THE EFFECT OF REACTANTS' INITIAL TEMPERATURES ON THE RATE CONSTANT AND CONVERSION OF SAPONIFICATION REACTION TAKING PLACE IN A NON-ISOTHERMAL AND NON-ADIABATIC BATCH REACTOR

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Abstract

This experimental research studied the saponification reaction of ethyl acetate with sodium hydroxide, which was carried out in a well-agitated non-isothermal and non-adiabatic batch reactor. As no isolation system was provided in this experiment, this study investigated other routes for boosting the reactants conversion. Subsequently, the effect of initial feed temperatures on the reaction rate constant and reaction conversion was assessed. For this purposes, the reaction rates of equimolar reactants were measured when they were heated from 20°C (ambient temperature) to 30°C, 40°C and 50°C. The decrease in the reactants concentrations throughout the reaction durationwas determined at equal time intervals by recording the electrical conductivity data of the reaction mixture. The results were represented graphically for time-conversion, temperature-conversion and temperature-rate constants profiles. They had shown that the reaction rate constant increased with rising of the initial feed temperatures. Even though, the conversion was boosted when the reactants were initially heated above 20°C, no significant change in conversion was achieved between 30, 40, and 50°C. The resulted value of activation energy was about 50 % less than the most accurate published values.

Keywords: Saponification reaction; batch reactor; rate constant; conversion.

Introduction

Saponification is commonly referred to as t he hydrolysis of a fat or oil in alkalinemedium to manufacture cleaning soap. The products of the saponification reactions have variety of applications such as textile, cosmetics, and paint industries. Even though, theend product is not soap, the hydrolysis of ethyl acetate ($CH_3OOC_2H_5$) in the presence of sodium hydroxide (NaOH) toproduce sodium acetate (CH_3COONa) and ethanol (C_2H_5OH) is considered as a type of saponification reaction (BursaliN., et al., 2006 and Kapoor, K. 2004). The ethyl acetate saponification reaction equation is written as follows

$$\mathbf{NaOH + CH_3COOC_2H_5 \rightarrow CH_3COONa + C_2H_5OH} \qquad \mathbf{(1)}$$

$$\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C} + \mathbf{D}$$

The reaction rate of the hydrolysis of ethyl acetate is represented in the literatureas amodel of an irreversible second order reaction (i.e. the reaction law is a function of the both reactants concentrations). The rate law for this reaction is given below as follows (Ikhazuangbe, et al., 2015).

$$-\mathbf{r} = -\mathbf{r_A} = \mathbf{kC_AC_B} \qquad \textbf{(2)}$$

Where ($-r_A$) is the rate of consumption of the reactant A, k is the reaction rate constant, and C_A and C_B are the instantaneous concentrations of reactants A and B respectively. In order to determine the reactantsconcentration at any time, the electrical conductivity of the reaction solution is continuously recorded. This method is called the conduct-metric technique, which was reported by Walker (1906). The kinetics and reaction mechanism of this reaction have been reported in numerous studies. The saponification reaction was investigated and monitored in a batch-reactor by the continuous recording of the electrical conductivity of the reaction mixture (Tsujikawa and Inoue 1966). The reaction rate constant at 25°C was found 0.112 L/mol.sec and its activation energy was 11.56 kcal/mol (Kuheli et al. 2011). Another experimental research has been conducted by Danish et al. (2015) to evaluate the parameters of the Arrhenius equation for the same reaction in a batch reactor. The implementation of the saponification reaction of ethyl acetate and sodium hydroxide in a continuous stirred tank reactor has also been investigated by Danish, et al. where they investigated the effect of the reaction temperature (ranged from 25°C to 35°C) on the rate constant and conversion. They found that an approximately linear increase in the reaction rate constant and conversion as the reaction temperature increased. However, the conversion decreased with increasing reactants flow rate because of decreasing the residence time. Modeling and simulation study of ethyl acetate saponification in continuous reactors using Aspen Plus was done by Wijayarathne et al. 2014. There was a close agreement between the simulated and experimental results. Additionally, it was found that the reaction rate increased with increasing reaction temperature.

