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Uncatalyzed esterification of biomass-derived carboxylic acids

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UNCATALYZED ESTERIFICATION OF BIOMASS-DERIVED CARBOXYLIC ACIDS

by

Kehinde Seun Bankole

An Abstract

Of a thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemical and Biochemical Engineering in the Graduate College of The University of Iowa

May 2011

Thesis Supervisors: Adjunct Associate Professor Gary A. Aurand
Professor Alec B. Scranton

ABSTRACT

To shift from a petroleum-based to a biomass-based economy will require the development not only of biofuels, but also of biorenewable replacements for petroleum-derived chemicals. In this regard, environmentally friendly biomass-derived esters may serve as alternatives to fossil-derived chemicals such as toxic halogenated solvents and glycol ethers. Therefore, esterification of various carboxylic acids that find significant applications in the chemical, pharmaceutical, petrochemical, food, and cosmetic industries has been initiated by the chemical industry.

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 to shift the equilibrium conversion. Heterogeneous or homogeneous acid catalysts are used to achieve acceptable reaction rates. The conventional acid-catalyzed process has been extensively developed; but it suffers from problems associated with the generation of side reactions, corrosion of equipment, expensive purification procedures, long reaction times and discharge of acidic wastes. Various attempts on esterification of carboxylic acids with ethanol have previously addressed important issues concerning product distribution, catalyst activity, and kinetics of acid-catalyzed esterification at lower reaction temperatures, but kinetics of uncatalyzed esterification at elevated reaction temperatures are still very limited. It is thus of great interest from a practical viewpoint that more information such as kinetic and thermodynamic parameters are required to develop a possible esterification process without using any catalyst.

In this work, therefore, a fundamental study on the uncatalyzed esterification of different aliphatic carboxylic acids with stoichiometric amounts of ethanol was undertaken to examine the possibility of converting the biomass-derived carboxylic acids to ethyl esters and to determine the kinetic and thermodynamic parameters for the uncatalyzed esterification. Experiments were conducted with isothermal batch reactors at temperatures ranging from 298 K to 623 K. A 2nd-order reversible kinetics rate expression was used to fit the experimental data. The thermodynamic and kinetic values estimated were found to vary for different esterification systems studied. The dependence of K_{eq} on temperature for esterification of short-chain and long-chain carboxylic acids varied. Despite the nonlinearity of the Van't Hoff plot for esterification of linoleic acid, the Arrhenius and Eyring plots were linear. Two thermodynamic paths were developed for estimating the equilibrium conversions, and the theoretical values compared well with the experimental results reported in this study.

Additional experiments performed to assess the corrosive and catalytic influences of metallic materials on esterification reaction indicated Inconel 625 alloy, nickel wire and stainless steel materials have potential corrosion problems on the uncatalyzed esterification reaction at elevated reaction. However, tantalum and grade 5 titanium materials showed acceptable level of compatibility for similar reaction conditions, and this can encourage the design of a flow reactor system.

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CERTIFICATE OF APPROVAL

PH.D. THESIS

This is to certify that the Ph.D. thesis of

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has been approved by the Examining Committee for the thesis requirement for the Doctor of Philosophy degree in Chemical and Biochemical Engineering at the May 2011 graduation.

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Humbly Dedicated
To My Loving Father and Mother

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ABSTRACT

To shift from a petroleum-based to a biomass-based economy will require the development not only of biofuels, but also of biorenewable replacements for petroleum-derived chemicals. In this regard, environmentally friendly biomass-derived esters may serve as alternatives to fossil-derived chemicals such as toxic halogenated solvents and glycol ethers. Therefore, esterification of various carboxylic acids that find significant applications in the chemical, pharmaceutical, petrochemical, food, and cosmetic industries has been initiated by the chemical industry.

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In this work, therefore, a fundamental study on the uncatalyzed esterification of different aliphatic carboxylic acids with stoichiometric amounts of ethanol was undertaken to examine the possibility of converting the biomass-derived carboxylic acids to ethyl esters and to determine the kinetic and thermodynamic parameters for the uncatalyzed esterification. Experiments were conducted with isothermal batch reactors at temperatures ranging from 298 K to 623 K. A 2^{nd}-order reversible kinetics rate expression was used to fit the experimental data. The thermodynamic and kinetic values estimated were found to vary for different esterification systems studied. The dependence of K_{eq} on temperature for esterification of short-chain and long-chain carboxylic acids varied. Despite the nonlinearity of the Van't Hoff plot for esterification of linoleic acid, the Arrhenius and Eyring plots were linear. Two thermodynamic paths were developed for estimating the equilibrium conversions, and the theoretical values compared well with the experimental results reported in this study.

Additional experiments performed to assess the corrosive and catalytic influences of metallic materials on esterification reaction indicated Inconel 625 alloy, nickel wire and stainless steel materials have potential corrosion problems on the uncatalyzed esterification reaction at elevated reaction. However, tantalum and grade 5 titanium materials showed acceptable level of compatibility for similar reaction conditions, and this can encourage the design of a flow reactor system.

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CHAPTER 1: INTRODUCTION

1.1. Motivation

The increased demand for energy, concerns about climate change, national security, energy dependence, and the need to reduce the environmental impacts from traditional fossil based chemicals, solvents, and fuels have led to a growing interest in alternative and renewable resources.[1-4] Among the several renewable resource options available, biomass is an important resource that can be converted to energy, chemicals, and petroleum compatible products. For example, polysaccharides, which are major components of biomass, can be converted to ethanol and various organic acids (carboxylic acids) useful for esterification. For the conversion of biomass-derived resources into useful chemicals, esterification of biomass-derived carboxylic acids has been initiated by the chemical industry to synthesize corresponding esters, which have significant applications in various areas like pharmaceuticals, plasticizers, solvents, food flavors, coating, and fragrance.[5-8] Some esters are converted into their derivatives, which are useful as chemical intermediates and monomers for resins and high molecular weight polymers.[9] Therefore, the conversion of biomass-derived ethanol and carboxylic acids into value-added esters has motivated the focus of this study.

1.2. Problem Identification

Esterification is a well-known process, from which important chemicals such as methyl, ethyl and butyl esters of carboxylic acids have been 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. This reaction is generally carried out in batch reactors in the presence of homogeneous or heterogeneous acid catalysts and also with supported heterogeneous acid catalysts in a fixed bed reactor with concurrent down-flow of the liquid phases to achieve acceptable reaction rates.[5-8, 10-37] Although the acid-catalyzed process has been extensively developed, it has at least the following inherently undesirable drawbacks:[11-18,29] 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 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 routes for synthesizing a wide variety of industrial products due to ease of separation and purification of the products without contamination is essential.

1.3. Research Justification

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. Performing reactions under supercritical conditions rather than in the conventional gas or liquid phase could be an interesting option for improving the equilibrium conversion, enhancing the reaction rate and making the process more environmentally friendly.[38] It has also been reported that at supercritical state, the dielectric constant of alcohol decreases, and this allows supercritical alcohol to become a better solvent for organic compounds, which consequently enables a homogeneous reaction system with more favorable kinetics.[39]

Supercritical ethanol (SC_{EtOH}), 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.[40-41] Ethanol has been a good choice as a reaction medium because presently, ethanol can be easily produced from biomass. Thus, ethanol will be used both as reactant and reaction medium for the uncatalyzed esterification reaction system.

In addition, research 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 at lower reaction temperatures, but kinetics of uncatalyzed esterification at elevated reaction temperatures is still very limited. It is thus of great interest from a practical point of view that more information such as kinetic and thermodynamic parameters are available to develop a possible esterification process without using any catalyst.

In this work, therefore, a fundamental study on the uncatalyzed esterification of different aliphatic carboxylic acids with stoichiometric amount of ethanol was undertaken to investigate the possibility of converting the biomass-derived carboxylic acids to ethyl esters and to determine the kinetic and thermodynamic parameters for the uncatalyzed esterification using isothermal batch reactors.

CHAPTER 2: BACKGROUND

2.1. Biomass-Derived products

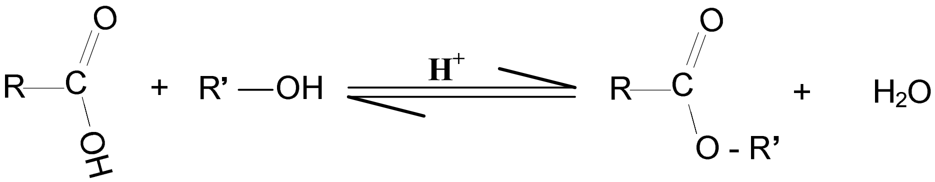
Biomass, being a viable alternative to fossil material, is a biological material derived from living organisms such as plant, waste and other derived organic matter available on a renewable basis. Of the types of biomass, lignocellulosic biomass (e.g. wood and switchgrass), which is the main naturally available biomass resource, has been used in a variety of applications ranging from engineering materials to a source of energy.

Lignocellulosic biomass is mainly a mixture of cellulose (38-50 wt%), hemicelluloses (23-32 wt%), and lignin (15-25 wt%) which are held together by covalent bonding, various intermolecular bridges, and van der Waals forces, forming a complex structure.[4] While lignocellulosic biomass material is not only useful as direct heating source, its degradation products are also potentially useful intermediates in industry.

The significance of glucose from cellulose hydrolysis is evident in its fermentation product, cellulosic ethanol. Glucose, which can be produced from hydrolysis of cellulose, can be degraded into other small molecules such as 5-hydroxymethylfurfural (5-HMF), lactic, acetic, formic and levulinic acids.[42] These acids have important economic values. These products from the degradation of lignocellulosic biomass have recently been obtained with supercritical fluid technology.[4, 42]

2.2. Catalysis of Esterification Reaction

Esterification can be defined as the transformation of carboxylic acids or their derivatives into esters, and esterification is an important class of reactions in which the kinetics have been investigated, dating back to the innovative efforts of Berthelot and Gilles in 1862.[43] There are many available reaction routes, such as solvolytic, condensations and free radical processes for the preparation of esters.[44] The most widely applied method is the direct esterification of carboxylic acid with alcohol in presence of homogeneous mineral acid or a heterogeneous catalyst. However, the conventional acid-catalyzed esterification system suffers from problems associated with the generation of side reactions (such as etherification, and dehydration), corrosion of equipments, expensive purification procedures, long reaction times and discharge of acidic wastes.[11-18, 29, 44] Synthesis of ester compounds by the treatment of carboxylic acids with alcohol is a reversible reaction, wherein water is a byproduct (Reaction 1).



Reaction 1. Esterification of Carboxylic Acid

Esterification reaction proceeds with or without a catalyst. However, at atmospheric conditions, the uncatalyzed esterification reaction is extremely slow, since its rate depends on the catalysis by the carboxylic acid itself. Therefore, esterification has been performed with external acid catalyst, which acts as a proton donor to the carboxylic acid. Some reported catalysts used for esterification reactions are listed in Table 1.

Esterification is usually carried out in a batch or continuous reactor depending on the scale of operation. It can also be carried out in the vapor phase by heating a mixture of acid, alcohol, and catalyst to the desired temperature. The rate of ester formation depends on the type of carboxylic acid and alcohol reacted. Primary alcohols react faster than secondary alcohols, while the secondary alcohols react faster than tertiary alcohols. Within each series, the reaction rate decreases with increasing molecular mass. Straightchain acids react more rapidly than branched acids; particularly, branching at the α-position lowers the rate of esterification. Esterification of aromatic acids, like benzoic acid, is generally slow. Esterification of benzoic acid with methanol containing isotopic oxygen (^{18}O) has shown that the oxygen in the water formed during acid-catalyzed esterification originates from the acid, not from the alcohol.[45] The mechanism of acid-catalyzed esterification reaction has been discussed in detail by Zimmermann and Rudolf.[46]

Table 1. Selected Catalysts for Esterification Systems

HOMOGENEOUS	HETEROGENEOUS
Sulfuric acid, Toluenesulfonic acid, Phosphoric acid, Hydrochloric acid, Ferric sulfate hydrate, Methyl thiosulphate, Aluminium trichloride, Niobic acid, Alkyl benzene sulfonic acid, Hydrogen Iodide.	Ion exchange resins, Enzymes, Ion exchange membranes, Solid super acids, Polyolefin supported sulfonic acid, Solid super acid of $Zr(OH)_4$ exposing with H_2SO_4 by calcinations, Solid acid having salts of $H_3PW_{12}O_{40}CS_2.5PW_{12}O_{40}$, Heteropolyacids supported on activated carbon, Solid acids of metal oxide promoted with SO_4^{2-}, H_3PO_4 supported on silica gel.

Esterification reaction is a slow equilibrium-limited reaction. The equilibrium must be shifted toward the product side by excess use of one of the reactants or continuous removal of one of the products, especially water, by azeotropic distillation. Ester synthesis through direct esterification between carboxylic acid and alcohol is conventionally conducted with the aid of external acid catalysts, but compatibility of the catalysts with other functional groups in the reaction medium is an important problem to address. Possible undesired side reactions of the conventional homogenously acid-catalyzed reaction are shown in Reactions 2 and 3.

$$C_2H_5OH + H_2SO_4 \rightarrow CH_2 = CH_2 + 2H_2O + SO_3$$
$$\text{Ethanol} + \text{SulfuricAcid} \rightarrow \text{Ethylene} + \text{Water} + \text{Sulfite} \quad (2)$$

$$C_2H_5OH + H_2SO_4 \rightarrow CH_3CH_2OCH_2CH_3 + 2H_2O + SO_3$$
$$\text{Ethanol} + \text{SulfuricAcid} \rightarrow \text{Diethyl ether} + \text{Water} + \text{Sulfite} \quad (3)$$

Reactions 2 and 3. Possible Side Reactions in Catalytic Esterification Reaction

Thus, the catalyst-free (uncatalyzed) reaction which provides cleaner routes for ester synthesis due to ease of separation and purification of the products without contamination is more desirable. Uncatalyzed reaction is enabled when reaction is carried out at high temperatures.

2.2.1. Homogeneous Acid-Catalyzed Esterification

Homogeneous catalysts such as sulfuric acid, hydrochloric acid, hydrogen iodide, phosphoric acid, *p*-toluenesulfonic acid, and mixtures of acids are efficient homogenous catalysts generally used for acid-catalyzed esterification. The homogenous acid-catalyzed esterification of carboxylic acids have been reported to give higher conversion than the heterogeneous acid-catalyzed esterification system, because the heterogeneous catalysts have been shown to exhibit limitations for catalyzing esterification due to low thermal stability, mass transfer resistance or loss of active acid sites (adsorption of reactants and swelling nature) in the presence of a polar medium.[14,36-37,76] But the disadvantage of homogenous mineral acids is their miscibility with the reaction medium leading to equipment corrosion and separation problems. The homogeneous method involves passing the alcohol through the mixture of carboxylic acid and homogenous acid catalyst already preheated to a temperature above the alcohol boiling temperature.[17, 31] Ronnback et al. studied the kinetics of esterification of acetic acid with methanol in presence of hydrogen iodide.

2.2.2. Heterogeneous Acid-Catalyzed Esterification

Heterogeneous acid-catalyzed esterification reactions have been investigated by various researchers. The process involves the reaction of carboxylic acid with alcohol in presence of insoluble solid acid catalyst at a temperature below the alcohol boiling temperature. Some of the solid-acid catalysts studied are ion-exchange resins,[5,11,15,18,22,32] acid-treated clays,[21] heteropolyacids,[20,29,30,34] Zeolite-T membrane,[33] and immobilized enzymes.[68] Nevertheless, of all the reported heterogeneous catalysts, ion-exchange resin and enzyme catalysts are reported to be most effective for heterogeneous phase esterification reactions. However, deactivation of solid catalysts does occur due to aging, aqueous adsorption, and swelling nature.[29, 66-68]

2.2.2.1. Ion exchange resins as catalysts

Ion exchange resin catalysts have been used for several years in esterification reactions. Ion exchange material is broadly defined as an insoluble matrix containing labile ions capable of exchanging with ions in the surrounding medium without major physical change in its structure.[77] Typical resin catalysts are sulphonic acids fixed to a polymer carrier, such as polystyrene cross-linked with divinylbenzene (DVB). Several commercially available catalysts are Amberlyst resins such as Amberlyst–15 and Amberlite IR-120. Unlike catalysis by dissolved electrolytes, with resins diffusion, adsorption, and desorption processes are present, and the concentration of the reactants at the active site of the catalyst (where the reaction takes place) may be different from that in the bulk solution. Also, the matrix with the fixed ionic group may have some influences that are not purely physical on the course of the reaction.[78]

2.2.2.2. Enzymes as catalysts

Enzymes have been widely used in esterification technology. In particular, lipase enzymes are used for the resolution of racemic alcohols and carboxylic acids through asymmetric hydrolysis of the corresponding esters. Yeast (*Candida cylindracea*) completely converts a carboxylic acid and an alcohol into the corresponding ester in the presence of organic solvents, in a highly stereoselective manner.[79] Enzymes are highly stable in organic solvents compared to water. To predict the behavior of batch enzymatic reactors, Mensah and co-workers developed a model incorporating reaction kinetics, water partitioning, and mass transfer effects. Also conducted were experimental and theoretical studies on immobilized enzyme catalyzed esterification of propionic acid with isoamyl alcohol in presence of hexane as solvent to understand the dynamic behavior of a continuous-flow packed-bed reactor.[80]

2.3. Development of Kinetic Model for Uncatalyzed Esterification Reaction

Kinetic analysis is to find a model that describes the rate of reaction as a function of system variables that define the chemical process. Kinetics of esterification between carboxylic acids and alcohols have been extensively studied. There are two different opinions about the ways in which hydrogen ion (H^+) in the catalyst performs its catalytic effect. One of the opinions is that the carboxylic acid molecule is initially activated by the H^+ ions before it is esterified with a molecule of alcohol. The other opinion is that the H^+ ions from the catalyst form complexes with the alcohol molecules, after which the esterification proceeds through interaction of molecules of the complex with the molecules of carboxylic acid. The rate of formation of ester in this case is thus related to the concentration of the carboxylic acid.[81] Studies on the kinetics of hydrogen ion catalyzed esterification of seven normal aliphatic carboxylic acids in methanol were reported, and the influence of acids and the length of the carbon chain of the acid on the rate of esterification system was emphasized.

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

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} E + W \tag{1}$$

Where, A and B are the reactants (carboxylic acid and alcohol), while E and W are the products (ester and water) in the reaction. Hence, the rate of forward reaction (r_f) depends on the concentrations of A and B (Equation 2) while the rate of reverse reaction (r_r) is a function of the concentrations of E and W (Equation 3).

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

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

The terms k_f and k_r are the forward rate constant and reverse rate constant, respectively, with units of mL/ (mol.min).

In the reversible reaction, each compound is being produced and consumed concurrently. For instance, compound A is being consumed in the forward reaction and simultaneously being produced in the reverse reaction. Therefore, the rate of change of concentration for compound A depends on both the forward and the reverse reaction rates. To evaluate the rate parameters in the kinetic model, the experimental concentration-time data are correlated using a batch reactor model under isothermal conditions as described in Equations 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 are: at t=0; $C_A=C_{A0}$, $C_B=C_{B0}$ and $C_E = C_W = 0$, Where, C_{A0} and C_{B0} are the initial concentrations of carboxylic acid and alcohol respectively.

When the esterification reaction reaches equilibrium, the rates of the forward reaction and reverse reaction are equal, and therefore the apparent equilibrium constant (K_{eq}) can be obtained from the equilibrium composition of the reaction mixture using Equation 9, which is obtained from Equation 8.

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

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

After some simple algebraic substitutions, the overall reaction rate of compound in the homogeneous reversible reaction can be written as Equation 10.

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

where r_i is the rate of formation of species i, C_i is the concentration of species i; t is reaction time, k_f is the forward reaction rate constant, K_{eq} is the reaction equilibrium constant, C_A, C_B, C_E, and C_W are concentrations of carboxylic acid, alcohol, ester, and water, respectively.

The value of K_{eq} varies with reaction temperature. If the reaction enthalpy is assumed to be constant with temperature, a simple relation to describe K_{eq} dependence on reaction temperature can be expressed by the Van't Hoff equation:

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

Where ΔG^o is reaction Gibbs free energy, ΔS^o is reaction entropy, ΔH^o is reaction enthalpy, and R is the universal gas constant with a value of 8.3145 J/(mol.K).

The value of forward reaction rate constant (k_f) is a function of temperature, and can be expressed by the Arrhenius equation:

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

Where A_o is the pre-exponential factor, T is the temperature, and E_a is the activation energy of the reaction.

The Eyring equation (Equation 13), which is similar to the Arrhenius equation, has been used to relate the rate constant to the temperature according to the transition state theory, and Equation 13 can be used to determine the activation parameters.

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

Where k_B is the Boltzmann constant, h is the Planck constant, $\Delta H^{\ddagger}$ is the enthalpy of activation, $\Delta S^{\ddagger}$ is the entropy of activation, T is the temperature, and (k_B*T/h) is the universal frequency factor.

2.4. Previous Kinetics Studies of Esterification Reactions

A kinetics study is essential in the analysis of a reaction system used in an industrial process. The goal of kinetic analysis is to find a model that describes the rate of reaction as a function of system variables that define the chemical process. Chemical kinetics are studied to gain fundamental insight into reaction mechanisms, and to aid reactor design for process development. When the esterification reaction is considered, the effects of reaction temperature, concentration of external acid catalyst, and reactant molar ratio have been previously investigated to some levels. The reaction has been studied using homogeneous and heterogeneous catalysts.

Sanz and co-workers[5] investigated the esterification kinetics of homogeneous and heterogeneous (Dowex 50W, ion exchange resin) acid-catalyzed esterification of lactic acid with methanol. The effects of catalyst type, stirrer speed, catalyst size, catalyst loading, reactant molar ratio and temperature on reaction kinetics were evaluated. Experimental reaction rates were correlated by some models based on homogeneous and heterogeneous catalytic reactions. Non-ideality of the liquid phase was taken into account by using activities instead of mole fractions. Prediction of the activity coefficients was made by UNIFAC. Parameters of the different models were obtained by the simplex search method.

Bart and co-workers[6] studied the esterification of levulinic acid (98.5 wt%) with butanol, using sulfuric acid as homogeneous catalyst. The kinetic data were correlated with a reversible second order reaction mechanism based on the compound concentrations. It was reported that the logarithm of the rate constant was proportional to the reciprocal of absolute temperature as per Arrhenius law of temperature dependence.

Delgado and co-workers[7] investigated the esterification of lactic acid (20 wt%) with ethanol and the hydrolysis of the ethyl lactate in the presence/absence of an ion-exchange resin, and the kinetics data were simultaneously correlated through heterogeneous Langmuir-Hinshelwood (LH) and Pseudo Homogeneous (PH) models.

Xu and Chang[13] investigated the kinetics study of Amberlyst-15 catalyzed esterification of dilute acetic acid with methanol at temperature range between 40 °C to 94 °C in a batch reactor. The internal mass transfer resistance was found to be insignificant to the reaction system. A kinetic equation was developed and proposed to be used in the design of a catalytic distillation column for removing dilute acetic acid from wastewater.

Lilja and co-workers[14] studied the esterification of acetic, propanoic and pentanoic acids with methanol, ethanol, 1-propanol, 2-propanol, butanol and 2-butanol in the presence of fibrous polymer-supported sulphonic acid catalyst (Smopex-101) at 60 °C with the equimolar initial ratio between the reactants. Higher reaction rate was reported as the acid and alcohol chain lengths reduce, and the branching of the alcohol chain also reduced the reaction rate.

Ronnback and co-workers[17] developed the kinetic model for the esterification of acetic acid with methanol in the presence of homogeneous hydrogen iodide acid catalyst at 30 °C to 60 °C. Possible reaction mechanisms for methyl acetate and methyl iodide formation were proposed. Rate equations, concentration-based, and activity-based, with UNIFAC activity coefficient estimations were derived, and the kinetics and equilibrium parameters included in the rate equations were estimated from experimental data with regression analysis.

Benedict and co-workers[17] investigated the esterification of lactic acid (88 wt%) and ethanol with/without a solid catalyst. A kinetic model based on compound concentrations was used to describe the reaction behavior, and the presence of oligomers was not mentioned in the study.

Yadav and co-workers[21] studied the esterification of lactic acid with isopropanol in the presence of various heterogeneous catalysts (Indion-130, Amberlyst-36, Amberlyst-15, Amberlite-120, Dowex 50W, Filtrol-44, 20% DTPA/K-10 and 20% DTPA/Filtrol-44). A theoretical kinetics model was developed for evaluating the reaction. The effects of various parameters on the reaction rate were evaluated. The reaction was found to be kinetically controlled and there were no external and internal mass transfer limitations on the reaction rate.

Troupe and Kobe[24] studied the esterification reaction of aqueous lactic acid (44 and 85 wt%) with ethanol in the presence of sulfuric acid as homogeneous catalyst. Based on the results, the data were fitted with an empirical equation and it was reported that the reaction mechanism changed when the reactants initial molar ratio exceeded 4.

Asthana and co-workers[27] investigated the esterification of different lactic acid concentrations (20, 50, and 88 wt%) with ethanol. The presence of oligomers was taken into account, and a simple reversible rate expression based on the compound concentration was used to describe the reaction kinetics. Zhang and co-workers[31] studied the esterification of aqueous lactic acid (80 wt%) with ethanol in the presence of five different cation-exchange resins. The LH-model mechanism was proposed to describe the kinetics behavior due to the adsorption of water and ethanol on the catalyst.

Tanaka and co-workers[33] studied the esterification of lactic acid (86 wt%) with ethanol in the presence of cation-exchange resins. The presence of oligomers was considered and the reaction kinetics were also described by a simple reversible second order reaction mechanism based on the compound concentration. Yadav and Borkar[68] investigated the esterification of levulinic acid with butanol using different immobilized lipases as catalyst and tetra-butyl methyl ether as solvent; the reaction kinetics were described through the “ping-pong bi-bi” mechanism based on alcohol inhibition.

Supercritical fluids like methanol and carbon dioxide have been applied to esterification of fatty acid compounds.[47, 49, 69,75] Srivastava and co-workers[75] investigated the influence of excess water and ethanol on the reaction kinetics of enzyme catalyzed esterification of myristic acid with ethanol in the presence of supercritical carbon dioxide. It was reported that the enzyme activity was retarded by addition of excess ethanol and water, and this reduced the conversion of myristic acid. On the contrary, higher yields of fatty acid ethyl esters from reacting soybean oil and ethanol in sub-critical and supercritical conditions have been reported.[41]

In summary, the results of most kinetics studies revealed an increase in reaction rate and conversion with increasing temperature and reactant molar ratio. Increasing the external acid catalyst has no significant effect on the equilibrium conversion.[6-7, 32] The Arrhenius law was used to express the relationship between rate constant and temperature. Since the polarity of reaction components, primarily water and alcohol, influences the number of accessible active acid sites of the resins to the reactants, [66-68] the activity of solid catalyst reduces (catalyst deactivation). Consequently solid catalysts are not practical in esterification reaction systems.

Nevertheless, in spite of several published reports on kinetics of esterification of carboxylic acids, the majority of the previous studies focused mainly on the low temperature range, used external acid catalyst and excess alcohol, and some observed side reactions.[13,15-17] Some of the authors did not include the reverse reaction rate constant in the kinetics model, and this assumption is only valid at low conversion, and/or if excess concentration of one of the reactants is used,[13,15] but not when equimolar concentrations of reactants are used. In some works, the authors did not report the values of the equilibrium constant[32] and thermodynamic parameters. Selected literature reports on kinetics of esterification of carboxylic acids with alcohols are listed in Table 2.

