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Effect of Operating Conditions on CSTR performance: an Experimental Study

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ABSTRACT
In this work, Saponification reaction of ethyl acetate by sodium hydroxide is studied experimentally in a continuous stirred tank reactor at 1 atmospheric pressure. The aim of this study is to investigate the influence of operating conditions on the conversion and specific rate constant. The parameters considered for analysis are temperature, feed flow rate, residence time, volume of reactor and stirrer rate. The steady state conversion of 0.45 achieved after a period of 30 minutes. Conversion decreases with increase of reactant flow rate due to decrease of residence time. The stirrer rate has a positive effect on the conversion and rate constant. Specific rate constant and conversion increase with temperature within the studied temperature range. Within the range of reactor volume selected for analysis, conversion increases with increase in reactor volume. The results obtained in this study may be helpful in maximizing the conversion of ethyl acetate saponification reaction at industrial scale in a CSTR.
***Keywords*–** Conductivity, Conversion, CSTR, Hydrolysis, Saponification**.**

I. Introduction

There are several types of reactors used in chemical or biochemical industries. Continuous stirred tank reactors in the form of either single tank or (or more often) tanks in series, are used widely and these are particular suitable for liquid phase reactions. These types of reactors are used generally in the organic chemicals industry and advantages include consistent product quality as compared with other type of reactors.

The hydrolysis of a fat or oil in alkaline condition produces soap for cleaning purpose and the reaction which occurs in the alkaline conditions is called saponification [1]. Saponification is the hydrolysis of an ester under basic conditions to form an alcohol and the salt of a carboxylic acid (carboxylates) and it is commonly used to refer to the reaction of a metallic alkali with a fat or oil to form soap. Thus, the hydrolysis of ethyl acetate ($CH_3OOC_2H_5$) by sodium hydroxide (NaOH) to produce sodium acetate (CH_3COON_A) and ethanol (C_2H_5OH) is saponification reaction although the end product is not soap. There are so many studies available in the literature on the process improvement for this saponification reaction.

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

The hydrolysis of ethyl acetate is one of the most well-known reactions and it is represented as a model of second order reaction in the literature dealing with chemical kinetics [2].This saponification reaction has been studied by several investigators at different temperatures using a variety of measurement techniques [3-4]. The technique reported by Walker [5] depends on conductometric measurements to determine the composition at any given time. This conductometric technique avoids periodic withdrawal of samples for analysis.

Investigators [6-7] focused their attention on online data acquisition using a conductometric technique to make the methodology much simpler. Various studies have been conducted by several investigators and data exhibit wide scatter in the saponification reaction of ethyl acetate and sodium hydroxide.

Kinetic studies on the saponification of ethyl acetate using innovative conductivity-monitoring instruments have been carried out by the investigator [8]. Rate constants of the saponification reaction in the temperature range at various temperatures (35-55 ^{0}C) were determined and it is noticed that results obtained are in agreement with some of the literature data. Modelling and simulation study of the CSTR for complex reaction has been carried out by the investigator [9] to determine the optimum operating conditions.

The effect of processing conditions on the performance of continuous stirred tank-ultrafiltration (CSTR-UF) was investigated [10] and it is found that lactose concentration in the permeate decreases with time due to concentration polarization and hydrolysis. The comparative study of acid–base ethyl acetate saponification reaction and an oxidation –reduction reaction has been carried out in a batch and semi-batch reactor [11]. Results obtained show that it is possible to operate the reactor in both modes of operation (batch and semi batch) for saponification reaction.

II. Materials and Methods

2.1 Chemicals

All chemical used to carry out research work are of AR grade. Ethyl acetate (99.5 %) from Sigma-Aldrich company and sodium hydroxide (98.0-100%) from Panreac Quimics company were used to carry out saponification reaction. The stock solutions of sodium hydroxide NaOH (~ 0.1 M) and ethyl acetate $CH_3COOC_2H_5$ (~ 0.1 M) were prepared using high purity distilled water.

2.2 Experimental Setup

The schematic diagram of the continuous stirred tank reactor (CSTR) unit is shown in Fig.1. The CSTR (ID: 0.153 m, maximum vessel depth: 0.108 m, maximum volume: 2.0 L) obtained from Armfield (U.K.), has been used for the experiments and specially designed to allow detailed study of the process. The reactor vessel is set on the base plate which is designed to be located on the four studs of the reactor service unit.