As the reaction will be carried out in non-isothermal and non-adiabatic conditions, therefore, neither reaction heat nor temperature will be maintained in the reactor container. This research aims to increase the reactants conversions even though if non-isolated batch reactor is used. The effect of initial heating of reactants on the reaction rate constant and conversion of the reactants will be reported. The activation energy of the studied reaction will be also estimated according to these imperfect conditions and the results will be compared with the reported literature studies.

Instrument Setup

A CSTR (Armfield, U.K) reactor will be used in this study and it will be adjusted to operate as a batch reactor by closing the feed inlet and products outlet connectors as showed in Figures (1) and (2). This adjustment will enable it to work as a closed system (i.e. batch reactor). The

reactant, A, concentration will be monitored throughout the reaction time by measuring the electrical conductivity through a conductivity sensor supported inside the reactor. An electrical digital water bath will be used to heat the reactants initially and prior to mixing them into the reactor tank.

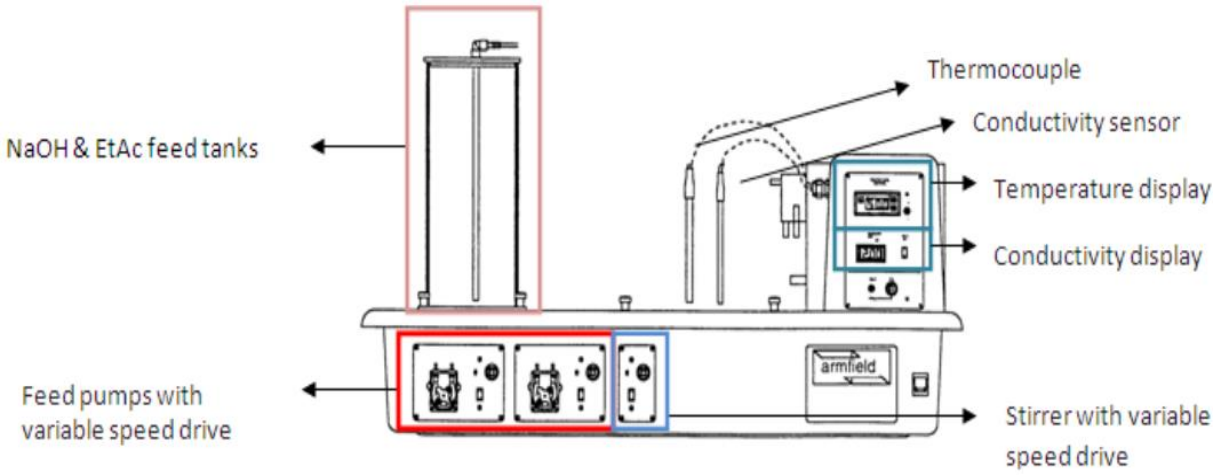


Figure (1): Batch Reactor Apparatus (Armfield CSTR instruction manual, 2006).

