Esterification of Maleic Acid with Butanol Catalyzed by Environmentally Friendly Catalysts

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Abstract

The esterification reaction between maleic acid and n-butanol is investigated using different environmentally friendly catalysts. Catalytic performance of Amberlyst 15-dry ,Amberlyst 15-wet, Amberlyst 131H+ and two deep eutectic solvents were studied at 1:10 molar ratio of acid to alcohol at temperature of 358 and 363 K and with catalyst loading of 0.0375 g/mL. Among the ion exchange resins studied, Amberlyst 131H+ was found to have the best performance and the effect of the water content in the reaction mixture was studied for this catalyst. The catalytic performance of DES's are found to be comparable and some cases significantly higher than the ion exchange resins.

Keywords: esterification, maleic acid, ion exchange resin, DES

1.Introduction

Esterification is the equilibrium reaction occurring between alcohol and acid which produces ester and water as reaction products. In industry, esterification reactions are widely applied in many different areas. Esters are common materials for many processes, they are used as plasticisers, solvents, flavor chemicals and in production of agrochemicals and various fine chemicals.

The esterification product, dibutyl maleate or maleic acid dibutyl ester, is used as an additive and intermediate for plastics, pigments, pharmaceuticals, and agricultural products. Dibutyl Maleate is an intermediate for the production of paints, adhesives and copolymers. It is used in many organic synthesis including as a dienophile for diene syntheses. [1]

Due to weak acidity of carboxylic acids esterification reaction cannot take place without the presence of the catalyst. Also the reaction rates are very slow and require several days to attain equilibrium [2]. Manufacturing esters from carboxylic acids and alcohols is possible with Fischer-Speier esterification. Acids such as sulfuric acid and hydrofluoric acid can be used as catalyst for this reactions.

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Although the catalytic performance of this acids are high [3] several problems such as recovery of catalyst, high volume of acidic waste generated and general difficulties caused by working with highly potent acids are making this catalysts unfavorable. Due to acid usage, these types of manufacturing processes require a large purification and treatment efforts for products and wastes.

Due to recent issues about the environmental pollution, ever growing industrial production and more stringent environmental regulations, environmentally friendly catalysts for industrial processes have gained more importance. Environmentally friendly heterogeneous catalysts like ion exchange resins and homogeneous catalyst such as ionic liquids and deep eutectic solvent offer some distinct advantages compared to the acid catalysts[4-5].

Ion exchange resins offer some advantages such as their non-toxic nature and ease of separation from the reaction mixture. But their rather low thermal stability prevents them from be employed at higher temperatures. Sert et al.[6] studied the kinetics of catalytic esterification of acrylic acid and n-butanol catalyzed by different ion exchange resins of Amberlyst 131, Amberlyst 15 and Dowex 50WX-400. They observed that the catalytic performance of Amberlyst 131 was the highest among the ion exchange resins studied. Yadav and Thathagar [7] studied the esterification of maleic acid with ethanol with the presence of ion exchange resins Amberlyst 36, Amberlyst 15 and Amberlite IRA 120 and observed the high catalytic potential of ion exchange resins.

Deep eutectic solvents (DES) are another candidate for catalysts in esterification reactions. They have negligible volatility, high thermal stability, high electric conductivity and high reusability[8]. DES is a type of ionic solvent composed of two components and has a lower melting point of either of the individual components. DES's can be prepared combining with a hydrogen bond donor (HBD) (amides, carboxylic acids) and hydrogen bond acceptor (HBA) (quaternary ammonium salts). In some ways DES's can be described as advanced ionic liquids (IL). Like IL's they have negligible volatility, high thermal stability and low cost. Although IL's can used as catalysts in esterificaiton reactions, the preparation of ILs often requires the use of organic solvents, and heat supply which make their usage unfavorable[9].

DES's are relatively new development [10], first one is described in early 2000's. De Santi et al.[11] studied esterification reactions between variety carboxylic acids and alcohols at molar ratio of 1:1and observed high yield with DES catalysts. Ease of recovery and reusability of DES with high activity makes this method efficient and eco-friendly in their study.

