## Research Article
## Kinetic and Thermodynamic Parameters for Uncatalyzed Esterification of Carboxylic Acid

Kehinde S. Bankole and Gary A. Aurand

Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa, 52242, USA

**Abstract:** A fundamental study on uncatalyzed esterification of various biomass-derived aliphatic carboxylic acids with stoichiometric amount of ethanol has been investigated in an isothermal batch reactor, with the objective to convert carboxylic acids to corresponding ethyl esters and to determine both the kinetic and thermodynamic parameters. The effects of temperature on the conversion of carboxylic acid, kinetic and thermodynamic parameters have been investigated. Temperature was found to have significant effect on the rate of reaction and conversion of carboxylic acid. A simple second order reversible kinetic model was developed to determine the kinetic and thermodynamic parameters. The thermodynamic and kinetic parameters varied for uncatalyzed esterification reaction of both short-chain and long-chain carboxylic acids considered. The predicted data from the kinetic model were correlated with experimental data and the two sets of data agreed reasonably well for the uncatalyzed esterification systems. It was observed that the Van't Hoff plot for uncatalyzed esterification of linoleic acid was non-linear curve, whereas for the Arrhenius and Eyring plots, they were linear. Additional experiments to assess the catalytic and corrosion effects of several metallic substances revealed Inconel 625 alloy, nickel wire and stainless steel materials were susceptible to corrosion problem with uncatalyzed esterification reaction at elevated reaction temperatures. However, tantalum and grade-5 titanium materials were corrosion resistance metals, suitable for similar reaction conditions and this can encourage the design of a flow reactor system. Although, uncatalyzed esterification of carboxylic acids at elevated reaction temperature is still at laboratory scale. It is our hope that the estimated kinetic and thermodynamic parameters would be the guiding tools for reactor scale-up, thus providing a new perspective into the conversion of biomass-derived carboxylic acids into value-added ester products under uncatalyzed esterification reaction system.

**Keywords:** Acid-catalyzed reaction, biomass derived-chemicals, catalysis reaction, esterification reaction, homogenous and heterogeneous catalyst, kinetic and thermodynamic parameters, uncatalyzed reaction

### INTRODUCTION

In recent years, chemical processing industry is facing a regulatory challenge to replace hazardous petroleum-derived solvents such as chlorofluorocarbons, ethylene glycol ethers, methylene chloride, chloroform and Methyl Ethyl Ketone (MEK) with environmentally friendly solvents and renewable chemicals (Argonne National Laboratory, 1998; Rathin and Shih-Perng, 1998; Carole et al., 2004). In this regard, the increased demand for value-added solvents and renewable chemicals has prompted the chemical industry to initiate the esterification of biomass-derived carboxylic acids to synthesize corresponding non-toxic biodegradable esters, which have significant applications in various areas like pharmaceuticals, plasticizers, solvents, food flavors, coating and fragrance (Bart et al., 1994; Sanz et al., 2002; Ayoub, 2005; Delgado et al., 2007).

Esterification is a well-known process, from which important chemicals such as methyl, ethyl and butyl esters of carboxylic acids can be produced. However, at atmospheric condition, esterification is a reversible reaction limited by the low equilibrium conversion and slow reaction rate and has recently been performed with excess alcohol and/or by continuous removal of water by azeotropic distillation to shift the equilibrium conversion. The esterification reaction is routinely performed in batch reactors with the presence of either homogeneous acid catalyst or heterogeneous acid catalyst to achieve acceptable reaction rates.

Though the acid-catalyzed process has been extensively developed, it has at least some inherently undesirable drawbacks (Choi et al., 1996; Xu and Chuang, 1996; Ronnback et al., 1997; Seo and Hong, 2000; LiIja et al., 2002; Benedict et al., 2003; Engin et al., 2003; Hoydonckx et al., 2004; Pipus et al., 2007). The homogeneous acid catalyst can erode process equipment; miscibility of acid catalyst with the reaction medium requires expensive downstream separation operations; there are possible side reactions such as dehydration and etherification; and acid

**Corresponding Author:** Kehinde S. Bankole, Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa, 52242, USA

disposal can be an environmental issue. In addition, the heterogeneous acid-catalyzed reactions can be mass transfer limited, require complex catalyst pre-treatment, suffer from deactivation of solid catalyst and require longer reaction time than the homogeneously acid-catalyzed esterification system. Hence, an uncatalyzed esterification reaction that provides cleaner route for synthesizing wide variety of industrial products due to ease of separation and purification of the products without contamination is essential.

Supercritical Fluid (SCF) technology has received considerable attention over the last few years in the chemical industry due to their favorable gas-like low mass transfer resistance and liquid-like high solvating capacity properties. Reactions at supercritical conditions have been reported as interesting options for improving equilibrium conversion, enhancing reaction rate and making the process more environmentally friendly (Jessop and Leitner, 1999). At supercritical state, dielectric constant of alcohol decreases and this allows supercritical alcohol to become a better organic solvent for organic homogeneous reaction systems (Gui *et al*., 2009).

Supercritical ethanol, whose critical temperature and pressure are 240°C and 6.15 MPa, respectively, has received attention as an alternative reaction medium because of its positive effects on the reaction rate, selectivity and yield (Isyama and Saka, 2008; Ignacio *et al*., 2008). Ethanol is a good choice for reaction medium because presently, ethanol is produce from biomass. Thus, ethanol was selected as both reactant and reaction medium for the uncatalyzed esterification reaction system.

Numerous efforts on production of esters from carboxylic acids and ethanol have addressed important issues concerning product distribution, catalyst activity and kinetic studies of acid-catalyzed esterification. These previous efforts only not covered low temperature range, utilized excess alcohol, but some of the acid-catalyzed esterification reactions suffered side reactions from external acidic catalyst (Xu and Chuang, 1996; Ronnback *et al*., 1997; Hoydonckx *et al*., 2004; Pipus *et al*., 2007).

Some of the previous, studies did not consider the reverse reaction rate constant in the kinetic model and this assumption is only valid at low conversion and/or if excess concentration of one of the reactants is used (Xu and Chuang, 1996; Pipus *et al*., 2007), but not when equimolar concentration of reactants is used. In addition, some previous studies did not report the values of the equilibrium constant (Zhang *et al*., 2004). Thermodynamic and kinetic parameters of uncatalyzed esterification at elevated reaction temperatures are very limited, thus, it is of great interest from a practical point of view to obtain kinetic and thermodynamic parameters for esterification reaction process without using external catalyst.

Presented in this study are the results of fundamental study on uncatalyzed esterification of

Table 1: Range of reaction conditions in batch reactors

| Temperature range (K) | Carboxylic acid | Alcohol | Reactants molar ratio |
|---|---|---|---|
| 298-523 | Lactic acid | Ethanol | 1:1 |
| 333-523 | Levulinic acid | Ethanol | 1:1 |
| 373-523 | Acetic acid | Ethanol | 1:1 |
| 373-523 | Formic acid | Ethanol | 1:1 |
| 373-623 | Linoleic acid | Ethanol | 1:1 |

different aliphatic carboxylic acids with stoichiometric amount of ethanol in an isothermal batch reactor. This study not only provides the proof of concept for converting biomass-derived carboxylic acids to corresponding esters without external catalyst, but also obtained both kinetic and thermodynamic parameters useful as predictive tools for reactor scale-up. Sealed quartz glass tube was used as batch reactor to prevent corrosion, metal catalytic influence and vaporization of reaction species. The reactor was fed with equimolar reactants under glove box circulated with inert gas. Presence of oligomers was ignored for the lactic acid esterification system, since total amount of lactic acid oligomers and their corresponding esters are negligible at equilibrium (Tanaka *et al*., 2002; Asthana *et al*., 2006). The conversion of carboxylic acid is highly dependent of temperature and time, hence; reaction time and temperature were varied for uncatalyzed esterification of different types of aliphatic carboxylic acids, to assess the effects of temperature, reaction time, carbon chain-length and functional group on the kinetic studies. Each reaction sample was analyzed to obtain the concentration-time data for specific reaction condition. Preliminary work on the esterification of lactic acid with stainless steel material 316 (SS 316) commonly used as reactor for high reaction conditions was performed, but it was observed that the SS-316 material was susceptible to progressive acid corrosion with increasing reaction time and temperature. Hence, this initiated the use of sealed quartz capillary tube, which has no corrosive susceptibility or catalytic activity at temperature above 300°C. Similar quartz tube as reactor has been used for gasification of methanol in supercritical water (DiLeo and Savage, 2006). Additionally, experiments with different metallic substances were also performed at selected temperature in order to assess their corrosive susceptibility and catalytic effect on uncatalyzed esterification reaction at elevated reaction temperature. Temperature range at which the study was performed is listed in Table 1.