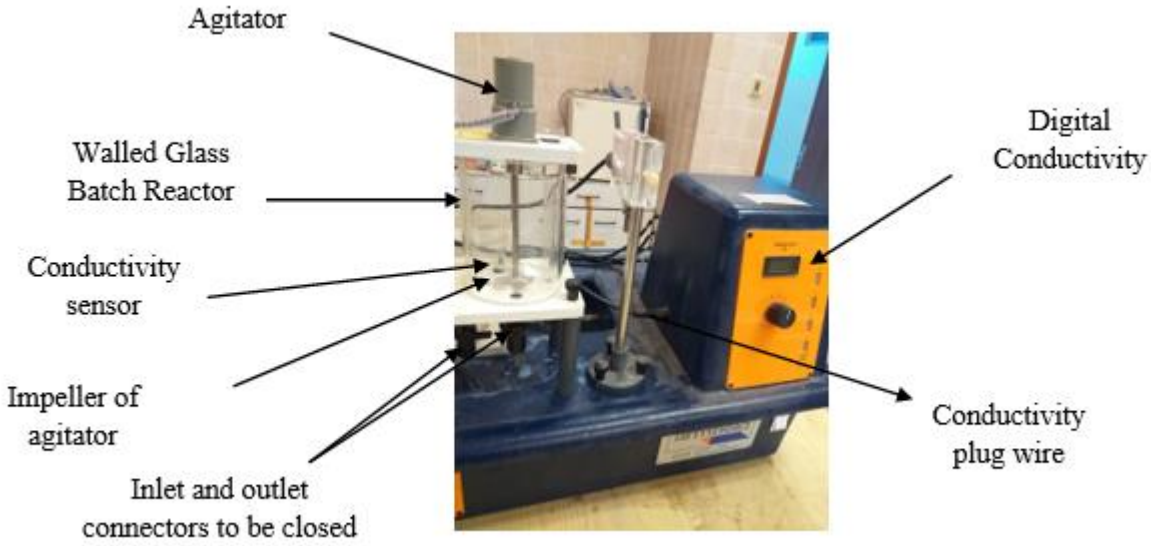


Figure (2): Armfield CSTR Reactor adjusted to work as a Batch Reactor used in this study.

Experimental Procedures and Methodology

Firstly, equimolar concentration solutions of (0.1 M) with 0.25 L of both reactants (ethyl acetate and sodium hydroxide) were prepared. Then, they were poured and mixed at once.

Once the saponification reaction had started, it was monitored immediately by recording the electrical conductivity of the reaction mixture along with reaction time. The collected electrical conductivity data of the chemical reaction were converted into concentration versus the reaction time. The initial reactants concentrations were fixed at 0.1 M in order to investigate the effect of reactants initial temperature on the reaction rate and conversion. The collected kinetic reaction rate data was used to estimate Arrhenius law parameters (i.e. the reaction activation energy, Ea, and the frequency factor, A_0,).

The Conductivity of the reaction mixture was recorded at different intervals of the reaction time. According to the chemical reaction mentioned above in equation1, sodium hydroxideNaOHin the reactants and sodium acetate CH_3COONa in the products are conducting charges where as the organic compounds of ethyl acetate $CH_3COOC_2H_5$ and ethanol C_2H_5OH are considered passive compounds because they have no effect on the conductivity resultant. Therefore, the overall conducitity at any time of the reaction was measured as in equation (3):

$$\boldsymbol{\Lambda = \Lambda_A + \Lambda_C} \qquad (\mathbf{3})$$

Where, Λ is the overall conductivity of the reaction mixture, Λ_A is the electrical conductivity of sodium hydroxide, and Λ_C is the electrical conductivity of sodium acetate. According to Armfield CSTR manual (2006), the measured values of the mixture electrical conductivity is mathematically converted into sodium hydroxide concentration and conversion by using equations4 and 5(Armfield CSTR instruction manual, 2006).

$$\boldsymbol{C_A = \left(C_{Af} - C_{A0}\right)\left[\frac{\Lambda_i - \Lambda_t}{\Lambda_i - \Lambda_\infty}\right] + C_{A0}} \qquad (\mathbf{4})$$

$$\boldsymbol{X_A = \frac{C_{A0} - C_A}{C_{A0}}} \qquad (\mathbf{5})$$

Where, C_A is the concentration of sodium hydroxide after a certain time (t) of the reaction, C_{Af} is the concentration of NaOH at completion of reaction, Λ_i is the initial reaction mixture conductivity at the starting of the reaction. mS, Λ_t is the recorded conductivity of the reaction mixture at a certain time of reaction. mS, Λ_∞ is the conductivity of the reaction mixture at a steady-state (i.e, the end of the reaction) mS, and X_A is sodium hydroxide`s conversion at any time during the saponification reaction.