Table 2. Published Kinetics Parameters for Esterification Reaction

Reference	Organic Acid Concentration (wt. %)	Reaction Temperature °C	Reactants	Ethanol / Acid Molar Ratio	Catalyst / Concentration	E_a (kJ/mol)	Frequency Factor (A_o)	Enthalpy of Reaction (kJ/mol)
25	85 wt.% lactic Acid	25-100	Lactic Acid / Ethanol	4	0.167 wt.% H_2SO_4	62	NA	NA
6	98.5 wt. % Levulinic Acid	23-118	Levulinic / Butanol	1	1 mol% H_2SO_4	54	286 087$(m^3)^2$ $kmol^{-2}s^{-1}$	7 ± 1 kJ /mol
7	20 wt.% lactic Acid	55-85	Lactic Acid / Ethanol	3	2.5 wt.% Cation Exchange Resin	52	NA	NA
7	20 wt.% lactic Acid	55-85	Lactic Acid / Ethanol	3	0	62	8.354×10^8 (mol $g^{-1}min^{-1}$)	NA
18	88 wt.% lactic Acid	75-95	Lactic Acid / Ethanol	1.2	5 wt. % Cation Exchange Resin	30	1.257 x 10^4 L/ kg-$_{cat}$./min	- 4.441
32	80 wt.% lactic Acid	60-88	Lactic Acid / Ethanol	3	4 wt.% Cation Exchange Resin	52	NA	NA
27	20 wt.% lactic Acid	62-90	Lactic Acid / Ethanol	3	3 wt. % Cation Exchange Resin	48	1.91 x 10^5 kg $_{sol}$/kg-$_{cat}$/s	NA
27	55 wt.% lactic Acid	62-90	Lactic Acid / Ethanol	3	3 wt.% Cation Exchange Resin	54	2.66 x 10^4 kg $_{sol}$/kg-$_{cat}$/s	NA
27	88 wt.% lactic Acid	62-90	Lactic Acid / Ethanol	3	3 wt. Cation Exchange Resin	74	1.24 x 10^7 kg $_{sol}$/kg-$_{cat}$/s	NA

2.5. Supercritical Fluids

A supercritical fluid (SCF) is a substance whose temperature and pressure are above its critical point.[a] The pressure-temperature phase diagram for a model supercritical fluid is represented in Figure 1. A pressure-density phase diagram for a model pure substance is shown in Figure 2. Figure 2 illustrates that fluid at its supercritical state has higher density than that of vapor. The critical temperature is the temperature above which a substance cannot exist as a liquid. The critical pressure is the pressure above which a substance will not boil.

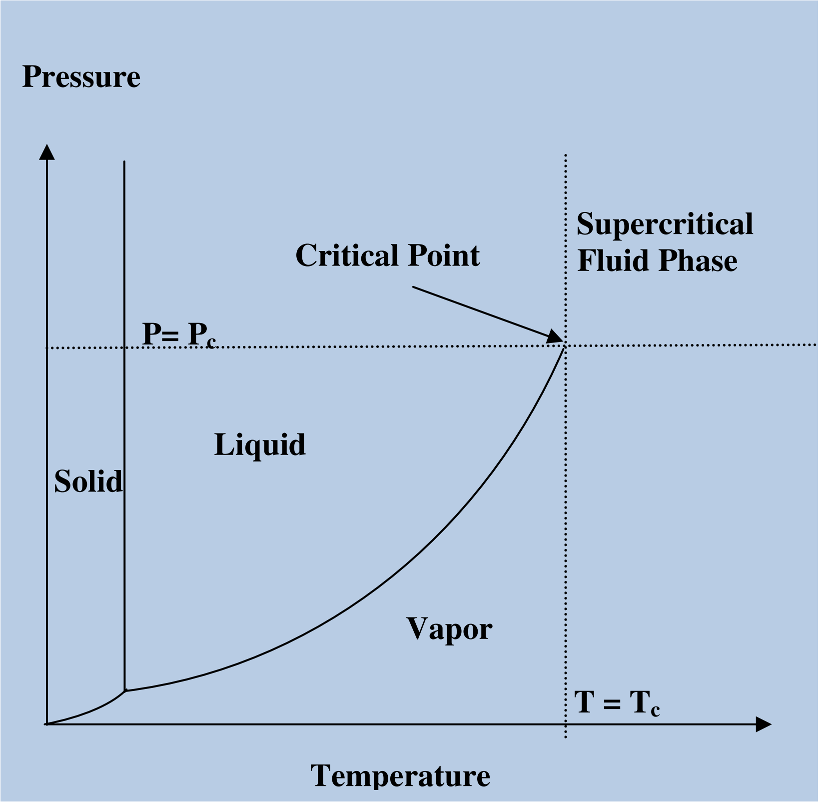


Figure 1. Pressure-Temperature Phase Diagram for model Supercritical Fluid

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[a] Critical point: This is a boundary at which a substance's gaseous and liquid phases merge together to become indistinguishable.

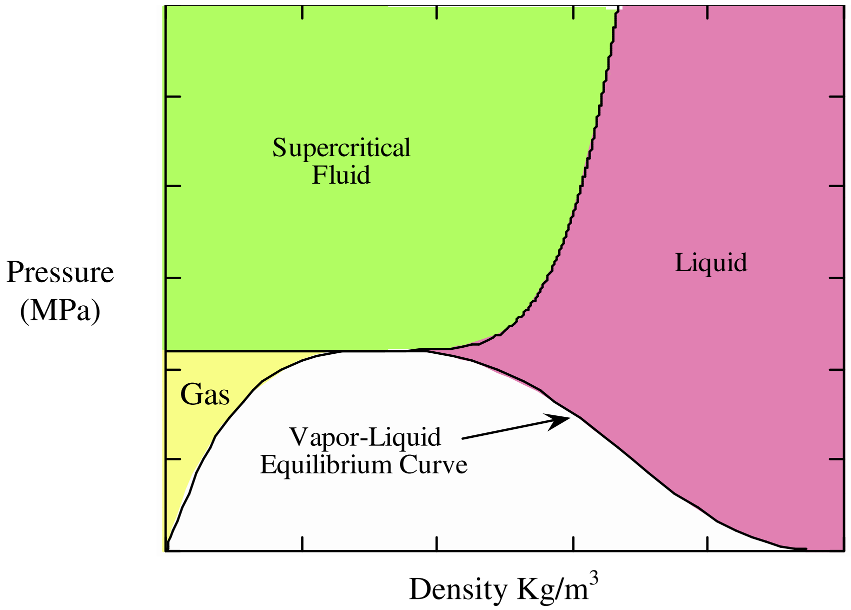


Figure 2. Pressure-Density Phase Diagram for Pure substance

Supercritical fluids (SCFs) possess gas-like low mass transfer resistance properties and liquid-like high solvating characteristics. The high diffusivity and low viscosity of SCFs allow them to enhance chemical reactions by reducing the mass transfer limitations, while the high density and compressibility typically influence the solubility of compounds to facilitate higher reaction rate and conversion. Table 3 compares the characteristics of the types of fluid phase. Typically, a supercritical fluid is an excellent medium for chemical reactions. Critical parameters of some commonly used supercritical fluids are listed in Table 4.

Table 3. Comparison of fluid-phase characteristics

Properties	SCF	Gas	Liquid	Affected Factor
Low Viscosity	X	X		Mass Transfer
High Diffusivity	X	X		Mass Transfer
High Compressibility	X	X		Solubility
High Density	X		X	Solubility

Table 4. Critical Parameters of Common Substances.[38, 53, 88]

Substance	Critical Temperature (°C)	Critical Pressure (MPa)	Critical Density (mol/cm^3)
Ethanol	240	6.15	0.006
Water	374	22.1	0.018
Methanol	239.5	8.08	0.0085
Carbon Dioxide	31.1	7.38	0.011
Ethane	32.2	4.87	0.0069
Isobutane	134.7	3.64	0.0038
Acetic Acid	230	5.79	0.0058
Ethyl Acetate	251	3.83	0.0035
Formic Acid	315	5.81	0.008
Ethyl Formate	235	4.74	0.0044
Methyl Formate	214	6	0.0058
Methyl Acetate	234	4.69	0.0044

Other attractive characteristics of SCFs are the ionization constant (K_w) and the dielectric constant (ε). A low dielectric constant allows supercritical fluids to dissolve organic compounds, while a high ionization constant allows supercritical fluids to provide an acidic medium for the reaction systems.[39, 53] In addition, the properties of supercritical fluids, such as viscosity, density, dielectric constant, ionization constant, and compressibility are adjustable by changing the system temperature and/or pressure. The applications of supercritical fluids as tunable solvents for extraction and chemical reactions have been demonstrated significantly in biocatalysis, polymerization, materials synthesis, and enzymatic reactions.[52-53] The main disadvantage of supercritical fluids is the high energy input required to achieve high pressure and high temperature; however, the required energy input is relatively lower than the energy required in the petrochemical industry.

2.5.1. Supercritical Alcohol

Application of supercritical methanol for the production of biodiesel (methyl esters) at a relatively fast rate without the presence of catalyst has been studied and reported. At the supercritical state of methanol, the methanol–oil mixture phase was found to be homogeneous, instead of the biphasic methanol–oil mixture generally observed at atmospheric conditions. The dielectric constant of methanol was reported to decrease at the supercritical region, and this allows supercritical methanol to become a better solvent for organic compounds, which consequently enables a homogeneous reaction system with more favorable kinetics.[39] 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.[40-41] Since the molecular structure of ethanol and methanol are in the same homologous series, the chemical and physical properties of both alcohols tend to be similar, therefore ethanol will be used both as reactant and reaction medium for the uncatalyzed esterification reaction system. Ethanol has been a good choice as a reaction medium because presently, ethanol can be easily produced from biomass. However, when ethanol is used, ethyl esters of respective carboxylic acids will be obtained as the products of the esterification reaction.

CHAPTER 3: RESEARCH OBJECTIVES

The review of literature on esterification of carboxylic acid presented above indicates the wide range of applications of esterification reactions in chemical industry. Being an equilibrium reaction, several reports have addressed important issues concerning product distribution, catalyst activity, and kinetics studies of acid-catalyzed esterification at lower reaction temperatures. High yields have also been reported on the production of esters of fatty acids from soybean oil in subcritical and supercritical ethanol. Nevertheless, kinetics of uncatalyzed esterification at elevated reaction temperatures are still limited. Thus, it is of great interest from a practical point of view that more information such as kinetic and thermodynamic parameters are required to develop a possible esterification process without using any catalyst.

Furthermore, facing the drawbacks on the acid-catalyzed esterification reaction (See section 1.2) and the depletion of fossil sources, which have caused instability to the supply and cost of products derived from fossil sources, the objectives of this work are:

(i) To examine the possibility of converting the biomass-derived carboxylic acids to value-added esters without using any catalyst.

(ii) To develop a kinetic model for uncatalyzed esterification at elevated temperatures.

(iii) To determine the thermodynamic and kinetic parameters for the uncatalyzed esterification reaction model.

The above objectives will be achieved by:

- Experimental conversion of different carboxylic acids into their corresponding esters at various reaction conditions.

- Analysis of reaction medium through analytical methods.
- Evaluating the effects of temperature and time on esterification of different carboxylic acids.
- Estimating the kinetic and thermodynamic parameters for each esterification system.
- Examining the effects of number of carbon atom and functional group on the kinetic study.

For all the systems under consideration, the reaction is assumed to proceed in the second order reversible reaction as a function of concentration of carboxylic acid and reaction temperature. Rate equations will be developed using experimentally measured concentration-time values over a wide range of temperature. Since the molar ratio of ethanol to carboxylic acid is set to be equal in this work, the contribution of equilibrium constant will be considered to develop the kinetic model.

CHAPTER 4: EXPERIMENTAL DESIGN AND DATA ANALYSIS

4.1. Design of Experiments

The uncatalyzed esterification experiments were performed in isothermally operated batch reactors. Since the estimation of the kinetic and thermodynamic parameters to describe the uncatalyzed esterification reaction remained the primary focus of this study, the experimental conditions were selected to avoid the use of excess ethanol, but ensure equilibrium conditions. In the case of the lactic acid esterification system, presence of oligomers was ignored, since it has been reported that the total amount of lactic acid oligomers and their esters are negligible at equilibrium.[27, 33] For a given carboxylic acid esterification system, the product distribution is a strong function of the reaction temperature and time. Thus, the experiments are set up such that the reaction time is much greater than the heat up time, so as to ensure isothermal conditions. The concentrations of carboxylic acid and ethanol in the uncatalyzed esterification have been limited to equimolar ratio, since the stoichiometric amount of the reactants is suitable for esterification reaction.

The conversion of the carboxylic acid is highly a function of the temperature and time, in this study; the reaction time and temperature were varied for uncatalyzed esterification of different types of aliphatic carboxylic acids, so as to assess the effects of temperature, reaction time, carbon chain-length and functional group on the kinetics studies. To obtain the concentration-time data for specific reaction condition, each reaction sample was analyzed through the analytical methods described in section 5.4.1.

Stainless steel material is a common reactor material for reaction systems at high temperature conditions. In this study, preliminary work on the esterification of lactic acid utilized a high pressure stainless steel 316 (SS 316) material as reactor, but it was observed that the SS-316 material was susceptible to progressive acid corrosion with increasing reaction time and temperature. This initiated the use of sealed quartz capillary tubes, which have no corrosive susceptibility or catalytic activity. DiLeo and Savage recently used similar reactors for the gasification of methanol in supercritical water.[83] Because of the small diameter and the properties of quartz, these reactors can withstand temperature above 300 °C. Additionally, experiments with different metallic substances were also performed at selected temperature in order to assess their corrosive susceptibility and catalytic effects on uncatalyzed esterification reactions at elevated reaction temperature.

4.2. 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 also in the evaluation of the effects of carbon chain-length and functional group on different uncatalyzed esterification systems. Concentrations at different times and the rate of disappearance of carboxylic acid were calculated from the stoichiometric material balance equation (Equation 14) and second order kinetics rate expression (Equation 10, Section 2.3) respectively:

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

where; C_{At} is the concentration of carboxylic acid at time t, C_{Ao} is the initial concentration of carboxylic acid at time t = 0, and X is the fractional conversion of carboxylic acid at time t.

For the calculation of the reaction rate constant at any given temperature, the concentration-time data obtained were correlated to second order kinetics rate equation (Equation 10, Section 2.3), and fit with the "LINEST" statistical function found in the Microsoft Excel software. The rate of the reaction was calculated based on the conversion of the carboxylic acid (X), which was calculated by Equation. 15:

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

The concentrations of the ester at different time (C_{Et}) were calculated by Equation 16:

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

With the use of a Runge-Kutta-Fehlberg 56 (RKF56) integration algorithm found in version 5.1 Polymath software package, the experimentally determined kinetic and thermodynamic parameters, reaction time, temperature, and initial concentration of carboxylic acid were fit to the model Equations 4 to 7 (See Section 2.3) to estimate the conversion, rate constants, equilibrium constants, and species concentrations. The confidence interval error values reported in this thesis were calculated with a function found in Microsoft Excel software using the number of experimental data points and standard deviation of the data set.

CHAPTER 5: KINETIC STUDIES OF UNCATALYZED ESTERIFICATION OF CARBOXYLIC ACIDS

In an effort to establish the possibility of the uncatalyzed esterification reaction at elevated reaction temperature, the uncatalyzed esterification reactions of five biomass-derived carboxylic acids (formic, acetic, lactic, levulinic, and linoleic acids) with biomass-derived ethanol at different temperatures have been conducted in this study. To avoid the vaporization of any compound from the reaction medium, experiments were carried out with sealed quartz capillary tubes. Additionally, experiments with metallic substances were also performed at selected temperatures to assess the corrosive and catalytic influences of the metallic material on esterification reactions. All reactors used in this study were fed with equimolar reactants under oxygen-free environment.

Since esterification of carboxylic acid is a reversible reaction, it was decided to use a second-order reversible kinetics model to describe the system. In each experiment, the concentrations of reactants and products were measured as a function of time to obtain the concentration-time profiles for each compound. To estimate the rate parameters, the experimental concentration-time data were correlated using an isothermal batch reactor kinetics model as described by Equations 4 to 7 (Section 2.3). The model calculated values for different operating conditions were compared with the experimental data. The data regarding the effect of reaction temperature on equilibrium conversion, kinetic, and thermodynamic parameters are presented in this chapter. The kinetic and thermodynamic results presented in this study will be valuable predictive tools in the design of uncatalyzed esterification reactions at elevated reaction temperatures. The range of reaction conditions under which this study was carried out is listed in Table 5.

Table 5. 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

5.1. Experimental Section

5.1.1. Materials

For the reactions, chemicals used in this study 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.

5.1.2. Experimental Setup and Procedure

Experiments in the temperature range of 333 K to 623 K were performed in capillary batch reactors made with corrosion-resistant quartz tubes (2 mm i.d. × 6 mm o.d). The reactors were flame sealed at one end and then fed with reactants under a nitrogen gas environment. Since the reaction pressures inside the reactor were 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 ends were flame sealed to 24 cm in length. The sealed capillary tubes were 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 the capillary 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. After the end of the desired reaction time, each capillary tube was removed and cooled by placing the tube into an ice bath. The cooled tubes were stored in the freezer to prevent further reaction before any analytical methods described below.

For reaction temperatures of 298 K and 313 K, serum bottles (Wheaton) were fed with equimolar ratios of reactants and capped under a nitrogen gas environment. The capped bottles were 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 any analysis. The pictorial diagram of the experimental setup is shown in Figure 3, and all reactions and analysis were conducted in duplicate.

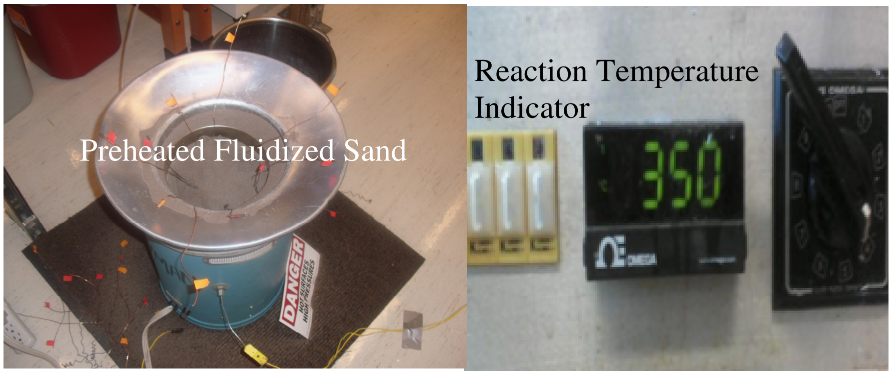


Figure 3. Experimental Setup of a Batch Reactor for Esterification Reaction

5.1.3. Catalysis and Corrosion Test

Several metals were evaluated 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). The metallic substances were weighed, placed in capillary reactor tubes fed with equimolar lactic acid/ethanol solution, and flame sealed at the end. The reactor tubes were then placed into the preheated fluidized sand bath and kept for 220 hr. The experiments were carried out at the temperatures of 423 K and 523 K under similar conditions described above (Section 5.1.2). The metals were subjected to different immersion/exposure periods. After the end of the desired exposure time, each reactor was removed and cooled to prevent further reaction. Liquid reaction samples were 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.

5.1.4. Component Analysis Methods

5.1.4.1. High Performance Liquid Chromatography

For this study to be significant, it is essential to determine the concentration of the reactants and products. A high performance liquid chromatography instrument was used to identify and quantify the components in the reaction samples of lactic acid, levulinic acid, and acetic acid esterification systems. From the stored reaction samples, about 0.1 mL from each sample was withdrawn and diluted with ultrapure water to 5 mL solution for analysis. The analysis of reactants and products was carried out using 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). A Waters Nova-Pak C-18 column (1.5 cm x 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 determined from the standard calibration curves generated by analyzing the authentic compounds with known concentrations. Procedures for preparing the standard calibration curves are presented in the Appendix (Section A.1.1). By this procedure, the concentration change of the reactants and products with time was recorded in all the experiments. Ethanol, carboxylic acid and ester were analyzed in each sample, and the amount of water was assumed to be stoichiometric. The conditions of HPLC analysis for each esterification system investigated are listed in Table 6.

Table 6. 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

5.1.4.2. Acid Base Titration of Esterification Reaction Sample

An acid-base titration method was used to quantify the conversion of formic acid from its esterification reaction system. To calculate the conversions of formic acid throughout the batch reactor experiments, the 0.1 N sodium hydroxide solution used in titration was standardized by using the standard 0.1 N hydrochloric acid solution and the normality of sodium hydroxide (NaOH) was calculated from Equation 17.

$$N_{NaOH} = \frac{V_{HCl} * N_{HCl}}{V_{NaOH}} \tag{17}$$

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.

At regular time intervals, about 0.1 mL from each reaction sample was withdrawn, weighed and diluted with deionized water to 5 mL solution for titration against 0.1 N standardized sodium hydroxide solution using phenolphthalein as an indicator. The concentration of formic acid was determined from the standard calibration curves generated by titration of authentic formic acid with known concentrations. A procedure for preparing the calibration curve for formic acid titration is presented in the Appendix (A.1.2). To assess the reliability of the titration method, unconverted formic acid was calculated by Equation 18.

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

F: Free Acidity as Formic Acid, wt%.

N_{NaOH}: Normality of NaOH solution, mol/L.

V_{NaOH}: volume of NaOH solution used for the titration, mL.

$MW_{Formic\ Acid}$: Molecular weight of Formic Acid, 46.02 g/mol

W_{Sample}: Sample weight, in g

Conversion (X %) at different time with respect to the formic acid is calculated by Equation 19.

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

5.1.4.3. Raman Analysis for Linoleic Acid Esterification

The reaction products obtained from the 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 components in the reaction samples. The power output of the laser was set at 200 mW. HoloGrams Software was used for data accumulation. The Raman peak intensities were examined at 1710 and 1740 cm^{-1} wavenumbers for COOH neat acid and C=O ester stretching, respectively.

All Raman spectra were obtained with the same conditions in triplicates by exposing each sample to the laser for 1 sec with 3 accumulations. With this procedure, the mole fraction of the ethyl linoleate produced at a given reaction time was determined during the batch reaction, and the rate of reaction was obtained. The mole fraction of ethyl linoleate was determined from the standard calibration curves generated by using several mixtures of authentic linoleic acid, ethyl linoleate, ethanol, and water with known molar ratio. Procedures for preparing the standard calibration curves are presented in the Appendix (Section A.1.3). The spectra of the standards are also shown in the Appendix.

5.2. Results and Discussions

5.2.1 Equilibrium Constant

The temperature and molar ratio of ethanol to carboxylic acid are two of the variables affecting the conversion of carboxylic acid. Theoretically, esterification of carboxylic acid is an equilibrium reaction. In this work, however equal amounts of ethanol and carboxylic acid were used at various temperatures to estimate the equilibrium constant

(K_{eq}) values from the equilibrium conversion (X_{eq}) of carboxylic acid. The equilibrium constant values were calculated by Equation 20.

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

The mean values of the experimental equilibrium constants ($K_{eq.exp}$) and calculated equilibrium constants ($K_{eq.calc}$) for uncatalyzed esterification of lactic acid (LAA), levulinic acid (LEA), acetic acid (ACA), formic acid (FA), and linoleic acid (LA) are listed in Tables 7. The reported errors are 95% confidence intervals.

As can be noticed in Table 7, the effect of temperature on the equilibrium constant for uncatalyzed esterification of carboxylic acid is shown. Though numerical values are different for different carboxylic acids, the trends are similar for the short-chain carboxylic acids (lactic acid, levulinic acid, acetic acid, and formic acid). The equilibrium constant (K_{eq}) value increases with temperature. However, 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) increases non-linearly as the temperature increases from 373 K to 473 K. However, as the reaction temperature increases from 523 K to 623 K, the K_{eq} value gradually decreases. 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 work, it was found that linoleic acid is a polyunsaturated carboxylic acid (2 double bond unsaturated carboxylic acid) with a longer carbon chain. Thus, decomposition reactions might have taken place at longer reaction times and higher temperature due to thermal degradation.

Table 7. 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	0.06 ± 0.01	0.07
333	0.13 ± 0.01	0.13
353	0.25 ± 0.01	0.25
373	0.50 ± 0.02	0.44
423	1.48 ± 0.08	1.4
473	3.8 ± 0.1	4
523	6.4 ± 0.2	7

(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
523	2.42 ± 0.03	2.4

(c) Acetic Acid (ACA)

T (K)	ACA $K_{eq.exp}$	ACA $K_{eq.calc}$
373	0.2 ± 0.2	0.3
423	0.85 ± 0.08	0.8
473	2 ± 1	2
523	4 ± 1	4

(d) Formic Acid (FA)

T (K)	FA $K_{eq.exp}$	FA $K_{eq.calc}$
373	2 ± 1	2
423	3.9 ± 0.1	4
473	6 ± 1	6
523	9 ± 2	9

(e) Linoleic Acid (LA)

T (K)	LA $K_{eq.exp}$	LA $K_{eq.calc}$
373	0.30 ± 0.04	0.26
423	0.6 ± 0.1	0.6
473	0.8 ± 0.1	0.8
523	0.4 ± 0.1	0.4
573	0.3 ± 0.1	0.3
623	0.23 ± 0.01	0.23

$K_{eq.exp}$: Experimental equilibrium constant value

$K_{eq.calc}$: Model calculated equilibrium constant value

5.2.2. Thermodynamic Parameters

Reaction enthalpy change of a reaction (ΔH) is the amount of heat absorbed or released in a reaction, and the ΔH parameter indicates whether a reaction is endothermic or exothermic depending if the enthalpy is required or released. Reaction ΔH and ΔS can be calculated for linear Van't Hoff plots using the equation given in Equation 11, section 2.3. Reaction ΔH and ΔS values at any given temperature can also be obtained theoretically from the formation enthalpies, formation entropies, and heat capacities, and residual properties. The effects of temperature on the equilibrium constant using the classical Van't Hoff plots are shown in Figure 4 in the form (ln K_{eq}) against (1/T). The Van't Hoff plots for the short-chain carboxylic acids were fitted to the least squares regression line.

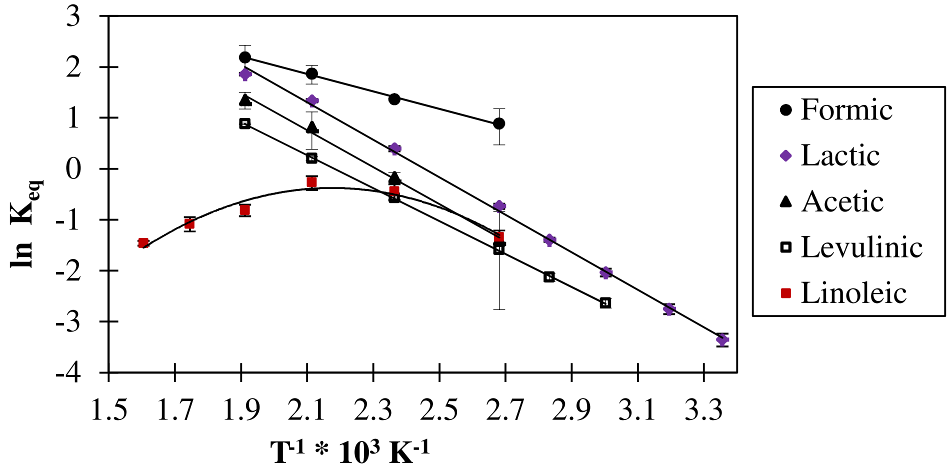


Figure 4. Effect of Temperature on Equilibrium Constant for Uncatalyzed Esterification of Carboxylic Acids with Ethanol

As can be noticed in Figure 4, ln K_{eq} shows linear dependence 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) indicates nonlinear Van't Hoff behavior. Nonlinear Van't Hoff plot may arise from temperature-dependent changes in enthalpy, and reduction in equilibrium constant (K_{eq}) at longer reaction time and higher temperature. The estimated reaction enthalpy (ΔH) and reaction entropy (ΔS) values, as well as their 95% confidence intervals error values from the classical linear Van't Hoff plot for uncatalyzed esterification of different short-chain carboxylic acids are listed in Table 8.

