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ESTERIFICATION REACTION OF ACETIC ACID AND ETHANOL WITH H_2SO_4: BATCH KINETICS AND SIMULATION APPROACH

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ABSTRACT

Esterification represents one of the most important reactions in chemical industry and the esters produced have applications in a variety of areas such as plasticizers, flavours and fragrances, pesticides, solvents, medicinal and surface active agents. The Esterification kinetics of acetic acid with ethanol in the presence of sulphuric acid as a homogenous catalyst was studied with batch experiments at four different temperatures and at a different molar ratio of ethanol to acetic acid with 5% catalyst loading. Investigation of kinetics of the reaction indicated that the increasing the [Ac/EtOH] molar ratio is favoured for esterification reaction, this is due to the reaction is catalyzed by acid. The maximum conversion, approximately 83% was obtained at 65°C for molar ratio of Ac/5EtOH. With the help of Aspen Plus we can design plants and can attempt profitability in existing plants. We can interactively change specifications, such as flow sheet Configuration, operating conditions, and feed compositions, to run new cases and analyze alternative. Sensitivity analysis predicts how much sensitive process or a model, to a particular variable. Using sensitivity analysis it is observed that the mole ratio is highly sensitive parameter while as temperature up to certain range is sensitive.

Keywords: Acetic Acid, Aspen Plus, Batch Kinetics, Esterification, Ethanol, Sensitivity.

I. INTRODUCTION

Esterification is a well-known process and a number of industrially important chemicals such as methyl, ethyl and butyl esters, alkyl t-butyl ethers (MTBE and ETBE) are produced using esterification reactions. Esters are important classes of chemicals have many applications in a variety of areas such as solvents, plasticizers, pharmaceuticals and intermediate for many industries (Kirk and Othmer 1980, Yadav and Metha, 1994). Sensitivity Analysis in ASPEN PLUS determines how a process reacts to varying key operating and design variables. We can use it to vary one or more flow sheet variables and study the effect of that variation on other flow sheet variables. It conveniently generates tables and plots showing how process performance varies with changes to selected equipment specifications and operating conditions. It has feature to run multiple simulations with different input for comparison and analysis. Design Specification capabilities to automatically calculate operating conditions or equipment parameters to meet specified performance targets. Sensitivity analysis is important to verify if the solution to a design specification lies within the range of the manipulated variable. It explored the Plant Operating Conditions that will maximize any objective function specified, including process yields, energy usage, stream purities and process economics.

II. EXPERIMENTATION

2.1 Kinetics of Esterification of Ethyl Alcohol by Acetic Acid

The Esterification kinetics of acetic acid with ethanol in the presence of sulphuric acid as a homogeneous catalyst was studied with isothermal batch experiments at 45-75^{0}C and at a different molar ratio of acetic acid to ethanol. The overall reaction between acetic acid and ethyl alcohol over a sulphuric acid catalyst is as follows:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Acetic acid + ethanol ⇌ ethyl acetate + water

(A) (B) (C) (D)

This reaction is reversible, exothermic and the equilibrium composition is a weak function of temperature. The reaction is acid catalysed, and as for most esterification usually strong mineral acids (hydrochloric acid, sulphuric acid) are used.

