

Experimental Study of the Influence of Process Conditions on Tubular Reactor Performance

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Abstract

This work presents an experimental study of the saponification reaction of ethyl acetate by sodium hydroxide in a tubular reactor at 1 atmosphere (atm) of pressure. The objective of this study is to analyze the effect of operating conditions on the rate constant and conversion in order to explore the tubular reactor performance. The temperature, reactant flow rate, and residence time are the parameters considered for analyzing the reactor performance. The steady-state conversion is achieved after a period of 30 minutes. Conversion decreases with the increased reactant flow rate, owing to the resulting decrease in residence time. The rate constant first decreases and then increases with feed flow rate. The rate constant and conversion increase with increased temperature within the studied temperature range. The residence time declines with increased reactants flow rates leading to decreased NaOH conversion. The obtained NaOH conversion values at different temperatures have been compared with literature data. The outcomes of this study may be useful in maximizing the conversion of ethyl acetate saponification reaction for industrial scale synthesis of sodium acetate and ethanol synthesis in a tubular reactor

Keywords: Saponification; Plug flow reactor (PFR); Conductivity; Conversion; Hydrolysis.

1. Introduction

Several types of reactors are used in chemical or petrochemical industries. Plug flow reactors (PFRs), also known as continuous tubular reactors, play a key role in chemical industries. Tubular reactors are often used when continuous operation is required but back-mixing of products and reactants is not desired. The use of plug flow reactors becomes especially important when continuous large-scale production is needed. PFRs are associated with high volumetric unit conversion because the occurrence of side

reactions is minimal. In plug flow reactors, reactants are fed from one end of reactor and flows continuously through the length of reactor as a series of plugs and the products are discharged from the other end of reactor.

Advantages of PFRs include high volumetric unit conversion and the capability of running for longer periods without any maintenance or less maintenance. For the same conversion and reaction conditions, PFR volume is usually lower than CSTR volume for isothermal reactions greater than zero order (Fogler, 2006). For the industrial

application, PFRs can be assembled as a single long tube or in the form of a coil. PFRs are extensively used in the industry for gaseous/liquid phase systems. PFRs are commonly used for gasoline production, oil cracking, oxidation of sulphur dioxide to sulphur trioxide, synthesis of ammonia and polymer manufacturing along with other applications.

According to Bursali et al., 2006, the hydrolysis of a fat or oil in alkaline condition produces soap and the reaction that occurs in alkaline conditions is known as saponification. Hydrolysis of an ester to produce an alcohol and the salt of a carboxylic acid, under basic conditions, is called saponification and it is normally referred as the reaction of antacid in the presence of fat/oil to produce soap. Saponification is the hydrolysis of ethyl acetate by sodium hydroxide to produce sodium acetate and ethanol. A lot of studies are available in the literature on the process improvement of this saponification reaction.

The effect of operating conditions on CSTR performance for ethyl acetate saponification has been investigated experimentally by Danish et al., 2015. The parameters selected for analysis were temperature, feed flow rate, residence time, reactor volume and stirrer rate. It was found that conversion decreases with increased flow rate due to decrease of residence time and agitation rate has a positive effect on the conversion and rate constant. It was also concluded that specific rate constant and conversion increases with increased temperature within the studied range.

The hydrolysis of ethyl acetate is one of the most important reactions, and it is characterized as second-order reaction in the literature (e.g. Kapoor, 2004). Various measurement techniques (Daniels et al., 1941; Schneider et al., 2005) have been used by several investigators at different temperatures to study saponification reaction. The techniques depend on the conductometric measurements to evaluate the composition at any time was reported by Walker, 1906 and this measurement approach circumvents regular removal of product samples for analysis.

Tsujikawa et al. 1966 estimated the rate constant and activated energy at an initial temperature of 25 °C as 0.112×10^{-3} m³/mol. sec and 8.37 KJ/mol respectively for alkaline hydrolysis of ethyl acetate in a polyethylene batch reactor. It was also observed that the reaction rate of ethyl acetate saponification is not expressed adequately by a second-order rate equation as given in literature (e.g Kapoor, 2004).