Table 8. Values of Thermodynamic Parameters for Esterification of Short-chain Carboxylic Acids

T (K)	Carboxylic Acid	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
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

As noted from Table 8, the ΔH values for the uncatalyzed esterification of short-chain carboxylic acids are positive. The positive values of ΔH indicate that the esterification of short-chain carboxylic acids considered in this study is endothermic. Some authors have reported endothermic reactions for lactic acid and levulinic acid esterification[6, 32] while some reported exothermic reactions for lactic acid esterification.[12, 18]

As previously presented in Figure 4, the relationship of ln K_{eq} on 1/T for the uncatalyzed esterification of long-chain carboxylic acid (linoleic acid) revealed a nonlinear Van't Hoff behavior. The reaction enthalpy change (ΔH) values at any temperature were estimated for the nonlinear Van't Hoff plot by fitting the data to Equation 21.

$$y = a + bx + cx^2 \tag{21}$$

Where x is T^{-1} and y is ln K_{eq}. Derivative of Equation 21 in term of ln K_{eq} with respect to 1/T gives a second equation that represents the negative enthalpy divided by the universal gas constant (R) as a function of temperature (Equation 22).

$$\frac{d\ln K_{eq}}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{R} = b + 2c\left(\frac{1}{T}\right) \tag{22}$$

The relationship of ln K_{eq} on 1/T obtained from the experimental data fitting is represented by Equation 23.

$$\ln K_{eq} = \left(\frac{-3.6087}{T^2}\right) + \left(\frac{15.7}{T}\right) - 17.452 \tag{23}$$

The correlation coefficient (R^2) for this fit is 0.95. The derivative of ln K_{eq} with respect to 1/T is given as Equation 24. The values of ΔH at each temperature were calculated from Equation 24.

$$\frac{d\ln K_{eq}}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{R} = 15.7 - \left(2 * \left(\frac{3.6087}{T}\right)\right) \tag{24}$$

Because the values of the activity coefficients for the considered systems at the reaction conditions are unknown, it is only possible to calculate the reaction Gibbs free energy change (ΔG) using Equation 25.

$$\Delta G = -RT * \ln K_{eq} \tag{25}$$

The reaction entropy change (ΔS) was calculated from the reaction enthalpy and Gibbs energy change values by Equation 26.

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (26)$$

The results of reaction enthalpy, Gibbs free energy, and entropy values calculated are presented in Table 9.

Table 9. Values of Thermodynamic Parameters for Esterification of Linoleic Acid

Temp	ΔH	ΔG	ΔS
K	kJ/mol	kJ/mol	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

As observed from Table 9, the reaction enthalpy and entropy changes decrease as the reaction temperature increases. The ΔH and ΔS values found in the Table 9 are 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 arise from a variety of sources, including temperature-dependent changes in enthalpy, and decrease in equilibrium constant (K_{eq}) at higher temperature. The ΔG values listed in Table 9 are positive at different temperatures, and the ΔG value decreases as temperature increases from 373 to 473 K, and thereafter increases as temperature increases from 523 to 623 K.

The trend observed for the ΔG may be related to the equilibrium constant (K_{eq}) values that increase as the temperature increases from 373 to 473 K, and gradually decrease as increases from 523 to 623 K (Table 7e, Section 5.2.1).

5.2.3. Theoretical Estimation of Thermodynamic Parameters

The thermodynamic properties (enthalpy and entropy) of a chemical reaction can be determined theoretically from the properties of formation, heat capacities, properties of vaporization, and residual properties. Thus, an attempt was made in this present work to estimate the equilibrium conversions from thermodynamic relationships. In the theoretical method, two different thermodynamic paths were applied to estimate the enthalpy and entropy of formation for carboxylic acid, alcohol, and ester in the reaction medium, since the thermodynamic properties are state functions, which are independent of the path between the initial and final states. The first estimation was based on an ideal gas temperature change (IGTC) thermodynamic path (Section 5.2.3.1), while the second estimation was constructed on a liquid temperature change (LTC) thermodynamic path (Section 5.2.3.2). The enthalpy and entropy change of formation for water at different temperatures were estimated with the use of steam table and standard enthalpy and entropy change of formation from its elements at 298 K and 1 bar (Section 5.2.3.3). A classical esterification reaction between acetic acid and ethanol has been selected as the demonstration system. The reaction enthalpies (ΔH) and reaction entropies (ΔS) were obtained from Equations 27 and 28:

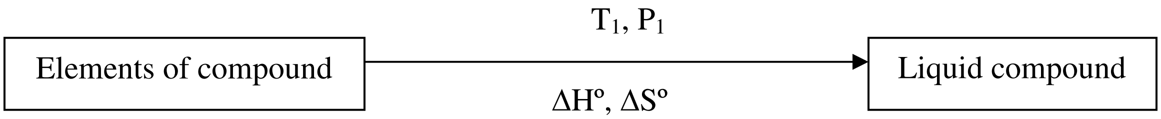
$$\Delta H_{Reaction} = \sum H_{products} - \sum H_{reactants} \tag{27}$$

$$\Delta S_{\mathrm{Reaction}} = \sum S_{\mathrm{products}} - \sum S_{\mathrm{reactants}} \tag{28}$$

5.2.3.1. Ideal Gas Temperature Change Thermodynamic Path

The values of enthalpy (ΔH) and entropy change (ΔS) of formation for acetic acid, ethanol, and ethyl acetate in the reaction mixture were obtained through the following steps:

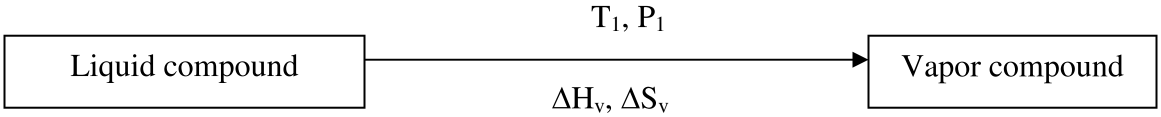
- A process of transforming the elements of a compound into liquid state of the compound at T_1 and P_1. The standard enthalpy and entropy changes of reaction for this process are calculated from the enthalpy and entropy of formation at standard state.



$$\Delta H^{\circ}_{\mathrm{reaction}} = H_{\mathrm{formation}_{\mathrm{compound}}}\left(T_o\right) - H_{\mathrm{formation}_{\mathrm{elements}}}\left(T_o\right) \tag{29}$$

$$\Delta S^{\circ}_{\mathrm{reaction}} = S_{\mathrm{formation}_{\mathrm{compound}}}\left(T_o\right) - S_{\mathrm{formation}_{\mathrm{elements}}}\left(T_o\right) \tag{30}$$

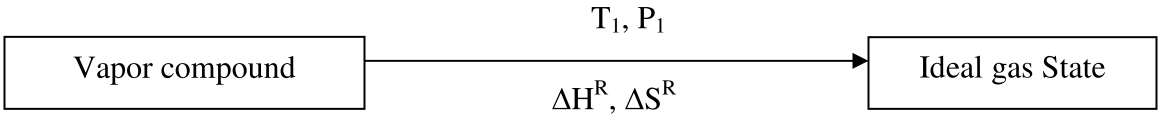
- Vaporization of the liquid compound at T_1 and $P_{1.}$ The enthalpy and entropy of vaporization for this process are calculated with the corresponding states equation developed by Pitzer, et.al.,[84]



$$\Delta H_v = RT_c*\left(7.08(1-T_r)^{0.354}+10.95*\omega(1-T_r)^{0.456}\right) \tag{31}$$

$$\Delta S_v = \frac{\Delta H_v}{T} \tag{32}$$

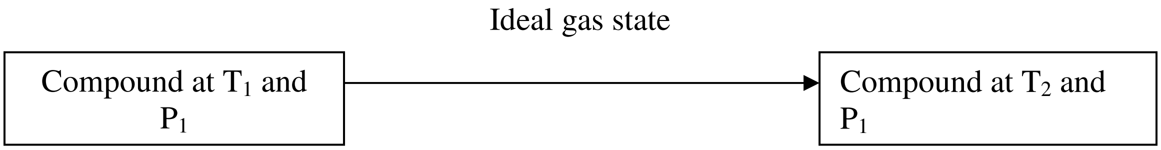
- A process of transforming the vapor compound into ideal gas state at T_1 and P_1. The enthalpy and entropy for this process are calculated with the Lee/Kesler correlation.[85-86]



$$\Delta H_1^R(T_1\ P_1) = \left(H^R\right)^0 + \omega*\left(H^R\right)^1 \tag{33}$$

$$\Delta S_1^R(T_1\ P_1) = \left(S^R\right)^0 + \omega*\left(S^R\right)^1 \tag{34}$$

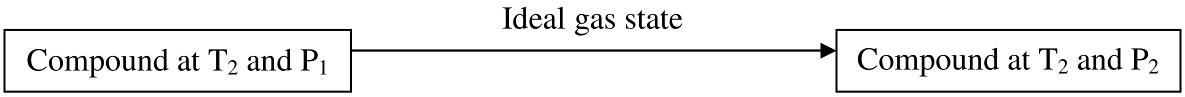
- A process of changing the compound in ideal gas state from T_1 and P_1 to T_2 and P_1. The enthalpy and entropy for this process are calculated by:



$$\Delta H^{ig} = \int_{T_1}^{T_2} C_{P_{compound}} \, dT \qquad (35)$$

$$\Delta S^{ig} = \int_{T_1}^{T_2} C_{P_{compound}} \frac{dT}{T} - R * \ln \frac{P_1}{P_1} \qquad (36)$$

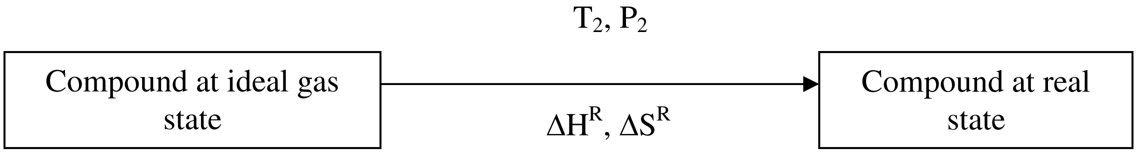
- A process of changing the compound in ideal gas state from T_2 and P_1 to T_2 and P_2. The enthalpy and entropy for this process are calculated by:



$$\Delta H = 0 \qquad (37)$$

$$\Delta S = -R * \ln \frac{P_2}{P_1} \qquad (38)$$

- A process of transforming the compound from ideal gas state to real state at T_2 and P_2. The enthalpy and entropy changes for this process are calculated with the Lee/Kesler correlation.[85-86]



$$-\Delta H_2^R\,(T_2\ P_2) = \left(H^R\right)^0 + \omega * \left(H^R\right)^1 \tag{39}$$

$$-\Delta S_2^R\,(T_2\ P2) = \left(S^R\right)^0 + \omega * \left(S^R\right)^1 \tag{40}$$

The combination of Equations 29, 31, 33, 35, 37, and 39 gives the enthalpy change of formation for specific compound at different temperatures (Equation 41). Similarly, combination of Equations 30, 32, 34, 36, 38, and 40 gives the entropy change of formation for specific compound at different temperatures (Equation 42).

$$\Delta H_{\text{compound}_i} = H_{\text{formation}_{\text{compound}_i(T_o)}} + \Delta H_v + H_1^R\,(T_1\ P_1) + \int_{T_1}^{T_2} C_{P_{\text{compound}_i}}\,dT - H_2^R\,(T_2\ P_2) \tag{41}$$

$$\Delta S_{\text{compound}_i} = S_{\text{formation}_{\text{compound}_i(T_o)}} + \Delta S_v + S_1^R\,(T_1\ P_1) + \int_{T_1}^{T_2} C_{P_{\text{compound}_i}}\,\frac{dT}{T} - R * \ln\frac{P_2}{P_1} - S_2^R\,(T_2\ P_2) \tag{42}$$

Where, The terms in Equations 27 to 42 denoted C_p as molar heat capacity, H^R as residual enthalpy, S^R as residual entropy, H_v and S_v as enthalpy and entropy of vaporization $H_{reactant}$ as reactant enthalpy, $H_{product}$ as product enthalpy, $S_{reactant}$ as reactant entropy, $S_{product}$ as product entropy, $H_{formation\ reactant}$ as reactant enthalpy of formation at standard state, $H_{formation\ product}$ as product enthalpy of formation at standard state, $S_{formation\ reactant}$ as reactant entropy of formation at standard state, $S_{formation\ product}$ as product entropy of formation at standard state, T as reaction temperature, T_o as atmospheric temperature, P is the estimated pressure, P_o is atmospheric pressure, R is the universal gas constant, and the subscript (i) denotes specific substance. Residual enthalpy and entropy for acetic acid, ethanol, and ethyl acetate were estimated with the use of three-parameter corresponding states correlation developed by Lee and Kesler.[85-86] The Lee/Kesler calculator found at www.macatea.com/wshop/lk/ was applied to the calculations. The dependence of C_p, H^R, and S^R on temperature, as well as the estimated parameters from respective equations are listed in the Appendix (Section A.4).The diagram for the ideal gas temperature change (IGTC) thermodynamic path described above; starting from initial state to the final state is presented in Figure 5.

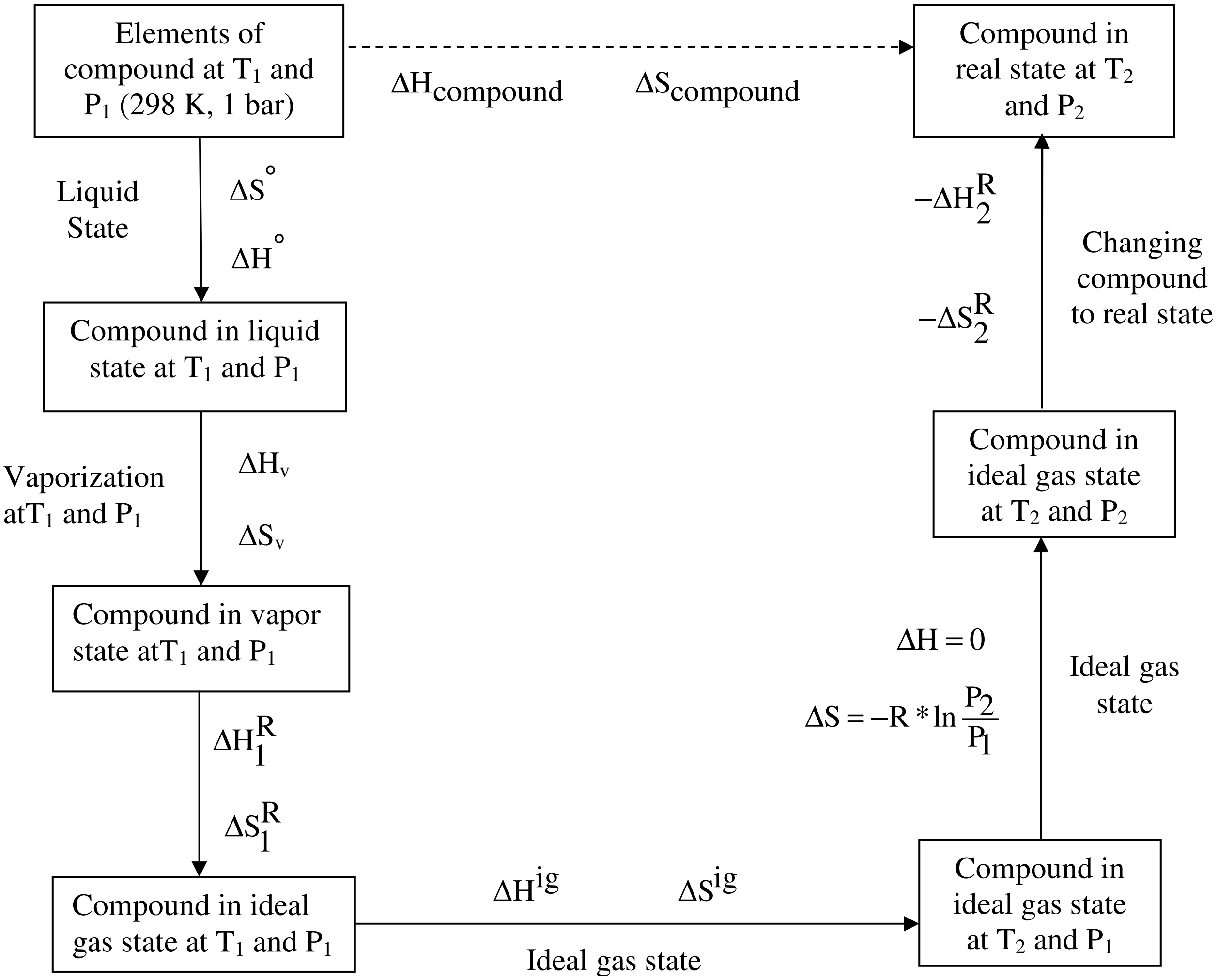
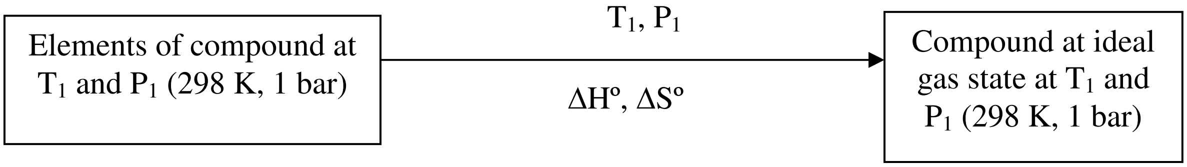


Figure 5. Ideal Gas Temperature Change Thermodynamic Path Diagram

5.2.3.2. Liquid Temperature Change Thermodynamic Path

The values of enthalpy (ΔH) and entropy change (ΔS) of formation for acetic acid, ethanol, and ethyl acetate in the reaction mixture were obtained through the following thermodynamic steps.

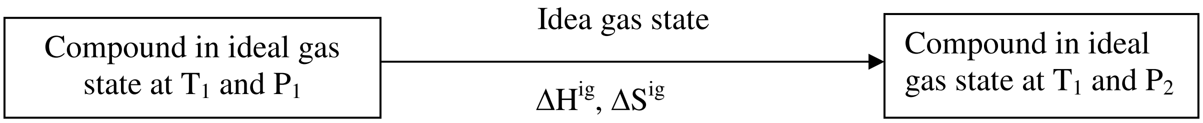
- A process of transforming the elements of a compound into ideal gas state at T_1 and P_1. The standard enthalpy and entropy changes of reaction for this process are calculated from the enthalpy and entropy of formation at standard state.



$$\Delta H^{\circ}_{reaction} = H^{ig}_{formation_{compound}}(T_o) - H^{ig}_{formation_{elements}}(T_o) \qquad (43)$$

$$\Delta S^{\circ}_{reaction} = S^{ig}_{formation_{compound}}(T_o) - S^{ig}_{formation_{elements}}(T_o) \qquad (44)$$

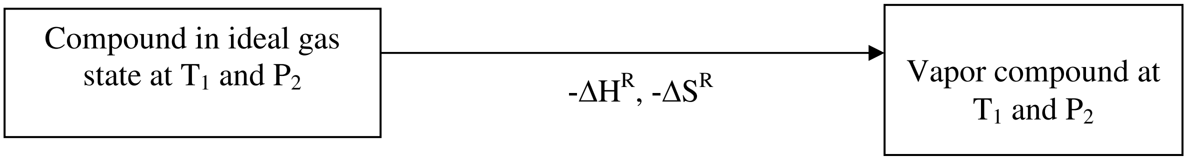
- A process of changing the compound in an ideal gas state from T_1 and P_1 to T_1 and P_2.



$$\Delta H^{ig} = 0 \qquad (45)$$

$$\Delta S^{ig} = -R * \ln \frac{P_2}{P_1} \qquad (46)$$

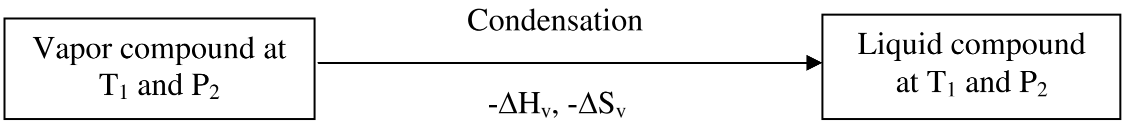
- A process of changing the compound in ideal gas state to vapor state at T_1 and P_2. The enthalpy and entropy for this process are calculated with the Lee/Kesler correlation.[85-86]



$$H^R(T_1\ P_2) = \left(H^R\right)^0 + \omega^*\left(H^R\right)^1 \tag{47}$$

$$S^R(T_1\ P_2) = \left(S^R\right)^0 + \omega^*\left(S^R\right)^1 \tag{48}$$

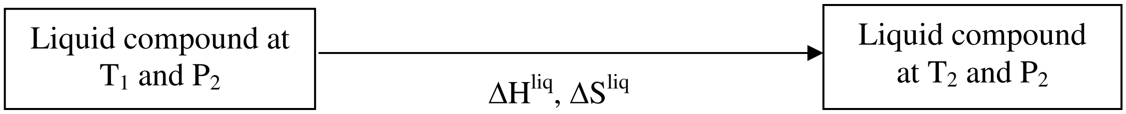
- Condensation of the vapor compound to liquid compound at T_1 and $P_{2.}$ The enthalpy and entropy for this process are calculated with the corresponding states equation developed by Pitzer, et.al.,[84]



$$\Delta H_c = -\Delta H_v = -RT_c{*}\left(7.08\left(1-T_r\right)^{0.354} + 10.95{*}\omega\left(1-T_r\right)^{0.456}\right) \tag{49}$$

$$\Delta S_c = -\Delta S_v = \frac{-\Delta H_v}{T} \tag{50}$$

- A process of changing the liquid compound at T_1 and P_2 to final at T_2 and P_2. The enthalpy and entropy changes for this process are calculated with the specific heat capacity of the liquid substance.



$$\Delta H^{liq} = \int_{T_1}^{T_2} C^{liq}_{P_{compound}} \, dT \qquad (51)$$

$$\Delta S^{liq} = \int_{T_1}^{T_2} C^{liq}_{P_{compound}} \frac{dT}{T} - R * \ln \frac{P_2}{P_2} \qquad (52)$$

The combination of Equations 43, 45, 47, 49 and 51 gives the enthalpy change of formation for specific compound at different temperatures (Equation 53). Similarly, combination of Equations 44, 46, 48, 50 and 52 gives the entropy change of formation for specific compound at different temperatures (Equation 54).

$$\Delta H_{compound_i} = H^{ig}_{formation_{compound_i(T_o)}} + \int_{T_1}^{T_2} C^{liq}_{P_{compound_i}} \, dT$$
$$- \Delta H_v - H^R \qquad (53)$$

$$\Delta S_{compound_i} = S^{ig}_{formation_{compound_i(T_o)}} + \int_{T_1}^{T_2} C^{liq}_{P_{compound}} \frac{dT}{T}$$
$$- R * \ln \frac{P_2}{P_1} - \Delta S_v - S^R \qquad (54)$$

The terms in Equations 43 to 52 are defined as the terms in Equations 27 to 42. The heat capacity for a substance in liquid state was evaluated from the residual heat capacity equation that was correlated with the corresponding states method.[84] The dependence of C_p, H^R, and S^R on temperature, as well as the estimated parameters from respective equations are listed in the Appendix (Section A.4).The diagram for the liquid temperature change (LTC) thermodynamic path described above, starting from initial state to the final state of is presented in Figure 6.

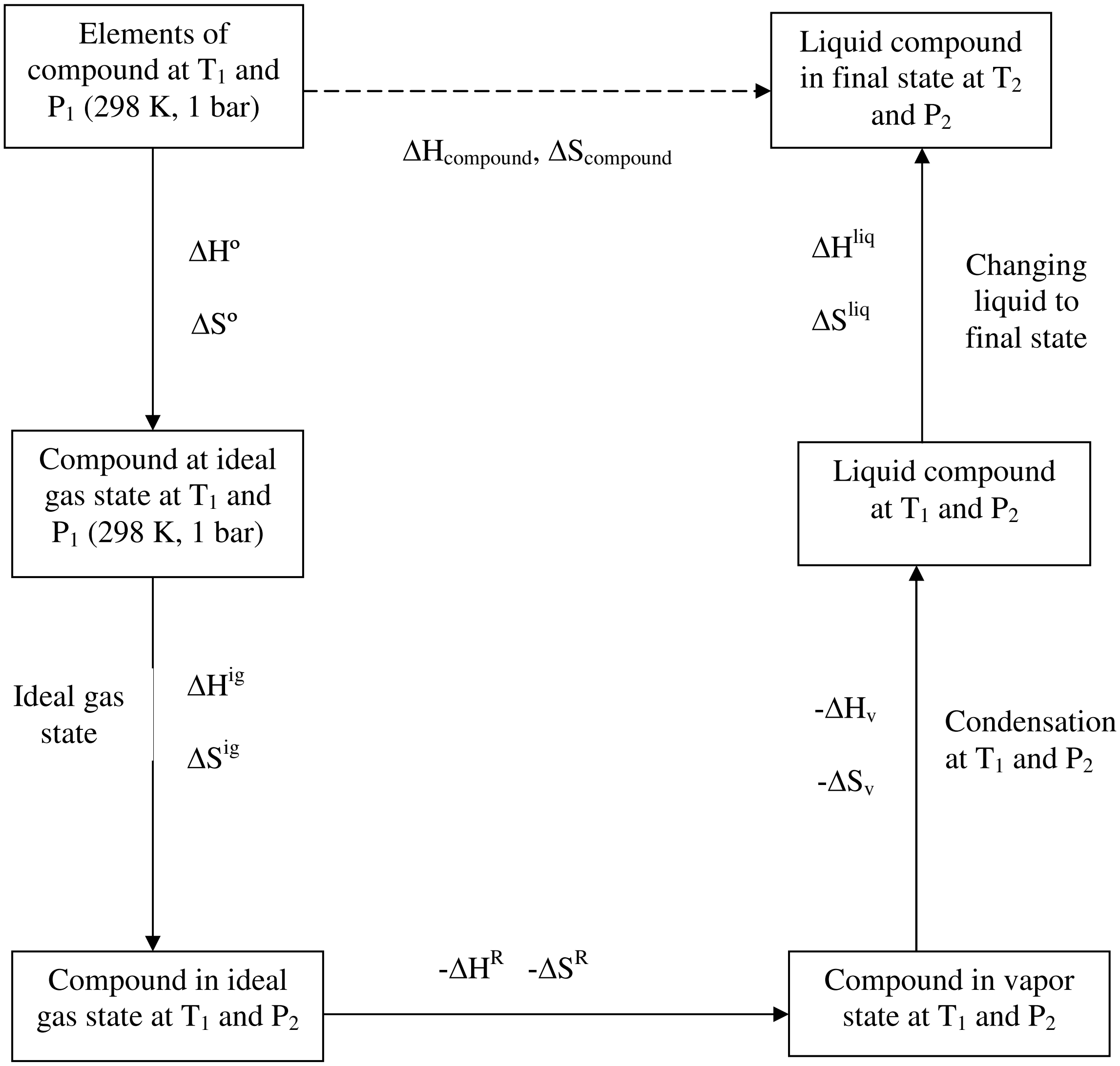


Figure 6. Liquid Temperature Change Thermodynamic Path Diagram

5.2.3.3. Thermodynamic Properties of Water

The values of enthalpy (ΔH) and entropy change (ΔS) of formation for water in the reaction mixture at different temperatures were obtained from the steam table. In order to ensure certainty, the (ΔH) and entropy (ΔS) values were adjusted to real state using the standard enthalpy and entropy change of formation of water from its elements at 298 K and 1 bar, through the following steps.

