 80.2% for 1.5 g of Dowex 50wx8-400. The reason behind this is attributed to the fact that with increasing catalyst the active sites where the reaction takes place also increases. This type of behaviors further indicates that mass transfer resistances are absent and the reaction is only controlled

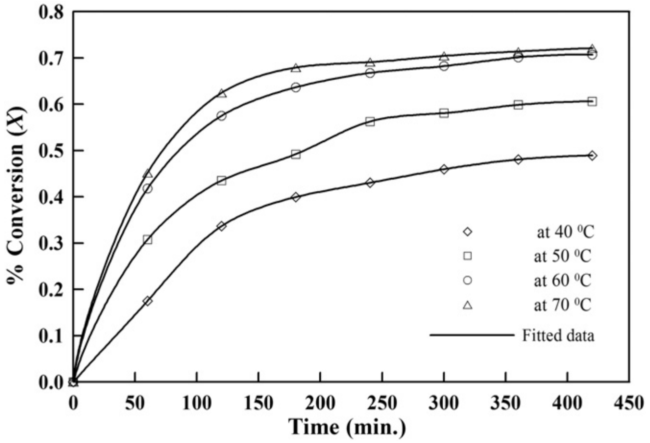

Fig. 1. Effect of temperature on the esterification of acetic acid and ethanol at conditions: $T = 313–343$ K; $C_{catalyst} = 11.3$ g/L of acetic acid.