A stainless steel coil inside the reactor provides the heat transfer for heating the chemical reactants. A turbine agitator works in the conjunction with a baffle arrangement to provide efficient mixing and heat transfer. The agitator is driven by an electric motor mounted on the lid of the reactor and motor is driven by a variable speed unit. Glands in the reactor lid house the conductivity and temperature sensors with service unit.

Saponification reaction of ethyl acetate and sodium hydroxide is monitored by conductivity probe as the conductivity of the solution changes with conversion of reactant to product. Temperature in the reactor is controlled by circulating hot water through internal coil and monitored via PID controller

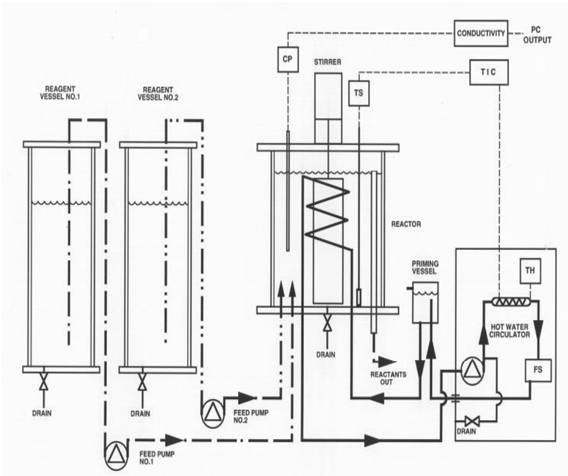

Figure 1 Schematic diagram of continuous stirred tank reactor (CSTR)

Priming vessel is used to fill the priming vessel and back into the hot water circulator. Stirring rate is adjusted by agitator speed control mounted with service unit. Two variables throughput peristaltic pumps are used to control the feed flow rate of reactants from the storage vessels and these pumps are calibrated so that exact flow rates can be maintained.

2.3 Experimental Procedure

Stock solutions of NaOH (~ 0.1M) and $CH_3COOC_2H_5$ (~ 0.1 M) are prepared to carry out the experiments at different operating conditions. Chemical reagents are pumped from the two feed tanks into the reactors separately in the base of reactor. As the reactants are pumped into the reactor, the level increases until it finally overflows the stand pipe.

After attaining desired operating conditions in the reactor, real time conductivity was monitored as displayed on control console. The extent of conversion of the reactants and hence the specific rate constant is determined using conductivity. Thus the sodium acetate, which is formed as a product in the above reaction, attributes for the conductivity at infinite time.

III. Results and Discussion

3.1 Steady state condition

Feed flow rates of 40 ml/min NaOH and 40 ml/min $CH_3COOC_2H_5$ were adjusted using peristaltic pumps. Solutions of concentration 0.1 M NaOH and 0.1 M $CH_3COOC_2H_5$ were used in the experiments. Saponification reaction was carried out at a constant temperature of 30 ^{0}C and with stirrer speed of 130 rpm. Real time conductivity of reaction mixture was recorded at every 5 minutes interval until steady state condition is reached.

The steady state condition is reached after a time period of 30 minutes from the start of experiment. Both sodium hydroxide and sodium acetate contribute conductance to the reaction solution whilst ethyl acetate and ethyl alcohol do not. The conductivity of a hydroxide solution at a given concentration and temperature, however, is not the same as that of a sodium acetate solution at the same morality and conversion. The variation of conductivity with time is shown in fig. 2.

The calculations are best carried out using spreadsheet. Conductivity of the reaction mixture decreases with time as reaction proceeds and it attains a steady state value of conductivity after a interval of about 30 minutes time. This is because as the reaction proceeds, concentration of NaOH

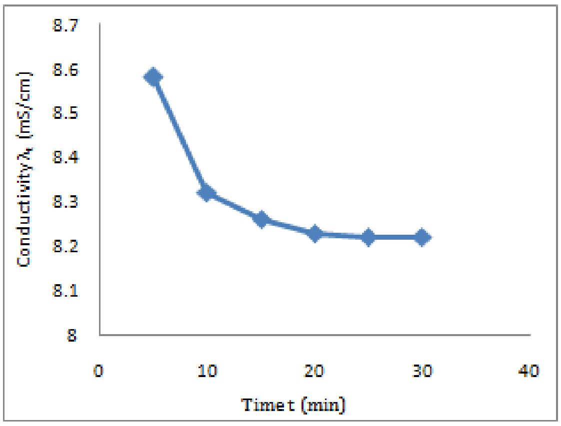

Figure 2 Conductivity vs. time curve for $CH_3COOC_2H_5$ hydrolysis with NaOH

decreases resulting a decrease of conductivity values. Conversion of sodium hydroxide X of 0.45 and specific rate constant k ~ 4.15 x 10^{-2} dm^3/mol.sec obtained at steady state conditions.

