



ENHANCEMENT OF ESTERIFICATION REACTION USING IONIC LIQUID AS CATALYST WITH SIMULTANEOUS REMOVAL OF WATER

Nithya Gopinath¹, Beula C²

^{1,2}Dept. of Chemical Engineering, Govt. Engg College, Kozhikode
Email:nithya117.chem@kongu.ac.in¹, beulaprasoon@gmail.com²

Abstract

Esterification reaction is one of the major reactions in the industries. These reactions are usually carried out conventionally by homogeneous catalysis and heterogeneous catalysis. These conventional methods have certain limitation. The phenomenon of green chemistry suggests a 'green catalyst' called ionic liquid that can be used as catalyst for this reaction. The yield of esterification reaction is convincingly high by using ionic liquid as catalyst. The simultaneous removal of water that is produced during the reaction also showed a remarkable increase in yield. These two methods of improving the reaction yield results in reduction of alcohol to acid ratio (M). The experimental results revealed that the reaction yield in the absence of adsorbent with molar ratio M as 6 is comparable with the yield obtained for the reaction in presence of adsorbent with molar ratio M as 3. Optimization and recycling studies of adsorbent were also conducted.

Keywords: Ethyl Oleate, Esterification, Ionic Liquid, Water Removal

I. INTRODUCTION

In this present world, the amount of waste produced is increasing day by day. Chemical industries are producing a huge bulk of wastes. Thus in the present scenario, the principles of green chemistry have been introduced to eliminate or at least to reduce the use of hazardous materials in chemical processes to

minimise the human and environmental impact without stifling scientific progress. One of the key areas of green chemistry is the replacement of hazardous solvent with environmentally benign ones. Recently, the progress in the field of ionic liquids (ILs) is gaining significance due to their unique properties. Ionic Liquids are salt-type compounds, which are liquids at room temperature and possessing low vapour pressure. Due to the lack of evaporation, they are considered as 'green solvents'. These compounds are known as environment friendly solvents or catalysts and much attention has currently been focused on the organic reactions with ILs as catalysts or solvents.

Esterification reactions are industrially important reactions and are studied widely. The reaction in which the two reactants i.e., an alcohol and an acid, reacts together to give an ester as the product is known as esterification. Esters are basically derived from an acid (organic or inorganic) from which at least one hydroxyl group is replaced by an alkoxy group [-OH group replaced by -O- group]. The commonly used acid is carboxylic acids.

The esterification reaction is endothermic, slow, and reversible in nature with high activation energy barrier in the absence of catalyst. The equilibrium constant of this reaction has very low value. So addition of catalyst, using excess alcohol and also removing the water produced by some physical means can be used to increase the amount of ester produced and thereby the equilibrium constant can be increased.

The catalysts used for the esterification reaction are homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts include sulphuric acid, hydrogen iodide etc. Heterogeneous catalysts include mainly ion exchange resins. But there are many disadvantages associated with these catalysts. Thus a new catalyst has been found out to carry out the esterification reaction that is the ionic liquid. This catalyst gives good conversion and purity of products. An ionic liquid (IL) is a salt in the liquid state. In some contexts, the term has been restricted to salts whose melting point is below some arbitrary temperature, such as 100 °C (212 °F). In general, ionic liquid is a liquid wholly composed of ions. Ionic liquid is called as the 'green catalyst'. There are many reasons for this. The first and foremost one is that ionic liquid possess negligible vapor pressure and hence they do not evaporate to the environment. The **functionalised ionic liquids** are one with functional group such as $-\text{SO}_3\text{H}$, $-\text{OH}$, $-\text{NH}$, $-\text{SH}$ etc. covalently attached to cations or anions or both. The ionic liquids with a built-in $-\text{SO}_3\text{H}$ group are acidic in nature and are called Bronsted Acid Ionic Liquid (BAIL). It can function as both catalyst and solvent. The first non-chloroaluminate room temperature acidic ionic liquid, i.e. SO_3H functionalised ionic liquid, was prepared by Forbes *et al.*

The equilibrium constant of the esterification reaction is very low. Thus to initiate or to increase the forward reactions, some steps taken are use of catalyst, using excess alcohol and simultaneous removal of water produced during the reaction. If the water produced during the reaction is removed simultaneously, then the conversion can be increased. Also the alcohol amount that is used can be reduced.

