Effect of Ion Exchange Resin Catalyst on Hydrolysis of Ethyl Acetate

U R Amarasinghe, M L S Gunasena and M Y Gunasekera

Abstract

Hydrolysis reaction of ethyl acetate is a reversible reaction with high activation energy. The reaction has a very slow reaction rate when carried out in the absence of a catalyst. Therefore, catalysts need to be used in industrial applications in order to increase the reaction rate. Traditionally homogenous catalysts are used in industry such as hydrochloric acid and sulphuric acid. The main problem related to homogeneous catalysis is the difficulty of separating the yield from reactants and catalyst mixture. This problem can be overcome by using heterogeneous catalysts. The main objective of this research is to study the polymeric resin Lewatit S1467, normally used for water treatment as an alternative heterogeneous catalyst for hydrolysis reaction of ethyl acetate. The resin had to be washed using sulphuric acid to give an H^+ charge on the catalyst. Experiments were carried out at a constant temperature to determine the suitable catalyst loading of dry resin. This research also focused on the ability of reusing the resin. The results show that increase in the solid resin catalyst loading increases the percentage of conversion. A maximum conversion of 52% was observed when 7.5 g of catalyst was used with 110ml of the reaction mixture. The catalyst reusability study with 7.5g of catalyst, showed a decrease in the conversion when the catalyst was reused.

1. Introduction[1]

Ethyl acetate hydrolysing reaction takes place as shown below;

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons C_2H_5O + CH_3COOH$$

This reaction is reversible and it has high activation energy. Therefore the reaction rate is very slow and hence this reaction cannot be used in industrial applications without using a catalyst. In the chemical industry, homogenous catalysts such as sulphuric acid or hydrochloric acid are used to catalyze this reaction. However, these catalysts cannot be separated from the reaction mixture since catalyst and the reaction yield are in the same phase. In order to overcome this problem, heterogeneous catalysts are used.

Hydrolysis of ethyl acetate using the solid resin catalyst, Amberlyst-15 at the temperatures ranging from 313.15K to 343 K has been studied by Ayyappan et al. [1]. Their research focused on the study of conversion of ethyl acetate for various catalyst loadings, molar feed ratios, reaction temperatures, feed concentrations and kinetics of the reaction. The results of their research prove that conversion increases with the catalyst loading, molar feed ratio of reactants namely water and ethyl acetate and temperature. Bamunusingha et al. [2] have analysed the kinetics of the esterification of acetic acid using acidic resin catalyst Trilite SCR-B in Na^+ and H^+ forms. This research analysed the reaction performance with catalyst loading, effect of temperature and reaction kinetics using Trilite SCR-B in H+ form. According to their results the conversion increases with catalyst loading and the optimum catalyst loading was found to be 7g. Furthermore, their results show that the conversion has increased with temperature. The optimum conversion obtained was at 335 K.

The solid ion exchange resins used as catalysts in catalytic reactions are available in the market at high costs. The ion exchange resins available in the market that are used in the water treatment industry are less costly. In this work a cation exchange resin used in the local water treatment industry namely Lewatit S1467 is studied for its applicability as a catalyst in the hydrolysis reaction of ethyl acetate. The reaction performance of this heterogeneous catalyst is looked at in order to identify a suitable catalyst loading and its re-using capability.

2. Methodology

2.1 Materials

The reagents used, ethyl acetate, sodium hydroxide, sulphuric acid and hydrochloric acid were analytical grade chemicals. The cation exchange resin Lewatit S1467 was used as the heterogeneous catalyst for the reaction. The cation exchange resin was soaked in sulphuric acid and the soaked resin was washed several times using de-ionized water. The resin was filtered and separated. The separated resin was then dried in the oven for 24 hours.

2.2 Hydrolysis of Ethyl Acetate without a Catalyst

The reactants with 10 ml of ethyl acetate (99% w/w) and 100 ml of water were mixed in a glass reagent bottle. The temperature of the solution was maintained at 37°C using a constant temperature water bath. The reactant solution in the bottle was continuously stirred. At different time intervals, 5ml samples were taken from the reactor bottle. These samples were titrated against 0.001 mol/dm^3 of NaOH and the relevant percentages of conversions of ethyl acetate were calculated.

[1] U. R. Amarasinghe, M. L. S. Gunasena and M. Y. Gunasekera are with the Department of Chemical & Process Engineering, University of Moratuwa, Sri Lanka.
(email: ur.amarasinghe.uom@gmail.com; lasithasandaruwan@gmail.com and manisha@uom.lk).