- A process of transforming the reactants (elements of water) at T_1 and P_1 to liquid state of the product (water) at T_1 and $P_{1.}$ The standard enthalpy and entropy changes of reaction for this process are calculated from the standard enthalpy and entropy of formation respectively.

$$\Delta H^{\circ}_{\text{reaction}} = H_{\text{formation}_{\text{products}}}(T_1) - H_{\text{formation}_{\text{reac tan ts}}}(T_1) \qquad (55)$$

$$\Delta S^{\circ}_{\text{reaction}} = S_{\text{formation}_{\text{products}}}(T_1) - S_{\text{formation}_{\text{reac tan ts}}}(T_1) \qquad (56)$$

- A process of transforming the product (water) from T_1 and P_1 to real state at T_2 and $P_{2.}$ The enthalpy and entropy changes are:

$$\Delta H = H\ (T_2,\ P_2) - H\ (T_1,\ P_1) \qquad (57)$$

$$\Delta S = S\ (T_2,\ P_2) - S\ (T_1,\ P_1) \qquad (58)$$

The combination of Equations 55 to 58 gives the enthalpy and entropy change of formation for water at different temperatures (Equations 59 and 60).

$$\Delta H_{water} = H_{formation_{water(T_1)}} - H_{formation_{reactant(T_1)}} + H(T_2,\ P_2) - H(T_1,\ P_1) \qquad (59)$$

$$\Delta S_{water} = S_{formation_{water(T_1)}} - S_{formation_{reactant(T_1)}} + S\,(T_2,\ P_2) - S\,(T_1,\ P_1) \qquad (60)$$

5.2.3.4 Comparison of Estimated Thermodynamic Properties

The experimental and theoretical thermodynamic parameters for uncatalyzed esterification of acetic acid with ethanol have been estimated. In the theoretical estimation method, two different thermodynamic paths were applied to estimate the enthalpy and entropy of formation for specific substance, except for water whose enthalpy and entropy of formation were estimated from the steam table. The first was based on the ideal gas temperature change (IGTC) path, which has its path starting from the elements of substance to liquid state at initial conditions (atmospheric conditions), followed by vaporization to ideal gas state, before transforming to real state at reaction conditions. It requires finding the thermodynamic properties of formation at liquid state, thermodynamic properties of vaporization, residual thermodynamic properties, and heat capacities at ideal gas state. The second was constructed on the liquid temperature change (LTC) path that has its path starting from the elements of substance to idea gas state at initial conditions, followed by condensation of the vapor substance to liquid state, before transforming to liquid state at final reaction conditions. It requires finding the thermodynamic properties of formation at ideal gas state, thermodynamic properties of condensation, residual thermodynamic properties, and heat capacities at liquid state.

The theoretical thermodynamic parameter values obtained from the IGTC and LTC methods, as well as the experimental equilibrium constant values for esterification of acetic acid with ethanol at different temperatures are listed in Tables 10 and 11.

Table 10. Theoretical Thermodynamic Values using IGTC Thermodynamic path

(a) Acetic Acid

Temp	ΔH	ΔS
K	kJ/mol	J/mol
373	-431	-182
423	-432	-202
473	-433	-217
523	-432	-232

(b) Ethanol

Temp	ΔH	ΔS
K	kJ/mol	J/mol
373	-273	-319
423	-268	-319
473	-262	-318
523	-254	-315

(c) Ethyl Acetate

Temp	ΔH	ΔS
K	kJ/mol	J/mol
373	-453	-447
423	-447	-444
473	-446	-450
523	-442	-461

(d) Water

Temp	ΔH	ΔS
K	kJ/mol	J/mol
373	-280	-147
423	-276	-138
473	-272	-129
523	-268	-120

(e) Thermodynamic Parameters and Equilibrium Constants of Reaction

Temp	ΔH_{rxn}	ΔS_{rxn}	$\Delta G_{rxn(calc)}$	$\Delta G_{rxn(exp)}$	Calculated	Experimental
K	kJ/mol	J/mol	kJ/mol	kJ/mol	$K_{eq(calc)}$	$K_{eq(exp)}$
373	-30	-94	5	4	0.2	0.2
423	-24	-60	2	1	0.6	0.8
473	-23	-44	-3	-3	2	2
523	-24	-35	-5	-6	4	4

Table 11. Theoretical Thermodynamic Values using LTC Thermodynamic path

(a) Acetic Acid

Temp	ΔH	ΔS
K	kJ/mol	J/mol
373	-435	-211
423	-431	-213
473	-427	-223
523	-422	-224

(b) Ethanol

Temp	ΔH	ΔS
K	kJ/mol	J/mol
373	-238	-220
423	-234	-234
473	-230	-240
523	-225	-251

(c) Ethyl Acetate

Temp	ΔH	ΔS
K	kJ/mol	J/mol
373	-434	-402
423	-428	-399
473	-420	-404
523	-403	-389

(d) Water

Temp	ΔH	ΔS
K	kJ/mol	J/mol
373	-280	-147
423	-276	-138
473	-272	-129
523	-268	-120

(e) Thermodynamic Parameters and Equilibrium Constants of Reaction

Temp	ΔH_{rxn}	ΔS_{rxn}	$\Delta G_{rxn(calc)}$	$\Delta G_{rxn(exp)}$	Calculated	Experimental
K	kJ/mol	J/mol	kJ/mol	kJ/mol	$K_{eq(calc)}$	$K_{eq(exp)}$
373	-41	-117	2	4	0.5	0.25
423	-39	-90	-1	0.6	1	1
473	-36	-69	-4	-3.2	2.5	2.3
523	-24	-34	-6	-6	4	4

It was noticed from Tables 10 and 11 that the enthalpy (ΔH) and entropy (ΔS) of reaction increase with temperature. The ΔH and ΔS values listed in the Tables 10 and 11 are negative from 373 to 523 K. The theoretical thermodynamic values from the IGTC (Table 10) thermodynamic path were estimated within the interval of -30 to -23 kJ/mol for ΔH, and -94 to -35 J/(mol.K) for ΔS at the temperature range of 373 and 523 K. The corresponding thermodynamic values from the LTC (Table 11) thermodynamic path were estimated within the interval of -41 to -24 kJ/mol for ΔH, and -117 to -34 J/(mol.K) for

ΔS. The experimental values estimated from the classical Van't Hoff plot are 30 ± 7 kJ/mol for ΔH and 70 ± 10 J/(mol.K) for ΔS.

The calculated and experimental Gibbs free energy change (ΔG) decrease as temperature increases. The estimated values of ΔG values from the IGTC and LTC thermodynamic paths were within the interval of 5 to -5 kJ/mol, and 2 to -6 kJ/mol, respectively, at the temperature range of 373 K to 523 K. The obtained experimental values of ΔG were within the interval of 4 to -6 kJ/mol.

In order to compare the estimated values with the experimental obtained values, the calculated values of the reaction enthalpies and entropies were included in the estimation of the equilibrium constants (K_{eq}) of the reaction by applying the thermodynamic property relation through some mathematical operations. It is worthy to note that the chemical equilibrium constants reported in this study have been estimated with the assumption of ideal solution behavior. However, the chemical equilibrium constant can be expressed in terms of composition and activity coefficient of reactants and products in order to account for the real behavior of the reaction system. In this study, the experimental chemical equilibrium constants were obtained with the experimental data.

To demonstrate the validity of the theoretical estimation methods in the calculation of the equilibrium constants for the uncatalyzed esterification reaction system, the calculated equilibrium constant values from the IGTC and LTC thermodynamic paths, along with the experimental equilibrium constants values were related to the equilibrium conversion (X_{eq}) of the carboxylic acid (Equation 20, Section 5.2.1). The values of equilibrium constants, equilibrium conversions, and percentage errors between experimental and the theoretical values are listed in Table 12. The IGTC method gave negative deviations, while the LTC method revealed positive deviations. These deviations became smaller at higher temperatures. Based on the agreement between the theoretical and experimental values, the thermodynamic paths would be useful in predicting the equilibrium conversions of uncatalyzed esterification reactions in general.

Table 12. Experimental and Calculated Equilibrium Constants and Equilibrium Conversion for Esterification of Acetic Acids

Temp (K)	Exp. K_{eq}	IGTC K_{eq}	LTC K_{eq}	Exp. X_{eq} %	IGTC X_{eq} %	LTC X_{eq} %	% Error IGTC	% Error LTC
373	0.25	0.17	0.49	33	29	41	-12	24
423	0.85	0.57	1.3	48	43	54	-10	12
473	2.3	1.9	2.5	60	58	61	-3	2
523	3.9	3.5	4	66	65	67	-1	1

The conclusion to be drawn from the estimation of thermodynamic parameters is that both the IGTC and LTC methods can be used to estimate the thermodynamic properties for esterification reaction at various reaction conditions. However, the LTC method seems to be less accurate than the IGTC method, because the estimated parameter values (equilibrium constants, equilibrium conversions, etc.) from the LTC thermodynamic path presented larger deviations from the experimental values. Thus, it will be preferred to apply the IGTC method to estimate the thermodynamic parameters for the esterification reaction system.

5.2.3.5. Theoretical Analysis of Equilibrium Constant from Activity Coefficient

It is worthy to note that the experimental and theoretical equilibrium constants reported in this study have been estimated with the assumption of ideal solution behavior.

However, the values of the equilibrium constants principally depend on the conditions of the mixture in the real state. In order to account for the real behavior of the mixture in the reactor, the equilibrium composition of the reacting species at vapor-liquid phases (VLE) will be desired.

For a mixture at VLE, the temperature and pressure are the same throughout all phases, and the chemical potentials of each component in all phases are equal. The chemical equilibrium constant can further be expressed in terms of the compositions and activity coefficients of reactants and products (Equation 61).

$$K_{eq} = \left(\frac{a_E * a_W}{a_A * a_B} \right)_{eq} \tag{61}$$

Where, $a_{E,}$ $a_{W,}$ $a_{A,}$ and a_B are activity of the ester, water, carboxylic acid, and ethanol, respectively.

The activities of specific substance at the vapor-liquid phase can be calculated in terms of fugacity coefficients (Equation 62).

$$a_i = y_i * \hat{\phi}_i * P = x_i * \gamma_i * f_i^0 \tag{62}$$

Where xi, $\gamma_{i,}$ f_i^0 are the mole fraction, activity coefficient of component *i*, and standard fugacity of component *i,* respectively, in liquid phase. $\acute{\o}_i$ and y_i are the fugacity coefficient and mole fraction of component i respectively, in vapor phase at system temperature and pressure.

The fugacity coefficients can be evaluated using the equation of state such as Peng-Robinson equation of state.[84] The activity coefficient (γ_i) of the component can be estimated using the UNIQUAC equation.[84] the activity coefficient of a substance consists of combinatorial (C) part and residual (R) parts (Equation 63).

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \tag{63}$$

Detailed equations for computing γ_i^C and γ_i^R can be found in the literature.[84] The appropriate parameters for estimating the γ_i^C and γ_i^R can be calculated using the UNIFAC group contribution method.[84] The activity coefficient depends on the mixture composition and the temperature. Therefore, it will be necessary to evaluate the activity coefficient for specific substance for each experimental temperature.

5.2.4. Reaction Rate Constant

In this study, the reaction rate of the uncatalyzed esterification was correlated using the simplified second order kinetics rate expression (Equation 10, Section 2.3). Integration of Equation 10 in terms of carboxylic acid conversion (X) gives,

$$\left(-\frac{1}{C_{A_0}(1-X)}\right) * \ln\left[\frac{\left((1-X)^2-\left(\frac{X^2}{K_{eq}}\right)\right)}{\left((1-X)-\left(\frac{X^2}{K_{eq}}\right)\right)}\right] = Y = t * k_f \tag{64}$$

Where C_{Ao} and X are initial concentration and fractional conversion of carboxylic acid, respectively. A derivation of Equation 64 is given in the Appendix (Section A.2) Equation 64 was used to estimate reaction rate constants 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 Figures 7 to 11. The forward reaction rate constant at each temperature was found from the slope of the line.

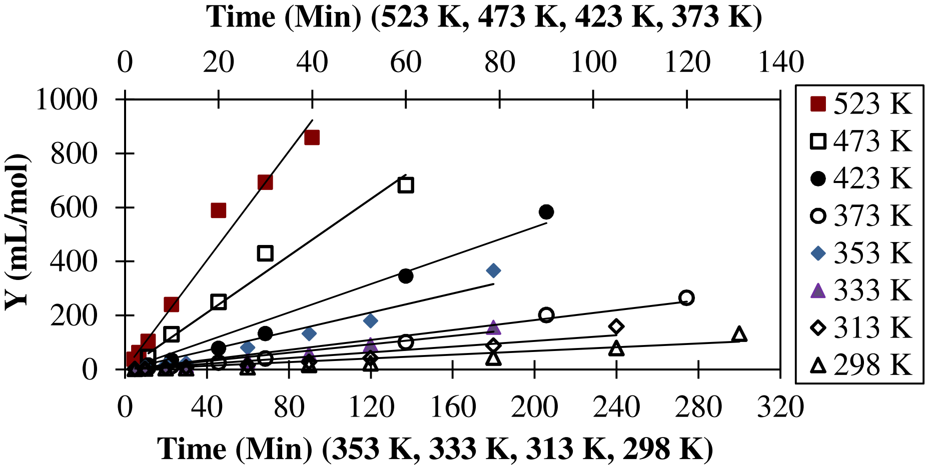


Figure 7. 2^{nd}-order rate plot for Uncatalyzed Esterification of Lactic Acid with Ethanol

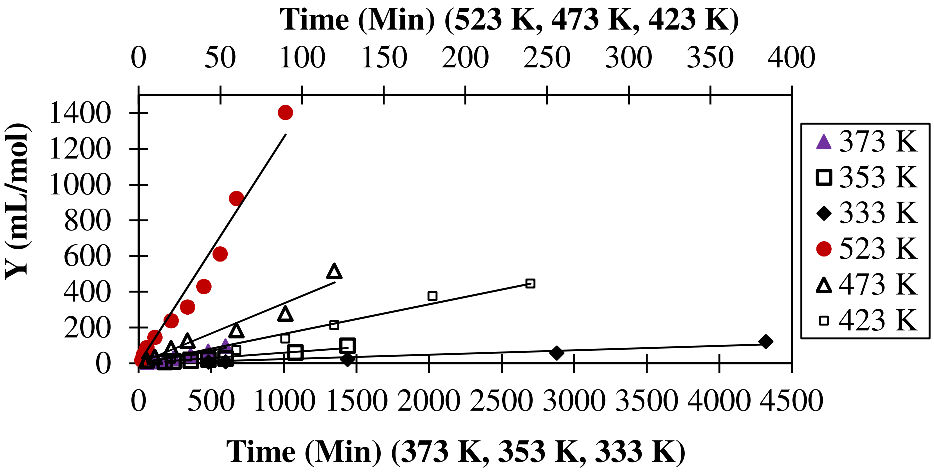


Figure 8. 2nd-order rate plot for Uncatalyzed Esterification of Levulinic Acid with Ethanol

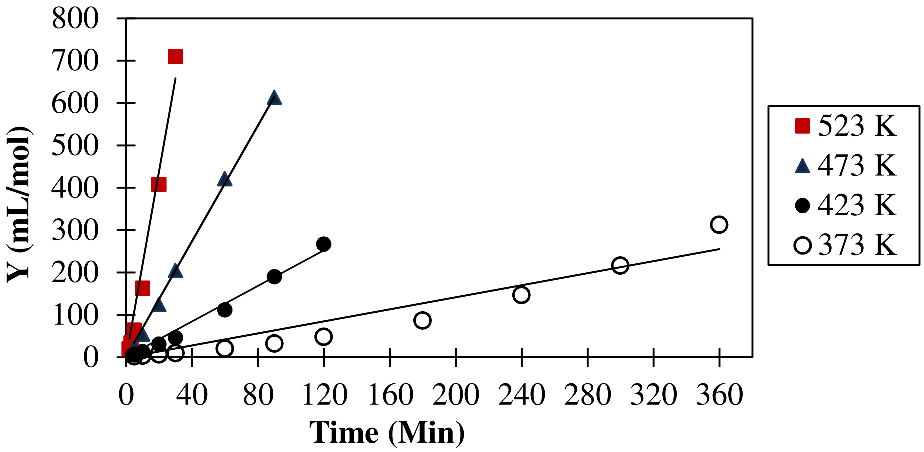


Figure 9. 2nd-order rate plot for Uncatalyzed Esterification of Acetic Acid with Ethanol

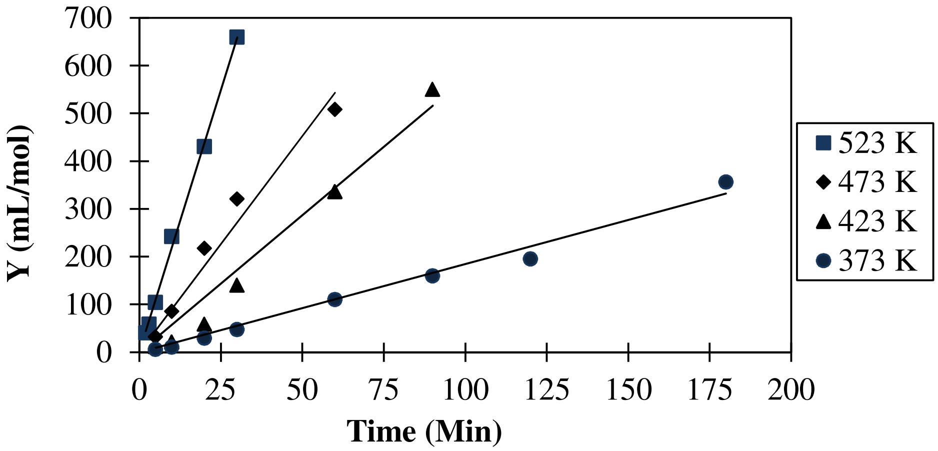


Figure 10. 2nd-order rate plot for Uncatalyzed Esterification of Formic Acid with Ethanol

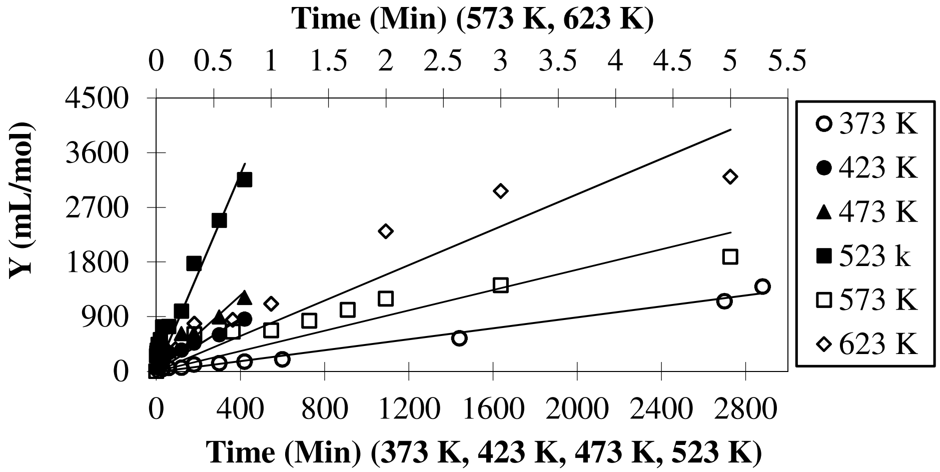


Figure 11. 2nd-order rate plot for Uncatalyzed Esterification of Linoleic Acid with Ethanol

The plots show that the 2nd-order model fits the data well, and Equation 10 is valid to describe the kinetics 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 of lactic acid (LAA), levulinic acid (LEA), acetic acid (ACA), formic acid (FA), and linoleic acid (LA) are listed in Table 13.

The reported errors in Table 13 are 95% confidence intervals. The reaction rate constant increases with increasing temperature for the esterification reactions studied in this work. At similar reaction temperature, Table 13 revealed that the reaction rate constant differs for esterification of different carboxylic acids. The differences in the rate constant may be explained by considering the different lengths of carbon chain in the carboxylic acid, attached functional group of the carboxylic acid, and difference in acid dissociation constant (pKa) values. It has been reported that the reaction rate decreases as the length of the carbon chain in the carboxylic acid increases, [14, 43, 76, 82] and the larger the pKa value of the acid, the slower the rate of reaction.

Table 13. 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	0.5
333	0.8 ± 0.1	0.9
353	1.8 ± 0.2	2
373	2.0 ± 0.2	2
423	6.0 ± 0.5	6
473	12 ± 1	12
523	23 ± 1	22

(b) Levulinic Acid

T (K)	LEA $k_{f.exp}$	LEA $k_{f.calc}$
333	0.025 ± 0.004	0.024
353	0.06 ± 0.01	0.07
373	0.14 ± 0.01	0.16
423	2.0 ± 0.1	1
473	3.8 ± 0.4	5
523	14 ± 1	15

(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
473	6 ± 3	8
523	22 ± 3	19

(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 ± 1	10
523	22 ± 1	20

(e) Linoleic Acid

T (K)	LA $k_{f.exp}$	LA $k_{f.calc}$
373	0.44 ± 0.03	0.51
423	2.2 ± 0.4	2
473	4 ± 1	5
523	10 ± 5	10
573	18 ± 9	19
623	30 ± 10	33

5.2.5 Kinetic Parameters

5.2.5.1. Activation Energy and Frequency Factor

The value of forward reaction rate constant (k_f) is a function of temperature, and was expressed by the Arrhenius equation (Equation 12, Section 2.3). The effect of temperature on the rate constants is shown in Figure 12 in the form of Arrhenius plots including the least squares fit.

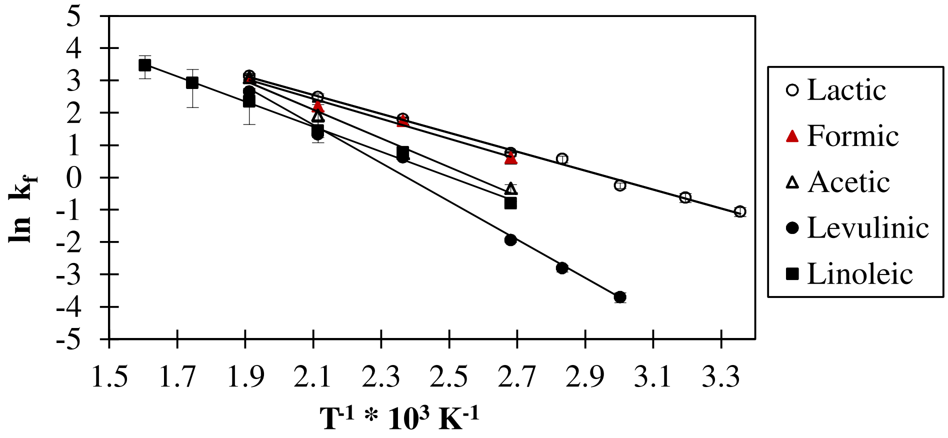


Figure 12. Arrhenius Plot for Uncatalyzed Esterification of Carboxylic Acids with Ethanol

It is evident from Figure 12 that the plot provided excellent linear fits for the esterification reaction systems considered in this work. The reaction rates for different esterification systems vary with an increase in rate constant as the temperature increases. The results of activation energy (E_a) and logarithm$_{10}$ of pre-exponential factor ($\log_{10} A_o$), as well as their 95% confidence intervals, evaluated for the uncatalyzed esterification of various carboxylic acids considered in this work are presented in Table 14. The dissociation constant (pK_a) Values at 25 °C for respective carboxylic acid are also listed in Table 14. It is noted from Table 14 that the activation energy for esterification of different carboxylic acids varies. This variation may arise from a variety of sources, including the difference in reaction temperature range, number of carbon atom, and pK_a values.

Table 14. 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 ± 1	3.74
373 – 523	Acetic Acid	40 ± 10	5 ± 1	4.76
298 – 523	Lactic Acid	24 ± 2	3.8 ± 0.2	3.85
333 – 523	Levulinic Acid	49 ± 8	6 ± 1	4.62
373 – 623	Linoleic Acid	32 ± 4	4.2 ± 0.4	7.90

The esterification of formic acid and lactic acid systems tends to have nearly equal activation energy, and this may be attributed to their nearly equal dissociation constant (pK_a) values. The pK_a values of formic acid and lactic acid at 25 °C are 3.74 and 3.85 respectively. In addition, the value of activation energy for esterification of acetic acid was expected to be lower than the activation energy value for the esterification of lactic acid, since it has been reported that the carboxylic acid with higher carbon chain tends to react slowly.[14, 43, 76, 82] However, the contrary was observed in this study, and this may be traced to the lower pK_a value of lactic acid, which possibly increases the acidity strength of the lactic acid. It is also observed that lower activation energy value was obtained for the linoleic acid esterification system as compare to esterification systems of acetic acid and levulinic acid. The reason for this trend could be related to difference in temperature range at which the esterification systems were conducted.

At the temperature of 328 and 358 K, using excess ethanol, Delgado and co-workers[7] obtained the activation energy values of 52 kJ/mol and 62 kJ/mol, respectively for catalyzed and uncatalyzed esterification of aqueous lactic acid. In this study, the estimated activation energy for uncatalyzed esterification of lactic acid is lower. The variation in the values of activation energy as reported by Delgado's group and this study may arise from difference in range of temperatures studied.

5.2.5.2. 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 equation, (Equation 13, Section 2.3). The Eyring plots generated by plotting ln (k_f *h/k_B*T) against T^{-1} (K^{-1}) are shown in Figure 13.

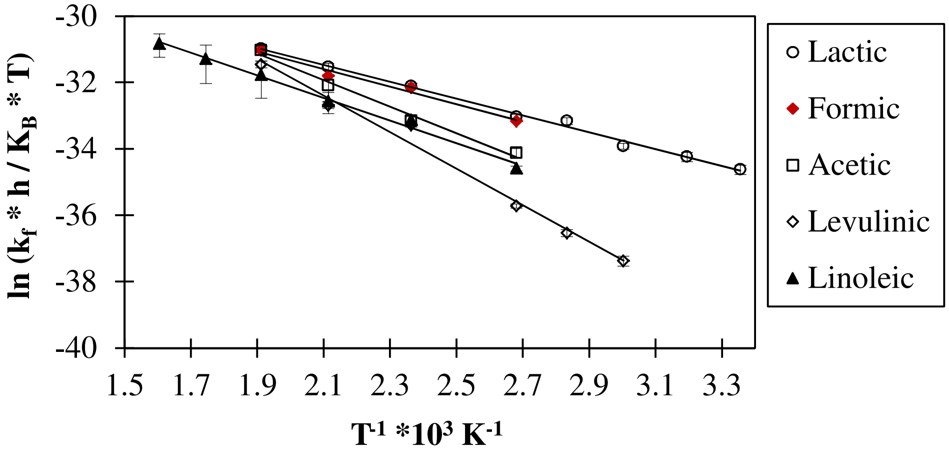


Figure 13. Eyring Plot for Uncatalyzed Esterification of Carboxylic Acids with Ethanol

Despite the nonlinearity of the Van't Hoff plot for esterification of linoleic cid, the Arrhenius and Eyring plots are linear. The linear Arrhenius and Eyring plots may arise from unchanging reaction mechanism. By the use of the least squares analysis, the activation enthalpies ($\Delta H^{\ddagger}$) and activation entropies ($\Delta S^{\ddagger}$) were evaluated with 95%

confidence interval error from the slope and intercept of the Eyring plot. The estimated values for the uncatalyzed esterification of formic acid, acetic acid, lactic acid, levulinic acid, and linoleic acid with ethanol are listed in Table 15.

Table 15. Values of Activation Enthalpy and Activation 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

As noted in Tables 14 and 15, 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 evident 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 the evaluated entropic terms; pre-exponential factor (A_o), and activation entropy ($\Delta S^{\ddagger}$) from respective plots. It has been recently stated that the reported negative values of $\Delta S^{\ddagger}$ corresponds to pre-exponential factors (A_o) smaller than the universal frequency factor (k_B*T_{ref}/h), whereas positive values signify situations wherein A_o is greater than k_B*T_{ref}/h.[87] Therefore, the 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. The negative signs of $\Delta S^{\ddagger}$ are indicative of associative mechanism for esterification of carboxylic acids as the activated complex in the transition state is more ordered than the reactants in the reaction system.

