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Experimental Study of Esterification of Carboxylic Acid with different alcohol using various Catalysts

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Abstract- **Esterification of carboxylic acids (acrylic acid, acetic, propionic, butryic) with different alcohols (ethanol, methanol and propanol) catalyzed by hydrochloric acid has been carried out in stirred batch reactor under atmospheric pressure. Effect of different catalysts was also studied in the present work. A comparison between homogeneous catalyst (HCL and Hydrogen iodide) and heterogeneous (Dowex) has been carried out. It is observed that HCL catalyzes esterification reaction rapidly followed by Hydrogen iodide and Dowex. The maximum conversion of 45.7% of acryilic acid is observed at 420 mins under operating conditions as molar ratio of reactants = 1, reaction temperature = 333.15K.**

Key words: **carboxylic acid, catalyst, esterification**

I. INTRODUCTION

Esterification is the process in which two reactants (alcohol and an acid) form an ester as the reaction product. The esterification is considered highly prominent in chemical industries. There are various applications of Esters (product out of esterification reaction). Some products of esters are solvents, flavors, plasticizers, pharmaceuticals, pesticides, monomers and emulsifiers. The limited conversion and large reaction time is required in the absence of catalyst because of low reaction rate and reversibility (Jyoti et al 2016). The addition of any acid catalyst enhances esterification as acid acts as a proton donor. The reaction parameters like the increase of temperatures, alcohol-to-acid ratios and more active catalyst can be useful in improving reaction rate while the catalyst is present. Wide literature regarding esterification of acrylic acid with various alcohols (methanol, ethanol, butanol) is present (Malshe and Chandalia 1977; Sert et al. 2013).
Homogeneous and heterogeneous catalysts have been used in the present work. Commonly used homogeneous catalysts are H2SO4, HCl, HI and para-toluene sulfonic acid (Chen, Xu, and Okuhara 1999; Ronnback et al. 1997; Lilja et al. 2002). HCl has been used for catalysis of reaction. This acid produces H+ ions and thereby protonate the carboxylic acid. Many authors have done comparative study of homogeneous and heterogeneous catalysts (Lilja et al. 2002; Liu, Lotero, and Goodwin (2006)).

Limited work related to esterification of acrylic acid and ethyl alcohol has been reported in literature (Malshe and Chandalia 1977, Jyoti et al. 2016). Esterification of carboxylic acids such as acrylic acid, acetic, propionic, butyric with different alcohols such as ethanol, methanol and propanol catalyzed by hydrochloric acid has been carried out in stirred batch reactor under atmospheric pressure. Effect of different catalysts was also studied in the present work. A comparison between homogeneous catalyst (HCL and Hydrogen iodide) and heterogeneous (Dowex) has been carried out. It is observed that HCL catalyzes esterification reaction rapidly followed by Hydrogen iodide and Dowex.

II. EXPERIMENTAL PROCEDURE

Carboxylic Acids (Acrylic acid, acetic, propionic, butyric) Alcohols (ethanol, methanol, propanol) and catalysts (sulphuric acid, hydrochloric acid, hydro iodic,Dowex acid) were of analytical grade and obtained from Merck. The setup consisted a batch reactor with 1,000 ml three necked ball glass flask equipped with magnetic stirrer (Remi 1 RML) has been used. For carrying out the reaction. The procedure is as follows:

- •Carboxylic acids in required amounts are heated up to the desire reaction temperature in the reactor.
- •Alcohols was heated in a separate conical flask.
- •Heated alcohols was charged to the reactor followed by addition of measured quantity of catalyst and from this moment the measurement of time was started.
- •A condenser was employed to prevent evaporation of any compounds during the reaction.
- •Sample of 1 ml was collected at regular intervals during the reaction using a sample bottle and immediately placed in a refrigerator in order to avoid any further reaction.
- •The samples were analyzed by NUCON series 5,700 gas chromatograph (GC) with porapak column (id 2 mm, od 1/8”, length 2 m) hydrogen gas taken as carrier gas with flow rate 60 ml/min equipped with a TCD detector.
- •1 µl sample is injected in chromatograph