A linear relationship between time and X_A/ (1-X_A) is achieved when the reaction is second. This linear relationship can be mathematically derived as follows

As it is know the conversion based on initial concentration

$$\mathbf{C_A = C_{A0}(1 - X_A)} \qquad \mathbf{(6)}$$

$$\mathbf{dC_A = -C_{A0}dX_A} \qquad \mathbf{(7)}$$

$$\mathbf{C_{A0} = C_{B0} \quad and \quad X_A = X_B} \qquad \mathbf{(8)}$$

By substituting in Eq. (2)

$$\frac{dX_A}{dt} = kC_{A0}(1 - X_A)^2 \qquad (9)$$

By integration of Eq. (9) from t = 0, to t = t,

$$\frac{X_A}{1-X_A} = kC_{A0}t \qquad (10)$$

Results and Discussion

The conductivity of reactionmixture had been recorded at every single minute intervaluntil the complete conversion condition was reached. The full conversion was achieved after approximately one hour. The change of the electrical conductivity with time is presented in Figure (3). The conductivity results were recorded since the begging of the reaction until 10 minutes to avoid high loss of heat from the reactor. As the reaction proceeded, more sodiumacetate was produced with less conductivity comparing to the conductivity of consumed sodium hydroxide. Thus, the solution conductivity decreased with time as it seems in the following chart.

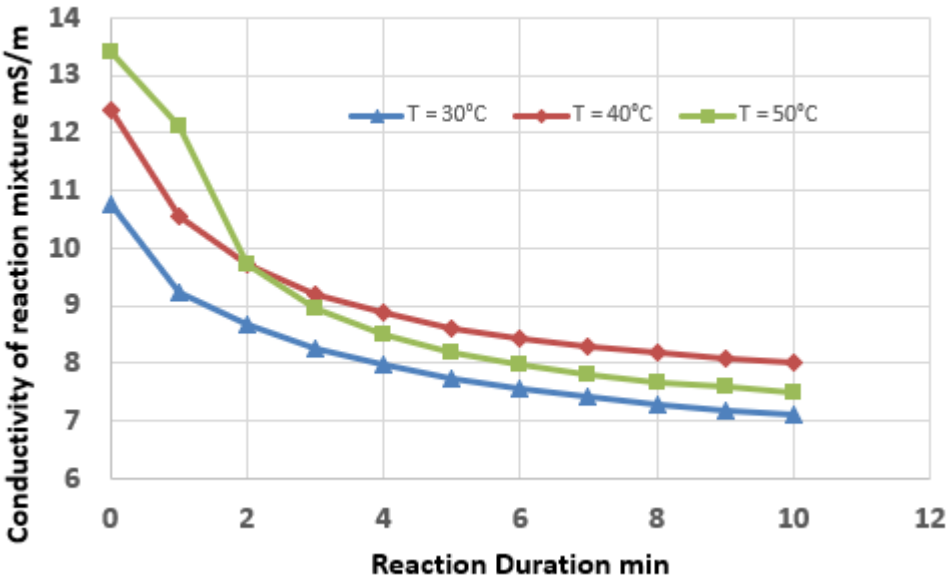


Figure (3): Conductivity Change with Time.

Representation of the conversion raise against time at each temperature is graphed in Figure (4). The general trend of the conversion curve indicates non-linear positive relationship between time and conversion. There is a wide variation in the final conversion at 10 minutes between the ambient temperature conversion, (0.8), and other higher temperatures conversions. However, when reactants were initially heated, and prior to mixing in the batch

reactor, to 30°C, 40°C and 50°C the conversions almost ended at the same point of 0.85. This can be attributed to the heat loss from the reactor. No significant change in conversion was achieved when operating between 30°C and 50°C.