## MATERIALS AND METHODS

**Chemicals and materials:** Chemicals used for reaction were lactic acid (>98%, Fisher Scientific), levulinic acid (>98%, Acros Chemicals), acetic acid (>98%, Fisher Scientific), formic acid (>98%, Acros), linoleic acid (>99%, Acros), anhydrous ethanol (AAPER Chemicals), ethyl levulinate (>99%, Acros Chemicals), ethyl lactate (>97%, Acros Chemicals), ethyl acetate

(>98%, Fisher Scientific), ethyl formate (>98%, Acros), ethyl linoleate (>99%, Fluka) and nitrogen gas (>99.99%, Airgas). Inconel 625 alloy, nickel wire (>99%) and grade-5 titanium wire were obtained from ESPI Metals. Stainless steel was obtained from engineering machine shop at the University of Iowa campus and tantalum sheet was obtained as a gift from Dr. Louis of chemistry department at the University of Iowa. Ultrapure water (18 MΩ-Cm) obtained from our laboratory was used to dilute reaction samples. Purified water (Optima Fisher Scientific) and helium gas (>99.99%, Airgas) were used for HPLC analysis. Sodium hydroxide pellets (Certified ACS grade, Fisher Scientific), 0.1 N hydrochloric acid standard solution (Fisher Scientific) and deionized water were used for titration analysis. Phenolphthalein (Certified ACS grade, Fisher Scientific) dissolved in 50% ethanol solution was used as indicator for titration analysis. All chemicals were used without further purification.

**Development of kinetic model:** Kinetic analyses find a model that describes rate of reaction as a function of system variables, which define the chemical process. Kinetic of esterification of carboxylic acid with alcohol has been extensively studied. Two different routes by which the hydrogen ion ($H^+$) in the catalyst performs its catalytic effect are:

- The carboxylic acid molecule is initially activated by the $H^+$ ions before it is esterified with a molecule of alcohol.
- The $H^+$ ions form complexes with the alcohol molecules, after which the esterification proceeds through interaction of molecules of the complex with the molecules of carboxylic acid.

Therefore, rate of formation of ester is related to the concentration of the carboxylic acid. Influence of various normal aliphatic carboxylic acids in methanol and their length of carbon-chain on reaction rate of catalyzed esterification system have been previously emphasized (Smith, 1939).

To establish a process for a chemical reaction useful to synthesize esters in large scale, information on the reaction kinetic is essential. This section presents a brief overview on the reaction rate for the kinetic of uncatalyzed homogeneous esterification of carboxylic acids. A generalized esterification reaction equation is written as:

$$A + B \rightleftarrows E + W \tag{1}$$

The forward reaction rate ($r_f$) depends on concentrations of reactants Eq. (2), while the reverse reaction rate ($r_r$) is a function of concentrations of products Eq. (3):

$$r_f = k_f C_A C_B \tag{2}$$

$$r_r = k_r C_E C_W \tag{3}$$

For reversible reaction, each compound is produced and consumed concurrently. Therefore, to evaluate the rate parameters in kinetic model, the experimental concentration-time data for individual compound are correlated to the batch reactor model under isothermal conditions as described by Eq. (4) to (7):

$$\frac{dC_A}{dt} = r_r - r_f = k_r C_E C_W - k_f C_A C_B \tag{4}$$

$$\frac{dC_B}{dt} = r_r - r_f = k_r C_E C_W - k_f C_A C_B \tag{5}$$

$$\frac{dC_E}{dt} = r_f - r_r = k_f C_A C_B - k_r C_E C_W \tag{6}$$

$$\frac{dC_W}{dt} = r_f - r_r = k_f C_A C_B - k_r C_E C_W \tag{7}$$

The initial conditions at $t$ = zero are; $C_A = C_{A0}$, $C_B = C_{B0}$ and $C_E = C_W$ = zero, where, $C_{A0}$ and $C_{B0}$ are the initial concentrations of carboxylic acid and alcohol, respectively.

When the esterification reaction reaches equilibrium, the forward reaction and reverse reaction rates are equal. Therefore, the apparent equilibrium constant ($K_{eq}$) from the reaction mixture is deduced from Eq. (8) to give (9):

$$r_f = r_r = k_f C_A C_B = k_r C_E C_W \tag{8}$$

$$K_{eq} = \frac{k_f}{k_r} = \frac{C_E C_W}{C_A C_B} \tag{9}$$

After some simple algebraic substitutions, the overall second order reaction rate of compound in homogeneous reversible reaction was written in form of Eq. (10):

$$r_i = \frac{dC_i}{dt} = k_f * \left( C_A C_B - \frac{C_E C_W}{K_{eq}} \right) \tag{10}$$

Assuming constant enthalpy with temperature, equilibrium constant ($K_{eq}$) as a function of reaction temperature expressed by Van't Hoff was given as Eq. (11):

$$K_{eq} = \exp\left( \frac{-\Delta G^o}{RT} \right) = \exp\left( \frac{T\Delta S^o - \Delta H^o}{RT} \right) \tag{11}$$

Relationship of forward reaction rate constant ($k_f$) with temperature expressed by Arrhenius was given as Eq. (12):

$$k_f = A_o * \exp\left(\frac{-E_a}{RT}\right) \tag{12}$$

According to the transition state theory, the Eyring's expression Eq. (13), similar to Arrhenius's expression used to relate rate constant to temperature was used to determine the activation parameters:

$$k_f = \left(\frac{k_B * T}{h}\right) \exp\left(\frac{\Delta S^{\mp}}{R}\right) \exp\left(\frac{-\Delta H^{\mp}}{RT}\right) \tag{13}$$

**Experimental data analysis:** The analysis of rate data is useful in understanding the dependence of the reaction rate on the kinetic and thermodynamic parameters and in the evaluating the effect of length of carbon chain and functional group on different uncatalyzed esterification systems. A concentration at each time was calculated from the stoichiometric material balance as expressed by Eq. (14) and the rate of disappearance of carboxylic acid were calculated from Eq. (10):

$$C_{A_t} = C_{A_o} - C_{A_o} * X \tag{14}$$

The reaction rate constant (K) at any given temperature was calculated by relating the concentration-time data to second order kinetic rate expression Eq. (10) and fit with the "LINEST" statistical function found in the Microsoft Excel software. The rate of reaction was calculated from conversion of the carboxylic acid (X), Eq. (15):

$$\text{Conversion}(X) = \frac{C_{A_o} - C_{A_t}}{C_{A_o}} \tag{15}$$

The concentration of the ester at each time ($C_{Et}$) was calculated by Eq. (16):

$$C_{Et} = C_{E_o} + C_{A_o} * X \tag{16}$$

To estimate the conversion, rate constants, equilibrium constants and species concentrations, the experimentally obtained kinetic and thermodynamic values, reaction time, temperature and initial concentration of carboxylic acid were related to the mathematical expressions in Eq. (4) to (7) with the use of a Runge-Kutta-Fehlberg 56 (RKF56) integration algorithm found in version 5.1 Polymath software package. The confidence interval error values were calculated with a function found in Microsoft Excel software using the number of experimental data points and standard deviation.



Fig. 1: Experimental setup of a batch reactor for esterification reaction

**Setup and procedures:** Experiments in the temperature range of 333 to 623 K were performed in capillary batch reactors made with corrosion-resistant quartz tube (2 mm i.d. ×6 mm o.d). The reactor was flame sealed at one end and then fed with reactants under a glove box circulated with inert nitrogen gas. Since the reaction pressure inside the reactor was not measurable, the increase in pressure at the reaction temperature was tolerated by partially filling the capillary tube with reactants. After adding the reactants, the open end was flame sealed to 24 cm in length. The sealed quartz tube was then immersed into an isothermal fluidized sand bath (SBS-4 Techne, U.S.A) that had been preheated to the desired temperature. The moment of immersing various quartz tubes into the fluidized sand bath was taken as zero reaction time. It was observed that the temperature change of the bath as a result of the immersion was negligible. At varied reaction time, each quartz tube was removed and cooled in an ice bath. Each cooled tube was stored in the freezer to prevent further reaction before sample analysis.

For reaction temperature range of 298 and 313 K, serum bottle (Wheaton) was fed with equimolar ratio of reactants and capped under a glove box circulated with inert nitrogen gas. Each capped bottle was then immersed into an isothermal oil bath shaker (C-76, New Brunswick Scientific, U.S.A.) that had been preset to the desired reaction temperature. Also, the moment of immersing the bottles into the oil bath shaker was taken as zero reaction time. Samples were withdrawn at regular time intervals and stored in the freezer to prevent further reaction before sample analysis. The pictorial diagram of the experimental setup is shown in Fig. 1 and all reactions and analysis were performed in duplicate.

Several metals were assessed for chemical compatibility as potential reactor materials. The metals were Inconel 625 (1.5 mm diameter), nickel wire (1 mm diameter), stainless steel 316 sheet, tantalum (1.5 mm diameter) and grade-5 titanium wire (1 mm diameter). A metallic substance was weighed and placed in corrosion-resistant quartz tube fed with equimolar lactic acid/ethanol solution and flame sealed at the open end. Each quartz tube was then placed into the preheated fluidized sand bath and kept for 220 h.