5.2.6. Effect of Temperature

5.2.6.1. Uncatalyzed Lactic Acid Esterification System

The temperature was varied from 298-523 K to study its effect on the rate of uncatalyzed esterification of 98% lactic acid with stoichiometric amount of ethanol. The results are shown in Figure 14. The reaction rate as well as the conversion of lactic acid to lactate increased with an increase in temperature. Higher reaction rate was observed at 523 K with the equilibrium conversion of approximately 70% conversion at nearly 60 min. At 298 K, the reaction reached equilibrium conversion at 480 min with approximately 15% conversion.

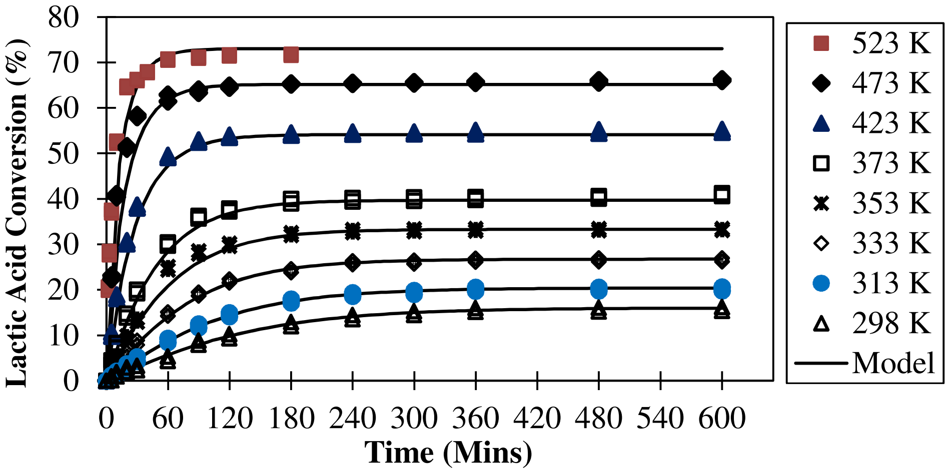


Figure 14. Conversion-time profile at various temperatures for Uncatalyzed Esterification of Lactic Acid with Ethanol. Molar ratio of 1:1. Continuous lines represent the kinetics model.

The kinetic model was plotted with the experimental data in Figures 14 using the fitting procedure described in section 4.2. A comparison of the calculated and experimental values for all reaction conditions shows a reasonable agreement between the model predictions and experiments. Thus, the second order reversible kinetics model applied in this study is reasonable for the uncatalyzed esterification of lactic acid system at the reaction temperatures considered in this study.

In this study, the measured concentrations of three species except water (lactic acid, ethanol and ethyl lactate) in the reaction samples were observed to follow the stoichiometric relation as indicated by nearly equal concentrations of lactic acid and ethanol. The amount of water produced by the reaction was not measured, but was assumed to be equal to the ethyl lactate on a molar basis. In the range of temperature considered in this study, side reactions were not observed, contrary to findings by some authors[11-12]

5.2.6.2. Uncatalyzed Levulinic Acid Esterification System

The effect of temperature on the formation of ethyl levulinate, esterification of levulinic acid was carried with equimolar amount of ethanol at different temperatures, ranging from 298 to 523 K. Figure 15 shows the obtained conversion of levulinic acid to ethyl levulinate as treated at various temperatures and reaction times. The experimental data are represented with the symbols, whereas the calculated model data are shown with the line. Increase in the reaction rate and conversion of levulinic acid as temperature increases is evident in Figure 15. Higher reaction rate was also obtained at 523 K, with 60% equilibrium conversion at nearly 90 min. It was noted that at 333 K, the equilibrium conversion of levulinic acid was approximately 21% after 120 hr reaction time. In this present study, the concentrations of ethyl levulinate at temperatures of 298 K and 313 K were below the detection limit of the applied HPLC analytical method.

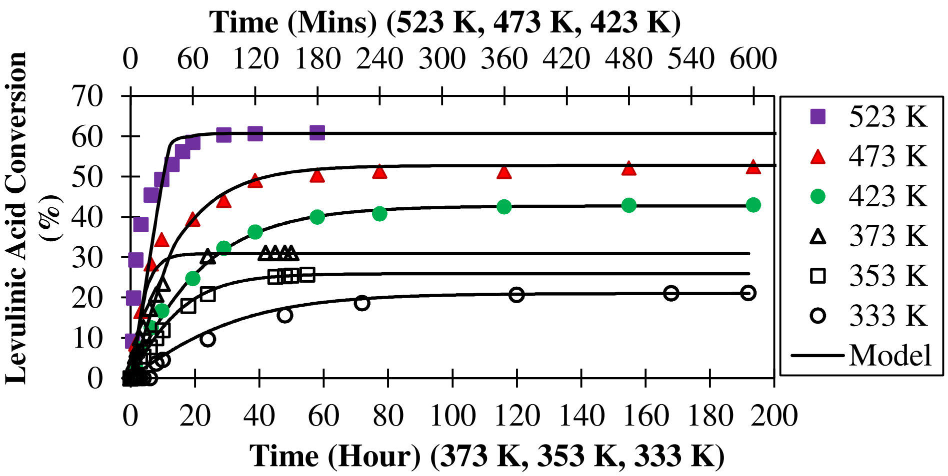


Figure 15. Conversion-time profile at various temperatures for Uncatalyzed Esterification of Levulinic Acid with Ethanol. Molar ratio of 1:1. Continuous lines represent the kinetics model.

The kinetic model was plotted with the experimental data in Figures 15 using similar fitting procedure described in section 4.2. A comparison of the model predictions with experiments for all reaction conditions shows a reasonable agreement between the experimental data and kinetics model. Thus, the second order reversible kinetics model applied in this study is reasonable for the uncatalyzed esterification of levulinic acid.

In this study, the measured concentrations of levulinic acid, ethanol and ethyl levulinate in the reaction samples were also noted to follow the stoichiometric relation, as indicated by equal concentrations of levulinic acid and ethanol. The amount of water produced by the reaction was not measured, but was assumed to be equal to the ethyl levulinate on a molar basis.

5.2.6.3. Uncatalyzed Acetic Acid Esterification System

To determine the effect of temperature on the ethyl acetate formation, uncatalyzed esterification reactions of acetic acid were carried out with equimolar amount of ethanol at various temperatures ranging from 373 to 523 K under similar conditions. Figure 16 shows the conversion of acetic acid to ethyl acetate as treated at various temperatures and reaction times. The experimental and model calculated data are represented by the symbols and continuous line respectively. The reaction rate, as well as the 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 recently reported the conversion of acetic to be higher in uncatalyzed esterification than when the reaction was catalyzed by acid resins, since the resins not only act as catalyst, bur also affect the equilibrium conversion due to their selective adsorption of reactants and swelling nature.[36]

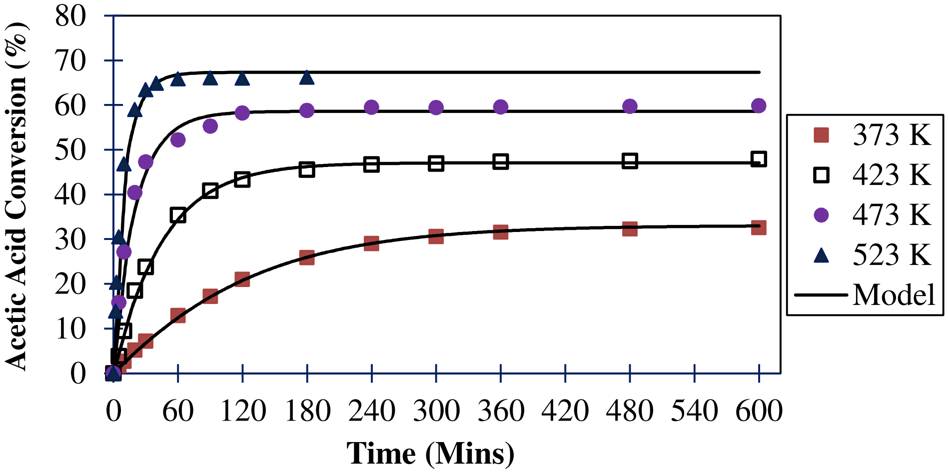


Figure 16. Conversion-time profile at various temperatures for Uncatalyzed Esterification of Acetic Acid with Ethanol. Molar ratio of 1:1. Continuous lines represent the kinetics model

The kinetic model was plotted with the experimental conversion-time data in Figure 16 using similar fitting procedure described in section 4.2. It is evident from the Figure that a comparison of the model values with experimental values for all reaction conditions shows a reasonable agreement between the experimental data and kinetics model. Therefore, the second order reversible kinetics model applied in this study is reasonable for the uncatalyzed esterification of acetic acid in the range of temperature considered in this study.

In the study of the uncatalyzed acetic acid esterification, the measured concentrations of acetic acid, ethanol and ethyl acetate in the reaction samples were observed to follow the stoichiometric relation, as evidenced by relatively equal concentrations of acetic acid and ethanol. The amount of water produced by the reaction was not measured, but was assumed to be equal to the ethyl acetate on a molar basis. In the range of temperature considered in this work, side reactions were not observed, contrary to findings by some authors.[13, 17]

5.2.6.4. Uncatalyzed Formic Acid Esterification System

The effect of temperature on the uncatalyzed esterification of 98% formic acid with ethanol at 1:1 mole ratio was studied at various temperatures varying from 373 to 523 K. The results on the conversion of formic acid, as well on the reaction rate at different temperatures are shown in Figure 17. While the experimental data are shown by symbols, the model values are represented by the lines. The conversion and reaction rate increase with an increase in temperature. Higher reaction rate was observed at 523 K and the equilibrium conversion was obtained at nearly 90 min with approximately 75%

conversion. The equilibrium conversion of the formic acid at 373 K was obtained after 360 min with approximately 55% conversion.

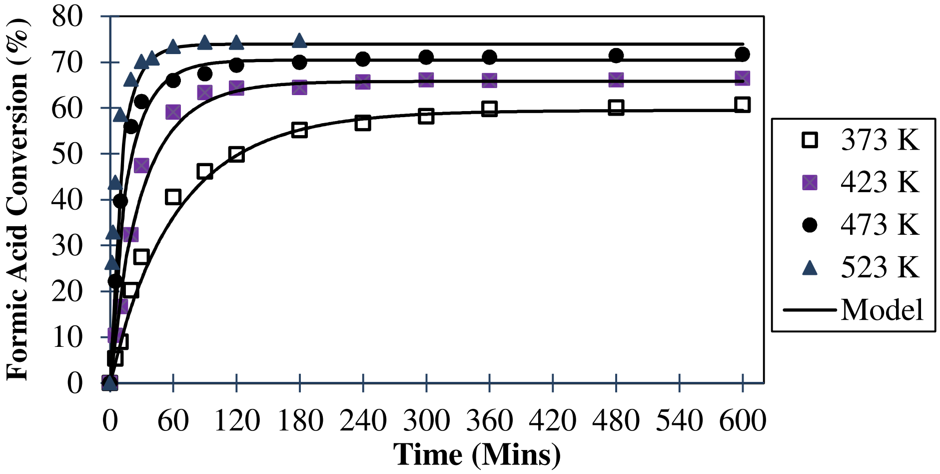


Figure 17. Conversion-time profile at various temperatures for Uncatalyzed Esterification of Formic Acid with Ethanol. Molar ratio of 1:1. Continuous lines represent the kinetics model.

The experimental conversion-time data in Figure 17 was plotted with the kinetic model using the fitting procedure described in section 4.2. As it can be noted, the experimental data agreed reasonably well with the kinetics model for all reaction conditions considered in this work. Hence, the second order reversible kinetic model applied in this study is reasonable for the uncatalyzed esterification of formic acid in the range of temperature considered.

5.2.6.5. Uncatalyzed Linoleic Acid Esterification System

To determine the effect of temperature on the ethyl linoleate formation, uncatalyzed esterification reactions of linoleic acid were carried out with equimolar amount of ethanol at various temperatures ranging from 373 to 623 K under similar conditions. Figure 18 shows the obtained conversion of linoleic acid to ethyl linoleate as treated at various temperatures and reaction times.

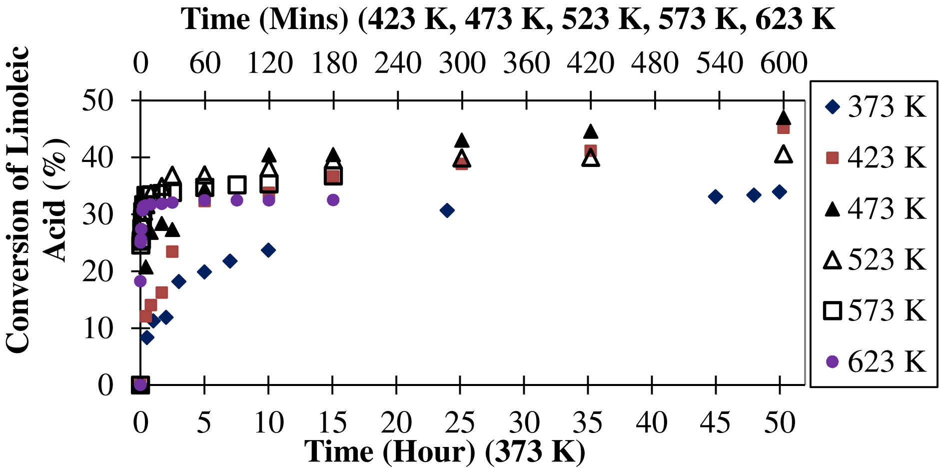


Figure 18. Conversion-time profile at various temperatures for Uncatalyzed Esterification of Linoleic Acid with Ethanol, molar ratio of 1:1

From Figure 18, it is evident that at the temperature range of 373 and 473 K, the conversion of linoleic acid increases with temperature, and 42% equilibrium conversion was obtained at nearly 300 min at 473 K. However, at temperatures above 473 K, significant reduction in the equilibrium conversion was noticed, but it was attained at shorter reaction time. In these conditions, equilibrium conversions are approximately 36%, 34%, and 32% at 523 K, 573 K, and 623 K, respectively, at 60 min reaction time. The decrease in equilibrium conversion might be related to the instability of the linoleic acid at longer reaction time and temperatures above 473 K. An important result observed in this work 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.

5.2.7. Effect of Metallic Substance

5.2.7.1. Conversion and Reaction Rate

In an effort to determine whether Inconel 625, nickel wire, stainless steel sheet, tantalum, and grade 5 titanium wires have catalytic or inhibitory effects and/or corrosion susceptibility with regard to the 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 Figures 19 and 20 respectively.

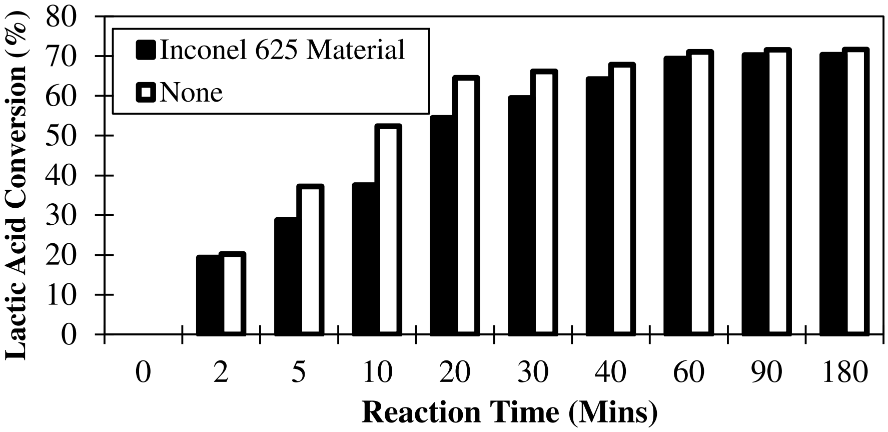


Figure 19. Conversion vs. time for Uncatalyzed Esterification of Lactic Acid with and without Inconel 625 material at 523 K. Initial reactant mole ratios: $n_{EtOH}/n_{LAA} = 1$

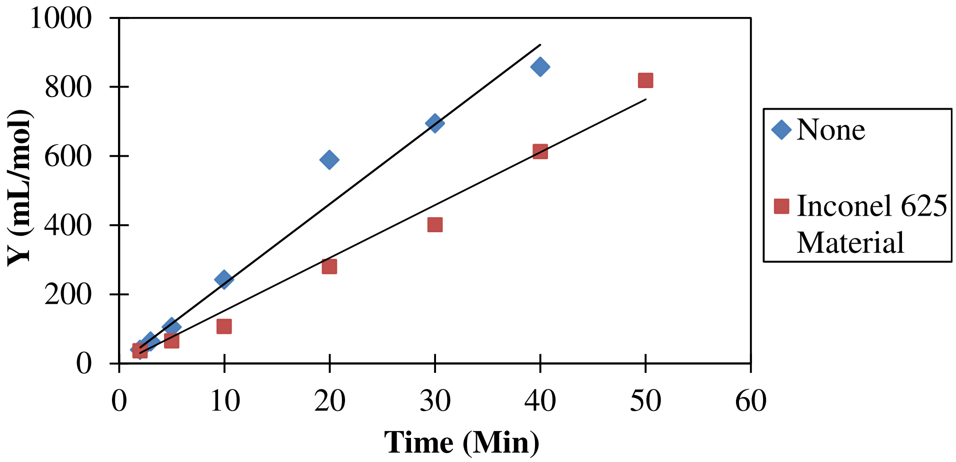
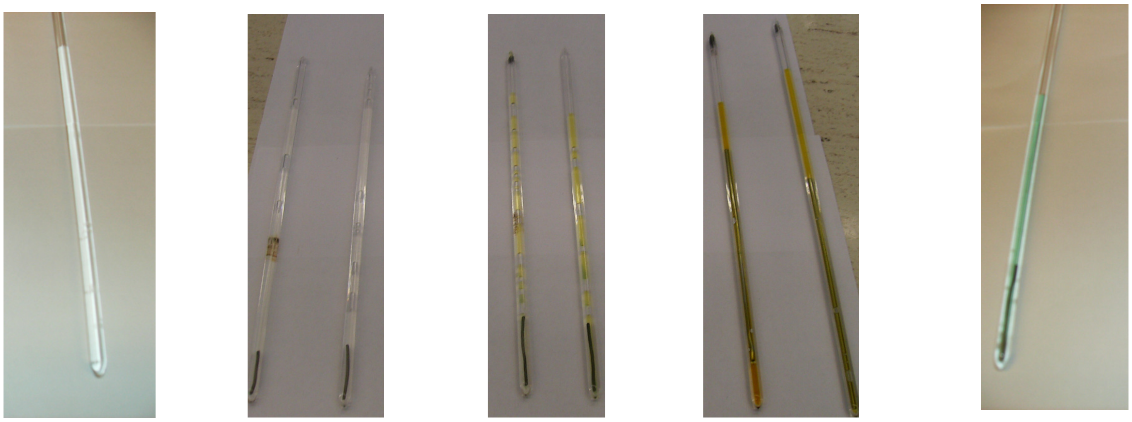


Figure 20. Reaction Rate Constant for Uncatalyzed Esterification of Lactic Acid with and without Inconel 625 material at 523 K. Initial reactant mole ratio: $n_{EtOH}/ n_{LAA} = 1$

When Inconel 625 material was added, the equilibrium conversion was nearly equal to that obtained in the absence of Inconel 625 material. However, the reaction rate constant was higher in the absence of 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 estimated from the experimental data 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 in the presence of Inconel 625 material may be attributed to reactant-metal surface contact that probably inhibits the reaction.

5.2.7.2. Corrosion

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 hr of exposure. At a reaction temperature of 473 K, color formation was not noticed until 100 hr reaction time. With stainless steel at 523 K, dark green color was noticed before 2 hr. The reaction tubes with intensity of green color formation are shown in Figure 21. The levels of color formation may arise from the potential corrosion problems associated with metallic materials commonly used for reactions with high pressure and high temperature.



(a) (b) (c) (d) (e)

Figure 21. Reactors with intensity of green color formation after Uncatalyzed Esterification of lactic Acid; (a) reactor with no metallic substance at 523 K, (b) reactor with Inconel 625 at 473 K and 72 hr, (c) reactor with Inconel 625 at 473 K and 100 hr, (d) reactor with Inconel 625 at 523 K and 20 hr, and (e) reactor with Stainless steel at 523 K and 2 hr.

Nevertheless, comparing the tantalum and grade 5 titanium materials with Inconel 625, nickel wire and stainless steel materials that are not compatible with uncatalyzed esterification of lactic acid with ethanol at elevated reaction temperatures, tantalum and grade 5 titanium materials indicated acceptable level of compatibility with uncatalyzed esterification of lactic acid with ethanol at 523 K since slight yellow color was observed after 220 hr of reaction time. The reactor tubes with various color formation for different metallic substances exposed to uncatalyzed esterification of lactic acid with ethanol at 523 K for 220 hr are shown in Figure 22. The corrosion resistance indicated by tantalum and grade 5 titanium materials could encourage the design of a flow reactor system for kinetics study of uncatalyzed esterification of carboxylic acids at elevated temperatures.

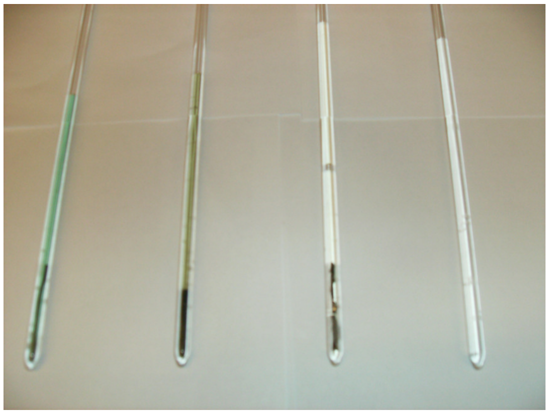


Figure 22. Reactors with different metallic substances exposed to Uncatalyzed Esterification of lactic acid at 523 K. From left are reactors with stainless steel, Inconel 625, tantalum sheet, and reactor with no metallic substance**.**

5.3. Conclusions

The kinetics for the uncatalyzed esterification of various biomass-derived carboxylic acids (formic, acetic, lactic, levulinic, and linoleic) with stoichiometric amounts of ethanol in isothermally operated non-catalytic capillary quart batch reactors have been successfully carried out. The effects of temperature, reaction time, number of carbon atom and functional group of carboxylic acid on the rate of reaction and conversion were emphasized.

The reaction rate has been found to increase with temperature for esterification of carboxylic acids considered in this study as indicated by linear Arrhenius and Eyring plots. The equilibrium constants for the esterification of short-chain carboxylic acids were 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) indicated a nonlinear Van't Hoff behavior.

The second order reversible reaction model was used to correlate the experimental kinetic data. The thermodynamic and kinetic parameters estimated were found to be varied for different esterification systems. The predicted conversions from the proposed kinetic model agree reasonably well with the experimental kinetic data.

Thermodynamic paths were developed for estimating the theoretical equilibrium conversions for uncatalyzed esterification of acetic acid with ethanol at different reaction conditions. This theoretical procedure incorporates the contributions of thermodynamic properties of formation, thermodynamic properties of vaporization, residual thermodynamic properties, and heat capacities. The theoretical estimated values of equilibrium conversion compared well with experimental results at different reaction conditions reported in this present study. Based on this agreement between the theoretical end experimental values, the thermodynamic paths would be useful in predicting the equilibrium conversions of uncatalyzed esterification reactions in general.

Additional experiments were carried out at selected elevated temperatures to assess the catalytic and corrosion effects of several metallic substances on esterification system. Tantalum and grade 5 titanium materials were identified as corrosion resistance metals, suitable for uncatalyzed esterification system at elevated temperatures.

CHAPTER 6: IMPACT AND FUTURE WORK

This research aims to study the kinetics of uncatalyzed esterification of biomass-based carboxylic acids, which provides cleaner routes for synthesizing valuable esters due to ease of separation and purification without contamination, and to establish the basic understanding on the variation of rate constants for different types of aliphatic carboxylic acids. Thus far, the results of this work have demonstrated the possibility to convert various biomass-derived carboxylic acids to their corresponding esters in an uncatalyzed esterification system. Also, two thermodynamic paths were developed for estimating the equilibrium conversions by applying the thermodynamic property relation.

Although, the uncatalyzed esterification of carboxylic acids at elevated reaction temperature is still at laboratory scale. It is our hope that the evaluated kinetic and thermodynamic parameters may be used as predictive tools for reactor scale-up, thus providing a new perspective into the conversion of biomass to useful chemicals and fuel.

Furthermore, since the domestically available biomass is an alternate renewable source to the fossil based chemicals and fuels, the potential esters of biomass-derived carboxylic acids, like ethyl lactate, ethyl levulinate, ethyl acetate, ethyl formate, and ethyl linoleate can be used as intermediates for fuels and chemicals like plasticizing agents, food preservatives, pharmaceutical formulation, plastics, cleaning solvents, fragrances, and biofuel. In addition, conversion of biomass resources to commercially viable chemicals through an uncatalyzed esterification system can provide opportunities to ensure improved economic growth and national security.

Acid-catalyzed esterification of carboxylic acids is an equilibrium-limited reaction, which appears to be performed within a reactive distillation column, an integrated process where both reaction and separation are carried out simultaneously. However, the reactive distillation process partially suffers from side reactions like etherification, or poor performance due to temperature limitations. In this context, the application of the uncatalyzed esterification system may be an interesting alternative.

Although significant amount of literature is available on esterification reaction, there is no comprehensive study on the kinetics and thermodynamics of uncatalyzed esterification of different aliphatic carboxylic acids with equimolar amount of alcohol to understand the effect of carbon chain length and functional group of carboxylic acids. Thus, the results presented in this study could lay the groundwork for future research opportunities into the kinetics and thermodynamics of uncatalyzed esterification of biomass-derived carboxylic acid at elevated temperatures.

With respect to esterification reaction rate, the synthesis of esters at elevated reaction conditions seems to show promising results over the acid-catalyzed approach, but due to the carboxylic acid-metal contact corrosion problem at very high reaction temperature, a detailed feasibility study to analyze the economics and environmental impact of both reaction systems are suggested for future work.

The uncatalyzed esterification of various carboxylic acids with ethanol at elevated temperatures has been conducted in this work a batch process. However, working at elevated reaction conditions with a batch reactor is complicated since the reaction temperature and pressure are not easy to monitor or control. Thus, a flow-type reactor that enables control of the temperature, pressure and flow rate is recommended for kinetic study of the uncatalyzed esterification system.

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APPENDIX

A.1. Preparation of Calibration Standards for Esterification of Carboxylic Acids

A.1.1. HPLC Standard Calibration Curves

Different weights of each standard compound were accurately weighed into the 50 mL flask and dissolved with 1 mL of water to give different concentration levels in g/mL. Calibration standard curve for each authentic compound was prepared by diluting about 0.1 mL of each sample with ultrapure water to 5 mL solution for analysis. A 1-mL of the diluted sample was placed into the HPLC vial tube and 10µL of the solution was injected into the HPLC column. The corresponding concentration levels for standard compounds are listed in Table A.1.

Table A.1. Concentrations of Standard Compounds for Calibration Curves

Compounds	Concentrations (g/mL)
Lactic acid	0.8, 0.4, 0.2, 0.1, and 0.05
Ethyl lactate	0.8, 0.4, 0.2, 0.1, and 0.05
Ethanol for lactic acid esterification	0.4, 0.2, 0.1, 0.05, and 0.025
Levulinic acid	1, 0.5, 0.25, 0.125, and 0.063
Ethyl levulinate	0.7, 0.35, 0.175, 0.088, and 0.044
Ethanol for levulinic acid esterification	0.7, 0.35, 0.175, 0.088, and 0.044
Acetic acid	0.6, 0.3, 0.2, 0.15, 0.099, 0.075, and 0.038
Ethyl acetate	0.88, 0.44, 0.29, 0.22, 0.145, 0.11, and 0.055
Ethanol for acetic acid esterification	0.46, 0.23, 0.15, 0.12, 0.076, 0.057, and 0.029

Calibration curves were obtained by plotting the average peak area of the standard compounds against the known concentrations. The concentration of each compound in the reaction sample was determined from the standard calibration curves. The standard calibration curves for esterification of lactic acid, levulinic acid, and acetic acid are shown in Figures A.1-A.9.