Other investigators focused their attention on online data recording, using a conductivity measurement technique to make the procedure much simpler. Researchers have conducted several studies on saponification reaction; the data exhibit wide scatter for the saponification of ethyl acetate with sodium hydroxide. Kuheli et al. 2011 conducted studies on the saponification of ethyl acetate by utilizing innovative conductivity-monitoring instruments. Rate constants of the saponification reaction at various

temperatures (range, 35°C to 55°C) were evaluated, and observed that outcomes were in agreement with some of the data reported in literature.

Ahmad et al. 2013 carried out a comparative study of ethyl acetate hydrolysis using full two level factorial design in batch (volume: $1 \times 10^{-3} \text{ m}^3$ and plug flow reactors (volume: $0.4 \times 10^{-3} \text{ m}^3$). The maximum fractional conversion of 0.97 was obtained at a residence time of 300 seconds in both type of reactors under optimum concentrations of NaOH (0.01 mol/L) and CH_3COONa (0.07 mol/L). It was also concluded that reaction conversion increases positively with increased absolute initial concentration of $\text{CH}_3\text{COOC}_2\text{H}_5$.

Saponification of ethyl acetate by sodium hydroxide to optimize the conversion in a continuous stirred tank reactor (CSTR) has been studied using two level factorial design and response surface methodology by Ullah et al., 2015. The maximum conversion of 96.71 % was obtained corresponding to sodium hydroxide and ethyl acetate concentration of 0.01 mol/L and 0.1 mol/L while it was suggested that the influence of feed ratio, agitation rate and temperature was insignificant which contradicts the findings (effect of reaction temperature on conversion) of other researchers (Wijayarathne et al., 2014; Danish et al., 2015). On other hand, the reactants concentration to maximize the conversion of sodium hydroxide reported by Ahmed et al. 2013 was different from the concentrations calculated by Ullah et al. 2015.

A comparative study of ethyl acetate saponification and an-oxidation-reduction reaction has been conducted in a batch and semibatch reactor by Grau et al., 2002. It was concluded that it is practicable to operate the reactor in both modes of operation to study the saponification reaction.

Hydrolysis of ethyl acetate by sodium hydroxide in a tubular reactor using Aspen Plus has been investigated by Wijayarathne and Wasalathilake, 2014. The simulated results were verified by the experimental data and it proves that predicted results were in agreement satisfactorily with experimental results. The model developed can be used as a reference to comprehend reaction kinetics of plug flow reactor. The objective of the current study is to investigate the influence of operating conditions on tubular reactor performance using hydrolysis of ethyl acetate by sodium hydroxide. The temperature, reactant flow rates and residence time are the parameters considered for analyzing the influence on steady-state conversion of NaOH and rate constant. The obtained result of sodium hydroxide conversion as a function of temperature of reaction mixture has been compared with literature data (Wijayarathne et al. 2014) in order to validate the outcome of current study.

2. Materials and methods

2.1 Chemicals

Analytical-grade reagents (AR) were used to carry out the research work. Ethyl acetate of purity 99.5% and sodium hydroxide of

concentration 98.0%-100% were utilized to conduct the experiments. The distilled water generated using distilled water unit (Type 2008,GFL) was used to prepare the solutions of sodium hydroxide NaOH (~ 0.1 M) and ethyl acetate $\text{CH}_3\text{COOC}_2\text{H}_5$ (~ 0.1 M).

2.2 Experimental Setup

The tubular reactor (reactor coil: length—20.9 m; internal diameter— 5.0×10^{-3} m; total volume of reactor V — 0.41×10^{-3} m³) obtained from Armfield (U.K.) has been used for the experiments for the investigation as shown in Fig.1 and designed properly to facilitate the detailed study.