3.2 Effect of reactants flow rate

Influence of reactants flow rate on the conversion and specific rate constant have been studied. Three different feed flow rates i.e. 40 ml/min, 50 ml/min and 60 ml/min selected to study the hydrolysis reaction. Experiment was conducted at a constant temperature of 35 ^{0}C and stirrer rate of 130 rpm. Real time conductivity data was recorded with reactants flow rate. Fig.3 shows the variation of specific rate constant and conversion with reactant flow rates .The specific rate constant first increases up to 5.27 x10^{-2} dm^3/mol.sec at reactants flow rates

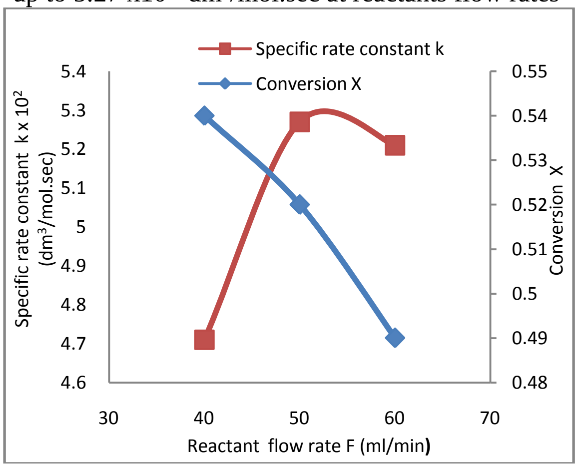

Figure 3 Effect of reactant flow rates on rate constant and conversion

of 50 ml/min and then starts decreasing. From the curve for conversion, it is clear that conversion decreases as flow rates of sodium hydroxide and ethyl acetate increase and reaches a value of 49% at flow rate of 60 ml/min of both reactants. This is because as flow rates of reactants are increased, the residence time decreases resulting in decrease of conversion value. It means that higher reactants flow rates are not always desirable for practical application.

3.3 Effect of Stirrer rate

Experiment was conducted at a flow rates of both sodium hydroxide and ethyl acetate equal to 60 ml/min. Temperature and volume of the reactor were adjusted at 30 ^{0}C and 1.43 dm^3 respectively. Fig. 4 shows the variation of conductivity and conversion with stirrer rate. Real time conductivity values were recorded and show a decline with stirrer rate and reach a value of 8.43 mS/cm at stirrer rate of 170

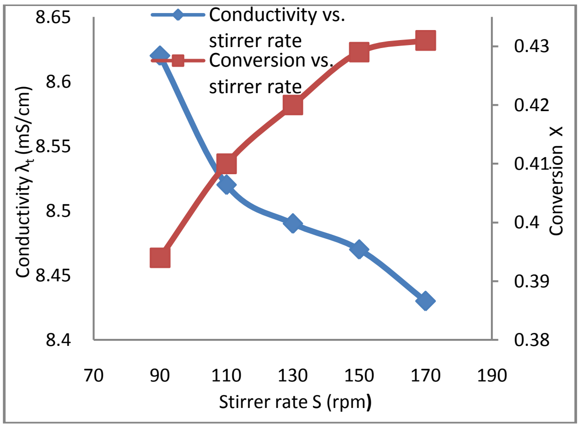

Figure 4 Variation of conductivity and conversion with stirrer rate

rpm. Dramatic decrease in conductivity values with stirrer rate highlight the significance of agitation and this result in achieving higher conversion as evident from the curve. The higher conversion achieved is 43.1 % at stirrer rate of 170 rpm as compared to conversion of 39.4% at stirrer rate of 90 rpm. Stirrer in conjunction with baffle arrangement is necessary for maintaining the uniform temperature throughout the reactor and hence the conversion of the reaction.