II. EXPERIMENTAL

A. Materials

The following chemicals were purchased from Sigma-Aldrich and used without purifying further: 1-methylimidazole (99%), 1-4 butane sultone (99%), pyridine (99.8%, anhydrous), triethyl amine (>99.5%, bioultra). Some other chemicals are also used for the preparation of catalysts that are: sulfuric acid (98 wt%, Himedia limited), diethyl ether (99.5 wt%, AR grade, Himedia limited) and cyclohexane (99.5

wt%, AR grade, Himedia limited). Oleic acid (technical grade, Merck & Co.), ethyl alcohol (absolute, Merck & Co.) were used without further purification. Acetonitrile (HPLC grade, Merck & Co.), dichloromethane (HPLC grade, Merck & Co.), potassium hydroxide salt (LR garde, Nice Chemicals Pvt. Ltd.), ethanol (60%), and phenolphthalein indicator were used for analysis. Sulphuric acid (98%, Himedia) as catalyst and as water removing agents, Silica gel (blue crystals, 3-8 mesh, Chemicals), anhydrous sodium sulphate (99%, Sigma Aldrich) are procured.

B. Experimental setup and procedure

Catalyst synthesis was carried out in a 100 mL single necked round bottom flask fitted with spiral coiled type condenser. To avoid the escape of volatile components from the reaction vessel, proper water circulation is provided through the condenser. An oil bath with magnetic stirrer was used to keep the isothermal condition of the reaction and also to provide the proper mixing of the reaction contents. The stirring piece was of cylindrical shape with Teflon coating. Stirring speed was kept constant throughout the reaction. The experimental set-up used was same as that used for synthesis of catalyst. But in esterification reaction 100 mL double-necked round bottom flask was used instead of 100 mL single-necked round bottom flask that was used in catalyst synthesis. In this double neck, one neck was to connect to the condenser and the other was to introduce catalyst to the reaction mixture. The synthesis of catalyst was done as per the procedure described by Zhou *et al.* FIL (a), FIL (b), and FIL (c) are prepared.

B1. Without Simultaneous Water Removal

Measured quantity of oleic acid and ethyl alcohol were fed into the batch reactor and the reaction mixture was allowed to reach the set temperature. Then the known amount of catalyst was added into the mixture and that was considered as the zero time. The stirring speed and temperature were kept constant. The reaction was carried out until the equilibrium was attained.

B2. With Simultaneous Water Removal

The procedure is same as before except that in the reaction mixture required quantity of the water removing agent is added and then

kept for stirring under constant temperature. Both silica gel and anhydrous sodium sulphate were used as simultaneous water removing agent to study about the reaction enhancement. The studies are done to find out whether the amount of excess alcohol can be reduced, because we are removing the water simultaneously that is produced during the reaction. To increase the rate of the forward reaction, catalyst can be used, excess alcohol can be used. Likewise, here acid to alcohol ratio is kept as 1:6, i.e. 6 times extra amount of alcohol is used. Thus the study is to find out whether we can reduce the acid to alcohol molar ratio.

Regeneration of the adsorbent is also done by heating the used silica gel esterification was monitored by determining the residual acid content of at 110⁰C for 50 minutes. And the reaction at optimized conditions was carried out.

C. Analysis of catalyst and sample

The catalyst synthesized was analysed using FT-IR analysis and TGA analysis.

The progress of the reaction by titration of 5 g samples with KOH (0.1N) using phenolphthalein as indicator and 25 mL of ethanol as quenching agent. The product was confirmed as butyl acetate from HPLC analysis.

III. RESULTS AND DISCUSSION

A. Effect of catalysts

The first set of reactions with oleic acid (0.1 mol, 31.56 mL) and ethanol (0.6 mol, 35 mL) using sulphuric acid (5 wt%, 1.4 mL) and FILs (1 gm) as catalyst are carried out keeping the reaction conditions as 80⁰C, with 2 rpm stirrer speed, and 1 hour reaction time. The qualitative and quantitative analyses of the samples obtained are then done. The maximum conversion was obtained for FIL (b) and minimum for the conventional catalyst sulfuric acid.

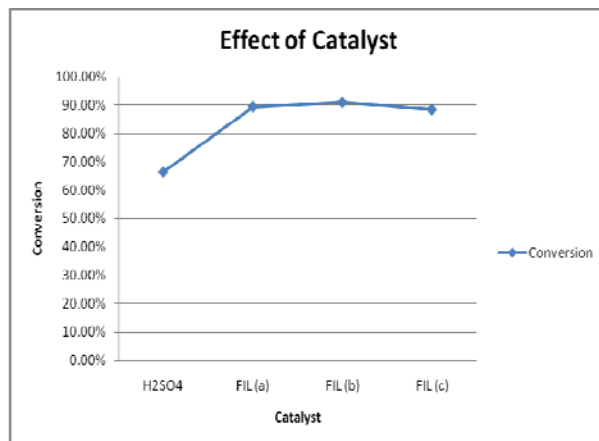


Fig. 1: Effect of Using Catalysts

B. Effect of drying agent

The second sets of reactions are carried out in the presence of drying agents. The drying agents used are anhydrous sodium sulphate and silica gel in the presence of FIL (b) which gave a better conversion. While carrying out the reaction, 10 gm of the drying agents are added. Out of the reactions, silica gel gave better conversion. So this is used for the reaction between oleic acid and ethanol (with the molar ratio M = 6) in the presence of other FILs.