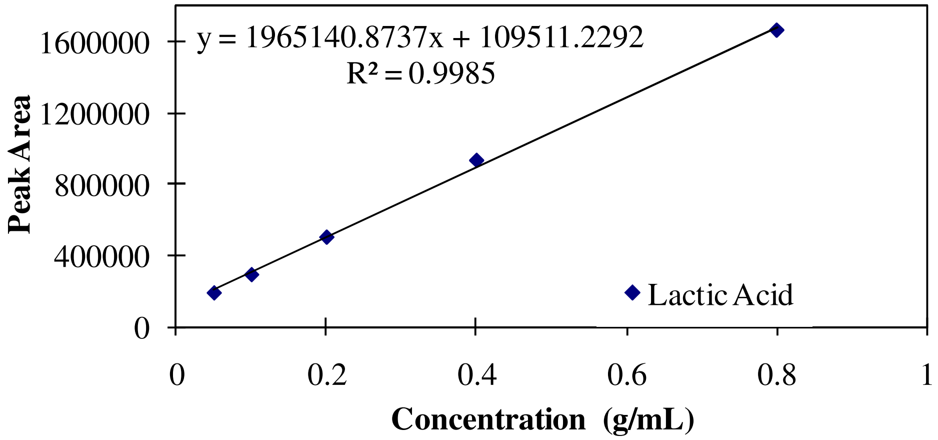

Figure A.1. Calibration Curve for Lactic Acid

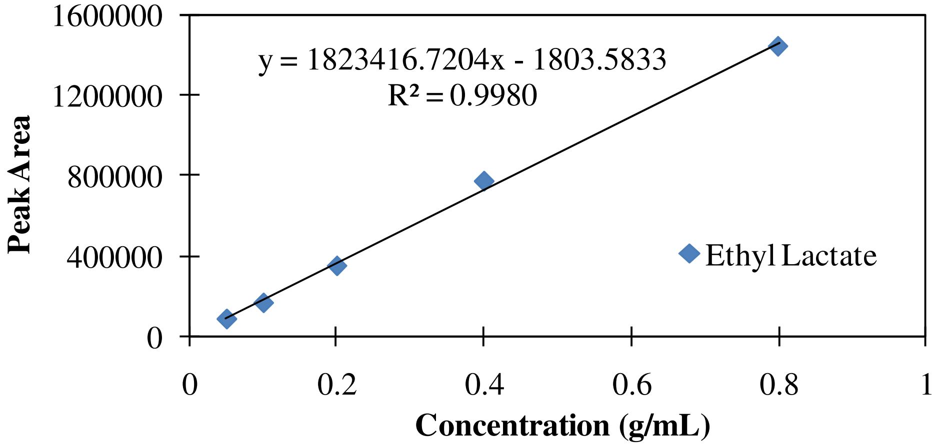

Figure A.2. Calibration Curve for Ethyl Lactate

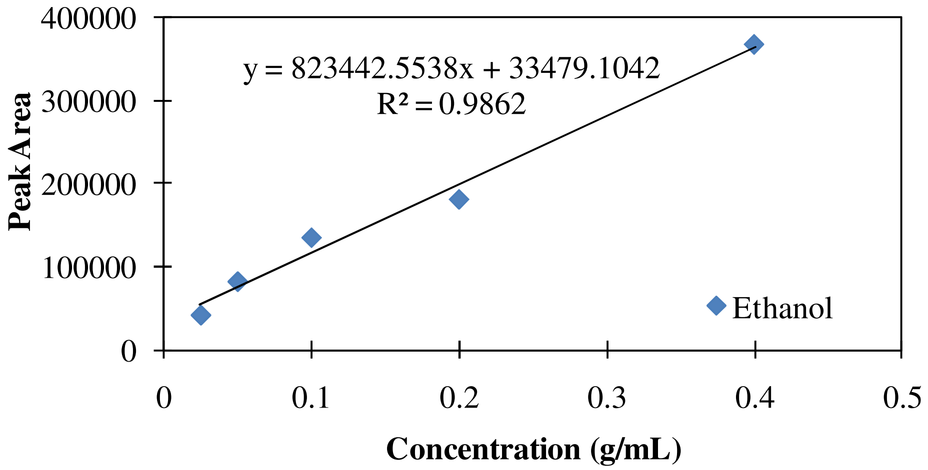

Figure A.3. Calibration Curve for Ethanol for lactic acid Esterification

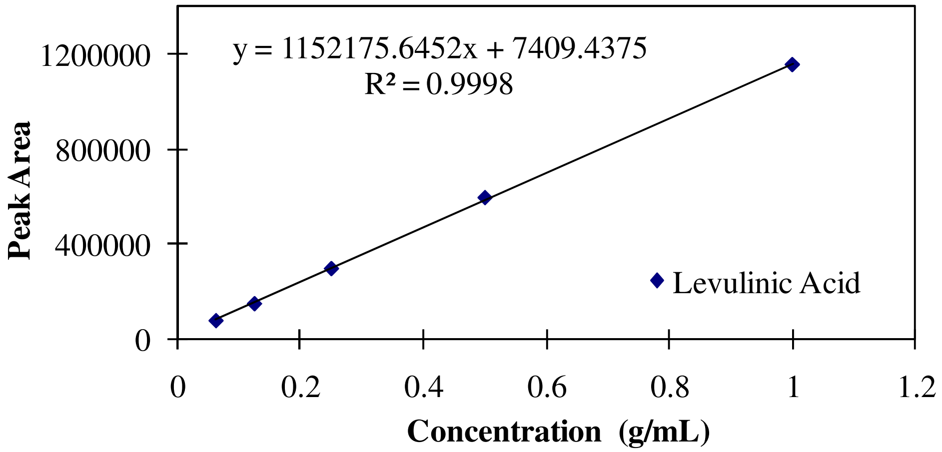

Figure A.4. Calibration Curve for Levulinic Acid

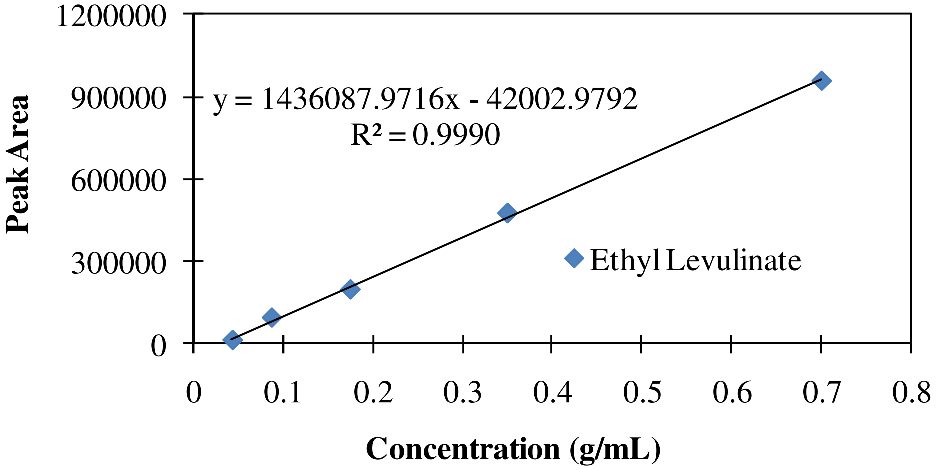

Figure A.5. Calibration Curve for Ethyl Levulinate

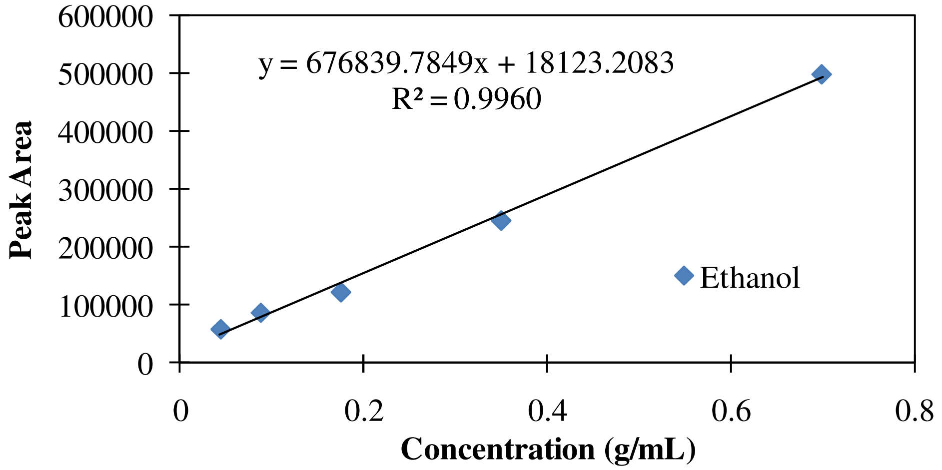

Figure A.6. Calibration Curve of Ethanol for Levulinic Acid Esterification

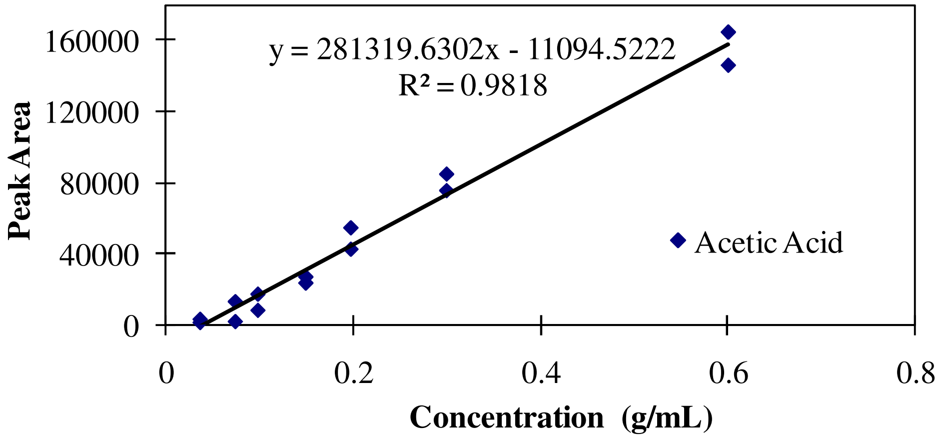

Figure A.7. Calibration Curve for Acetic Acid

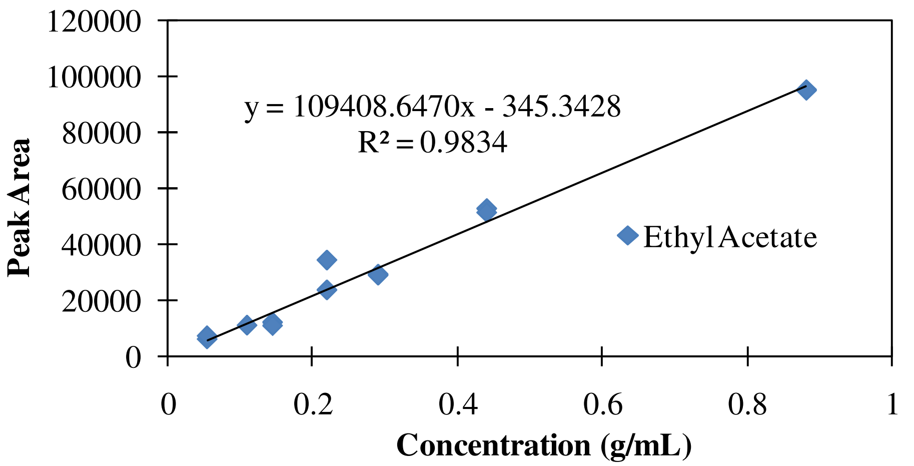

Figure A.8. Calibration Curve for Ethyl Acetate

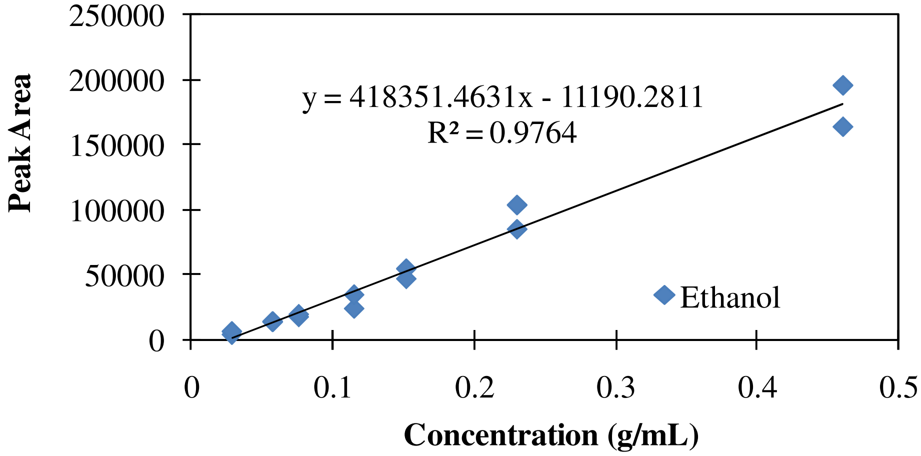

Figure A.9. Calibration Curve of Ethanol for Acetic Acid Esterification

A.1.2. Standard Calibration Curve for Formic Acid Titration

Different weights of standard formic acid were accurately weighed into the 50 mL flask and dissolved with 1 mL of water to give different concentrations. The corresponding concentration levels for standard formic acid are listed in Table A.2.

Table A.2. Concentrations of Standard Formic Acid for Calibration Curves

Compound	Concentration (g/mL)
Formic acid	0.477, 0.313, 0.196, 0.1, and 0.055

Calibration standard curve for formic acid was prepared by diluting about 0.1 mL of each sample with deionized water to 5 mL solution for titration against 0.1 N standardized sodium hydroxide solution using phenolphthalein as an indicator. Unconverted formic acid was found by using the following formulas:

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

F: Free Acidity as Formic Acid, wt%, N_{NaOH}: Normality of NaOH solution, mol/L, V_{NaOH}: volume of NaOH solution used for the titration, mL, $MW_{Formic\ Acid}$: Molecular weight of Formic Acid, 46.02 g/mol, and W_{Sample}: Sample weight, in g.

Calibration curve was obtained by plotting the average unconverted formic acid against the known concentrations of the formic acid. The concentration of formic acid in the reaction medium was determined from the standard calibration curve. The standard calibration curve is shown in Figure A.10.

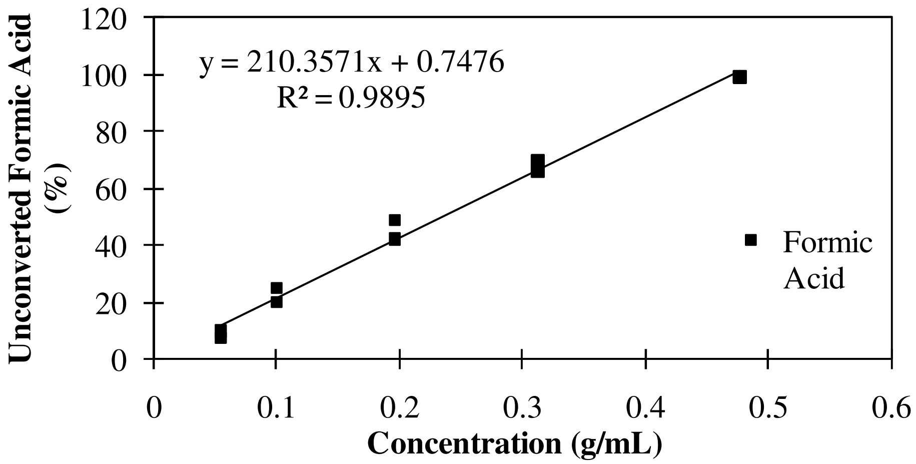

Figure A.10. Titration of standard Formic Acid

A.1.3. Raman Spectroscopy Standard Calibration Curves

A standard calibration curve for Raman spectroscopy analysis was developed by using several mixtures of authentic linoleic acid, ethyl linoleate, ethanol, and water. The molar ratios of the mixtures are listed in the Table A.3.

Table A.3. Molar Ratio of Calibration Mixtures

	Moles				
Acid	1	0	0.25	0.5	0.75
Ester	0	1	0.75	0.5	0.25
Ethanol	1	0	0.25	0.5	0.75
Water	0	1	0.75	0.5	0.25

The Raman peak intensities were examined at 1710 and 1740 cm^{-1} wavenumbers for COOH neat acid and C=O ester stretching, respectively. A constant wavenumber equation was used to calculate the intensity ratio because the peaks were shifting to the right hand side.

$$\begin{array}{c}\text{Constant Wavenumber}\\ \text{Intensity Ratio}\end{array} = \frac{I_{1740}}{I_{1710} + I_{1740}}$$

The spectra of the standards and the standard calibration curve are shown in Figure A.11 and Figure A.12 respectively. All spectra were obtained with the same condition in triplicates from each standard mixture to ensure reproducibility. The mole fraction of the ethyl linoleate in the each reaction sample was determined from the standard calibration curve.

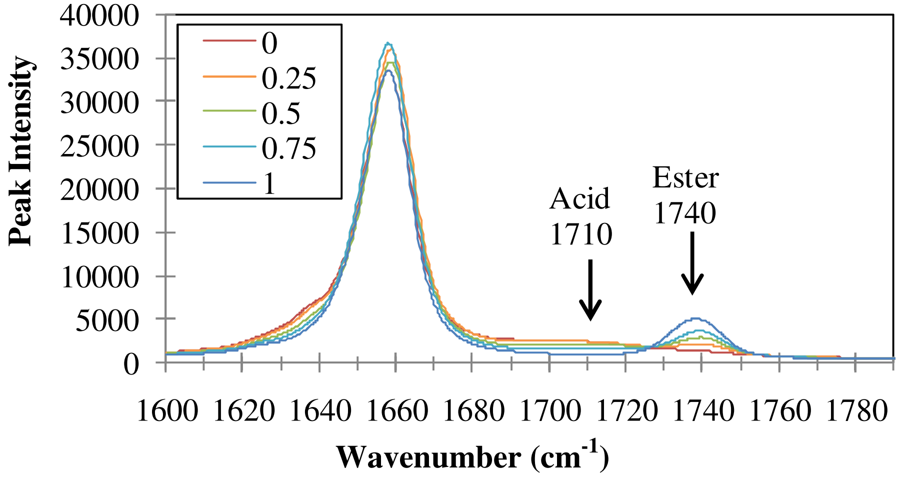

Figure A.11. Spectra of standard mixtures of linoleic acid and ethyl linoleate in ethanol

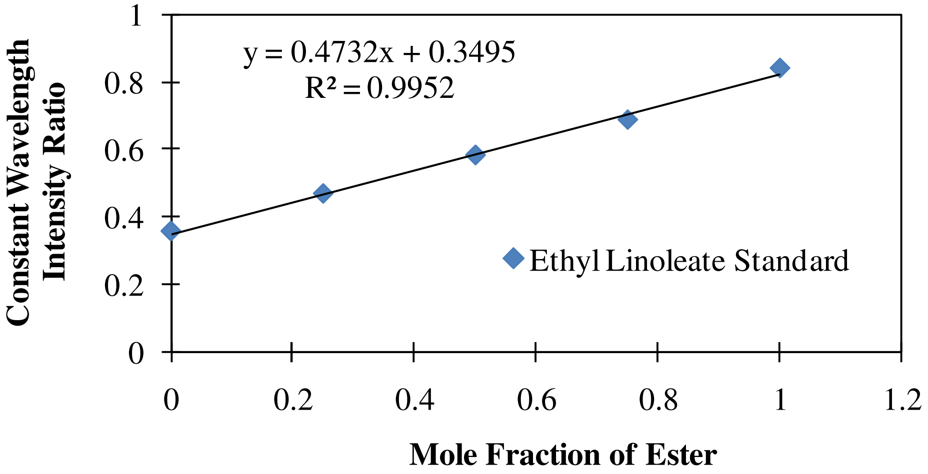

Figure A.12. Calibration curve for the conversion of linoleic acid to ethyl linoleate

A.2. Derived Equation for Reaction Rate Constant in term of Carboxylic Acid Conversion

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} E + W \qquad (A1)$$

$$-r_A = -\frac{dC_A}{dt} = k_f C_A C_B - k_r C_E C_W \tag{A2}$$

$$-r_A = -\frac{dC_A}{dt} = k_f \left(C_A C_B - \frac{k_r C_E C_W}{k_f} \right) \tag{A3}$$

$$-r_A = -\frac{dC_A}{dt} = k_f \left(C_A C_B - \frac{C_E C_W}{K_{eq}} \right) \tag{A4}$$

$$\text{Where, } K_{eq} = \frac{k_f}{k_r}$$

$$-r_A = -\frac{dC_A}{dt} = \left(k_f C_A C_B - \frac{k_f C_E C_W}{K_{eq}} \right) \tag{A5}$$

From Equation (A5), Let

$$\left.\begin{array}{l} \dfrac{k_f C_E C_W}{K_{eq}} = M \\[2em] C_A = Y \\[2em] k_f C_B = L \\[2em] t = X \end{array}\right| \tag{A6}$$

Therefore, Equation (A5) becomes

$$-r_A = -\frac{dY}{dX} = YL - M \tag{A7}$$

$$-\frac{dY}{YL - M} = dX \tag{A8}$$

By Integrating Equation (A8)

$$-\int_{Y_0}^{Y} (YL - M)^{-1} dY = \int_{X_0}^{X} dX$$

$$-\left[\frac{\ln(YL - M)}{L}\right]_{Y_0}^{Y} = X \tag{A9}$$

Substitute the terms in Equation (A6) into Equation (A9)

$$-\ln\left[k_f C_A C_B - \frac{k_f C_E C_W}{K_{eq}}\right]_{C_{A0}}^{C_A} = t * k_f * C_B \tag{A10}$$

Canceling out the like terms, Equation 10 becomes

$$-\frac{1}{C_B}\ln\left[\frac{\left(C_A C_B - \frac{C_E C_W}{K_{eq}}\right)}{\left(C_{A_0} C_B - \frac{C_E C_W}{K_{eq}}\right)}\right] = t * k_f \tag{A11}$$

From Stoichiometry relationship,

$C_A = C_B$

$C_E = C_w$

$$r_A = -\frac{1}{C_A}\ln\left[\frac{\left(C_A^2 - \frac{C_E^2}{K_{eq}}\right)}{\left(C_{A_0} C_A - \frac{C_E^2}{K_{eq}}\right)}\right] = t * k_f \tag{A12}$$

Since,

$$X = \frac{C_{A_0} - C_A}{C_{A_0}}$$

$$C_A = C_{A_0}(1 - X)$$

$$C_E = C_{A_0}X + C_{E_0}$$

For $C_{E_0} = 0$

Therefore, by mathematical substitution, Equation (A12) becomes

$$r_A = -\frac{1}{C_{A_0}(1-X)}\ln\left[\frac{\left(C_{A_0}^2(1-X)^2 - \frac{C_{A_0}^2X^2}{K_{eq}}\right)}{\left(C_{A_0}^2(1-X) - \frac{C_{A_0}^2X^2}{K_{eq}}\right)}\right] = t * k_f \qquad \text{(A13)}$$

Canceling the like terms, Equation (A13) becomes

$$r_A = -\frac{1}{C_{A_0}(1-X)}\ln\left[\frac{\left((1-X)^2 - \frac{X^2}{K_{eq}}\right)}{\left((1-X) - \frac{X^2}{K_{eq}}\right)}\right] = t * k_f \qquad \text{(A14)}$$

A.3. Experimental Results for Uncatalyzed Esterification Reaction

Table A.4. Formic Acid Conversion at 373 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Formic Acid	Ethanol	Ethyl Formate	Water	Formic	Ethanol	Ethyl Formate	Water	Formic	Ethanol	Ethyl Formate	Water	Formic	
(Mins)	Concentration	Concentration	Concentration	Concentration	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.01040456	0.010404563	0	0	0.0025	0.0025	0	0	0.5	0.5	0	0	0	0
5	0.00984315	0.009843151	0.00056141	0.0005614	0.00237	0.00237	0.0001349	0.00013	0.47302	0.47302	0.02697912	0.02698	5.39582	5.64451
10	0.00946798	0.009467984	0.00093658	0.0009366	0.00227	0.00227	0.00022504	0.00023	0.45499	0.45499	0.04500807	0.04501	9.00161	10.1542
20	0.00829678	0.008296784	0.00210778	0.0021078	0.00199	0.00199	0.00050646	0.00051	0.39871	0.39871	0.10129109	0.10129	20.2582	29.221
30	0.00754826	0.007548262	0.0028563	0.0028563	0.00181	0.00181	0.00068631	0.00069	0.36274	0.36274	0.13726196	0.13726	27.4524	46.7527
60	0.00618202	0.006182018	0.00422254	0.0042225	0.00149	0.00149	0.00101459	0.00101	0.29708	0.29708	0.20291793	0.20292	40.5836	109.803
90	0.00560001	0.005600014	0.00480455	0.0048045	0.00135	0.00135	0.00115443	0.00115	0.26911	0.26911	0.23088665	0.23089	46.1773	159.311
120	0.00521896	0.005218962	0.0051856	0.0051856	0.00125	0.00125	0.00124599	0.00125	0.2508	0.2508	0.24919841	0.2492	49.8397	194.836
180	0.0046655	0.004665495	0.00573907	0.0057391	0.00112	0.00112	0.00137898	0.00138	0.2242	0.2242	0.27579572	0.2758	55.1591	356.39
240	0.00450914	0.004509144	0.00589542	0.0058954	0.00108	0.00108	0.00141655	0.00142	0.21669	0.21669	0.2833093	0.28331	56.6619	508.439
300	0.00435381	0.004353809	0.00605075	0.0060508	0.00105	0.00105	0.00145387	0.00145	0.20923	0.20923	0.29077404	0.29077	58.1548	680.65
360	0.00418682	0.004186819	0.00621774	0.0062177	0.00101	0.00101	0.00149399	0.00149	0.2012	0.2012	0.2987989	0.2988	59.7598	867.636
480	0.00415766	0.004157657	0.00624691	0.0062469	0.001	0.001	0.001501	0.0015	0.1998	0.1998	0.30020031	0.3002	59.9799	921.153
600	0.0040952	0.004095204	0.00630936	0.0063094	0.00098	0.00098	0.00151601	0.00152	0.1968	0.1968	0.30320152	0.3032	60.7005	#NUM!