The tubular reactor in which the chemical reaction takes place made up of a pliable coil. The volume of the reactor in the form of coil is 0.41×10^{-3} m³. The conductivity and temperature sensors are inserted into the gland for online data acquisition. In order to conduct an experiment at a fixed

temperature, the reactor coil is immersed in water, which is maintained at a fixed temperature by temperature controller. Water enters the reactor through non-return valve and this valve prevents water draining back from reactor when pump is under switch off position.

The reactants i.e. NaOH and $\text{CH}_3\text{COOC}_2\text{H}_5$ enter the reactor coil from one end and leave the reactor vessel through the other end of the coil. The conductivity probe housing allows the conductivity probe to be fixed in the stream of products mixture coming out from the reactor coil. The progress of the hydrolysis reaction is recorded by conductivity probe as the conductivity of solution varies with conversion. The conductance of the reaction mixture varies with conversion. Priming vessel attached with reactor service unit is used to fill the reactor coil and returned back into the hot water circulator system. The reactants flow rates from the storage vessel

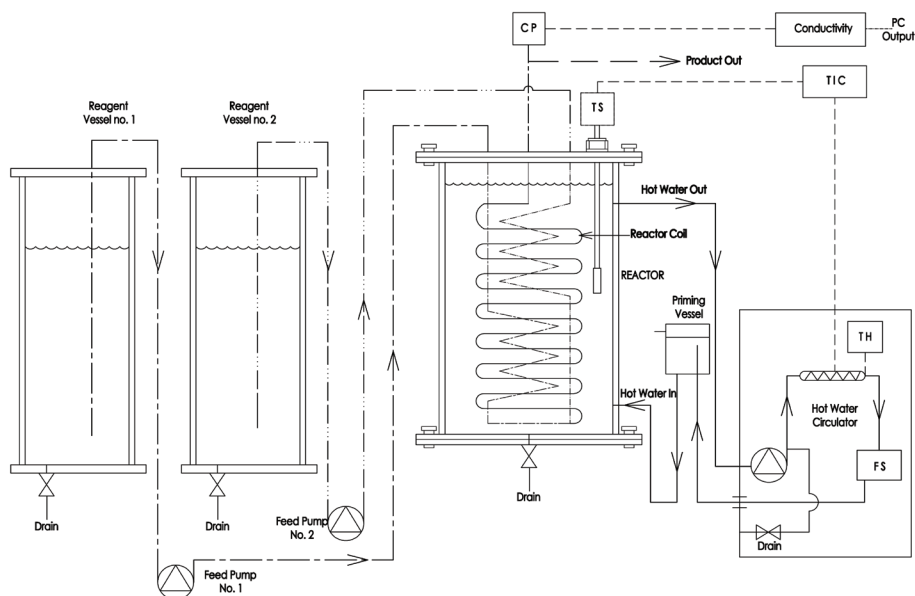


Fig. 1: Setup diagram of tubular reactor (adopted from Armfield, U.K.)

are controlled by using two peristaltic pumps; these pumps are calibrated so that any desired reactants flow rate can be adjusted.

2.3 Experimental Procedure

Solutions of sodium hydroxide and ethyl acetate were prepared to perform the experiments under different process conditions. Two peristaltic pumps were used to pump the reactant from feed tanks and enter the reactor vessel. The reactants pass through pre-heating coils submerged in the water; here, the reactants are individually brought up to the desired reaction temperature. The reactants are mixed together at the inlet of reactor coil and reaction proceeds as reaction mixture pass through the reactor coil.

After acquiring the required process conditions in the reactor, actual-time conductivity was recorded by the probe and displayed on control panel. The degree of conversion and hence, rate constant are tabulated by utilizing the conductivity data. One of the products of saponification reaction i.e. the sodium acetate ascribes for the conductivity after infinite time.