2.3 Hydrolysis of Ethyl Acetate Using HCl as a Catalyst

The reactants with 10 ml of ethyl acetate (99% w/w) and 100 ml of water were mixed and prepared as above. In addition, 5ml of 1M HCl was added to the solution to act as a homogeneous catalyst. Reaction was carried out at 37^0C and samples of 5ml were taken at different time intervals. Samples were titrated with 0.001 mol/dm^3 of NaOH to find the ethyl acetate conversion.

2.4 Weight of Lewatit S1467 Resin for Hydrolysis of Ethyl Acetate

Four solutions with 10 ml of ethyl acetate (99% w/w) and 100 ml of water were prepared. The heterogeneous catalyst (Lewatit S1467) in quantities of 1g, 3g, 7.5g and 10g were added to each of the four solutions. The reaction was carried out at 37^0C and from the time of addition of the catalyst, 5ml samples were taken at regular time intervals. The samples were analyzed by the titration procedure used for determining ethyl acetate conversion described in section 2.3 above.

2.5 Reuse of Resin

Ethyl acetate solution was prepared and 7.5g (8.4% w/w) of resin was used as catalyst. As described above in section 2.3, titration of samples was done until steady state was reached in the reaction. Resin used once was separated and dried for 24 hours in the oven. Then it was taken from the oven and weight was measured. The makeup resin was added to maintain the constant resin quantity of 7.5g. Above reuse procedure was repeated for new solutions four times.

2.6 Experimental Setup

Stoppered reaction bottles of 500ml were used to carry out the experimental reactions. The reactants in the bottles were heated to the desired temperature and kept at a constant temperature throughout the experiment by placing the bottles in a temperature controllable water bath. The reactants in the bottle were mixed manually using a glass rod.

3. Results and Discussion

The results of the hydrolysis of ethyl acetate using the cationic ion exchange resin are presented in this section. The cation resin Lewatit S1467 was in Na^+ form when it was purchased from the local market. Literature reveals that the catalytic action in ion exchange resins is best observed in chemical reactions when the resin has the H^+ form [3][4]. Therefore this resin was soaked in sulphuric acid to obtain an acidic cation exchange resin. The Lewatit S1467 resin in H^+ form is examined for its performance and reusability. Initially the hydrolysis reaction of ethyl acetate was carried out without a catalyst to facilitate comparison of reaction performance with and without a catalyst. Further the hydrolysis of ethyl acetate using the homogeneous catalyst HCl was also looked at and the results are discussed.

3.1 Ethyl Acetate Hydrolysis in the Absence of a Catalyst and with HCl Catalyst

The hydrolysis of ethyl acetate reaction when a catalyst is not present, gives very low conversions of ethyl acetate as shown in Figure 1. After 200 minutes from the start of the reaction a conversion of about 0.16% is achieved. This shows that the reaction needs to be studied in the presence of a catalyst.

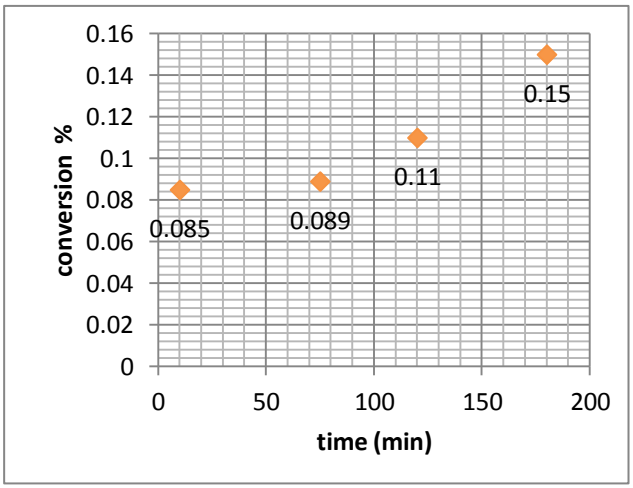

Figure 1: Ethyl acetate conversion % for hydrolysis of ethyl acetate without a catalyst

The liquid phase hydrolysis using the homogeneous catalyst, hydrochloric acid is carried out. For a solution consisting of 10 ml of ethyl acetate, 100 ml of water and 5ml of 1M HCl catalyst, the ethyl acetate conversions observed are shown in Figure 2. With this strong acid catalyst very high reaction conversions of ethyl acetate are shown after about 90 minutes from the start of the reaction.