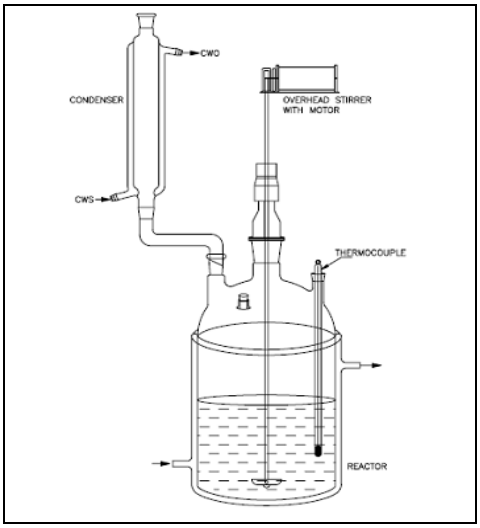

Fig 2.1: Schematic Representation of Batch Kinetics Setup

2.1.1 Materials and Catalyst

All the reagents were of synthesis grade and obtained from Merck AG. Acetic acid and ethyl alcohol, respectively was 99.98 % w/w and 96 % w/w and rest being water. The experimental assembly consisted of a 250 ml reactor fitted with a long reflux condenser to prevent any loss of products and a thermometer pocket. Aliquots of sample were taken via reflux condenser. A steel stirrer was used to stir the reaction mixture. The reaction vessel was placed in a thermostat bath with an electronic temperature regulator (+/- 0.10 K). Experiments were conducted at various molar ratios of acetic acid and ethyl alcohol in the temperature range of 318.15K, 328.15K, 338.15K, 348.15K, and 358.15 K using 5% catalyst concentrations. The sulphuric acid catalyst is used for the production of ethyl acetate. The amount of catalyst used is 5% of limiting reactant i.e. acetic acid.

2.1.2 Effect of Temperature

In order to study the effect of temperature on the reaction, experiments were carried out over a range of temperatures (318-358 K). Figure shows the plot of conversion vs. time at different temperatures. As expected, the rate of reaction and hence conversion increases as temperature is increased from 318.15 to 358.15 K. since this is a reaction with no observable side reaction; it is clear that higher the temperature more is the conversion.

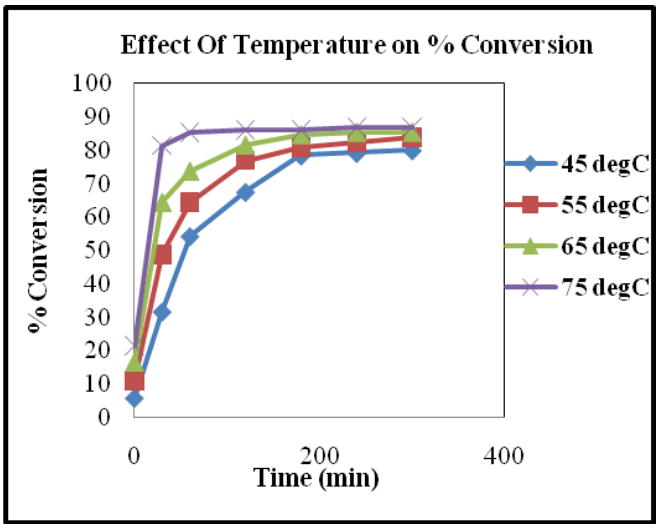

Fig 2.2: Effect of Temperature on % conversion

2.1.3 Effect of Reaction Time

To study the effect of time on the reaction, experiment was carried out for 5 hour at 65^0C temperature. Figure shows the plot of conversion vs. time at 65^0C temperature. As expected, the rate of reaction and hence conversion increases as time is increased.

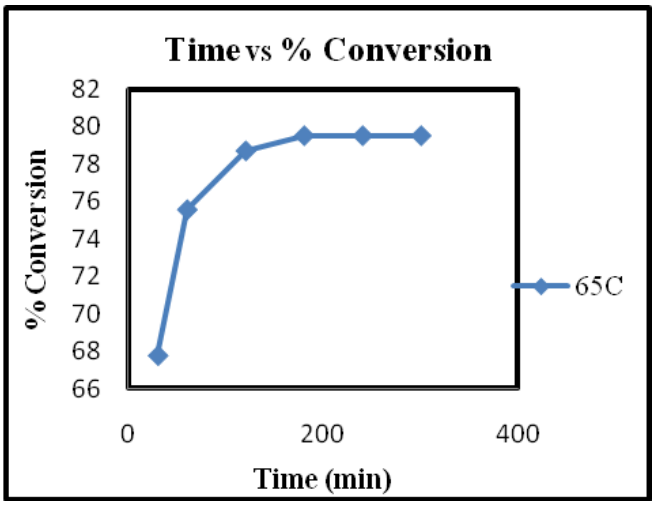

Fig 2.3: Effect of Reaction Time

Since this is a reaction with no observable side reaction; it is clear that as the time increases conversion also increases.

2.1.4 Effect of Mole Ratio

In order to study the effect of mole ratio on the reaction, experiments were carried out over a range of mole ratio 1:1, 1:2, 1:3 and 1:5. Figure shows the plot of conversion vs. mole ratio. As expected, the rate of reaction and hence conversion increases as the mole ratio is increased from 1:1 to 1:5. Since this is a reaction with no observable side reaction; it is clear that higher the mole ratio more is the conversion.