Table 2: HPLC analysis conditions for esterification systems

| Esterification system | Mobile phase flow rate (mL/min) | Column temperature (°C) | Analysis run time (min) |
|---|---|---|---|
| Lactic acid/ethanol | 0.10 | 40 | 60 |
| Levulinic acid/ethanol | 0.15 | 40 | 100 |
| Acetic acid/ethanol | 0.10 | 45 | 60 |

Experiment was performed at temperature of 423 and 523 K under similar conditions previously described for the kinetic studies. Each metallic substance was exposed to varied reaction time. At varied reaction time, each reactor was removed and cooled in an ice bath to prevent further reaction. Liquid reaction sample was withdrawn and stored in the freezer before HPLC analysis. The exposed metallic substance was removed, washed with ultrapure water, dried and weighed to obtain percentage weight loss.

**Analytical methods:** For the study to be significant, it is essential to determine the concentration of each reactant and product. A high performance liquid chromatography analytical technique was used to identify and quantify the compounds in reaction samples for lactic acid, levulinic acid and acetic acid esterification systems. From the stored reaction samples, 0.1 mL of each sample was withdrawn and diluted to 5 mL solution with ultrapure water for analysis. A reverse-phase HPLC system consisting of a Shimadzu Liquid Chromatography pump (LC-10ADvp), System Controller (SCL-10Avp), auto-injector (SIL-10AF) and Refractive Index Detector (RID-10A) was used for the HPLC analytical procedure. A Waters Nova-Pak C-18 column (1.5 cm×3.9 mm, particle size 4 μm) was used for separation. The mobile phase was 5 mM sulfuric acid in purified water, degassed with helium. The concentration of each compound in the reaction sample was quantified from standard calibration curves obtained by analyzing known concentrations of authentic compounds. With this procedure, the concentration change of ethanol, carboxylic acid and ester with time from each sample was recorded, while the amount of water was assumed stoichiometric. The conditions of HPLC analysis for each esterification system investigated are listed in Table 2.

An acid-base titration method was used to quantify the conversion of formic acid for the formic acid esterification reaction system. To calculate the conversion of formic acid, 0.1 N sodium hydroxide solution was standardized by using the standard 0.1 N hydrochloric acid solution and the normality of Sodium Hydroxide (NaOH) was calculated from Eq. (17):

$$N_{NaOH} = \frac{V_{HCl} * N_{HCl}}{V_{NaOH}} \quad (17)$$

At regular time intervals, 0.1 mL of each reaction sample was withdrawn, weighed and diluted to 5 mL
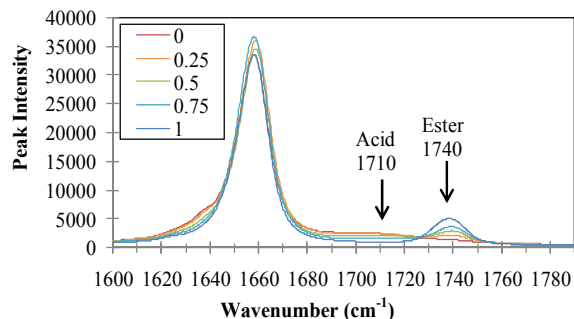


Fig. 2: Spectra of standard mixtures of linoleic acid and ethyl linoleate in ethanol

solution with deionized water and titrated with 0.1 N standardized sodium hydroxide solution using phenolphthalein as indicator. Concentration of formic acid was determined from standard calibration curve, obtained by titrating known concentrations of authentic formic acid. To ensure reliability of the titration, unconverted formic acid was calculated from Eq. (18):

$$F(wt\%) = \frac{N_{NaOH}(mol/L) * V_{NaOH}(mL) * MW_{FormicAcid}(g/mol) * 100\%}{W_{Sample}(g) * 1000(mL/L)} \quad (18)$$

Conversion (X%) at different time with respect to the formic acid is calculated from Eq. (19):

$$X(\%) = 100 - F(w\%) \quad (19)$$

The reaction products obtained from esterification of linoleic acid were analyzed using a Raman spectroscopic system consisting of a Holospec VPT spectrometer and an Invictus laser operating at 785 nm (Kaiser Optical Systems Inc., Ann Arbor, MI) in order to quantify the compounds in reaction sample. The power output of the laser was set at 200 mW. Holo Grams Software was used for data accumulation. The Raman peak intensities were examined at 1710 and 1740 cm$^{-1}$ wave numbers, respectively, for COOH neat acid and C = O ester stretching.

All Raman spectra were obtained with the same conditions in triplicates by exposing each sample to the laser for 1-sec with three accumulations. With this procedure, the mole fraction of the ethyl linoleate produced during the batch reaction at a given reaction time was determined and the reaction rate was obtained. Mole fraction of ethyl linoleate was determined from the standard calibration curve, obtained by using several mixtures of authentic linoleic acid, ethyl linoleate, ethanol and water with known molar ratio. The spectra for the standard are shown in Fig. 2.

## RESULTS AND DISCUSSION

**Equilibrium constant:** The temperature and molar ratio of ethanol to carboxylic acid are two variables affecting the conversion of carboxylic acid. Theoretically, esterification reaction is an equilibrium reaction. However, in this study, equal amount of ethanol and carboxylic acid was used to estimate the equilibrium constant ($K_{eq}$) values from the equilibrium conversion ($X_{eq}$) of carboxylic acid at various temperatures. The equilibrium constant values were calculated from Eq. (20):

$$K_{eq} = \frac{\left(X_{eq}\right)^2}{\left(1 - X_{eq}\right)^2} \qquad (20)$$

The experimental equilibrium constants ($K_{eq.exp}$) and calculated equilibrium constants ($K_{eq.calc}$) mean values for uncatalyzed esterification of Lactic Acid (LAA), Levulinic Acid (LEA), Acetic Acid (ACA), Formic Acid (FA) and Linoleic Acid (LA) are listed in Table 3.

It is noted from Table 3 that equilibrium constant ($K_{eq}$) values varied for different carboxylic acids. The $K_{eq}$ value increased with temperature for the esterification reaction system of short-chain carboxylic acids (formic acid, acetic acid, lactic acid and levulinic acid), while the temperature dependence of $K_{eq}$ for the long-chain carboxylic acid (linoleic acid) deviates from the trend revealed by short-chain carboxylic acids. The $K_{eq}$ value for the long-chain carboxylic acid (linoleic acid) increased non-linearly as the temperature increased from 373 to 473 K. However, as the reaction temperature increased from 523 to 623 K, the $K_{eq}$ value gradually decreased. The reason for a trend of linoleic acid is not known, but from an examination of the length of carbon-chain for the carboxylic acids considered in this study, it was found that linoleic acid is a polyunsaturated carboxylic acid (2 double bond unsaturated carboxylic acid) with a longer carbon chain. Thus, decomposition reaction might have taken place at longer reaction time and higher temperature due to thermal degradation.

**Thermodynamic parameters:** Reaction enthalpy change of a reaction ($\Delta H$) is the amount of heat absorbed or released in a reaction and $\Delta H$ parameter indicates whether a reaction is endothermic or exothermic depending if the enthalpy is required or released. The effects of temperature on the equilibrium constant using the classical Van't Hoff plots are shown in Fig. 3 in the form (ln $K_{eq}$) against (1/T).

Figure 3 showed that natural log (ln) $K_{eq}$ is linearly dependent on 1/T for the short-chain carboxylic acids, while the relationship of ln $K_{eq}$ on 1/T for the long-chain carboxylic acid (linoleic acid) revealed nonlinear Van't Hoff behavior. The nonlinear Van't Hoff

Table 3: Values of equilibrium constants for esterification of carboxylic acids

(a) Lactic Acid (LAA)

| T (K) | LAA $K_{eq.exp}$ | LAA $K_{eq.calc}$ |
|---|---|---|
| 298 | 0.035±0.004 | 0.04 |
| 313 | 0.060±0.010 | 0.07 |
| 333 | 0.130±0.010 | 0.13 |
| 353 | 0.250±0.010 | 0.25 |
| 373 | 0.500±0.020 | 0.44 |
| 423 | 1.480±0.080 | 1.40 |
| 473 | 3.800±0.100 | 4.00 |
| 523 | 6.400±0.200 | 7.00 |

(b) Levulinic Acid (LEA)

| T (K) | LEA $K_{eq.exp}$ | LEA $K_{eq.calc}$ |
|---|---|---|
| 333 | 0.07±0.01 | 0.07 |
| 353 | 0.12±0.01 | 0.12 |
| 373 | 0.20±0.01 | 0.20 |
| 423 | 0.57±0.03 | 0.56 |
| 473 | 1.22±0.05 | 1.00 |
| 523 | 2.42±0.03 | 2.40 |