3. Results and Discussion

3.1 Steady-State Condition

Feed flow rates of $13.33 \times 10^{-7} \text{ m}^3/\text{sec}$ sodium hydroxide and $13.33 \times 10^{-7} \text{ m}^3/\text{sec}$ ethyl acetate were fixed using peristaltic pumps. Solutions of 0.1M NaOH and 0.1M $\text{CH}_3\text{COOC}_2\text{H}_5$ were used for conducting the experiments; and the saponification reaction were performed at a fixed temperature of 30°C . Conductance of reaction mixture was recorded

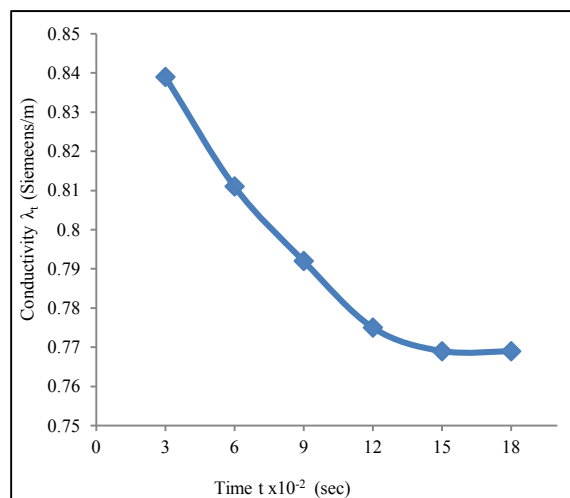


Fig.2: Conductivity versus time curve for $\text{CH}_3\text{COOC}_2\text{H}_5$ hydrolysis by NaOH

at 5-minute intervals until steady-state condition was reached. The steady-state condition was reached after 30 minutes as shown in Fig.2.

Sodium hydroxide and sodium acetate contributed conductance to the reaction mixture and on the other hand, ethyl acetate and ethyl alcohol do not. The sodium hydroxide solution conductivity at a given concentration and temperature is not equal to that of CH_3COON_A solution at the same concentration and reaction conversion.

The rate constant and reaction conversion were calculated at steady-state conditions. Reaction mixture conductivity decreases with time as the reaction proceeds, and it attains a steady-state value of conductivity after approximately 30 minutes. This occurs because as the reaction proceeds, the concentration of NaOH decreases, resulting in decreased conductivity values. A conversion of sodium hydroxide $X \sim 0.727$; and rate constant $k \sim 1.27 \times 10^{-3} \text{ m}^3/\text{mol}\cdot\text{sec}$ were obtained under steady state conditions.

3.2 Reactant Flow Rate

Influence of the flow rates of NaOH and CH₃COOC₂H₅ on the conversion and rate constant were investigated. Three different feed flow rates (i.e. 6.67x10⁻⁷ m³/sec, 8.33x10⁻⁷ m³/sec and 10.0x10⁻⁷ m³/sec) were selected to analyze the reaction performance and the experiments were conducted at a fixed temperature of 30°C. Actual-time conductivity data were collected with the different flow rates. Fig.3 shows the variation of conductivity and conversion with various reactant flow rates.