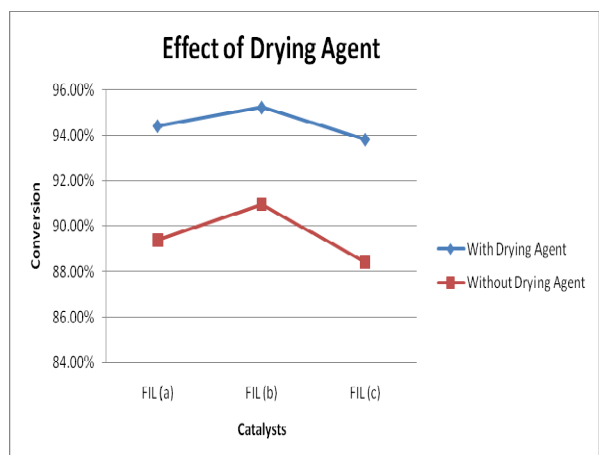


Fig. 2: Effect of Adding Drying Agent

C. Effect of temperature

The esterification reaction carried out in the presence of FIL (a) catalyst for 1 hour with 10 gm of adsorbent in the reaction mixture at the temperatures, 60⁰C, 70⁰C and 80⁰C. The maximum conversion was obtained at 80⁰C.

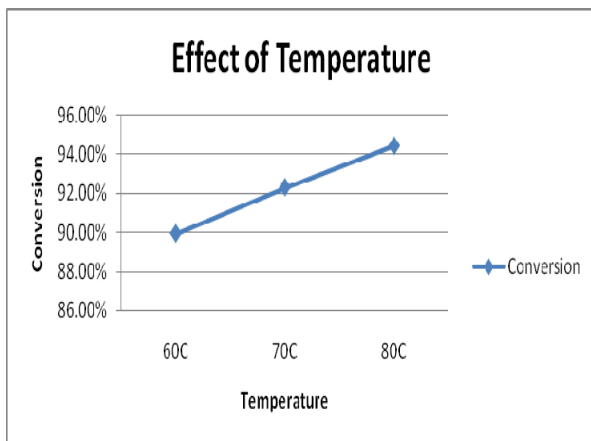


Fig. 3: Effect of Temperature

D. Effect of adsorbent concentration

The effect of amount of adsorbent is also studied by varying the amount of adsorbent used from 5 gm to 15 gm. The reaction is carried out at 80°C for 1 hour. The conversion increases as the amount of adsorbent increases from 5 gm to 10 gm. But if the amount of adsorbent is increased further no much change are there in conversion.

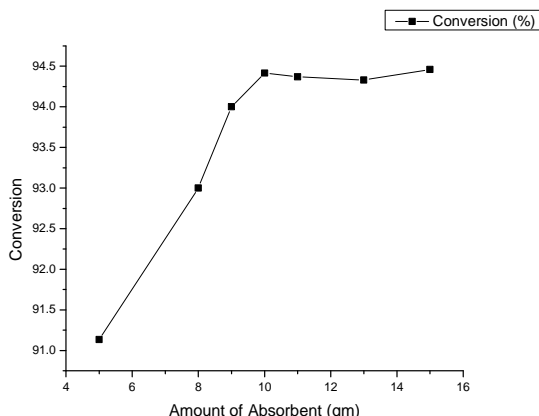


Fig. 4: Effect of adsorbent

E. Effect of catalyst concentrations

The effect of the concentration change of the catalyst on the esterification reaction is studied. The catalyst concentrations taken are 0.5 gm, 0.75 gm, 1 gm, and 1.25 gm. The conversion increases as the catalyst concentration is increased but as the concentration is increased above 1 gm the conversion gradually decreases. Thus the optimum is 1 gm of catalyst.

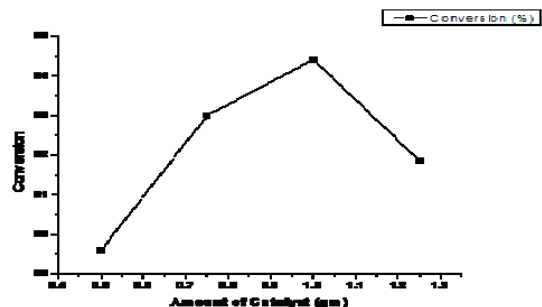


Fig. 5: Effect of catalyst concentrations

F. Effect of Molar Ratio

To find out whether the molar ratio of acid to alcohol can be reduced, keeping all the optimised conditions that we obtained till now is used to conduct the reaction at molar ratio $M=4$ and 3 . The reaction was previously done at $M=6$.