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III. RESULTS AND DISCUSSIONS

Effect of varying the catalysts

Efficiency of different types of catalysts both homogenous (HCl, HI) and heterogeneous (Dowex 50WX8), was investigated. Conversion effects shown by various catalysts for the esterification of acrylic acid with ethanol at 333.15K, molar ratio RE/A =1 is just one part of efficiency measurement. The catalyst loading for homogenous catalyst is 3 vol% and 20g/l for Dowex 50WX8. The conversion obtained after 7 hours of the reaction for homogenous catalyst is shown in Fig.1 where HCl, HI showed 46%, and 49% and conversions respectively. The reason for this difference in the conversion is the difference in the acidity of the catalyst which is dependent on both the pKa value of the acid and its concentration. HCl though has very low concentration but a high pKa (-6.3) increases its acidity and so it gives conversion higher than Dowex 50WX8.

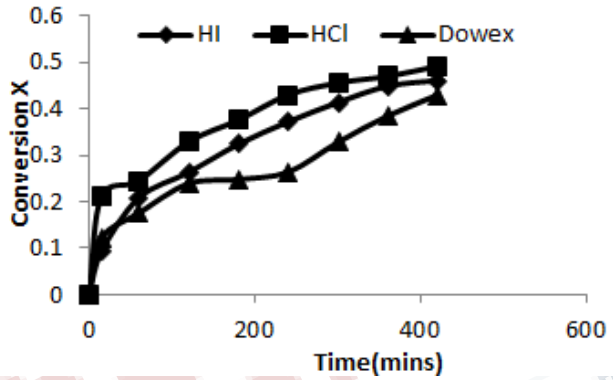


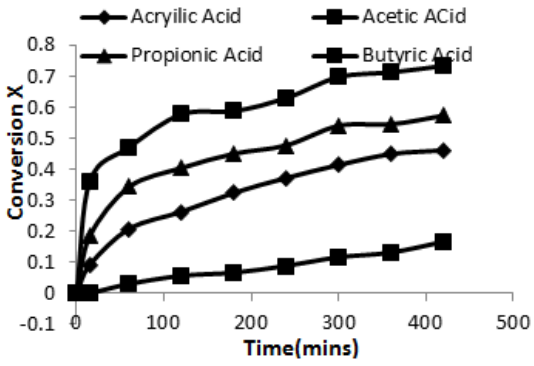
Fig.1 Effect of the different types of catalyst used for the esterification reaction. Reaction condition: RE/A = 1; temperature = 333.15K.

Liquid mineral acid catalysts though suffer from some drawbacks such as a corrosive nature, and separation problem, but high conversion, low cost and solubility makes its more preferable. The conversion obtained by Dowex after 7 hours was 43% which is least of all the conversions obtained. The reason for this observation may be the fact that the homogenous catalysts have greater density of acid sites per gram. Calculation of turnover frequencies (TOFs) provides a comprehensive way to make catalyst comparisons on a per site basis. Liu et al., (2006) calculated the catalytic activity of H2SO4 and found it to be greater than the heterogeneous catalyst by a factor of 3. Because of their selective adsorption of reactants and swelling nature, these resins not only catalyze the esterification reaction but also affect the equilibrium conversion [Liu and Tan, 2001]. Shortcomings include insufficient thermal resistance, which limits the reaction temperature to 120OC, preventing widespread use in industry. It was studied that although the catalysts HCl, HI and H2SO4 drove the reaction to a high yield, hydrochloric acid was the only catalyst that could be considerably recovered and reused.