2. Materials and Method

2.1 Materials

Reactants

n-Butanol(Merck) and maleic acid(ABCR) were used as reactans.

Deep Eutectic Solvents

For DES preparation, p-toluene sulfonic acid monohydrate (ABCR), benzyltrimethylammonium chloride (Merck) and Benzyltriethylammonium chloride (Merck) were used.

Ion Exchange Resins

In the experiments three ion exchange resins were used; Amberlyst 15-dry, Amberlyst 15-wet and Amberlyst 131. The properties of the resins are shown in Table 1.

Table 1. Properties of ion exchange resins used

	Amberlyst 15 DRY	Amberlyst 15 WET	Amberlyst 131 H+
Manufacturer	Rohn & Haas	Rohn & Haas	Sigma Aldrich
Active Group	Sulfonic Acid	Sulfonic Acid	Sulfonic Acid
Concentration of acid sites	≥4.7 meq/g	≤4.7 meq/g	4.8 meq/g

2.1 DES Preparation

The ingredients for DES are placed on a flask at molar ratio of 1:2 HBA to HBD and to confirm the homogeneity, the mixture is mixed. The solid mixture is heated to 80 °C and stirred on a temperature controlled magnetic stirrer until all the solid is dissolved and mixture attained a consistent structure. Prepared DES's are allowed to cold down to confirm their liquidity at room temperature. Prior the usage, pH measurements of each DES have been made to ensure their acidic properties.

Table 2. Compositions of DES's

	DES 1	DES 2
HBD	p-Toluenesulfonic acid	p-Toluenesulfonic acid
HBA	benzyltrimethylammonium chloride	benzyltriethylammonium chloride
pH	0.72	0.38
Appearance	pale pink	pale yellow

2.2 Experimental Procedure

Experiments were performed at a reactor which placed upon a magnetic heater stirrer and consisted of a 500 ml flash fitted with condenser to prevent loss of material during experiment. Also to prevent concentration gradients across the reaction mixture vigorous stirring was employed at 1000 rpm. In experiments, reactants were quickly heated to the reaction temperature and catalyst are added at that point. The catalyst loading was 0.0375 g/L. The ion exchange resins were dried in an oven at 70°C to ensure the absence of any moisture content. To promote maleic acid conversion excess n-butanol were used. The molar ratio of acid to alcohol was 1:10. The temperature is controlled by a temperature controller. The samples were taken during the experiment for gas chromatographic analysis.

Analyses of the samples were performed on Agilent 7890A chromatograph. The conversion of limiting reactant (maleic acid) was calculated.

3. Results and Discussion

3.1 Effect of Catalyst

Different catalysts, Amberlyst 15-dry, Amberlyst 15-wet, Amberlyst 131H+ and DES1 and DES2 are used in the experiments at a temperature of 363 K with catalyst loading of 0.0375 g/mL. The results are given in Figure 1. As shown in the figure, the maximum value of maleic acid conversion was achieved by DES1.