(c) Acetic Acid (ACA)

| T (K) | ACA $K_{eq.exp}$ | ACA $K_{eq.calc}$ |
|---|---|---|
| 373 | 0.20±0.20 | 0.3 |
| 423 | 0.85±0.08 | 0.8 |
| 473 | 2.00±1.00 | 2.0 |
| 523 | 4.00±1.00 | 4.0 |

(d) Formic Acid (FA)

| T (K) | FA $K_{eq.exp}$ | FA $K_{eq.calc}$ |
|---|---|---|
| 373 | 2.0±1.0 | 2 |
| 423 | 3.9±0.1 | 4 |
| 473 | 6.0±1.0 | 6 |
| 523 | 9.0±2.0 | 9 |

(e) Linoleic Acid (LA)

| T (K) | LA $K_{eq.exp}$ | LA $K_{eq.calc}$ |
|---|---|---|
| 373 | 0.30±0.04 | 0.26 |
| 423 | 0.60±0.10 | 0.60 |
| 473 | 0.80±0.10 | 0.80 |
| 523 | 0.40±0.10 | 0.40 |
| 573 | 0.30±0.10 | 0.30 |
| 623 | 0.23±0.01 | 0.23 |

$K_{eq.exp}$: Experimental equilibrium constant value; $K_{eq.calc}$: Model calculated equilibrium constant value; 95% confidence intervals error values
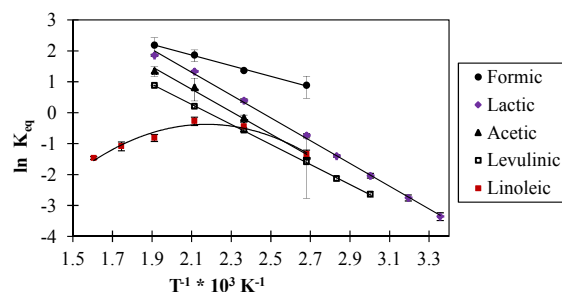


Fig. 3: Effect of temperature on equilibrium constant for uncatalyzed esterification of carboxylic acids with ethanol

behavior may be attributed to temperature-dependent changes in enthalpy and reduction of equilibrium constant ($K_{eq}$) at longer reaction time and higher temperature.

The estimated reaction enthalpy ($\Delta H$) and reaction entropy ($\Delta S$) values and the 95% confidence intervals

Table 4: Thermodynamic parameters for esterification of short-chain carboxylic acids

| T (K) | Carboxylic acid | ΔH (kJ/mol) | ΔS (J/mol/K) |
|---|---|---|---|
| 373-523 | Formic acid | 14±2 | 45±6 |
| 373-523 | Acetic acid | 30±7 | 70±10 |
| 298-523 | Lactic acid | 30±1 | 75±3 |
| 333-523 | Levulinic acid | 27±1 | 58±1 |

Table 5: Values of thermodynamic parameters for esterification of linoleic acid

| Temp K | ΔH kJ/mol | ΔG kJ/mol | ΔS J/ (mol.K) |
|---|---|---|---|
| 373 | 30 | 4 | 70 |
| 423 | 11 | 2 | 23 |
| 473 | -4 | 1 | -10 |
| 523 | -16 | 4 | -37 |
| 573 | -26 | 5 | -54 |
| 623 | -34 | 8 | -67 |

error values from the linear Van't Hoff plot for uncatalyzed esterification of different short-chain carboxylic acids are listed in Table 4.

As noted from Table 4, the ΔH values for the uncatalyzed esterification of short-chain carboxylic acids are positive. Thus, the esterification of short-chain carboxylic acids considered in this study is endothermic. Previous studies have reported endothermic reaction for lactic acid and levulinic acid esterification systems (Bart *et al*., 1994; Zhang *et al*., 2004).

The ΔH values for uncatalyzed esterification of linoleic acid at varied reaction temperatures were estimated from the nonlinear Van't Hoff plot by fitting the data to Eq. (21), deduced from derivative of ln $K_{eq}$ with respect to 1/T:

$$\frac{d \ln K_{eq}}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{R} = 15.7 - \left(2 * \left(\frac{3.6087}{T}\right)\right) \quad (21)$$

Because the values of activity coefficients at reaction conditions for the esterification systems are unknown, reaction Gibbs free energy change (ΔG) was calculated from Eq. (22):

$$\Delta G = -RT * \ln K_{eq} \quad (22)$$

Therefore, the ΔS for the uncatalyzed esterification of linoleic acid was calculated with the ΔH and ΔG values from Eq. (23):

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (23)$$

The calculated values of ΔH, ΔG and ΔS for the uncatalyzed esterification of linoleic acid are presented in Table 5.

As observed from Table 5, the reaction enthalpy and entropy decreased as the reaction temperature increased. The ΔH and ΔS values in the Table 5 are
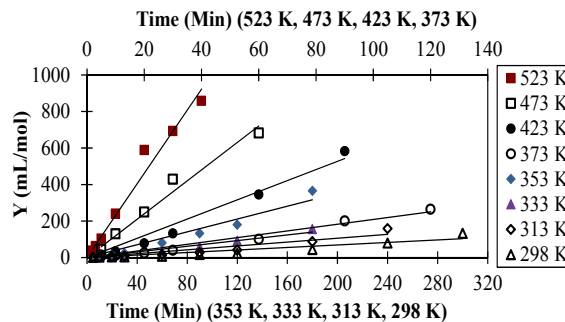


Fig. 4: 2nd-order rate plot for uncatalyzed esterification of lactic acid with ethanol
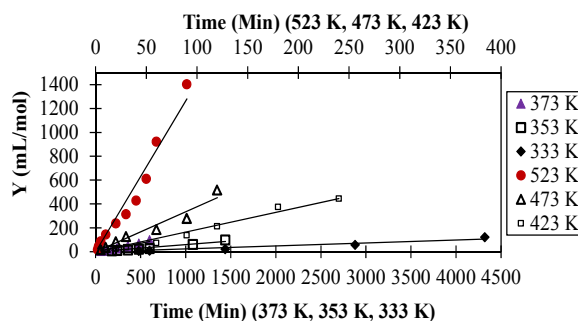


Fig. 5: 2nd-order rate plot for uncatalyzed esterification of levulinic acid with ethanol
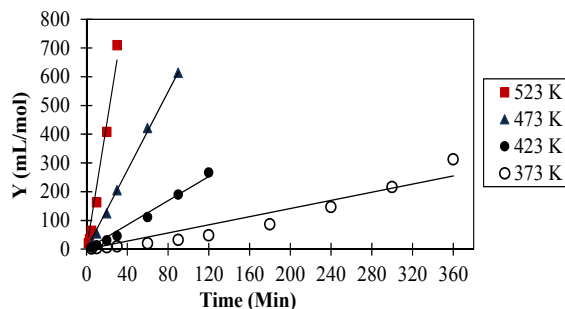


Fig. 6: 2nd-order rate plot for uncatalyzed esterification of acetic acid with ethanol

positive from 373 to 423 K and then become negative from 473 to 623 K. The change of sign from positive to negative values in ΔH as a function of temperature may be attributed to variety of sources, including temperature-dependent changes in enthalpy and reduction of equilibrium constant ($K_{eq}$) at higher temperature. The ΔG values in Table 5 are positive at different temperatures and the ΔG value decreased as temperature increased from 373 to 473 K and thereafter increased as temperature increased from 523 to 623 K. The trend observed for the ΔG may relate to the equilibrium constant ($K_{eq}$) values that increased as temperature increased from 373 to 473 K and gradually decreased as temperature increased from 523 to 623 K.
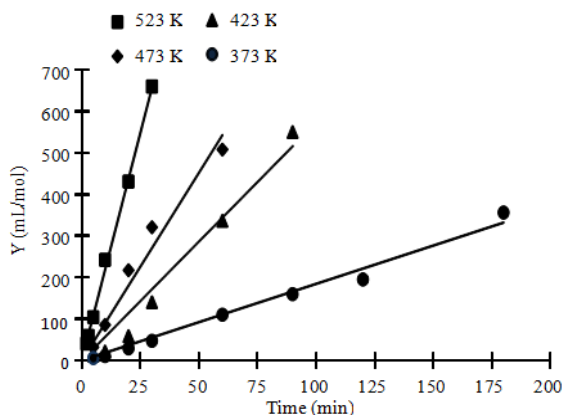
Fig. 7: $2^{nd}$-order rate plot for uncatalyzed esterification of formic acid with ethanol
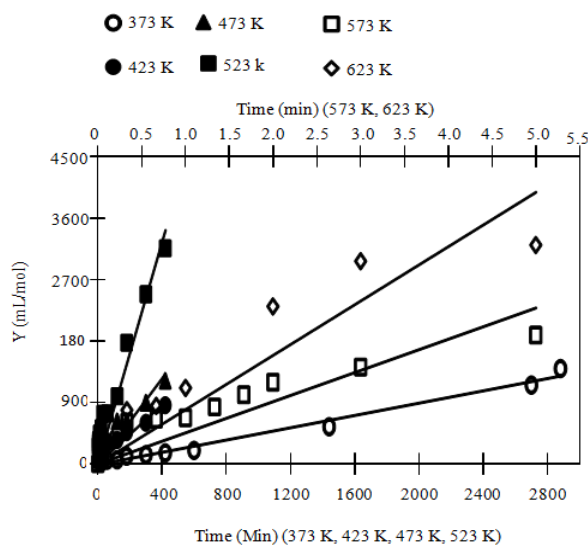