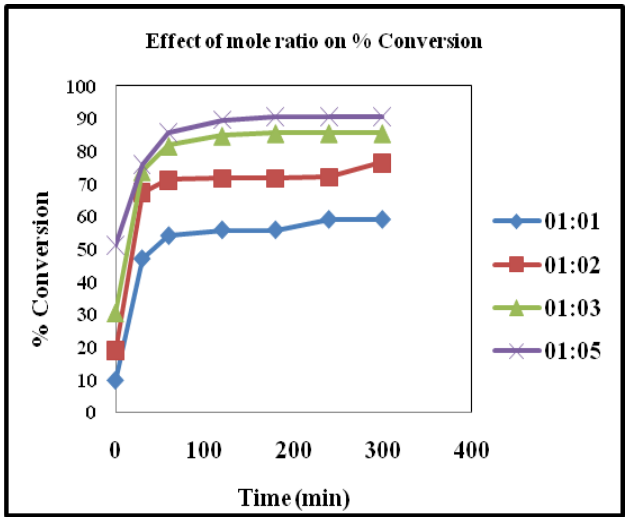

Fig 2.4: Effect of Mole Ratio

III. SENSITIVITY ANALYSIS

Here, Sensitivity analysis will be introduced with esterification reaction in batch reactor. In this task the effect of change in manipulated variable like temperature and mole flow of ethanol in RBATCH block B1 on the product concentration is to be done, also the effect of mole flow rate of acetic acid on the concentration of product in the reactor outlet. For doing the sensitivity analysis of esterification reaction, basic simulation of that reaction must be encountered.

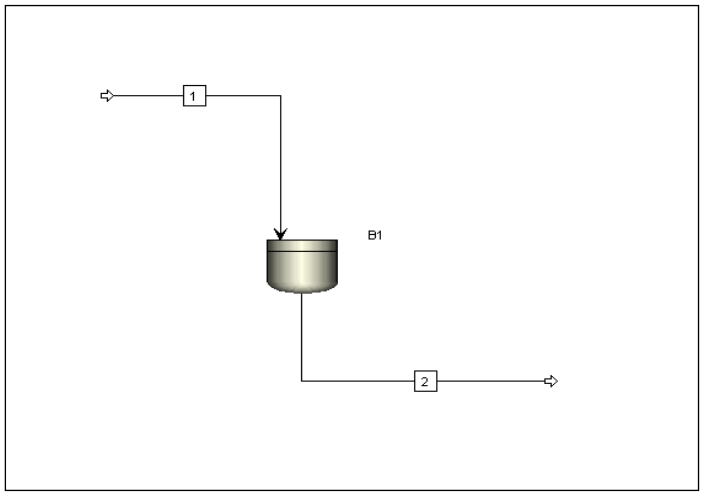

Fig 3.1: Process Flow Sheet Window

3.1 Manipulated Variable: Reaction Temperature:

Reaction temperature	Pressure (atm)	Acetic Acid (gm)	Ethanol (gm)	Water (gm)	Mass of solution (gm)	Reaction Time (hr)
45^0C -85^0C	1	43	131	2.15	176.15	5

3.2 Manipulated Variable: Mass flow rate of Ethanol

Ethanol (Kg/ hr)	Reaction temperature (^{0}C)	Pressure (atm)	Water (gm)	Reaction Time (hr)
0.043 – 0.180	65^0C	1	2.15	5 hr

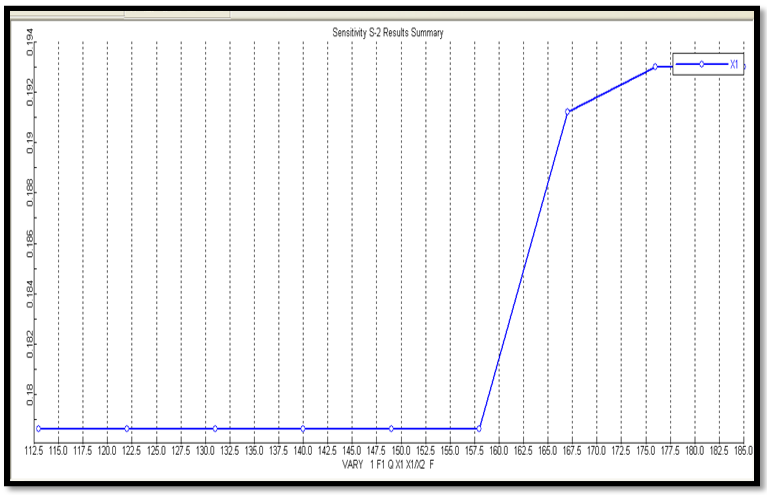

Fig 3.2: Sensitivity Analysis (Change in Reaction Temperature on Mole Fraction of Ethyl Acetate)