3.4 Effect of Temperature

Experiment was conducted at flow rate of 40 ml/min of both reactants i.e. sodium NaOH and $CH_3COOC_2H_5$ and with stirrer rate of 130 rpm. Volume of the reactor was adjusted and kept equal to 1.43 dm^3.Variation of conversion and specific rate with temperature is shown in fig. 5.The specific rate constant is a strong function of reaction temperature and variation is almost linear as shown in figure and its value varies from 3.69x10^{-2} dm^3/mol.sec at a temperature of 25 ^{0}C to 8.49 x10^{-2} dm^3/mol.sec at a temperature of 35 ^{0}C.Conversion of saponification

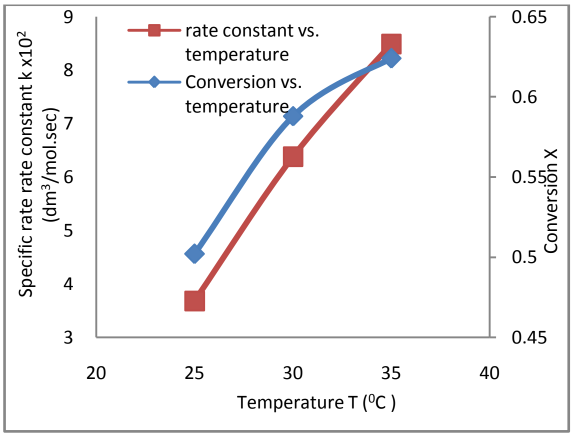

Figure 5 Specific rate constant and conversion vs. temperature curves

reaction is also increases with increase of reaction temperature. Change of conversion with temperature is not as much profound as in case of specific rate constant. Conversion attains a value of 63.3 % at 35 ^{0}C as compared to conversion of 50.2 % at a temperature of 25 ^{0}C.

3.5 Effect of reactor volume

Experiment was conducted to analyze the effect of reactor volume on conversion and specific rate constant. Volumetric reactant flow rate of 40 ml/min was selected for both the reactants and a reaction temperature of 30 ^{0}C was maintained at a stirrer rate of 130 rpm.

The effect of reactor volume on CSTR performance has been studied as shown in fig. 6.The specific rate constant varies almost linearly with reactor volume and it reaches a value of 4.71x10^{-2} dm^3/mol.sec at a volume of 2.06 dm^3 as compared to a value of 3.84 x10^{-2} dm^3/mol.sec at a reactor volume of 1.26 dm^3.It is also clear from the conversion vs. volume curve

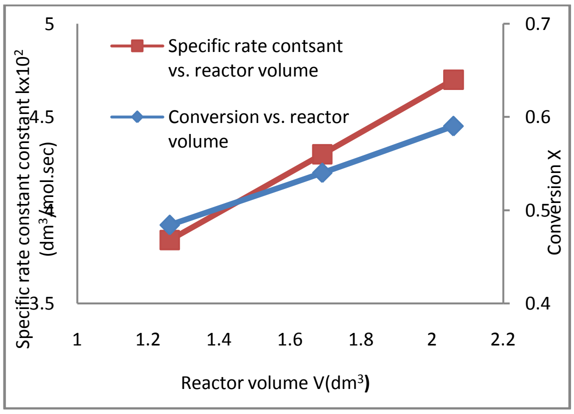

Figure 6 Variation of rate constant and conversion with reactor volume

that conversion increases from 48.4 % to almost 59% for a change of reactor volume from 1.26 dm^3 to 2.06 dm^3. More experimental work must be carried out to determine the optimum volume of the reactor.

IV. Conclusion

In this investigation, hydrolysis of ethyl acetate (~ 0.1 M) with sodium hydroxide (~0.1 M) has been studied. Progress of the saponification reaction was monitored by recording real time conductivity data under different operating conditions. Both sodium hydroxide and sodium acetate contribute conductance to the reaction. All the experiments were conducted at a pressure of 1 atmosphere. The influence of operating conditions like reactants flow rate, stirrer rate, reaction temperature and reactor volume on conversion and specific rate constant has been analyzed. The research findings may be summarized as follows:

- Decline in the value of real time conductivity with time indicates the progress of the hydrolysis reaction.
- Conversion value of 45 % and specific rate constant equal to 4.15 x10^{-2} dm^3/mol.sec were achieved under steady state condition after time interval of 30 minutes.
- The reaction conversion decreases with increase in reactants flow rate and this is because of decrease of residence time. On the other hand, value of specific rate constant first increases and then shows a decline with reactant flow rate.
- The conductivity decreases dramatically with stirrer rate and results in achieving higher conversion as evident from the curve. The stirrer is necessary to provide efficient mixing and maintain uniform temperature throughout the reactor.
- Specific rate constant and conversion increase almost linearly with temperature. Conversion increases from 50.2 % to 58.8 % corresponding to a temperature change from 25 ^{0}C to 30 ^{0}C. But for a reaction temperature more than 30 ^{0}C, behaviour of conversion change became more sluggish.
- Increase of reactor volume also has positive effect on the conversion and specific rate constant. Conversion and rate constant increase with increase in volume from 1.26 dm^3 to 2.06 dm^3.

V. Acknowledgement

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