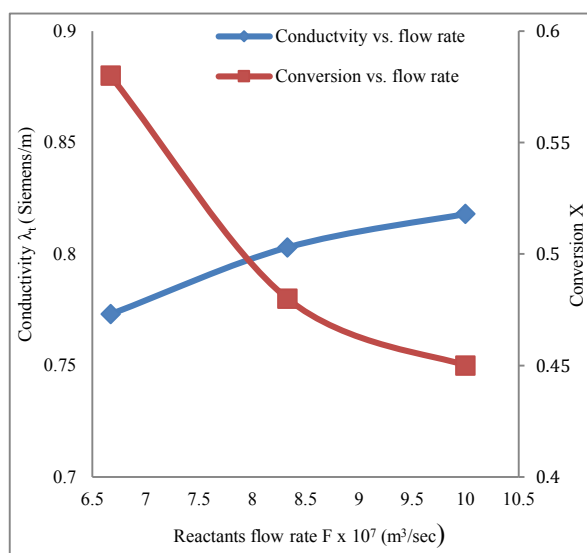


Fig.3: Effect of reactant flow rates on conductivity and conversion

The conductivity increases with reactant flow rate upto 0.818 Siemens/m at flow rates of both reactants equal to 10.0x10⁻⁷ m³/sec as compared with 0.773 Siemens/m at a flow rate of 6.67x10⁻⁷ m³/sec. A decrease of conductivity with an increased feed flow rate signifies the formation of less desired products. The conversion curve shows a decline with increased flow rate. Conversion

reaches a value of X~ 45% at a flow rate of 10.0x10⁻⁷ m³/sec in comparison with a value of X~ 58 % at a flow rate of 6.67x10⁻⁷ m³/sec.

Residence time decreases with increased reactant flow rate and reaches a value of 205 sec at a flow rate of 10.0x10⁻⁷ m³/sec of both sodium hydroxide and ethyl acetate, as shown in Fig.4. As flow rates of reactants are increased, residence time decreases, resulting in decreased conversion value. Thus higher reactants flow rates are not always desirable for practical application.

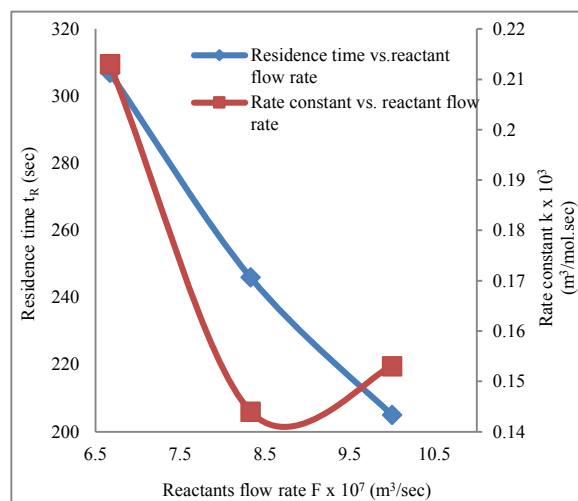


Fig. 4: Variation of residence time and rate constant with reactants flow rate

3.3 Temperature

The experiment was conducted at a flow rate of 10.0x10⁻⁷ m³/sec for both reactants i.e., NaOH and CH₃COOC₂H₅. Concentration of both reactants was adjusted equal to 0.1 M NaOH and 0.1 M CH₃COOC₂H₅. Variation of rate constant and conversion with temperature is shown in Figure 5. It is found that the reaction conversion is a strong function of

reaction temperature, and variation is almost linear.

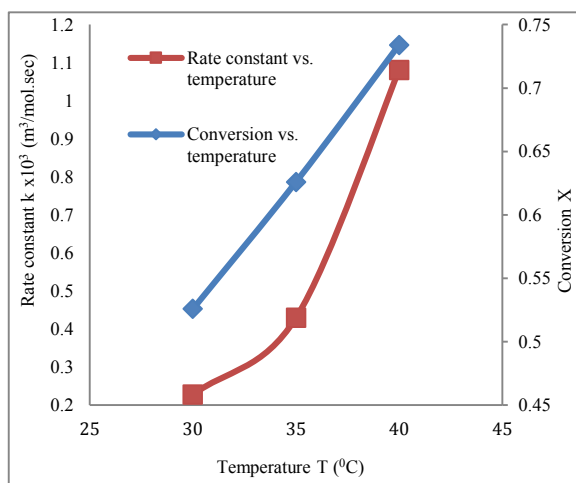


Fig.5: Rate constant and conversion versus temperature curves

Conversion varies from 52.6% at a temperature of 30 °C to 73.4% at a temperature of 40 °C. The rate constant of the saponification reaction increased from 0.228×10^{-3} m³/mol.sec to 1.081×10^{-3} m³/mol.sec with an increased temperature from 30 °C to 40 °C respectively. The change in conversion with temperature is more profound than the change with specific rate constant.