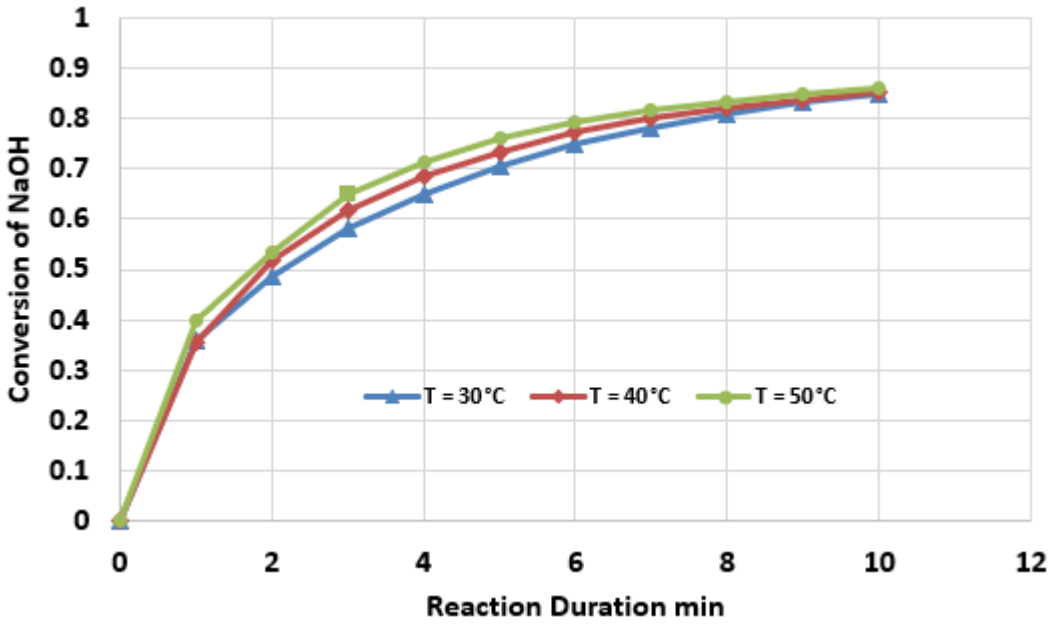


Figure (4): Conversion Change with Time and Temperature.

The saponification reaction is well known as a model of an elementary overall second order reaction. That means the mathematical solution of the rate equation should generate a linear relationship between time scalar and the inverse of the instaneous concentration ($1/C_A$), which is expressed in terms of conversion as (X/(1-X)). this strong linearity is almost confirmed by Figure (5) for all the temperatures tested. The reaction rate constant, k, was estimated at each temperature by fitting to straight line taking the slope and dividing by the initial concentration. The rate constant found at 20, 30, 40 and 50°C were 0.043, 0.080, 0.096 and 0.105 L/mol/s respectively.

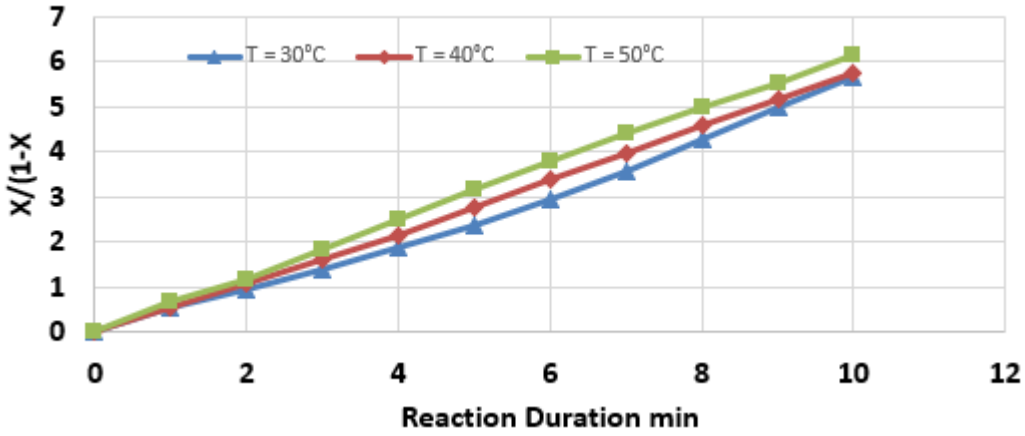


Figure (5): Change of Concentration Inverse (as Conversion) with Time.

The effect of temperature on the reaction rate constant is shown in Figure (6). The experiments were run for 10 minutes to avoid heat losing from the reactor. The specific rate constant increased from 0.043 L/mol s at 20°C (not used in previous figures) to 0.105 L/mol s at 50°C. The current study results are compared with the experimental work results of Çitak and Kivrak, 2019. The differences in the outcomes between the two studies are understood due to insufficient isolation (non-isothermal operation) of the reactor system at which the reaction temperature could not be maintained throughout the reaction time. The reaction`s rate constant change with temperature was used to calculate the parameters of Arrhenius equation, the frequency factor and the reaction activation energy. It was done by plotting the inverse of absolute temperature against the natural logarithm of the rate constant values, Figure (6). Even thought, the ideal results should generate a straight line with a negative slope for this correlation, the deviations shown in the figure can be attributed to the imperfect conditions of the experiment. The calculated activation energy was 22780 J/mol which is less than the real value by about 50%. The activation energy with the value of 29775 J/mol was obtained by Çitak and Kivrak 2019.