Fig. 8: $2^{nd}$-order rate plot for uncatalyzed esterification of linoleic acid with ethanol

**Reaction rate constant:** The integration of second order reaction rate expressed with Eq. (10) in terms of carboxylic acid conversion (X) yields Eq. (24):

$$\left(-\frac{1}{C_{A_0}(1-X)}\right)*\ln\left[\frac{\left[(1-X)^2-\left(\frac{X^2}{K_{eq}}\right)\right]}{\left[(1-X)-\left(\frac{X^2}{K_{eq}}\right)\right]}\right] = Y = t*k_f \tag{24}$$

Equation (24) was used to estimate reaction rate constant from the experimental conversion of carboxylic acids with time at each reaction temperature. The plots of the left term "Y" against reaction time "t" at various temperatures for uncatalyzed esterification of lactic acid, levulinic acid, acetic acid, formic acid and linoleic acid are respectively represented in Fig. 4 to 8. The forward reaction rate constant at each temperature was estimated from the slope of the plot.

Table 6: Values of forward reaction rate constants ($k_f$) for esterification of carboxylic acids

(a) Lactic acid

| T (K) | LAA $k_{f.exp}$ | LAA $k_{f.calc}$ |
|---|---|---|
| 298 | 0.3±0.1 | 0.33 |
| 313 | 0.5±0.1 | 0.50 |
| 333 | 0.8±0.1 | 0.90 |
| 353 | 1.8±0.2 | 2.00 |
| 373 | 2.0±0.2 | 2.00 |
| 423 | 6.0±0.5 | 6.00 |
| 473 | 12.0±1.0 | 12.0 |
| 523 | 23.0±1.0 | 22.0 |

(b) Levulinic acid

| T (K) | LEA $k_{f.exp}$ | LEA $k_{f.calc}$ |
|---|---|---|
| 333 | 0.025±0.004 | 0.024 |
| 353 | 0.060±0.010 | 0.070 |
| 373 | 0.140±0.010 | 0.160 |
| 423 | 2.000±0.100 | 1.000 |
| 473 | 3.800±0.400 | 5.000 |
| 523 | 14.000±1.000 | 15.000 |

(c) Acetic acid

| T (K) | ACA $k_{f.exp}$ | ACA $k_{f.calc}$ |
|---|---|---|
| 373 | 0.7±0.1 | 0.6 |
| 423 | 2.0±0.3 | 3.0 |
| 473 | 6.0±3.0 | 8.0 |
| 523 | 22±3.0 | 19.0 |

(d) Formic acid

| T (K) | FA $k_{f.exp}$ | FA $k_{f.calc}$ |
|---|---|---|
| 373 | 2.0±0.3 | 2 |
| 423 | 6.0±0.6 | 5 |
| 473 | 9.0±1.0 | 10 |
| 523 | 22.0±1.0 | 20 |

(e) Linoleic acid

| T (K) | LA $k_{f.exp}$ | LA $k_{f.calc}$ |
|---|---|---|
| 373 | 0.44±0.03 | 0.51 |
| 423 | 2.20±0.40 | 2.00 |
| 473 | 4.00±1.00 | 5.00 |
| 523 | 10.00±5.00 | 10.00 |
| 573 | 18.00±9.00 | 19.00 |
| 623 | 30.00±10.00 | 33.00 |

The plots showed that the $2^{nd}$-order model related well with the data, thus, Eq. (10) is appropriate to describe the kinetic of the reaction. The mean values of the experimental forward reaction rate constants ($k_{f.exp}$) and calculated forward reaction rate constants ($k_{f.calc}$) for uncatalyzed esterification systems considered in this study are listed in Table 6.

The reported errors in Table 6 are 95% confidence intervals. The reaction rate constant for the esterification reactions increased with increasing temperature. At similar reaction temperature, Table 6 revealed that the reaction rate constant varied for esterification of different carboxylic acids. The differences in the rate constant may be attributed to varied number of carbon-chain of the carboxylic acid, attached functional group of the carboxylic acid and difference in acid dissociation constant (pKa) values. Previous studies have reported that reaction rate decreases as number of carbon chain of carboxylic acid increases and rate of reaction declines as the pKa value of the acid increases (Christian, 1990; LiIja *et al.*, 2002; Zaidi *et al.*, 2002; Liu *et al.*, 2006).
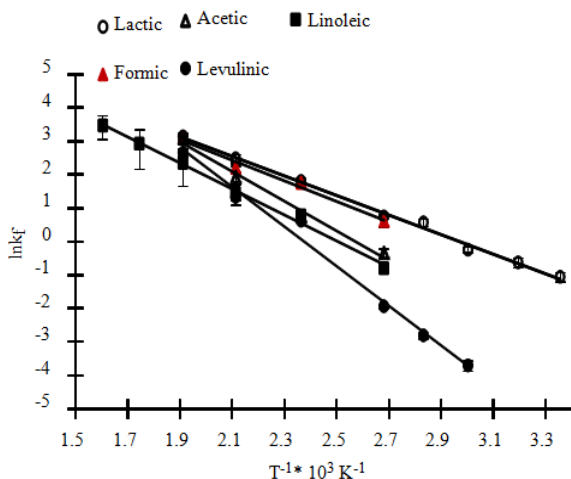
Fig. 9: Arrhenius plot for uncatalyzed esterification of carboxylic acids with ethanol
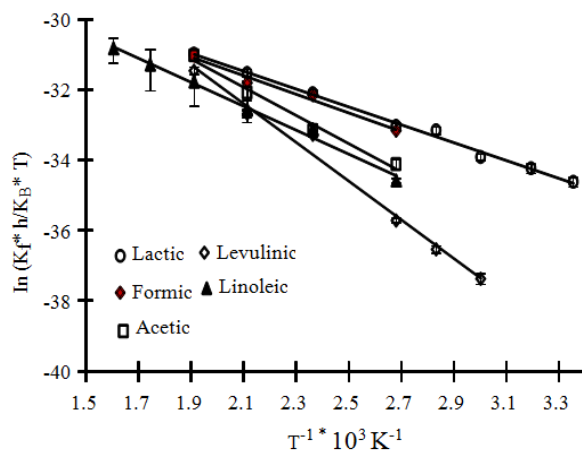


Fig. 10: Eyring plot for uncatalyzed esterification of carboxylic acids with ethanol

**Activation energy and frequency factor:** The value of forward reaction rate constant ($k_f$) is a function of temperature and this was mathematically represented by Arrhenius's expression Eq. (12). Effect of temperature on rate constants is shown in Fig. 9 in the form of Arrhenius plot, including the least squares fit.

The plots from Fig. 9 provided excellent linear fits for uncatalyzed esterification reaction systems. Reaction rates for different esterification systems varied and increased as temperature increased. Results of activation energy ($E_a$), logarithm$_{10}$ of pre-exponential factor ($\log_{10} A_o$) and 95% confidence interval values, evaluated for the uncatalyzed esterification of various carboxylic acids are presented in Table 7. The dissociation constant ($pK_a$) Values at 25°C for respective carboxylic acid are also listed in Table 7.

From Table 7, the activation energy for esterification of different carboxylic acids varied. This variation may be attributed to varied range of reaction temperatures, number of carbon chain and $pK_a$ values.