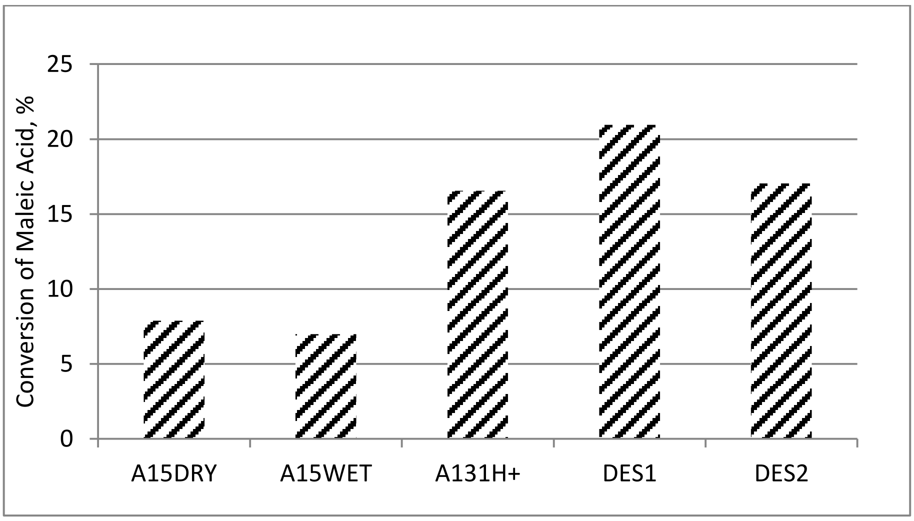

Figure 1. Effect of catalyst on the conversion of maleic acid at a temperature of 363 K

3.2 Effect of Temperature

To investigate the effect of temperature, experiments were performed at temperatures of 358 and 363 K. The results are given in Figure 2.

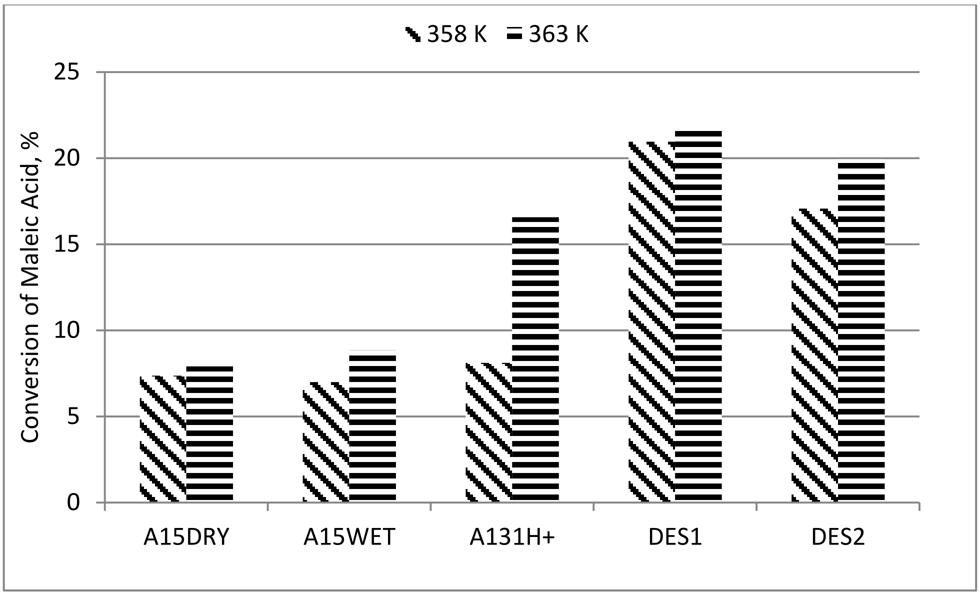

Figure 2. Effect of temperature on the conversion of maleic acid

Temperature increases the number of collisions between the molecules, so conversion increases as expected.

3.3 Effect of Time

During the experiments, samples were taken at different time intervals to explore the effect of time.