Table A.5. Formic Acid Conversion at 423 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Formic Acid	Ethanol	Ethyl Formate	Water	Formic	Ethanol	Ethyl Formate	Water	Formic	Ethanol	Ethyl Formate	Water	Formic	
(Mins)	Concentratior	oncentratio	Concentration	oncentratio	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversion	Y
0	0.0104046	0.0104	0	0	0.0025	0.0025	0	0	0.5	0.5	0	0	0	0
5	0.0093199	0.00932	0.00108466	0.001085	0.00224	0.00224	0.00026062	0.00026	0.44788	0.44788	0.05212443	0.05212	10.42489	11.939
10	0.0086725	0.00867	0.0017321	0.001732	0.00208	0.00208	0.00041619	0.00042	0.41676	0.41676	0.0832373	0.08324	16.64746	21.1985
20	0.0070389	0.00704	0.00336565	0.003366	0.00169	0.00169	0.0008087	0.00081	0.33826	0.33826	0.16173931	0.16174	32.34786	58.5729
30	0.0054695	0.00547	0.00493509	0.004935	0.00131	0.00131	0.0011858	0.00119	0.26284	0.26284	0.23715993	0.23716	47.43199	139.972
60	0.0042621	0.00426	0.00614244	0.006142	0.00102	0.00102	0.0014759	0.00148	0.20482	0.20482	0.29518004	0.29518	59.03601	336.004
90	0.0038196	0.00382	0.00658497	0.006585	0.00092	0.00092	0.00158223	0.00158	0.18355	0.18355	0.31644628	0.31645	63.28926	550.086
120	0.0037189	0.00372	0.00668571	0.006686	0.00089	0.00089	0.00160644	0.00161	0.17871	0.17871	0.32128747	0.32129	64.25749	667.809
180	0.0037009	0.0037	0.00670368	0.006704	0.00089	0.00089	0.00161076	0.00161	0.17785	0.17785	0.32215106	0.32215	64.43021	702.694
240	0.0035788	0.00358	0.00682576	0.006826	0.00086	0.00086	0.00164009	0.00164	0.17198	0.17198	0.32801765	0.32802	65.60353	980.526
300	0.0035234	0.00352	0.00688115	0.006881	0.00085	0.00085	0.0016534	0.00165	0.16932	0.16932	0.33067929	0.33068	66.13586	1250.29
360	0.0035416	0.00354	0.00686301	0.006863	0.00085	0.00085	0.00164904	0.00165	0.17019	0.17019	0.32980774	0.32981	65.96155	1115.13
480	0.0035293	0.00353	0.00687525	0.006875	0.00085	0.00085	0.00165198	0.00165	0.1696	0.1696	0.3303957	0.3304	66.07914	1224.64
600	0.0034934	0.00349	0.00691115	0.006911	0.00084	0.00084	0.0016606	0.00166	0.16788	0.16788	0.33212092	0.33212	66.42418	#NUM!

Table A.6. Formic Acid Conversion at 473 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Formic Acid	Ethanol	Ethyl Formate	Water	Formic	Ethanol	Ethyl Formate	Water	Formic	Ethanol	Ethyl Formate	Water	Formic	
(Mins)	Concentration	Concentration	Concentration	Concentration	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversion	Y
0	0.01040456	0.01040456	0	0	0.0025	0.0025	0	0	0.5	0.5	0	0	0	0
5	0.00809891	0.00809891	0.00230565	0.00230565	0.00195	0.00195	0.000554	0.00055	0.3892	0.3892	0.11080009	0.1108	22.16002	31.6204
10	0.00627314	0.00627314	0.00413143	0.00413143	0.00151	0.00151	0.0009927	0.00099	0.30146	0.30146	0.19853913	0.198539	39.70783	85.2435
20	0.00458774	0.00458774	0.00581683	0.00581683	0.0011	0.0011	0.00139766	0.0014	0.22047	0.22047	0.27953249	0.279532	55.9065	216.684
30	0.0040175	0.0040175	0.00638706	0.00638706	0.00097	0.00097	0.00153468	0.00153	0.19306	0.19306	0.30693561	0.306936	61.38712	320.762
60	0.00354013	0.00354013	0.00686443	0.00686443	0.00085	0.00085	0.00164938	0.00165	0.17012	0.17012	0.32987612	0.329876	65.97522	508.119
90	0.00338623	0.00338623	0.00701834	0.00701834	0.00081	0.00081	0.00168636	0.00169	0.16273	0.16273	0.33727209	0.337272	67.45442	615.684
120	0.00319642	0.00319642	0.00720814	0.00720814	0.00077	0.00077	0.00173197	0.00173	0.15361	0.15361	0.34639332	0.346393	69.27866	777.11
180	0.00312907	0.00312907	0.0072755	0.0072755	0.00075	0.00075	0.00174815	0.00175	0.15037	0.15037	0.34963011	0.34963	69.92602	914.035
240	0.00305897	0.00305897	0.0073456	0.0073456	0.00074	0.00074	0.00176499	0.00176	0.147	0.147	0.35299883	0.352999	70.59977	1065.06
300	0.00301059	0.00301059	0.00739397	0.00739397	0.00072	0.00072	0.00177662	0.00178	0.14468	0.14468	0.35532333	0.355323	71.06467	1422.1
360	0.00301484	0.00301484	0.00738973	0.00738973	0.00072	0.00072	0.0017756	0.00178	0.14488	0.14488	0.35511953	0.35512	71.02391	1224.53
480	0.00297783	0.00297783	0.00742673	0.00742673	0.00072	0.00072	0.00178449	0.00178	0.1431	0.1431	0.35689794	0.356898	71.37959	1498.84
600	0.00294569	0.00294569	0.00745888	0.00745888	0.00071	0.00071	0.00179221	0.00179	0.14156	0.14156	0.35844251	0.358443	71.6885	#NUM!

Table A.7. Formic Acid Conversion at 523 K, 1:1 Molar Ratio in the absence of Catalyst

Time (Mins)	Formic Acid Concentration (mol/mL)	Ethanol Concentration (mol/mL)	Ethyl Formate Concentration (mol/mL)	Water Concentration (mol/mL)	Formic Amount mol	Ethanol Amount mol	Ethyl Formate Amount mol	Water Amount mol	Formic mole Fraction	Ethanol mole Fraction	Ethyl Formate mole Fraction	Water mole Fraction	Formic % Conversion	Y
0	0.0104046	0.0104046	0	0	0.0025	0.0025	0	0	0.5	0.5	0	0	0	0
2	0.0076665	0.0076665	0.00273811	0.0027381	0.00184	0.00184	0.00065791	0.00066	0.36842	0.36842	0.131582224	0.13158	26.31644	40.35155
3	0.0069798	0.0069798	0.00342477	0.0034248	0.00168	0.00168	0.0008229	0.00082	0.33542	0.33542	0.164580388	0.16458	32.91608	58.52742
5	0.0058454	0.0058454	0.00455914	0.0045591	0.0014	0.0014	0.00109547	0.0011	0.28091	0.28091	0.219093286	0.21909	43.81866	104.1536
10	0.00431	0.00431	0.0060946	0.0060946	0.00104	0.00104	0.00146441	0.00146	0.20712	0.20712	0.292881039	0.29288	58.57621	241.7792
20	0.0035153	0.0035153	0.00688924	0.0068892	0.00084	0.00084	0.00165534	0.00166	0.16893	0.16893	0.331068198	0.33107	66.21364	430.4692
30	0.0031052	0.0031052	0.00729938	0.0072994	0.00075	0.00075	0.00175389	0.00175	0.14922	0.14922	0.350777631	0.35078	70.15553	660.0245
40	0.003025	0.003025	0.00737956	0.0073796	0.00073	0.00073	0.00177316	0.00177	0.14537	0.14537	0.354631179	0.35463	70.92624	809.6485
60	0.0027643	0.0027643	0.00764029	0.0076403	0.00066	0.00066	0.0018358	0.00184	0.13284	0.13284	0.367160738	0.36716	73.43215	1150.81
90	0.0026699	0.0026699	0.00773467	0.0077347	0.00064	0.00064	0.00185848	0.00186	0.1283	0.1283	0.371695983	0.3717	74.3392	1650.283
120	0.0026685	0.0026685	0.00773603	0.007736	0.00064	0.00064	0.00185881	0.00186	0.12824	0.12824	0.371761477	0.37176	74.3523	1856.726
180	0.0026243	0.0026243	0.00778031	0.0077803	0.00063	0.00063	0.00186945	0.00187	0.12611	0.12611	0.373889397	0.37389	74.77788	#NUM!

Table A.8. Acetic Acid Conversion at 373 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Acetic	Ethanol	Ethyl Acet	Water	Acetic	Ethanol	Ethyl Acet	Water	Acetic	Ethanol	Ethyl Acet	Water	Acetic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00864	0.00864	0	0	0.0025	0.0025	0	0	0.5	0.5	0	0	0	0
5	0.00849	0.00855	0.00015	0.00015	0.00246	0.00247	4.2E-05	4.2E-05	0.49154	0.49454	0.00846	0.00846	1.69284	2.01413
10	0.00841	0.00846	0.00023	0.00023	0.00243	0.00245	6.8E-05	6.8E-05	0.48648	0.48949	0.01352	0.01352	2.70338	3.27222
20	0.00819	0.00827	0.00045	0.00045	0.00237	0.00239	0.00013	0.00013	0.4741	0.47861	0.0259	0.0259	5.17952	6.58057
30	0.00802	0.00808	0.00062	0.00062	0.00232	0.00234	0.00018	0.00018	0.46391	0.46766	0.03609	0.03609	7.2179	9.60977
60	0.00752	0.00772	0.00112	0.00112	0.00218	0.00223	0.00032	0.00032	0.43531	0.44657	0.06469	0.06469	12.938	20.3169
90	0.00716	0.00728	0.00148	0.00148	0.00207	0.00211	0.00043	0.00043	0.41408	0.42159	0.08592	0.08592	17.1838	32.0578
120	0.00683	0.00694	0.00181	0.00181	0.00198	0.00201	0.00052	0.00052	0.39504	0.40187	0.10496	0.10496	20.9917	47.839
180	0.00641	0.00646	0.00223	0.00223	0.00185	0.00187	0.00065	0.00065	0.37079	0.3738	0.12921	0.12921	25.8412	86.8058
240	0.00613	0.00615	0.00251	0.00251	0.00178	0.00178	0.00072	0.00072	0.35502	0.35577	0.14498	0.14498	28.9953	146.822
300	0.006	0.00604	0.00264	0.00264	0.00174	0.00175	0.00076	0.00076	0.34728	0.34953	0.15272	0.15272	30.5443	216.181
360	0.00591	0.00595	0.00273	0.00273	0.00171	0.00172	0.00079	0.00079	0.34228	0.34453	0.15772	0.15772	31.544	312.528
480	0.00585	0.00589	0.00279	0.00279	0.00169	0.00171	0.00081	0.00081	0.3388	0.34107	0.1612	0.1612	32.2393	510.751
600	0.00583	0.00587	0.00281	0.00281	0.00169	0.0017	0.00081	0.00081	0.33732	0.33957	0.16268	0.16268	32.5368	#NUM!

Table A.9. Acetic Acid Conversion at 423 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Acetic	Ethanol	Ethyl Acet	Water	Acetic	Ethanol	Ethyl Acet	Water	Acetic	Ethanol	Ethyl Acet	Water	Acetic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00864	0.00864	0	0	0.0025	0.0025	0	0	0.5	0.5	0	0	0	0
5	0.00831	0.00786	0.00033	0.00033	0.0024	0.00227	9.6E-05	9.6E-05	0.48076	0.45496	0.01924	0.01924	3.84718	4.87544
10	0.00782	0.00738	0.00082	0.00082	0.00226	0.00214	0.00024	0.00024	0.45255	0.42711	0.04745	0.04745	9.4893	13.0942
20	0.00704	0.00684	0.0016	0.0016	0.00204	0.00198	0.00046	0.00046	0.40766	0.39576	0.09234	0.09234	18.4688	30.9103
30	0.00658	0.00636	0.00206	0.00206	0.00191	0.00184	0.00059	0.00059	0.38107	0.36826	0.11893	0.11893	23.7856	45.8831
60	0.00558	0.00551	0.00306	0.00306	0.00161	0.00159	0.00089	0.00089	0.32283	0.31889	0.17717	0.17717	35.4333	111.255
90	0.00511	0.00511	0.00353	0.00353	0.00148	0.00148	0.00102	0.00102	0.29579	0.29594	0.20421	0.20421	40.8428	189.96
120	0.0049	0.00486	0.00374	0.00374	0.00142	0.00141	0.00108	0.00108	0.28339	0.28137	0.21661	0.21661	43.3221	266.727
180	0.00471	0.00452	0.00393	0.00393	0.00136	0.00131	0.00114	0.00114	0.27234	0.26183	0.22766	0.22766	45.5324	393.62
240	0.00461	0.00435	0.00403	0.00403	0.00133	0.00126	0.00117	0.00117	0.26653	0.25164	0.23347	0.23347	46.6937	510.662
300	0.00459	0.00431	0.00405	0.00405	0.00133	0.00125	0.00117	0.00117	0.26545	0.24953	0.23455	0.23455	46.9096	550.911
360	0.00455	0.00428	0.00409	0.00409	0.00132	0.00124	0.00118	0.00118	0.26323	0.24758	0.23677	0.23677	47.3542	749.751
480	0.00454	0.00427	0.0041	0.0041	0.00131	0.00124	0.00119	0.00119	0.26249	0.24706	0.23751	0.23751	47.5011	815.01
600	0.0045	0.00427	0.00414	0.00414	0.0013	0.00124	0.0012	0.0012	0.26047	0.2474	0.23953	0.23953	47.9059	#NUM!

Table A.10. Acetic Acid Conversion at 473 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Acetic	Ethanol	Ethyl Acet	Water	Acetic	Ethanol	Ethyl Acet	Water	Acetic	Ethanol	Ethyl Acet	Water	Acetic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00864	0.00864	0	0	0.0025	0.0025	0	0	0.5	0.5	0	0	0	0
5	0.00727	0.00727	0.00137	0.00137	0.0021	0.0021	0.0004	0.0004	0.42095	0.42095	0.07905	0.07905	15.8092	24.2284
10	0.0063	0.0063	0.00234	0.00234	0.00182	0.00182	0.00068	0.00068	0.36431	0.36431	0.13569	0.13569	27.1373	53.8906
20	0.00515	0.00515	0.00349	0.00349	0.00149	0.00149	0.00101	0.00101	0.2978	0.2978	0.2022	0.2022	40.44	124.196
30	0.00456	0.00456	0.00408	0.00408	0.00132	0.00132	0.00118	0.00118	0.26365	0.26365	0.23635	0.23635	47.2704	205.104
60	0.00413	0.00413	0.00451	0.00451	0.00119	0.00119	0.00131	0.00131	0.23899	0.23899	0.26101	0.26101	52.202	420.756
90	0.00387	0.00387	0.00477	0.00477	0.00112	0.00112	0.00138	0.00138	0.22372	0.22372	0.27628	0.27628	55.2557	613.29
120	0.00361	0.00361	0.00503	0.00503	0.00104	0.00104	0.00146	0.00146	0.20889	0.20889	0.29111	0.29111	58.2215	800.223
180	0.00356	0.00357	0.00508	0.00508	0.00103	0.00103	0.00147	0.00147	0.20627	0.2064	0.29373	0.29373	58.747	890.614
240	0.0035	0.0035	0.00514	0.00514	0.00101	0.00101	0.00149	0.00149	0.20258	0.20275	0.29742	0.29742	59.484	1134.09
300	0.00351	0.00351	0.00513	0.00513	0.00101	0.00102	0.00149	0.00149	0.20287	0.20321	0.29713	0.29713	59.4269	1098.61
360	0.00349	0.0035	0.00515	0.00515	0.00101	0.00101	0.00149	0.00149	0.2021	0.20269	0.2979	0.2979	59.5795	1229.12
480	0.00348	0.00349	0.00516	0.00516	0.00101	0.00101	0.00149	0.00149	0.20131	0.20213	0.29869	0.29869	59.7378	1528.58
600	0.00347	0.00349	0.00517	0.00517	0.001	0.00101	0.0015	0.0015	0.20083	0.20199	0.29917	0.29917	59.8343	#NUM!

Table A.11. Acetic Acid Conversion at 523 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Acetic	Ethanol	Ethyl Acet	Water	Acetic	Ethanol	Ethyl Acet	Water	Acetic	Ethanol	Ethyl Acet	Water	Acetic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00864	0.00864	0	0	0.0025	0.0025	0	0	0.5	0.5	0	0	0	0
2	0.00744	0.0072	0.0012	0.0012	0.00215	0.00208	0.00035	0.00035	0.43029	0.41695	0.06971	0.06971	13.9426	20.3329
3	0.00688	0.00665	0.00176	0.00176	0.00199	0.00192	0.00051	0.00051	0.39821	0.38477	0.10179	0.10179	20.3575	33.6704
5	0.006	0.0058	0.00264	0.00264	0.00174	0.00168	0.00076	0.00076	0.34748	0.33594	0.15252	0.15252	30.5047	63.6718
10	0.00459	0.00469	0.00405	0.00405	0.00133	0.00136	0.00117	0.00117	0.26586	0.27153	0.23414	0.23414	46.8277	162.96
20	0.00354	0.00375	0.0051	0.0051	0.00103	0.00108	0.00147	0.00147	0.20513	0.21689	0.29487	0.29487	58.9738	407.699
30	0.00316	0.00347	0.00548	0.00548	0.00092	0.001	0.00158	0.00158	0.18304	0.20054	0.31696	0.31696	63.391	710.088
40	0.00304	0.00323	0.0056	0.0056	0.00088	0.00093	0.00162	0.00162	0.17568	0.18679	0.32432	0.32432	64.8638	992.278
60	0.00295	0.00313	0.00569	0.00569	0.00085	0.0009	0.00165	0.00165	0.17064	0.18098	0.32936	0.32936	65.8721	1565.32
90	0.00293	0.00304	0.00571	0.00571	0.00085	0.00088	0.00165	0.00165	0.16975	0.17605	0.33025	0.33025	66.0503	2165.64
120	0.00294	0.00301	0.0057	0.0057	0.00085	0.00087	0.00165	0.00165	0.17004	0.17437	0.32996	0.32996	65.9916	2283.28
180	0.00292	0.00297	0.00572	0.00572	0.00084	0.00086	0.00166	0.00166	0.16895	0.17164	0.33105	0.33105	66.2092	#NUM!

Table A.12. Lactic Acid Conversion at 298 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00749	0.00749	0	0	0.1	0.1	0	0	0.5	0.5	0	0	0	0
5	0.00746	0.00699	3.7E-05	3.7E-05	0.0995	0.0933	0.0005	0.0005	0.4975	0.46649	0.0025	0.0025	0.50024	0.67781
10	0.00739	0.00691	0.0001	0.0001	0.09861	0.09218	0.00139	0.00139	0.49306	0.46088	0.00694	0.00694	1.38893	1.91246
20	0.00731	0.00668	0.00018	0.00018	0.09758	0.08916	0.00242	0.00242	0.48791	0.44579	0.01209	0.01209	2.41749	3.41729
30	0.00728	0.00667	0.00021	0.00021	0.09722	0.08903	0.00278	0.00278	0.48611	0.44517	0.01389	0.01389	2.77872	3.97187
60	0.00713	0.00658	0.00036	0.00036	0.09518	0.08787	0.00482	0.00482	0.4759	0.43934	0.0241	0.0241	4.82083	7.48028
90	0.00687	0.00641	0.00063	0.00063	0.09163	0.08556	0.00837	0.00837	0.45815	0.42781	0.04185	0.04185	8.37089	16.5466
120	0.00676	0.00626	0.00073	0.00073	0.09023	0.08361	0.00977	0.00977	0.45117	0.41803	0.04883	0.04883	9.7657	22.3637
180	0.00656	0.00625	0.00093	0.00093	0.08757	0.08339	0.01243	0.01243	0.43787	0.41696	0.06213	0.06213	12.4255	44.1787
240	0.00645	0.00609	0.00105	0.00105	0.08603	0.08127	0.01397	0.01397	0.43015	0.40634	0.06985	0.06985	13.9696	79.3315
300	0.00638	0.0059	0.00111	0.00111	0.08518	0.07868	0.01482	0.01482	0.4259	0.3934	0.0741	0.0741	14.8197	132.147
360	0.00633	0.00576	0.00116	0.00116	0.08447	0.07692	0.01553	0.01553	0.42235	0.38459	0.07765	0.07765	15.5309	310.678
480	0.00632	0.00578	0.00117	0.00117	0.08437	0.07712	0.01563	0.01563	0.42184	0.38559	0.07816	0.07816	15.6325	411.642
600	0.00631	0.00578	0.00118	0.00118	0.08427	0.07707	0.01573	0.01573	0.42134	0.38536	0.07866	0.07866	15.7312	#NUM!

Table A.13. Lactic Acid Conversion at 313 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00749	0.00749	0	0	0.1	0.1	0	0	0.5	0.5	0	0	0	0
5	0.00744	0.00739	5.7E-05	5.7E-05	0.09924	0.09869	0.00076	0.00076	0.49621	0.49343	0.00379	0.00379	0.75868	1.03135
10	0.00737	0.00716	0.00012	0.00012	0.0984	0.09559	0.0016	0.0016	0.49202	0.47794	0.00798	0.00798	1.59546	2.19768
20	0.00725	0.00693	0.00024	0.00024	0.09679	0.09254	0.00321	0.00321	0.48393	0.46268	0.01607	0.01607	3.21429	4.59258
30	0.00714	0.0068	0.00036	0.00036	0.09525	0.09078	0.00475	0.00475	0.47624	0.45388	0.02376	0.02376	4.75171	7.10275
60	0.00683	0.00673	0.00066	0.00066	0.09118	0.08976	0.00882	0.00882	0.45588	0.4488	0.04412	0.04412	8.82482	15.7451
90	0.00659	0.00667	0.0009	0.0009	0.08795	0.08897	0.01205	0.01205	0.43977	0.44485	0.06023	0.06023	12.0465	26.9216
120	0.00641	0.00661	0.00108	0.00108	0.08553	0.08816	0.01447	0.01447	0.42764	0.44079	0.07236	0.07236	14.4727	41.7891
180	0.00618	0.00652	0.00131	0.00131	0.08252	0.08699	0.01748	0.01748	0.41258	0.43495	0.08742	0.08742	17.4849	87.2207
240	0.00607	0.00642	0.00142	0.00142	0.08106	0.08565	0.01894	0.01894	0.40529	0.42825	0.09471	0.09471	18.9422	158.428
300	0.00604	0.00637	0.00145	0.00145	0.0806	0.08497	0.0194	0.0194	0.40298	0.42486	0.09702	0.09702	19.4045	213.016
360	0.00599	0.00607	0.00151	0.00151	0.07988	0.08096	0.02012	0.02012	0.39941	0.40478	0.10059	0.10059	20.118	617.871
480	0.00598	0.00604	0.00151	0.00151	0.07984	0.08064	0.02016	0.02016	0.39922	0.40322	0.10078	0.10078	20.1567	846.891
600	0.00598	0.00608	0.00151	0.00151	0.07983	0.08119	0.02017	0.02017	0.39915	0.40594	0.10085	0.10085	20.1696	#NUM!

Table A.14. Lactic Acid Conversion at 333 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00749	0.00749	0	0	0.00237	0.00237	0	0	0.5	0.5	0	0	0	0
5	0.00738	0.00695	0.00011	0.00011	0.00233	0.00219	3.4E-05	3.4E-05	0.49276	0.46364	0.00724	0.00724	1.44865	1.9856
10	0.00727	0.00687	0.00022	0.00022	0.0023	0.00217	6.9E-05	6.9E-05	0.48531	0.45824	0.01469	0.01469	2.93803	4.13622
20	0.00706	0.00671	0.00043	0.00043	0.00223	0.00212	0.00014	0.00014	0.47125	0.44798	0.02875	0.02875	5.74997	8.63387
30	0.00687	0.0067	0.00062	0.00062	0.00217	0.00212	0.0002	0.0002	0.45836	0.44733	0.04164	0.04164	8.32703	13.4851
60	0.0064	0.00661	0.0011	0.0011	0.00202	0.00209	0.00035	0.00035	0.4268	0.44089	0.0732	0.0732	14.6409	31.2996
90	0.00607	0.0063	0.00142	0.00142	0.00192	0.00199	0.00045	0.00045	0.40492	0.42021	0.09508	0.09508	19.0156	56.2782
120	0.00585	0.00622	0.00164	0.00164	0.00185	0.00196	0.00052	0.00052	0.39057	0.41504	0.10943	0.10943	21.8863	91.1144
180	0.00568	0.00605	0.00181	0.00181	0.00179	0.00191	0.00057	0.00057	0.37932	0.40364	0.12068	0.12068	24.1363	155.728
240	0.00555	0.00591	0.00194	0.00194	0.00175	0.00186	0.00061	0.00061	0.37042	0.39414	0.12958	0.12958	25.9153	342.674
300	0.00554	0.00568	0.00195	0.00195	0.00175	0.00179	0.00062	0.00062	0.36987	0.379	0.13013	0.13013	26.026	374.417
360	0.00551	0.00549	0.00198	0.00198	0.00174	0.00173	0.00063	0.00063	0.3678	0.36637	0.1322	0.1322	26.4399	673.41
480	0.00551	0.00537	0.00199	0.00199	0.00174	0.00169	0.00063	0.00063	0.36741	0.35809	0.13259	0.13259	26.5186	1077.73
600	0.00551	0.00524	0.00199	0.00199	0.00174	0.00165	0.00063	0.00063	0.36736	0.34971	0.13264	0.13264	26.5279	#NUM!

Table A.15. Lactic Acid Conversion at 353 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00749	0.00749	0	0	0.00237	0.00237	0	0	0.5	0.5	0	0	0	0
5	0.00731	0.00746	0.00019	0.00019	0.00231	0.00236	5.9E-05	5.9E-05	0.4875	0.49792	0.0125	0.0125	2.50029	3.48131
10	0.00712	0.00735	0.00037	0.00037	0.00225	0.00232	0.00012	0.00012	0.47525	0.49055	0.02475	0.02475	4.95057	7.21347
20	0.00679	0.00677	0.00071	0.00071	0.00214	0.00214	0.00022	0.00022	0.45295	0.45156	0.04705	0.04705	9.4107	15.2008
30	0.0065	0.00633	0.001	0.001	0.00205	0.002	0.00031	0.00031	0.43353	0.42267	0.06647	0.06647	13.2943	24.1013
60	0.00564	0.00576	0.00185	0.00185	0.00178	0.00182	0.00058	0.00058	0.3766	0.38429	0.1234	0.1234	24.6791	80.9078
90	0.00538	0.00561	0.00211	0.00211	0.0017	0.00177	0.00067	0.00067	0.35913	0.37435	0.14087	0.14087	28.1738	132.165
120	0.00526	0.00537	0.00224	0.00224	0.00166	0.00169	0.00071	0.00071	0.35086	0.35821	0.14914	0.14914	29.8283	179.826
180	0.00508	0.00505	0.00241	0.00241	0.0016	0.00159	0.00076	0.00076	0.33898	0.33677	0.16102	0.16102	32.2038	364.756
240	0.00503	0.00485	0.00246	0.00246	0.00159	0.00153	0.00078	0.00078	0.33562	0.32345	0.16438	0.16438	32.8751	566.388
300	0.00502	0.00446	0.00248	0.00248	0.00158	0.00141	0.00078	0.00078	0.33469	0.29765	0.16531	0.16531	33.062	743.771
360	0.00501	0.00432	0.00249	0.00249	0.00158	0.00136	0.00078	0.00078	0.33415	0.28845	0.16585	0.16585	33.1704	969.559
480	0.005	0.00432	0.00249	0.00249	0.00158	0.00136	0.00079	0.00079	0.33396	0.28814	0.16604	0.16604	33.2079	1329.45
600	0.005	0.0043	0.00249	0.00249	0.00158	0.00136	0.00079	0.00079	0.33386	0.28705	0.16614	0.16614	33.228	#NUM!