Table 7: Values of kinetic parameters for uncatalyzed esterification of carboxylic acids

| T (K) | Carboxylic acid | $E_a$ (kJ/mol) | $\log_{10} (A_o)$ (mL/ (mol.min) | pKa values at 25°C |
|---|---|---|---|---|
| 373-523 | Formic acid | 26±10 | 4.0±1.0 | 3.74 |
| 373-523 | Acetic acid | 40±10 | 5.0±1.0 | 4.76 |
| 298-523 | Lactic acid | 24±2 | 3.8±0.2 | 3.85 |
| 333-523 | Levulinic acid | 49±8 | 6.0±1.0 | 4.62 |
| 373-623 | Linoleic acid | 32±4 | 4.2±0.4 | 7.90 |

Table 8: Activation enthalpy and entropy for uncatalyzed esterification of carboxylic acids

| T (K) | Carboxylic acid | $\Delta H^{\ddagger}$ (kJ/mol) | $\Delta S^{\ddagger}$ (J/ (mol.K) |
|---|---|---|---|
| 373-523 | Formic acid | 20±10 | -220±20 |
| 373-523 | Acetic acid | 30±10 | -190±30 |
| 298-523 | Lactic acid | 21±1 | -217±4 |
| 333-523 | Levulinic acid | 45±7 | -170±20 |
| 373-623 | Linoleic acid | 28±3 | -210±8 |

The esterification of formic acid and lactic acid tends to have nearly equal activation energy and this may be attributed to nearly equal values of dissociation constant ($pK_a$). The $pK_a$ values of formic acid and lactic acid at 25°C are 3.74 and 3.85, respectively. The expected lower activation energy for esterification of acetic acid, as compared the activation energy value for esterification of lactic acid showed the contrary. This may be traced to lower $pK_a$ value of lactic acid, which possibly increased the acidity strength of the lactic acid. The lower activation energy value obtained for the linoleic acid esterification system as compare to esterification systems of acetic acid and levulinic acid could be related to varied temperature range at which the esterification systems were performed.

At the temperature of 328 and 358 K, using excess ethanol, Delgado and co-workers obtained the activation energy values of 52 and 62 kJ/mol, respectively for catalyzed and uncatalyzed esterification of aqueous lactic acid (Delgado *et al.*, 2007), while the estimated activation energy for uncatalyzed esterification of lactic acid in this study is 24±2 kJ/mol. The variation in the values of activation energy may be related to varied temperature range studied.

**Activation enthalpy and activation entropy:** The temperature dependence of forward rate constants ($k_f$) was determined and the activation enthalpies and activation entropies for esterification of different carboxylic acids were determined graphically from the Eyring plot according to the Eyring's expression Eq. (13). The Eyring plots generated by plotting ln ($k_f$ $*h/k_B*T$) against $T^{-1}$ ($K^{-1}$) are shown in Fig. 10.

Despite the nonlinearity of the Van't Hoff plot for esterification of linoleic acid, the Arrhenius and Eyring plots are linear. The linear Arrhenius and Eyring plots may be attributed to the unchanged reaction mechanism. Using the least squares analysis, the activation enthalpies ($\Delta H^{\ddagger}$) and activation entropies ($\Delta S^{\ddagger}$) from the slope and intercept of the Eyring plot respectively, are listed in Table 8. The error values were evaluated with 95% confidence interval.

As noted in Table 7 and 8, the activation energy ($E_a$) deduced from Arrhenius plot is nearly equal to the activation enthalpy ($\Delta H^{\ddagger}$) deduced from Eyring plot and this is shown by similar trend observed for both the Arrhenius and Eyring plots. Therefore, major difference between the two analyses of the temperature dependence of rate constants depends in the interpretation of entropic terms such as pre-exponential factor ($A_o$) and activation entropy ($\Delta S^{\ddagger}$) from respective plots. Negative $\Delta S^{\ddagger}$ values obtained in this study may be associated to the lower values of pre-exponential factors ($A_o$) as compared to the universal frequency factor ($k_B * T_{ref}/h$) values (Winzor and Jackson, 2006). The negative $\Delta S^{\ddagger}$ value indicates an associative mechanism for esterification of carboxylic acids, which the activated complex in the transition state is more ordered than the reactants in the reaction system.

**Effect of temperature:** Presented in Fig. 11 are the results showing the effect of temperature from 298 to 523 K on uncatalyzed esterification of lactic acid with stoichiometric amount of ethanol. Reaction rate and conversion of lactic acid to ethyl lactate increased with increasing temperature. At 523 K, equilibrium conversion of approximately 70% conversion was attained at nearly 60 min, while at 298 K; equilibrium conversion of approximately 15% at 480 min was reached.

Using the Runge-Kutta-Fehlberg 56 (RKF56) integration algorithm found in version 5.1 Polymath software package, the kinetic model predicted data and experimental data for various reaction conditions showed reasonable agreement. Thus, the second order reversible kinetic model applied in this study is suitable for the uncatalyzed esterification of lactic acid system.

Presented in Fig. 12 is the effect of temperature on uncatalyzed esterification of levulinic acid with equimolar amount of ethanol at varied temperatures, from 298 to 523 K. The results show the conversion of levulinic acid to ethyl levulinate. The symbols represented experimental data, while the continuous line represented the calculated model data. The reaction rate and conversion of levulinic acid increased as temperature increased. Obtained at reaction temperature of 523 K was 60% equilibrium conversion at nearly 90 min, while at 333 K, the equilibrium conversion of levulinic acid was approximately 21% after 120 h reaction time. In the present study, the concentrations of ethyl levulinate at temperatures of 298 and 313 K were below the detection limit of the applied HPLC analytical method. A comparison of the model predictions with experiments for different reaction conditions showed reasonable agreement between the experimental data and kinetic model. Thus, the second order reversible kinetic model applied in the study is practical for the uncatalyzed esterification of levulinic acid.

Presented in Fig. 13 is the effect of temperature on uncatalyzed esterification of acetic acid with equimolar
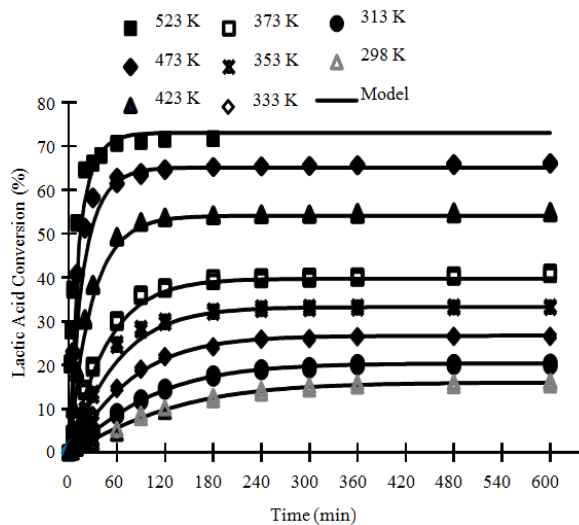


Fig. 11: Conversion-time profile for uncatalyzed esterification of lactic acid with ethanol at various temperatures. Continuous lines represent the kinetic model
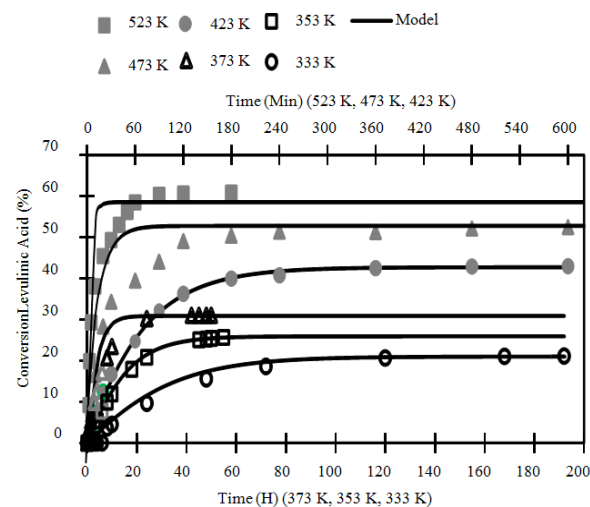


Fig. 12: Conversion-time profile for uncatalyzed esterification of levulinic acid with ethanol at various temperatures. Continuous lines represent the kinetic model

amount of ethanol at varied temperatures, from 373 to 523 K. Figure 13 showed the conversion of acetic acid to ethyl acetate. Depicted also on Fig. 13 are experimental and calculated data, represented by symbols and continuous line respectively. The reaction rate and conversion increased with increasing temperature. The equilibrium conversion approximately increased from 30% at 373 K after 360 min to 65% at 523 K after 60 min. For the esterification of acetic acid with ethanol, Calvar and co-workers had reported higher conversion of acetic acid in uncatalyzed esterification, when compared to acid resin-catalyzed esterification of acetic acid. The resins not only act as
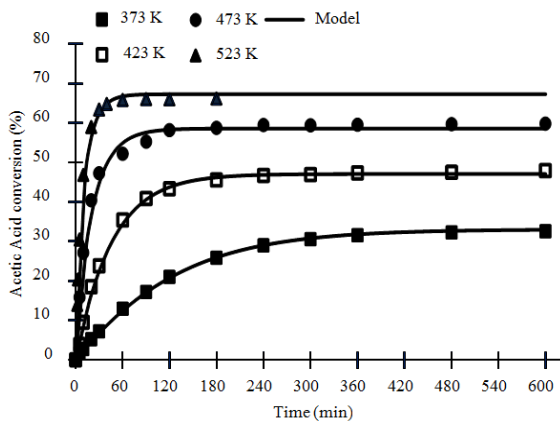
Fig. 13: Conversion-time profile for uncatalyzed esterification of acetic acid with ethanol at various temperatures. Continuous lines represent the kinetic model
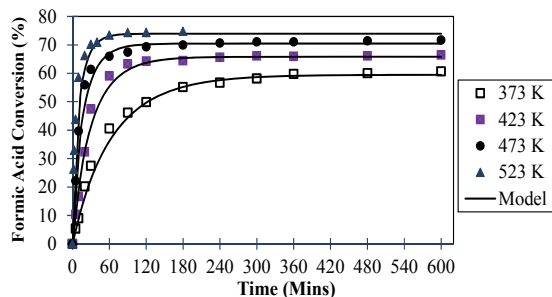