Effect of using different acids

The effect of chain length of different mono-carboxylic acids (acetic, propionic, acrylic and butyric) on the esterification reaction with ethanol at 333.15K, molar ratio RE/A =1and 3 vol% of HCl was studied. As shown in Fig.2 the conversion of the acids increased from 16% to 73% as the chain length of the acid decreased from butyric acid to acetic acid. This can be explained by the polar and steric effect of the α-substitution to the carboxylic group. There may two main factors that contribute to the reduction in carboxylic acid reactivity with size: an inductive effect and a steric effect. The inductive effect lowers the electrophilicity of the carboxyl chain, resulting in the rate-limiting nucleophilic attack to be more energy hindered. The steric effect basically disturbs the bonding interaction.

The equilibrium conversion decreased from 73% of acetic acid to 57% of propionic acid as the chain length increased from 2 carbon system to 3 carbon system. Again conversion decreased to 46% for acrylic acid due to increase in both the carbon chain as well as the branching in the structure. The lowest conversion was achieved for butyric acid of 16.7% as its chain consists of four carbons. Similar results were seen by Ali et al., (2007). It was found that at 4 h of reaction, the equilibrium conversion of acetic acid was 62%, propionic acid 48% and butyric acid 31% with 1-propanol. Lilja et al., (2002) stated that the reaction rate was higher by shorter alcohol chain lengths, and branching of the alcohol chain retarded the reaction rate for esterification process.



Fig, 2 Effect of different type of mono-carboxylic acids used in the esterification reaction with ethanol. Reaction condition: RE/A = 1; HCl as catalyst; temperature = 333.15K.

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Effect of using different alcohols

The the effect of chain length of alcohols was investigated by performing multiple experiments with different alcohols(methanol, ethanol and 2-propanol) with acrylic acid at 333.15K, molar ratio RE/A = 1 and catalyst loading of 3 vol% HCl. Increasing the chain length of alcohol decreased the conversion of acrylic acid as shown in Fig.3. The equilibrium conversion of acrylic acid after 7 hours of reactionwas observed to be 58% for methanol and decreased to 46% for ethanol as the chain increased from one carbon system to 2 carbon system. Further, 30% equilibrium conversion was obtained for 2-propanol due to branching and increase in chain length. Here both branching and longer carbon chain cause the decrease in conversion due to increasing steric hinderance.

The propionic acid conversion at 4 h of reaction was 67%, 55%, 48%, 46% when reacting withmethanol, ethanol, 1-propanol and 1-butanol, respectively in the investigation done by Ali et a., (2007) giving resuts in support. Lilja et al., (2002) had similar results for the esterification of acetic acid with methanol,ethanol, 1-propanol, 2-propanol and butanol at 60 ◦C with theinitial molar ratio of 1:1 between the reactants.

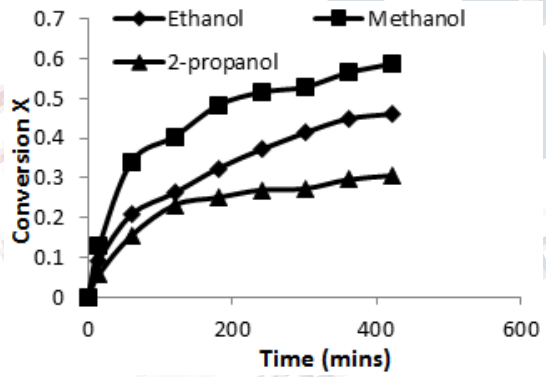

Fig.3 Effect of varying the type of alcohols used. Reaction condition: RE/A = 1; HCl as catalyst; temperature = 333.15 K.

CONCLUSION

It was observed that higher conversion for the esterification of acrylic acid was obtained when HCl was used rather than HI and Dowex. Ethanol was used as the other reactant.
For the carboxylic acid conversions were found to be highest for Acetic acid followed by propionic acid, acrylic acid and butyric acid respectively (ethanol as other reactant) using HCl as catalyst.

For the esterification of acrylic acid with various alcohols conversions were found to be highest for methanol followed by ethanol and 1 propanol using HCl as catalyst.

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