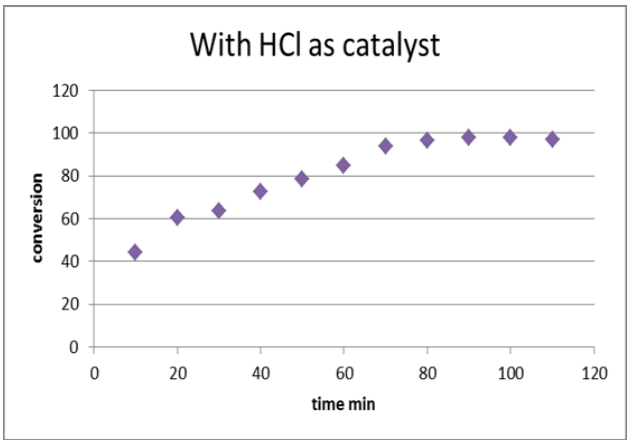

Figure 2: Ethyl acetate conversion % for hydrolysis of ethyl acetate with HCl catalyst

Maximum conversion observed was about 98% of ethyl acetate. The conversion increases with time and reaches a

maximum within a short time about 1.5 hours. A similar study done by Thilakarathna *et al* [5] for the hydrolysis of ethyl acetate using 0.1M HCl had shown conversions of about 60% to 70%. The main objective of this study is to observe the performance of a low cost cationic ion exchange resin as a solid catalyst for this hydrolysis reaction. The observations made with the solid resin Lewatit S1467 in the hydrolysis reaction are discussed in the following section.

3.2 Study of Different Amounts of the Catalyst

The amount of catalyst present in the reaction mixture is an important parameter that influences the rate of reaction. The amount of solid catalyst determines the amount of surface area of the catalyst and the number of sites available for the reaction. When the amount of catalyst increases the amount of sites available for the reactants to get adsorbed onto and react also increases. The weights of Lewatit S1467 resin, 1g, 3g, 5g and 7.5g were used in this study. Four samples of reactant solutions consisting of 10 ml of ethyl acetate and 100 ml of water each along with the solid catalyst were reacted. The conversions of the ethyl acetate observed for different catalyst weights are shown in Figure 3.

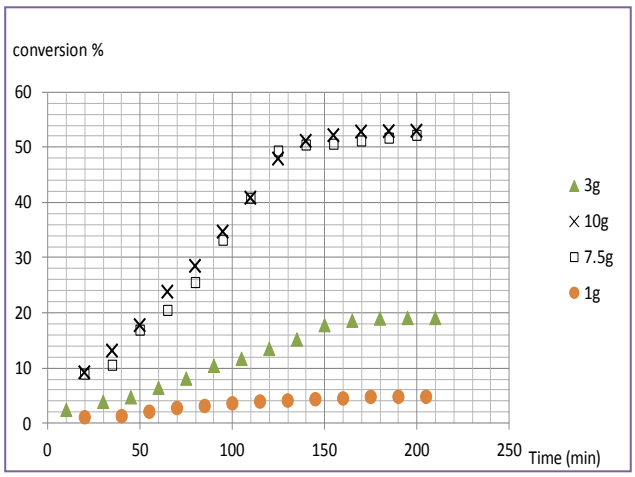

Figure 3: Ethyl acetate conversion for different catalyst weights

According to the Figure 3, conversion rate of hydrolysis reaction is significantly low when quantity of catalyst used is 1g and 3g. The conversion observed after 150 minutes from the start of the reaction for 3g of catalyst was about 18% and that for 1g of catalyst was about 4%. When 10g or 7.5g is used, conversion observed after 150 minutes was about 52% for both cases. The conversion shows an increase with the time for all four weights of resin. However the rate at which it increases is high for 7.5g and 10g of the catalyst. Similar results have been observed in the work carried out by Thilakarathna et al [5] using the treated ion exchange resin, Trilite SCR-B for the same hydrolysis reaction. The research done on esterification reaction using the cation exchange resin Trilite by Bamunusinghe et al [2] has shown similar result, an increase in the reaction rate with the increase of catalyst loading. Since 7.5g and the 10g of resin show similar conversion patterns the quantity of catalyst weight 7.5g that is 8.4%w/w is considered for use as the suitable weight of the catalyst in the following study on catalyst reuse. In order to determine the optimum loading more trial experiments using catalyst weights between 3g and 7.5g need to be carried out. Further it is recognised that the effect of different temperatures on the catalyst performance is an important aspect that needs to be looked at in the future work of this study.

3.3 Reuse of the Solid Catalyst

The ion exchange resin catalyst, once used in the reaction, can be separated from the reactions mixture as it is heterogeneous. However whether it could be reused for the same purpose is one aspect that must be explored. The hydrolysis reaction for which 7.5g of catalyst has been used is recovered and reused several times while adding fresh catalyst to make up for the amount lost during the reaction process. The Figure 4, Figure 5, Figure 6 and Figure 7 show the conversion results of ethyl acetate when the catalyst is used for the first time, reused or in the second use, third use and the fourth use respectively. According to the results in these figures the conversion shows a decrease with the number of reused times. After the third reuse the conversion observed is significantly low, about 6.4% after 280 minutes (Figure 7). The results show that the resin catalyst could be reused twice with some make up catalyst.