Fig. 14: Conversion-time profile for uncatalyzed esterification of formic acid with ethanol at various temperatures. Continuous lines represent the kinetic model
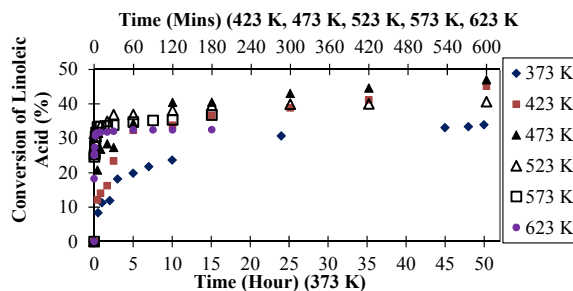


Fig. 15: Conversion-time profile for uncatalyzed esterification of linoleic acid with ethanol at various temperatures



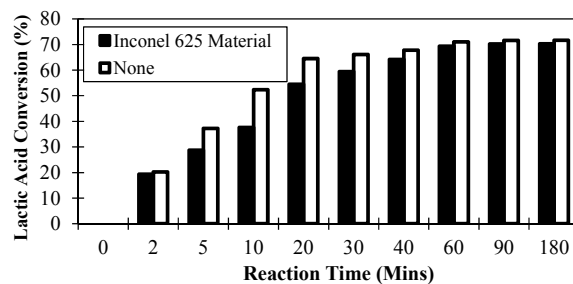Fig. 16: Conversion vs. time for uncatalyzed esterification of lactic acid with and without inconel 625 material at 523 K

catalyst, but also affect the equilibrium conversion due to their selective adsorption of reactants and swelling nature (Calvar *et al.*, 2007). A comparison of the model-calculated values with experimental values showed reasonable agreement between the experimental data and kinetic model. Therefore, the second order reversible kinetic model applied is also satisfactory for the uncatalyzed esterification of acetic acid.

Presented in Fig. 14 is the effect of temperature on uncatalyzed esterification of formic acid with ethanol at 1:1 mole ratio at temperatures varying from 373 to 523 K. While the symbols represent the experimental data, the continuous line represents the model values. The conversion and reaction rate increased with an increase in temperature. At 523 K, the equilibrium conversion obtained at 90 min was approximately 75% conversion. The equilibrium conversion of formic acid at 373 K after 360 min was approximately 55% conversion. As noted from Fig. 14, the experimental data agreed reasonably well with the predicted data. Thus, the devised second order reversible kinetic model is applicable for uncatalyzed esterification of formic acid.

To determine the effect of temperature on the ethyl linoleate formation, uncatalyzed esterification of linoleic acid was performed with equimolar amount of ethanol at temperatures ranging from 373 to 623 K. Figure 15 showed the conversion of linoleic acid to ethyl linoleate. The conversion of linoleic acid increased as temperature increased from 373 to 473 K, with approximately 42% equilibrium conversion at nearly 300 min at 473 K. However, as the temperature increased above 473 K, the equilibrium conversion significantly declined at shorter reaction time. The equilibrium conversions at 523, 573 and 623 K were approximately 36, 34 and 32%, respectively at 60 min reaction time. The reduction in equilibrium conversion could be attributed to instability of linoleic acid at longer reaction time and temperature above 473 K. An important result observed in this study for the linoleic acid esterification system is that a reaction temperature of 523 K appears to be the optimum condition for the uncatalyzed production of ester.

**Effect of metallic substance:** In an effort to determine whether various metals such as Inconel 625, nickel, stainless steel, tantalum and grade-5 titanium wires have catalytic or inhibitory effects and/or corrosion susceptibility on uncatalyzed esterification of carboxylic acids at elevated reaction conditions, experiments were conducted by inserting the metallic substance into the reactor tube. The results on the conversion of lactic acid and the reaction rate at 523 K are shown in Fig. 16 and 17 respectively.
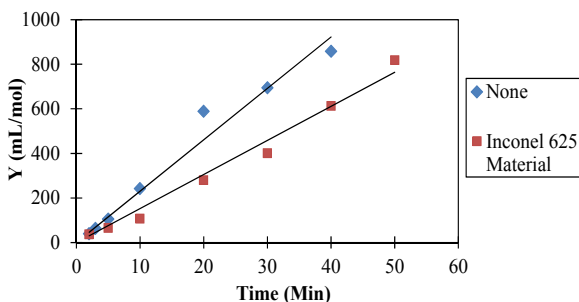
Fig. 17: Reaction rate constant for uncatalyzed esterification of lactic acid with and without inconel 625 material at 523 K
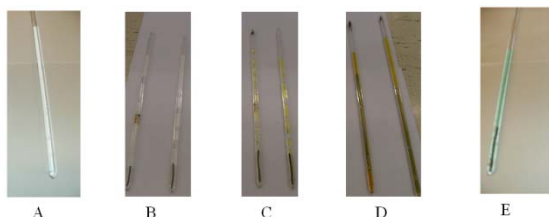


Fig. 18: Reactors with intensity of color formation after uncatalyzed esterification of lactic acid. (A) no metallic substance at 523 K, (B) with inconel 625 at 473 K and 72-h, (C) with inconel 625 at 473 K and 100-h, (D) with inconel 625 at 523 K and 20-h and (E) with stainless steel at 523 K and 2-h



Fig. 19: Reactors with different metallic substances exposed to uncatalyzed esterification of lactic acid at 523 K. From left are reactors with stainless steel, inconel 625, tantalum sheet and reactor with no metallic substance

When Inconel 625 material was added, the equilibrium conversion was nearly equal to that obtained without Inconel 625 material. However, the reaction rate constant was higher with Inconel 625 material. For the reaction with added Inconel 625 material, the equilibrium conversion achieved at 90 min was 70%, while the reaction without Inconel-625 material reached the same equilibrium conversion at 60 min. The reaction rate constants at 523 K are 23±1 mL/ (mol.min) for reaction without Inconel 625 and 15±1 mL/ (mol.min) for reaction with Inconel 625 material. The lower reaction rate constant obtained for reaction with Inconel 625 material may be attributed to reactant-metal surface contact that probably inhibits the reaction.

When the Inconel 625 alloy or nickel wire were added to the reaction medium at 523 K, pale green color was observed in the reactor after 20-h of exposure, whereas, at 473 K, color formation was not noticed until 100-h reaction time. With stainless steel at 523 K, dark green color was noticed before 2-h. The tubes with intensity of green color formation are shown in Fig. 18. The levels of color formation may be attributed to potential corrosion problems associated with metallic substances at elevated temperature.

Nevertheless, comparing tantalum and grade-5 titanium materials with Inconel 625, nickel wire and stainless steel materials, tantalum and grade-5 titanium materials showed acceptable level of compatibility with uncatalyzed esterification of lactic acid with ethanol at 523 K since slight yellow color was observed after 220-h. The tubes with color formation for different metallic substances exposed to uncatalyzed esterification of lactic acid with ethanol at 523 K for 220-h are shown in Fig. 19. The corrosion resistance shown with tantalum and grade-5 titanium materials could encourage the design of flow reactor system for kinetic study of uncatalyzed esterification of carboxylic acids at elevated temperatures.

## CONCLUSION

The kinetic for uncatalyzed esterification of various biomass-derived carboxylic acids (formic, acetic, lactic, levulinic and linoleic) with stoichiometric amounts of ethanol in non-catalytic isothermal batch reactor has been successfully performed. A kinetic model based on second order reversible reaction system has been devised for the process and the kinetic and thermodynamic parameters have been determined as functions of temperature. The estimated thermodynamic and kinetic parameters varied for different uncatalyzed esterification systems. The data calculated from the model have been compared with the experimental data and the two set of data agreed reasonably well for the uncatalyzed esterification systems at varied temperatures.

The reaction temperature was found to affect the reaction rate and equilibrium conversion of carboxylic acid as indicated by linear Arrhenius and Eyring plots. The equilibrium constant for the esterification of short-chain carboxylic acid was found to increase with temperature as indicated by the linear Van't Hoff plots, while the relationship between equilibrium conversion and temperature for the esterification of long-chain carboxylic acid (linoleic acid) showed nonlinear Van't Hoff behavior.