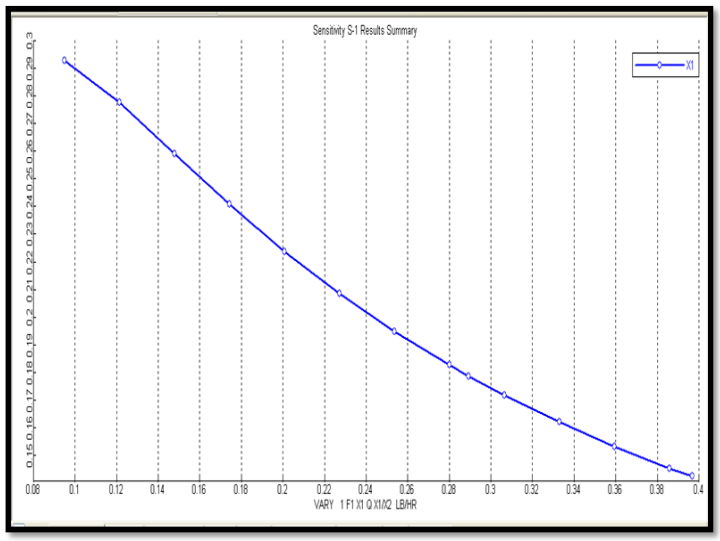

Figure 3.3: Sensitivity Analysis (Effect of Change in Mole Flow of Ethanol on Mole Fraction of Ethyl Acetate)

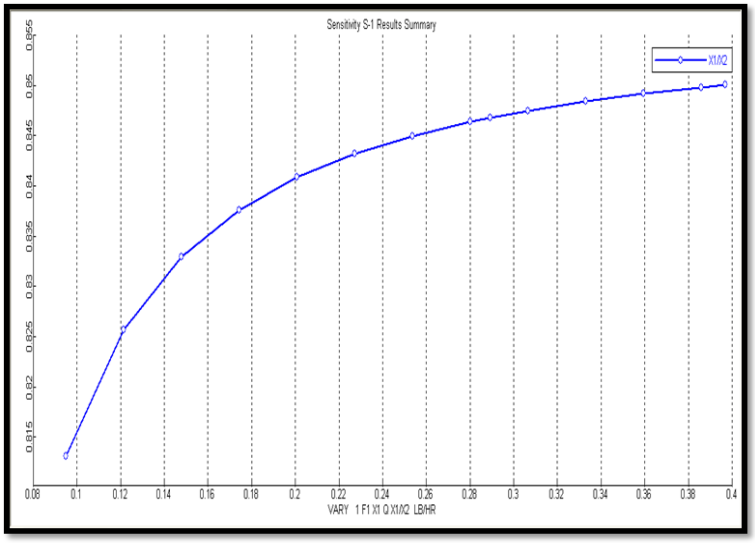

Figure 3.4: Effect of Change in Mole Flow of Ethanol on Ratio of Mole Fraction of Ethyl Acetate and Water

IV. CONCLUSION

The simulation work has been carried out for esterification of acetic acid and ethanol reaction at various temperature and mole ratio of reactant. To verify the simulation results, experiments are also carried out at some temperature and mole ratio conditions. For an esterification reaction of 5 hour at 65^0C the conversion of 85% is observed. It will matches with the literature. While doing the experiments it is also observed that upto certain limitation if time and mole ratio increases, the conversion also increases. It is reported in literature for 1:10 ratio, the conversion is around 87%. While as for my experimental studies I have taken 1:3.

It is also observed that, the experimental and simulation results are fairly matching. Simulation sensitivity analysis is also performed. From sensitivity analysis it is observed that the mole ratio is highly sensitive parameter while as temperature up to certain range is sensitive.

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