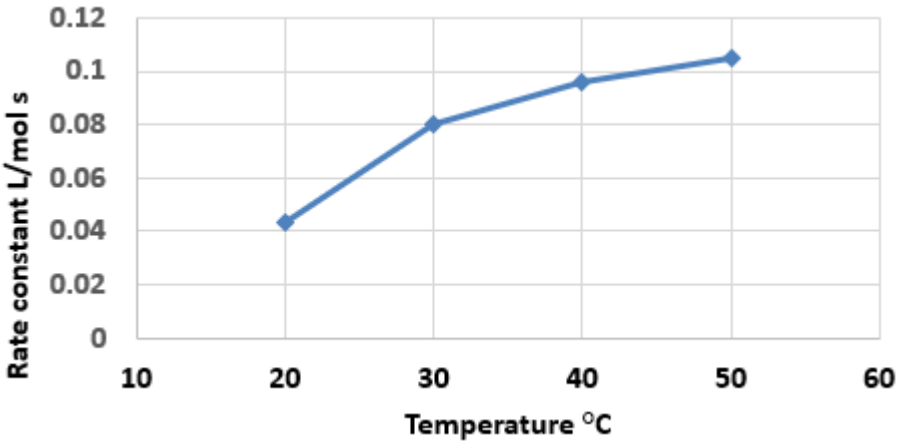


Figure (6): Change of Rate Constant with Temperature.

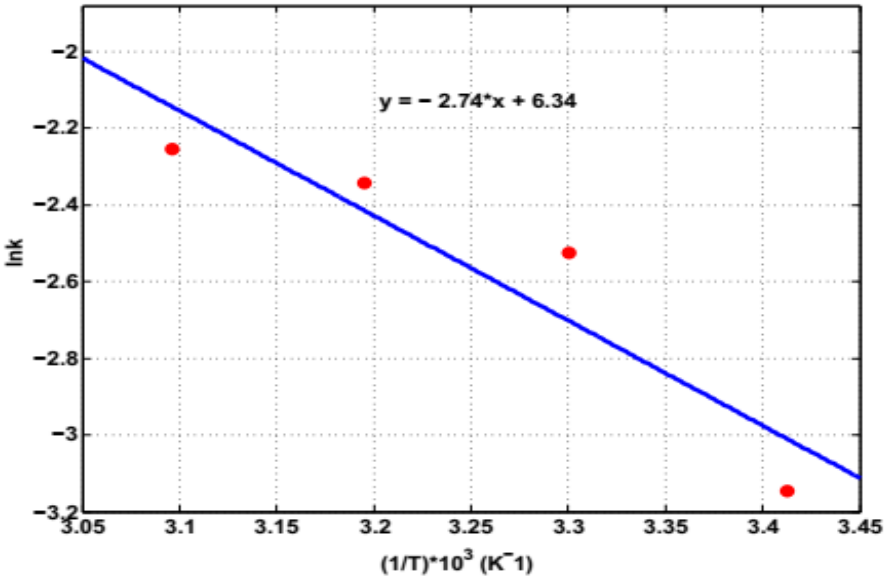


Figure (7): Data Fitting for Arrhenius Equation.

Conclusion

Saponification reaction of ethyl acetate by sodium hydroxide taking place in a batch reactor has been experimentally studied. The purpose of the work was to investigate the effect of the initial reactants temperature on the reaction rate constant and conversion. The increase of the rate constant with temperature was used to estimate the reaction activation energy. Nonlinearity of the relation used was attributed to the heat loss from the reactor due to the bad insulation efficiency. Nevertheless, the well-known second order of the reaction was confirmed by the resulting linear relationship between temperature and the concentration inverse after converting to conversion expression. The overall outcomes showed that the

conversion can be insignificantly affected by the reactants initial temperature when the insulation condition is imperfect. However, the rate constant increased with increasing the reactants initial temperature.

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