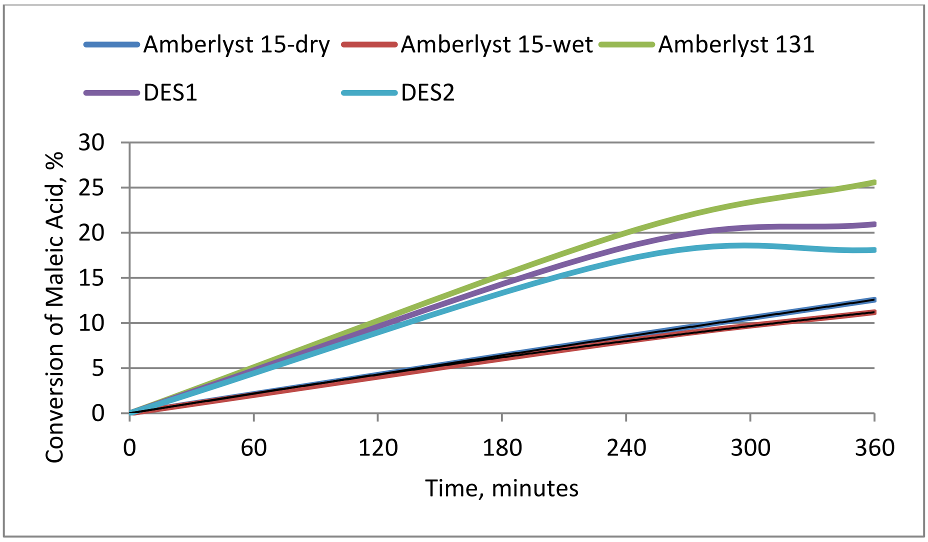

Figure 3. Effect of time on the conversion of maleic acid at a temperature of 363 K

At the beginning, the reaction rate is faster, after 3 hours, reaction starts to reach the plateau.

3.4 Effect of Water in the Reaction Mixture

Esterification reactions are equilibrium reactions which produce water. According to Le Chatelier's principle any water content in the reaction mixture would force the equilibrium towards the reactants hence lowers the conversion of maleic acid. Maleic acid can be obtained as solution which is coming from any process in industry. One way of recovery of maleic acid is to react with alcohol to obtain corresponding ester. Amberlyst 131H+ has the best performance among the three ion exchange resins. Therefore to observe effect of water on the conversion, Amberlyst 131H+ catalyst was selected. Maleic acid is diluted 75% by mass water and charged into the reactor. As it can be seen on the Figure 4. presence of water in the reaction mixture has great effect on the conversion of maleic acid. But, by changing the operational conditions such as catalyst loading or temperature this situation may be compensated.

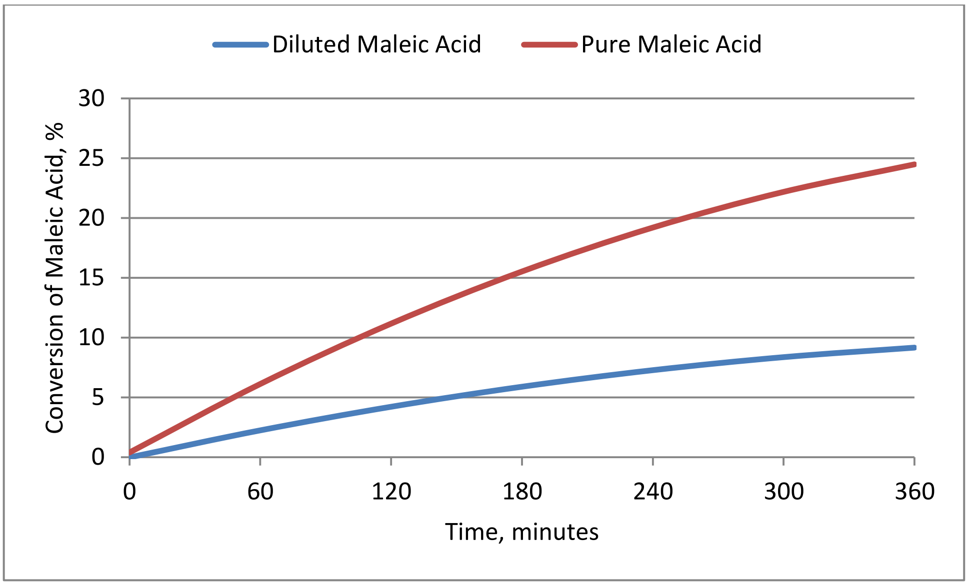

Figure 4. Effect of water in the reactor mixture on the maleic acid conversion at a temperature of 363 K

4.0 Conclusion

Esterification reaction between maleic acid and n-butanol was studied using different environmentally friendly catalysts. Experiments were carried out in a batch reactor at two different temperatures. Two deep eutectic solvents were prepared. The performances of DES’s were found to be higher than the ion exchange resins. Effect of water in the reaction mixture is also studied with the Amberlyst 131 H+ catalyst and showed decreasing maleic acid conversion with the presence of water.

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