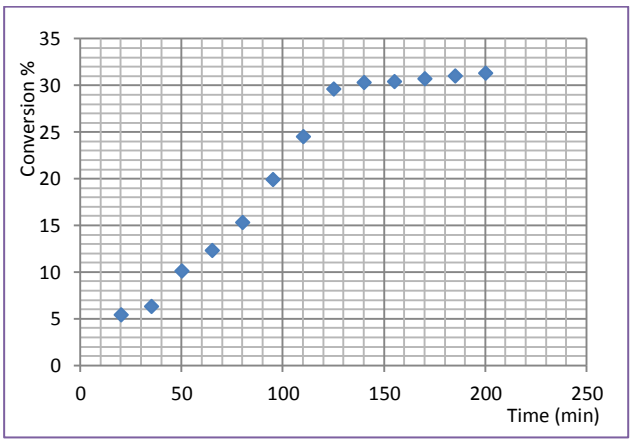

Figure 4: Conversion % for the first use of the 7.5g of catalyst

Although the reusability of the catalyst was studied using the catalyst loading of 7.5g in this work, it is recognized that the study of the same using other loadings also needs to be carried out to determine the performance characteristics of the solid resin Lewatit S1467 as a catalyst.

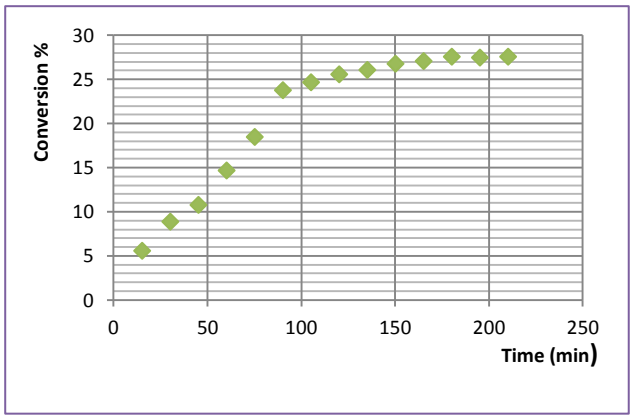

Figure 5: Conversion % for the second use of the 7.5g of catalyst

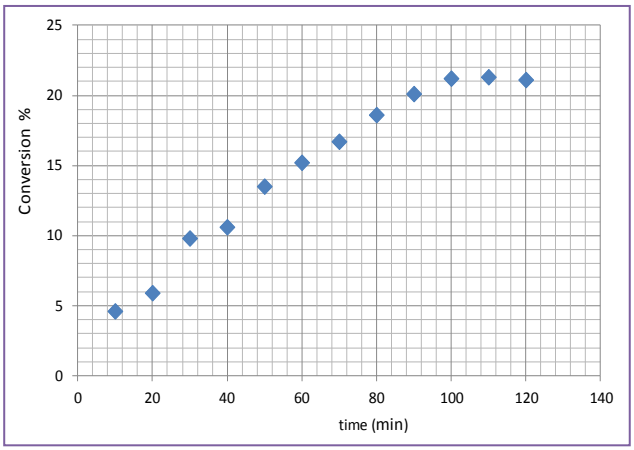

Figure 6: Conversion % for the third use of the 7.5g of catalyst

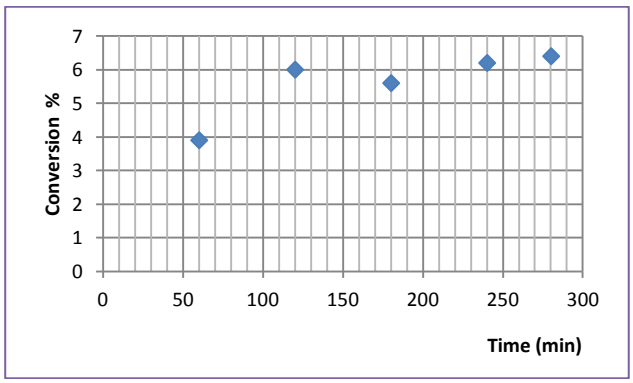

Figure 7: Conversion % for the fourth use of the 7.5g of catalyst

4. Conclusions

The hydrolysis rate of ethyl acetate in the absence of a catalyst is very low and that with a homogeneous catalyst HCl is very high. When the Lewatit S1467 resin in its H^+ form is used as a catalyst for the same reaction, a conversion higher than the conversion seen in the absence of a catalyst is observed. However the conversions were not as high as that was observed in the case where HCl was used as a catalyst. The catalyst Lewatit S1467 resin in H^+ form can be reused twice with some makeup catalyst satisfactorily.

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