Additional experiments performed at selected temperature to assess the catalytic and corrosion effects of different metallic substances on esterification system showed tantalum and grade-5 titanium to be corrosion resistance metals, suitable for uncatalyzed esterification system at elevated temperature.

## NOMENCLATURES

| | |
|---|---|
| A | = Carboxylic acid |
| B | = Alcohol |
| E | = Ester |
| W | = Water |
| $r_f$ | = Rate of forward reaction, (mol/min) |
| $r_r$ | = Rate of reverse reaction, (mol/min) |
| $k_f$ | = Forward rate constant, (mL/(mol.min)). |
| $k_r$ | = Reverse rate constant, (mL/(mol.min)) |
| $C_{At}$ | = Concentration of carboxylic acid at time t, (mol) |
| $C_{Ao}$ | = Initial concentration of carboxylic acid at time t = 0, (mol) |
| $C_{B0}$ | = Initial concentration of alcohol at time t = 0, (mol) |
| X | = Fractional conversion of carboxylic acid at time t |
| $r_i$ | = Rate of formation of species i, (mol/min) |
| $C_i$ | = Concentration of species I, (mol) |
| t | = Reaction time, (min) |
| $K_{eq}$ | = Equilibrium constant |
| T | = Temperature (K) |
| $\Delta G^o$ | = Reaction Gibbs free energy, (kJ/mol) |
| $\Delta S^o$ | = Reaction entropy, (J/(mol.K) |
| $\Delta H^o$ | = Reaction enthalpy, (kJ/mol) |
| $A_o$ | = Pre-exponential factor, (mL/(mol.min) |
| $E_a$ | = Activation energy of the reaction, (kJ/mol) |
| $\Delta H^{\ddagger}$ | = Enthalpy of activation, (kJ/mol) |
| $\Delta S^{\ddagger}$ | = Entropy of activation, (J/(mol.K) |
| R | = Universal gas constant with a value of 8.3145 J/ (mol.K) |
| $k_B$ | = Boltzmann constant value, ($1.3806488 \times 10^{-23}$ J/K |
| h | = Planck constant value, ($6.62606957 \times 10^{-34}$ J.sec |
| $N_{NaOH}$ | = Normality of NaOH solution, (mol/L) |
| $N_{HCl}$ | = Normality of HCl solution, (mol/L) |
| $V_{NaOH}$ | = Volume of NaOH solution used for the titration, (mL) |
| $V_{HCl}$ | = Volume of HCl solution used for the titration, (mL) |
| F | = Free Acidity as Formic Acid, (wt %) |
| $MW_{Formic Acid}$ | = Molecular weight of Formic Acid, (46.02 g/mol) |
| $W_{Sample}$ | = Sample weight, (g) |
| $C_A$, $C_B$, $C_E$ and $C_W$ | = Concentrations of carboxylic acid, alcohol, ester and water, respectively |

## REFERENCES

Argonne National Laboratory, 1998. Novel Membrane based Process for Producing Lactate Esters. Retrieved form: www.epa.gov/oppt/green chemistry (Accessed on: February, 2007).

Asthana, N.S., A.K. Kolah, D.T. Vu, C.T. Lira and D.J. Miller, 2006. A kinetic model for the esterification of lactic acid and its Oligomers. Ind. Eng. Chem. Res., 45: 5251.

Ayoub, P.M., 2005. Process for the reactive extraction of levulinic acid. World Patent 2005/070867A1.

Bart, H.J., J. Reidetschlager, K. Schatkaj and A. Lehmann, 1994. A kinetic of esterification of levulinic acid with n-butanol by homogeneous catalysis. Ind. Eng. Chem. Res., 33: 21-25.

Benedict, D.J., S.J. Parulekar and S.P. Tsai, 2003. Esterification of lactic acid and ethanol with/without pervaporation. Ind. Eng. Chem. Res., 42: 2282-2291.

Calvar, N., B. Gonzalez and A. Dominquez, 2007. Esterification of acetic acid with ethanol: Reaction Kinetic and operation in a packed bed reactive distillation column. Chem. Eng. Proc., 46: 1317-1323.

Carole, T.M., J. Pellegrino and M.D. Paster, 2004. Opportunities in the industrial biobased products industry. Appl. Biochem. Biotech., 115: 871.

Choi, J.I., W.H. Hong and H.N. Chang, 1996. Reaction kinetic of lactic acid with methanol catalyzed by acid resins. Int. J. Chem. Kinet., 28: 37.

Christian, R., 1990. Solvents and Solvent Effects in Organic Chemistry. 2nd Edn., Wiley-VCH, New York.

Delgado, P., M.T. Sanz and S. Beltran, 2007. Kinetic study for esterification of lactic acid with ethanol and hydrolysis of ethyl lactate using an ion-exchange resin catalyst. Chem. Eng. J., 126: 111.

DiLeo, G.J. and P.E. Savage, 2006. Catalysis during methanol gasification in supercritical water. J. Supercrit. Fluid., 39: 228-232.

Engin, A., H. Haluk and K. Gurkan, 2003. Production of lactic acid esters catalyzed by heteropoly acid supported over ion-exchange resins. Green Chem., 5: 460-466.

Gui, M.M., K.T. Lee and S. Bhatia, 2009. Supercritical ethanol technology for the production of biodiesel: Process optimization studies. J. Supercrit. Fluid., 49: 286-292.

Hoydonckx, H.E., D.E. DeVos, S.A. Chavan and P.A. Jacobs, 2004. Esterification and transesterification of renewable chemicals. Top. Catal., 27: 83.

Ignacio, V.I., C. Silva, G.R. Borges, F.C. Corazza, V. Oliveira, M.A. Grompone and J.I. Iva´n, 2008. Continuous production of soybean biodiesel in supercritical ethanol-water mixtures. J. Energ. Fuels, 22: 2805-2809.

Isyama, Y. and S. Saka, 2008. Biodiesel production by supercritical process with crude bio-methanol prepared by wood gasification. Bioresource Technol., 99: 4775-4779.

Jessop, P.G. and W. Leitner, 1999. Chemical Synthesis Using Supercritical Fluids. Wiley-VCH, New York, pp: 1-30.

LiIja, J., D.Y. Murzin, T. Salmi, J. Aumo, P. Maki-Arvela and M. Sundell, 2002. Esterification of different acids over heterogeneous and homogeneous catalysts and correlation with the Taft equation. J. Mol. Catal. A-Chem., 182: 555-563.

Liu, Y., E. Lotero and J.G. Goodwin, 2006. Effect of carbon chain length on esterification of carboxylic acids with methanol using acid catalysis. J. Catal., 243: 221-228.

Pipus, G., I. Plazl and T. Koloini, 2007. Esterification of benzoic acid in microwave tubular flow reactor. Chem. Eng. J., 6: 239.

Rathin, D. and T. Shih-Perng, 1998. Esterification of fermentation-derived acids via pervaporation. U.S. Patent 05723639.

Ronnback, R., T. Salmi, A. Vuori, H. Haario, J. Lehtonen, A. Sundqvist and E. Tirronen, 1997. Development of a kinetic model for the esterification of acetic acid with methanol in the presence of a homogeneous acid catalyst. Chem. Eng. Sci., 52: 3369-3381.

Sanz, M.T., R. Murga, S. Beltran and J.L. Cabezas, 2002. Auto catalyzed and ion exchange resin catalyzed esterification kinetic of lactic acid with methanol. Ind. Eng. Chem. Res., 41: 512.

Seo, Y. and W.H. Hong, 2000. Kinetic of esterification of lactic acid with methanol in the presence of cation exchange resin using a pseudo-homogenous model. J. Chem. Eng. Jpn., 33: 128.

Smith, H.A., 1939. Kinetic of the catalyzed esterification of normal aliphatic acids in methyl alcohol. J. Am. Chem. Soc., 61: 254-260.

Tanaka, K., R. Yoshikawa, C. Ying, H. Kita and K. Okamoto, 2002. Application of zeolite T membrane to vapor-permeation-aided esterification of lactic acid with ethanol. Chem. Eng. Sci., 57: 1577.

Winzor, D.J. and C.M. Jackson, 2006. Interpretation of the temperature dependence of equilibrium and rate constants. J. Mol. Recognit., 19: 389-407.

Xu, Z.P. and K.T. Chuang, 1996. Kinetic of acetic acid esterification over ion exchange catalysts. Can. J. Chem. Eng., 74: 493.

Zaidi, A., J.L. Gainer, G. Carta, A. Mrani, T. Kadiri, Y. Belarbi and A. Mir, 2002. Esterification of fatty acids using nylon-immobilized lipase in *n*-hexane: Kinetic parameters and chain-length effects. J. Biotechnol., 93: 209-216.

Zhang, Y., L. Ma and J. Yang, 2004. Kinetic of esterification of lactic acid with ethanol catalyzed by cation-exchange resins. React. Funct. Polym., 61: 101-114.