The results obtained at different temperatures of reaction mixture have been compared with findings reported by Wijayarathne et al. 2014 as shown in Fig. 6. Results reported by Wijayarathne et al. 2014 were obtained under a flow rate of 6.67×10^{-7} m³/s with a reactor volume of 0.44×10^{-3} m³. The NaOH conversion reported by Wijayarathne et al. 2014 is higher (80 % at 40 °C) compared with the value obtained in present

study (73.4 % at 40 °C) and it may be due to the large volume of reaction mixture and lower reactant flow rate compared with. Residence time increases with decreased flow rate and this leads to increased reaction conversion.

The effect of reaction mixture temperatures on reactor performance have not been explored by the researchers (Ahmed et al. 2013) although it was suggested that conversion increases with increased temperatures of reaction mixtures (Ullah et al., 2015; Wijayarathne et al., 2014).

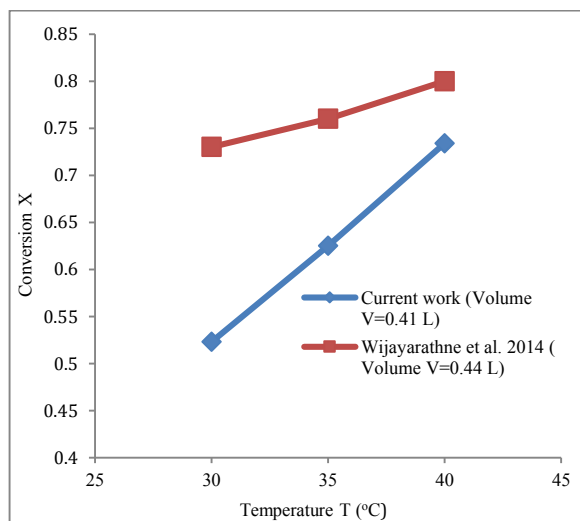


Fig.6: Comparison of NaOH conversion at different temperatures of reaction mixture with literature data (Wijayarathne et al. 2014)

4. Conclusions

In this investigation, hydrolysis of ethyl acetate (~0.1 M) with sodium hydroxide (~0.1 M) has been studied. The advancement of the saponification reaction was observed by monitoring conductivity data under different process conditions. Sodium hydroxide and sodium acetate impart conductance to the

hydrolysis reaction. Experiments were performed at a pressure of 1 atmosphere (atm) and a concentration of 0.1 M of both reactants. The influence of operating conditions such as reactant flow rate, residence time, and temperature on conversion and specific rate constant has been analyzed. The research outcomes may be outlined as follows:

- Decline in the value of actual time conductivity with time signifies the progress of the hydrolysis reaction.
- A steady-state conversion value of 72.7% and specific rate constant equal to 1.27×10^{-3} m³/mol.sec were achieved after time interval of 30 minutes.
- The reaction conversion diminishes with an increased reactant flow rate; this is due to the decrease of residence time.
- On the other hand, the rate constant first decreases and then increases within the studied range of reactant flow rates.
- Conversion increases almost linearly with temperature, from 0.526 to 0.734 for a temperature change from 30°C to 40°C. The maximum fractional conversion of 0.734 was achieved at a temperature of 40 °C under studied range of temperatures.
- The specific rate constant also increases with increased temperature but not as profoundly as does conversion.

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Nomenclature

M	Reactants concentration	mol/liter
V	Volume of reactor	m ³
F	Reactant flow rate	m ³ /sec
X	Reaction conversion	(-)
t _r	Residence time	sec
k	Rate constant	m ³ /mol.sec
T	Temperature	°C
t	Time	sec

Greek Symbols

λ	Conductivity	Siemens/m
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