The conversion decreased but the conversion that is obtained at $M=3$ in the presence of drying agent is comparable with the conversion i.e. is obtained at $M=6$ without the presence of water absorbing agent. Therefore, if simultaneous water removal is there, then the alcohol used can be reduced.

The reaction is again done at $M=3$, in the presence of the water absorbing agent for simultaneous water removal, using the alcohol which was treated with 10 gm of silica gel prior to the reaction. Any water content in ethanol is removed silica gel is added to it. Thus the conversion we obtained is **89.43%** which is slightly more than the conversion obtained for the reaction done at the same conditions except that the ethanol was not treated with silica gel for water absorption prior to the reaction.

At all these optimised conditions, the reactions are done using the other two ionic liquids as catalysts.

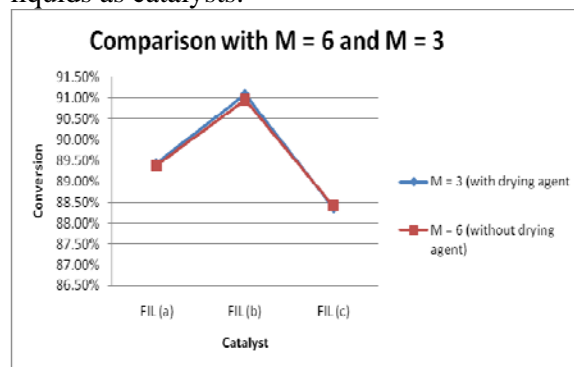


Fig. 6: Change in Molar Ratio with and without Drying Agent

G. Regeneration of adsorbent

The adsorbent regeneration was done and 10 gm of regenerated adsorbent is used and the reaction is carried out in all the optimised conditions in the presence of the catalyst FIL (a) at $M = 3$ using the ethanol which is treated priorly. The Conversion obtained is: **87.425%**.

When the reaction is carried out at $M = 6$, the conversion obtained is: **91.9%**.

H. Characterization of Ethyl oleate

From HPLC analysis the presence of ethyl oleate is confirmed. HPLC analysis for the known standard solution of ethyl oleate was done and the peak was obtained at 1.7 minutes. Then for the sample also the analysis was done and the peak was obtained in that time range itself. Hence the presence of ethyl oleate is confirmed.

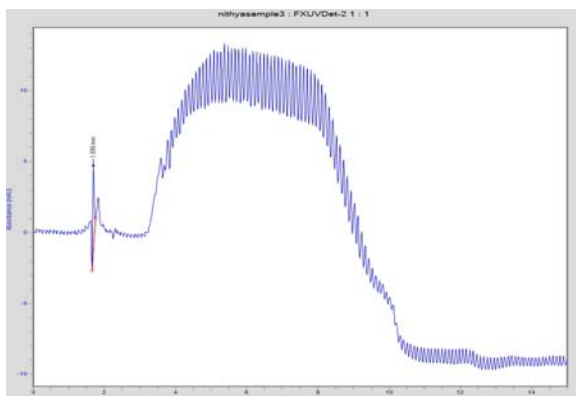


Fig. 7: Characterization of Ethyl Oleate

IV. CONCLUSIONS

The esterification reaction was carried out between ethanol and oleic acid. The comparison of the conventional catalyst H_2SO_4 and the three FILs were done. Among three FILs, FIL (b), with pyridinium catalyst gave the highest conversion.

The water adsorbent such as silica gel and anhydrous sodium sulfate were added for the simultaneous removal of water from the reaction mixture. Among these two, silica gel gave good conversion. Then the optimisation studies were done using silica gel.

Effects of temperature, catalyst concentration and adsorbent concentration were studied and optimised conditions are found out as $80^\circ C$, 1 gm of catalyst and 10 gm of adsorbent.

The simultaneous use of ionic liquid as catalyst and removal of water formed during reaction reduce the amount of excess alcohol used during the reaction. The alcohol to acid molar ratio initially used was 6: 1. The experiments were conducted at $M = 3$, and 4 in the presence of drying agent. The results showed that the conversion obtained when $M = 3$ in the presence of drying agent was comparable with $M = 6$ for the reaction without drying agent. The reaction was conducted again in the same reaction conditions after treating the alcohol with silica gel prior to the reaction. This gave a conversion slightly higher than before. At all these optimised conditions the reactions were carried out using the other two FILs as catalysts. In all cases, a good conversion was observed.

The regeneration of adsorbent was done by simply heating the used silica gel at $110^\circ C$ for 50 minutes. And this regenerated adsorbent was used to carry out the reaction. It was observed that the reactions were carried not much reduction in efficiency for second regeneration of adsorbent.

The present work concluded that Ionic Liquids as catalyst gives a good conversion. The efficiency of reaction is further improved by using drying agents such as silica gel and anhydrous sodium sulfate. The incorporation of above two methods of increasing the reaction rates result in the reduction of excess usage alcohol or alcohol to acid ratio.

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