Table A.16. Lactic Acid Conversion at 373 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00749	0.00749	0	0	0.00237	0.00237	0	0	0.5	0.5	0	0	0	0
5	0.00719	0.00732	0.0003	0.0003	0.00227	0.00231	9.5E-05	9.5E-05	0.47994	0.48873	0.02006	0.02006	4.01103	5.71821
10	0.00691	0.0069	0.00058	0.00058	0.00218	0.00218	0.00018	0.00018	0.4612	0.46037	0.0388	0.0388	7.75984	11.8622
20	0.00642	0.00685	0.00107	0.00107	0.00203	0.00216	0.00034	0.00034	0.42868	0.45731	0.07132	0.07132	14.2645	25.3204
30	0.00603	0.00631	0.00147	0.00147	0.0019	0.00199	0.00046	0.00046	0.40213	0.42135	0.09787	0.09787	19.5748	40.6751
60	0.00525	0.00563	0.00225	0.00225	0.00166	0.00178	0.00071	0.00071	0.35001	0.37584	0.14999	0.14999	29.9978	100.546
90	0.0048	0.00549	0.00269	0.00269	0.00152	0.00173	0.00085	0.00085	0.32042	0.36612	0.17958	0.17958	35.9167	200.931
120	0.00468	0.00515	0.00281	0.00281	0.00148	0.00162	0.00089	0.00089	0.31221	0.3434	0.18779	0.18779	37.5581	264.563
180	0.00453	0.00467	0.00296	0.00296	0.00143	0.00147	0.00093	0.00093	0.30256	0.31131	0.19744	0.19744	39.4873	425.914
240	0.00451	0.00471	0.00298	0.00298	0.00142	0.00149	0.00094	0.00094	0.30109	0.31456	0.19891	0.19891	39.7818	470.771
300	0.0045	0.0043	0.00299	0.00299	0.00142	0.00136	0.00094	0.00094	0.30023	0.28708	0.19977	0.19977	39.9542	504.873
360	0.00449	0.004	0.003	0.003	0.00142	0.00126	0.00095	0.00095	0.29965	0.26686	0.20035	0.20035	40.0703	531.038
480	0.00447	0.00394	0.00302	0.00302	0.00141	0.00124	0.00095	0.00095	0.29844	0.26277	0.20156	0.20156	40.3122	602.203
600	0.00443	0.00393	0.00307	0.00307	0.0014	0.00124	0.00097	0.00097	0.29541	0.26222	0.20459	0.20459	40.9183	#NUM!

Table A.17. Lactic Acid Conversion at 423 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00749	0.00749	0	0	0.00237	0.00237	0	0	0.5	0.5	0	0	0	0
5	0.00673	0.00726	0.00077	0.00077	0.00212	0.00229	0.00024	0.00024	0.44891	0.48457	0.05109	0.05109	10.2181	16.1625
10	0.00611	0.00677	0.00138	0.00138	0.00193	0.00214	0.00044	0.00044	0.40769	0.45205	0.09231	0.09231	18.4618	34.4917
20	0.00521	0.00661	0.00228	0.00228	0.00165	0.00209	0.00072	0.00072	0.3478	0.44106	0.1522	0.1522	30.4409	78.1233
30	0.00462	0.00598	0.00287	0.00287	0.00146	0.00189	0.00091	0.00091	0.30848	0.39877	0.19152	0.19152	38.3041	131.775
60	0.0038	0.0048	0.0037	0.0037	0.0012	0.00152	0.00117	0.00117	0.25325	0.32039	0.24675	0.24675	49.3504	345.23
90	0.00354	0.00455	0.00395	0.00395	0.00112	0.00144	0.00125	0.00125	0.23642	0.30351	0.26358	0.26358	52.7162	582.85
120	0.00347	0.00425	0.00403	0.00403	0.00109	0.00134	0.00127	0.00127	0.23125	0.28328	0.26875	0.26875	53.7505	762.203
180	0.00343	0.00407	0.00407	0.00407	0.00108	0.00128	0.00128	0.00128	0.22872	0.27144	0.27128	0.27128	54.2563	929.825
240	0.00341	0.00391	0.00408	0.00408	0.00108	0.00123	0.00129	0.00129	0.22781	0.26079	0.27219	0.27219	54.4389	1028.23
300	0.00341	0.00381	0.00408	0.00408	0.00108	0.0012	0.00129	0.00129	0.22761	0.254	0.27239	0.27239	54.4772	1054.15
360	0.0034	0.00358	0.0041	0.0041	0.00107	0.00113	0.00129	0.00129	0.22666	0.239	0.27334	0.27334	54.6677	1242.99
480	0.00339	0.00343	0.00411	0.00411	0.00107	0.00108	0.0013	0.0013	0.22589	0.22899	0.27411	0.27411	54.8219	1600.61
600	0.00338	0.00357	0.00411	0.00411	0.00107	0.00113	0.0013	0.0013	0.22544	0.23802	0.27456	0.27456	54.9125	#NUM!

Table A.18. Lactic Acid Conversion at 473 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00749	0.00749	0	0	0.00237	0.00237	0	0	0.5	0.5	0	0	0	0
5	0.00579	0.00537	0.00169	0.00169	0.00183	0.0017	0.00053	0.00053	0.38626	0.35864	0.11285	0.11285	22.7471	45.5082
10	0.00444	0.00493	0.00288	0.00288	0.0014	0.00156	0.00091	0.00091	0.29642	0.32904	0.19239	0.19239	40.7158	130.332
20	0.00365	0.00442	0.00383	0.00383	0.00115	0.00139	0.00121	0.00121	0.24347	0.29467	0.25583	0.25583	51.3069	249.872
30	0.00313	0.00401	0.00435	0.00435	0.00099	0.00127	0.00137	0.00137	0.20903	0.26756	0.29031	0.29031	58.1932	429.431
60	0.00283	0.00352	0.0046	0.0046	0.00089	0.00111	0.00145	0.00145	0.18916	0.23504	0.30698	0.30698	62.1688	681.826
90	0.00272	0.00294	0.00471	0.00471	0.00086	0.00093	0.00149	0.00149	0.18164	0.19645	0.31398	0.31398	63.6727	861.434
120	0.00265	0.0028	0.00484	0.00484	0.00084	0.00088	0.00153	0.00153	0.17663	0.18659	0.32275	0.32275	64.6749	1073.85
180	0.0026	0.00254	0.00488	0.00488	0.00082	0.0008	0.00154	0.00154	0.1738	0.16922	0.32559	0.32559	65.2401	1261.16
240	0.00259	0.00251	0.00489	0.00489	0.00082	0.00079	0.00154	0.00154	0.17304	0.16774	0.32625	0.32625	65.3918	1338.64
300	0.00259	0.00251	0.00489	0.00489	0.00082	0.00079	0.00154	0.00154	0.17252	0.16757	0.32658	0.32658	65.4952	1402.8
360	0.00257	0.00244	0.0049	0.0049	0.00081	0.00077	0.00155	0.00155	0.17176	0.16306	0.32687	0.32687	65.6481	1517.99
480	0.00256	0.00246	0.0049	0.0049	0.00081	0.00078	0.00155	0.00155	0.171	0.16424	0.32706	0.32706	65.7997	1684.23
600	0.00254	0.0025	0.00491	0.00491	0.0008	0.00079	0.00155	0.00155	0.16951	0.16712	0.32791	0.32791	66.0989	#NUM!

Table A.19. Lactic Acid Conversion at 523 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00749	0.00749	0	0	0.00237	0.00237	0	0	0.5	0.5	0	0	0	0
2	0.00598	0.00533	0.00152	0.00152	0.00189	0.00168	0.00048	0.00048	0.39887	0.3558	0.10113	0.10113	20.2261	38.155
3	0.0054	0.00497	0.0021	0.0021	0.0017	0.00157	0.00066	0.00066	0.36002	0.33167	0.13998	0.13998	27.9967	62.1399
5	0.0047	0.00472	0.00279	0.00279	0.00148	0.00149	0.00088	0.00088	0.31393	0.31518	0.18607	0.18607	37.2136	103.489
10	0.00357	0.00426	0.00393	0.00393	0.00113	0.00134	0.00124	0.00124	0.23802	0.28411	0.26198	0.26198	52.3955	240.466
20	0.00266	0.00284	0.00484	0.00484	0.00084	0.0009	0.00153	0.00153	0.1773	0.18954	0.3227	0.3227	64.5403	588.372
30	0.00254	0.0024	0.00495	0.00495	0.0008	0.00076	0.00156	0.00156	0.16945	0.15993	0.33055	0.33055	66.1092	693.119
40	0.00241	0.00219	0.00508	0.00508	0.00076	0.00069	0.0016	0.0016	0.16086	0.14642	0.33914	0.33914	67.8282	857.738
60	0.0022	0.00205	0.00529	0.00529	0.00069	0.00065	0.00167	0.00167	0.14675	0.13675	0.35325	0.35325	70.6499	1490.15
90	0.00217	0.00201	0.00532	0.00532	0.00068	0.00063	0.00168	0.00168	0.14476	0.13399	0.35524	0.35524	71.0486	1731.38
120	0.00213	0.002	0.00536	0.00536	0.00067	0.00063	0.00169	0.00169	0.14226	0.13364	0.35774	0.35774	71.5478	2521.19
180	0.00212	0.002	0.00537	0.00537	0.00067	0.00063	0.00169	0.00169	0.14166	0.13359	0.35834	0.35834	71.6674	#NUM!

Table A.20. Lactic Acid Conversion at 523 K in the presence of Inconel 625 Material

Time	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	Ethanol	Ethyl Lac	Water	Lactic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.00749	0.00749	0	0	0.00237	0.00237	0	0	0.5	0.5	0	0	0	0
2	0.00604	0.00579	0.00145	0.00145	0.00191	0.00183	0.00046	0.00046	0.40329	0.38635	0.09671	0.09671	19.343	35.9085
5	0.00534	0.00478	0.00215	0.00215	0.00169	0.00151	0.00068	0.00068	0.35638	0.3189	0.14362	0.14362	28.7248	65.0163
10	0.00468	0.00417	0.00282	0.00282	0.00148	0.00132	0.00089	0.00089	0.31209	0.2783	0.18791	0.18791	37.5812	106.281
20	0.00342	0.00298	0.00408	0.00408	0.00108	0.00094	0.00129	0.00129	0.22791	0.19898	0.27209	0.27209	54.4182	280.053
30	0.00304	0.00262	0.00445	0.00445	0.00096	0.00083	0.00141	0.00141	0.20283	0.17479	0.29717	0.29717	59.4346	400.554
40	0.00269	0.00227	0.00481	0.00481	0.00085	0.00072	0.00152	0.00152	0.17923	0.1513	0.32077	0.32077	64.1545	613.239
50	0.00251	0.00212	0.00499	0.00499	0.00079	0.00067	0.00157	0.00157	0.16732	0.14163	0.33268	0.33268	66.5362	818.76
60	0.0023	0.00206	0.00519	0.00519	0.00073	0.00065	0.00164	0.00164	0.15353	0.13752	0.34647	0.34647	69.2945	1422.29
90	0.00223	0.00203	0.00526	0.00526	0.00071	0.00064	0.00166	0.00166	0.14906	0.13518	0.35094	0.35094	70.1874	2519.47
180	0.00223	0.00203	0.00527	0.00527	0.0007	0.00064	0.00166	0.00166	0.14862	0.13527	0.35138	0.35138	70.2766	#NUM!

Table A.21. Levulinic Acid Conversion at 333 K, 1:1 Molar Ratio in the absence of Catalyst

Time (Mins)	Levulinic Conc (mol/mL)	Ethanol Conc (mol/mL)	Ethyl Levulinate Conc (mol/mL)	Water Conc (mol/mL)	Levulinic Amount mol	Ethanol Amount mol	Ethyl Levulinate Amount mol	Water Amount mol	Levulinic mole Fraction	Ethanol mole Fraction	Ethyl Levulinate mole Fraction	Water mole Fraction	Levulinic % Conversion	Y
0	0.0062	0.0062	0	0	0.00196	0.00196	0	0	0.5	0.5	0	0	0	0
60	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
90	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
120	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
180	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
240	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
360	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
480	0.00598	0.00601	0.000225519	0.00023	0.00189	0.0019	0.00007126	0.00007126	0.48182187	0.48424308	0.018178133	0.01818	3.63563	6.33082
600	0.00593	0.00596	0.000277719	0.00028	0.00187	0.00188	0.00008776	0.00008776	0.47761424	0.48001431	0.022385762	0.02239	4.47715	7.98271
1440	0.0056	0.00496	0.000598319	0.0006	0.00177	0.00157	0.000189062	0.0001891	0.451772	0.3998922	0.048228019	0.04823	9.6456	21.352
2880	0.00524	0.00478	0.000964219	0.00096	0.00166	0.00151	0.000304683	0.0003047	0.4222783	0.3849195	0.077721724	0.07772	15.5443	57.2922
4320	0.00505	0.00458	0.001152719	0.00115	0.0016	0.00145	0.000364247	0.0003642	0.4070841	0.3688988	0.092915939	0.09292	18.5832	120.937
7200	0.00492	0.00434	0.001280519	0.00128	0.00156	0.00137	0.00040463	0.0004046	0.3967826	0.3498544	0.103217375	0.10322	20.6435	359.653
10080	0.0049	0.00423	0.001305319	0.00131	0.00155	0.00134	0.000412467	0.0004125	0.3947836	0.3412186	0.105216402	0.10522	21.0433	766.953
11520	0.00489	0.00416	0.001308619	0.00131	0.00155	0.00131	0.000413509	0.0004135	0.3945176	0.3350367	0.105482401	0.10548	21.0965	#NUM!

Table A.22. Levulinic Acid Conversion at 353 K, 1:1 Molar Ratio in the absence of Catalyst

Time (Mins)	Levulinic Conc (mol/mL)	Ethanol Conc (mol/mL)	Ethyl Levulinate Conc (mol/mL)	Water Conc (mol/mL)	Levulinic Amount mol	Ethanol Amount mol	Ethyl Levulinate Amount mol	Water Amount mol	Levulinic mole Fraction	Ethanol mole Fraction	Ethyl Levulinate mole Fraction	Water mole Fraction	Levulinic % Conversion	Y
0	0.0062	0.0062	0	0	0.00196	0.00196	0	0	0.5	0.5	0	0	0	0
60	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
90	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
120	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
180	0.00595	0.00595	0.000252519	0.00025	0.00188	0.00188	0.00007979	0.00007979	0.47965	0.47965	0.020354493	0.02035	4.0709	7.1003
240	0.00587	0.00587	0.000330019	0.00033	0.00186	0.00186	0.000104282	0.0001043	0.4734	0.4734	0.026601451	0.0266	5.32029	9.56822
360	0.00573	0.00573	0.000476419	0.00048	0.00181	0.00181	0.000150543	0.0001505	0.4616	0.4616	0.038402158	0.0384	7.68043	14.7992
480	0.00559	0.00559	0.000610619	0.00061	0.00177	0.00177	0.000192949	0.0001929	0.45078	0.45078	0.049219472	0.04922	9.84389	20.5057
600	0.00547	0.00547	0.000732719	0.00073	0.00173	0.00173	0.000231531	0.0002315	0.44094	0.44094	0.059061454	0.05906	11.8123	26.813
1080	0.0051	0.00538	0.001107319	0.00111	0.00161	0.0017	0.000349901	0.0003499	0.41074	0.43405	0.08925643	0.08926	17.8513	60.5781
1440	0.00491	0.00523	0.001288519	0.00129	0.00155	0.00165	0.000407158	0.0004072	0.39614	0.42184	0.103862223	0.10386	20.7724	98.8342
2700	0.00465	0.00497	0.001552319	0.00155	0.00147	0.00157	0.000490516	0.0004905	0.37487	0.40083	0.125126063	0.12513	25.0252	407.424
2880	0.00464	0.00456	0.001566019	0.00157	0.00147	0.00144	0.000494845	0.0004948	0.37377	0.36734	0.126230364	0.12623	25.2461	500.79
3000	0.00463	0.00439	0.001573619	0.00157	0.00146	0.00139	0.000497247	0.0004972	0.37316	0.35413	0.126842969	0.12684	25.3686	586.042
3300	0.00462	0.00438	0.001588019	0.00159	0.00146	0.00138	0.000501797	0.0005018	0.372	0.35279	0.128003695	0.128	25.6007	#NUM!

Table A.23. Levulinic Acid Conversion at 373 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Levulinic	Ethanol	Ethyl Levulinate	Water	Levulinic	Ethanol	Ethyl Levulinate	Water	Levulinic	Ethanol	Ethyl Levulinate	Water	Levulinic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversion	Y
0	0.0062	0.0062	0	0	0.00196	0.00196	0	0	0.5	0.5	0	0	0	0
60	0.00598	0.00511	0.000226119	0.00023	0.00189	0.00161	0.00007145	0.00007145	0.48177	0.41186	0.018226497	0.01823	3.6453	6.26474
90	0.00587	0.00505	0.000330819	0.00033	0.00186	0.0016	0.00010454	0.0001045	0.47333	0.40733	0.026665936	0.02667	5.33319	9.48699
120	0.00577	0.00489	0.000431019	0.00043	0.00182	0.00154	0.0001362	0.0001362	0.46526	0.39407	0.034742649	0.03474	6.94853	12.8272
180	0.00559	0.00482	0.000617319	0.00062	0.00177	0.00152	0.00019507	0.0001951	0.45024	0.38864	0.049759531	0.04976	9.95191	19.9161
240	0.00542	0.00456	0.000785219	0.00079	0.00171	0.00144	0.00024812	0.0002481	0.43671	0.36745	0.063293265	0.06329	12.6587	27.6725
360	0.00513	0.00427	0.001068819	0.00107	0.00162	0.00135	0.00033774	0.0003377	0.41385	0.34404	0.086153103	0.08615	17.2306	45.7511
480	0.00491	0.00411	0.001289519	0.00129	0.00155	0.0013	0.00040747	0.0004075	0.39606	0.33135	0.103942828	0.10394	20.7886	68.0866
600	0.00475	0.00409	0.001457819	0.00146	0.0015	0.00129	0.00046066	0.0004607	0.38249	0.33001	0.117508804	0.11751	23.5018	95.6241
1440	0.00432	0.00406	0.001878719	0.00188	0.00137	0.00128	0.00059365	0.0005937	0.34856	0.32686	0.151435835	0.15144	30.2872	455.397
2520	0.00428	0.00394	0.001925119	0.00193	0.00135	0.00124	0.00060832	0.0006083	0.34482	0.31731	0.155175949	0.15518	31.0352	1196.74
2700	0.00428	0.00383	0.001926019	0.00193	0.00135	0.00121	0.0006086	0.0006086	0.34475	0.30902	0.155248494	0.15525	31.0497	1358.39
2880	0.00428	0.00372	0.001926619	0.00193	0.00135	0.00118	0.00060879	0.0006088	0.3447	0.30017	0.155296858	0.1553	31.0594	1615.04
3000	0.00428	0.00367	0.001926919	0.00193	0.00135	0.00116	0.00060889	0.0006089	0.34468	0.29573	0.15532104	0.15532	31.0642	#NUM!

Table A.24. Levulinic Acid Conversion at 423 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Levulinic	Ethanol	Ethyl Levulinate	Water	Levulinic	Ethanol	Ethyl Levulinate	Water	Levulinic	Ethanol	Ethyl Levulinate	Water	Levulinic	
(Mins)	Conc	Conc	Conc	Conc	Amount	Amount	Amount	Amount	mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversion	Y
0	0.006203	0.006203	0	0	0.00196	0.00196	0	0	0.5	0.5	0	0	0	0
5	0.006055	0.005797	0.000147635	0.000148	0.001913	0.001832	0.00004665	0.00004665	0.4881	0.467282	0.011900294	0.0119003	2.380059	3.989017
10	0.005747	0.005705	0.000456194	0.000456	0.001816	0.001803	0.000144152	0.0001442	0.463228	0.459863	0.036771913	0.0367719	7.354383	13.44506
20	0.005431	0.005632	0.000772334	0.000772	0.001716	0.00178	0.000244049	0.000244	0.437745	0.453948	0.062254696	0.0622547	12.45094	25.3446
30	0.005167	0.005547	0.001035828	0.001036	0.001633	0.001753	0.000327311	0.0003273	0.416506	0.447129	0.083493894	0.0834939	16.69878	37.8298
60	0.004673	0.005364	0.001530043	0.00153	0.001477	0.001695	0.000483477	0.0004835	0.376669	0.432399	0.123330558	0.1233306	24.66611	72.64535
90	0.004209	0.005088	0.001994207	0.001994	0.00133	0.001608	0.000630148	0.0006301	0.339255	0.410128	0.160744903	0.1607449	32.14898	137.8508
120	0.003959	0.00494	0.002244265	0.002244	0.001251	0.001561	0.000709164	0.0007092	0.319099	0.398187	0.18090106	0.1809011	36.18021	212.0419
180	0.003727	0.004119	0.002475787	0.002476	0.001178	0.001302	0.000782322	0.0007823	0.300437	0.332019	0.199563112	0.1995631	39.91262	374.0885
240	0.003679	0.003574	0.002524319	0.002524	0.001162	0.001129	0.000797658	0.0007977	0.296525	0.288057	0.203475014	0.203475	40.695	443.8939
360	0.00357	0.003376	0.002633319	0.002633	0.001128	0.001067	0.0008321	0.0008321	0.287739	0.272136	0.212261059	0.2122611	42.45221	853.062
480	0.003546	0.003261	0.002656819	0.002657	0.001121	0.00103	0.000839526	0.0008395	0.285845	0.262829	0.214155298	0.2141553	42.83106	1338.564
600	0.003541	0.003073	0.002661819	0.002662	0.001119	0.000971	0.000841106	0.0008411	0.285442	0.247673	0.214558328	0.2145583	42.91167	#NUM!

Table A.25. Levulinic Acid Conversion at 473 K, 1:1 Molar Ratio in the absence of Catalyst

Time (Mins)	Levulinic Conc (mol/mL)	Ethanol Conc (mol/mL)	Ethyl Levulinate Conc (mol/mL)	Water Conc (mol/mL)	Levulinic Amount mol	Ethanol Amount mol	Ethyl Levulinate Amount mol	Water Amount mol	Levulinic mole Fraction	Ethanol mole Fraction	Ethyl Levulinate mole Fraction	Water mole Fraction	Levulinic % Conversion	Y
0	0.0062	0.0062	0	0	0.00196	0.00196	0	0	0.5	0.5	0	0	0	0
5	0.00567	0.00504	0.000529641	0.00053	0.00179	0.00159	0.000167361	0.000167	0.45731	0.40593	0.042692197	0.04269	8.53844	15.8476
10	0.00517	0.00475	0.001029194	0.00103	0.00163	0.0015	0.000325214	0.000325	0.41704	0.38262	0.082959089	0.08296	16.5918	36.1458
20	0.00444	0.00421	0.001760201	0.00176	0.0014	0.00133	0.000556205	0.000556	0.35812	0.33941	0.141882601	0.14188	28.3765	84.3548
30	0.00407	0.00417	0.002134789	0.00213	0.00129	0.00132	0.00067457	0.000675	0.32792	0.33596	0.17207662	0.17208	34.4153	127.152
60	0.00375	0.00365	0.002454653	0.00245	0.00118	0.00115	0.000775644	0.000776	0.30214	0.29448	0.197859552	0.19786	39.5719	186.115
90	0.00346	0.00356	0.002739306	0.00274	0.00109	0.00113	0.000865591	0.000866	0.2792	0.287	0.220804273	0.2208	44.1609	278.07
120	0.00316	0.00319	0.003047645	0.00305	0.001	0.00101	0.000963023	0.000963	0.25434	0.25702	0.245658237	0.24566	49.1316	515.113
180	0.00307	0.00317	0.003132284	0.00313	0.00097	0.001	0.000989768	0.00099	0.24752	0.2554	0.252480627	0.25248	50.4961	671.452
240	0.00301	0.00306	0.003190052	0.00319	0.00095	0.00097	0.001008022	0.001008	0.24286	0.24687	0.257137086	0.25714	51.4274	870.749
360	0.00302	0.003	0.00318686	0.00319	0.00095	0.00095	0.001007014	0.001007	0.24312	0.24171	0.256879794	0.25688	51.376	855.529
480	0.00296	0.0031	0.003238917	0.00324	0.00094	0.00098	0.001023463	0.001023	0.23892	0.25018	0.261075843	0.26108	52.2152	1308.41
600	0.00295	0.00304	0.003256986	0.00326	0.00093	0.00096	0.001029173	0.001029	0.23747	0.24479	0.262532373	0.26253	52.5065	#NUM!

Table A.26. Levulinic Acid Conversion at 523 K, 1:1 Molar Ratio in the absence of Catalyst

Time (Mins)	Levulinic Conc (mol/mL)	Ethanol Conc (mol/mL)	Ethyl Levulinate Conc (mol/mL)	Water Conc (mol/mL)	Levulinic Amount mol	Ethanol Amount mol	Ethyl Levulinate Amount mol	Water Amount mol	Levulinic mole Fraction	Ethanol mole Fraction	Ethyl Levulinate mole Fraction	Water mole Fraction	Levulinic % Conversion	Y
0	0.0062	0.0062	0	0	0.00196	0.00196	0	0	0.5	0.5	0	0	0	0
2	0.00563	0.00561	0.000568287	0.00057	0.00178	0.00177	0.000179573	0.00018	0.45419	0.45245	0.045807317	0.04581	9.16146	17.2089
3	0.00497	0.00496	0.001230267	0.00123	0.00157	0.00157	0.000388751	0.00039	0.40083	0.40002	0.099166831	0.09917	19.8334	45.4938
5	0.00439	0.00469	0.001814032	0.00181	0.00139	0.00148	0.000573215	0.00057	0.35378	0.37803	0.146221707	0.14622	29.2443	88.0615
10	0.00384	0.0038	0.00236053	0.00236	0.00121	0.0012	0.000745902	0.00075	0.30973	0.30633	0.19027268	0.19027	38.0545	144.186
20	0.00339	0.00345	0.002815054	0.00282	0.00107	0.00109	0.000889527	0.00089	0.27309	0.27833	0.226910018	0.22691	45.382	236.513
30	0.00314	0.00326	0.003058625	0.00306	0.00099	0.00103	0.000966493	0.00097	0.25346	0.26247	0.246543291	0.24654	49.3087	313.234
40	0.00292	0.00322	0.003286418	0.00329	0.00092	0.00102	0.001038473	0.00104	0.2351	0.25918	0.264904742	0.2649	52.9809	427.737
50	0.00272	0.00301	0.003483396	0.00348	0.00086	0.00095	0.001100716	0.0011	0.21922	0.24294	0.280782305	0.28078	56.1565	610.151
60	0.00258	0.00291	0.003624451	0.00362	0.00081	0.00092	0.001145288	0.00115	0.20785	0.23427	0.292152201	0.29215	58.4304	921.126
90	0.00247	0.00297	0.003737181	0.00374	0.00078	0.00094	0.001180909	0.00118	0.19876	0.2398	0.301238913	0.30124	60.2478	1401.08
120	0.00245	0.003	0.003757187	0.00376	0.00077	0.00095	0.001187231	0.00119	0.19715	0.24216	0.302851478	0.30285	60.5703	1773.01
180	0.00243	0.00311	0.003774802	0.00377	0.00077	0.00098	0.001192797	0.00119	0.19573	0.25064	0.304271338	0.30427	60.8543	#NUM!

Table A.27. Linoleic Acid Conversion at 373 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	
(Mins)	Conc	Conc	Conc	Conc	mole	Mole	mole	Mole	Mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.0027	0.0027	0	0	0.00075	0.00075	0	0	0.5	0.5	0	0	0	0
30	0.00248	0.00248	0.00023	0.00023	0.00069	0.00069	6.3E-05	6.3E-05	0.4583	0.4583	0.0417	0.0417	8.34046	36.2517
60	0.0024	0.0024	0.0003	0.0003	0.00067	0.00067	8.4E-05	8.4E-05	0.44386	0.44386	0.05614	0.05614	11.2285	52.6735
120	0.00238	0.00238	0.00032	0.00032	0.00066	0.00066	8.9E-05	8.9E-05	0.44056	0.44056	0.05944	0.05944	11.8889	56.8602
180	0.00221	0.00221	0.00049	0.00049	0.00061	0.00061	0.00014	0.00014	0.40921	0.40921	0.09079	0.09079	18.1581	109.181
300	0.00217	0.00217	0.00054	0.00054	0.0006	0.0006	0.00015	0.00015	0.40074	0.40074	0.09926	0.09926	19.8529	129.356
420	0.00212	0.00212	0.00059	0.00059	0.00059	0.00059	0.00016	0.00016	0.39133	0.39133	0.10867	0.10867	21.7348	156.853
600	0.00206	0.00206	0.00064	0.00064	0.00057	0.00057	0.00018	0.00018	0.38178	0.38178	0.11822	0.11822	23.6443	192.665
1440	0.00187	0.00187	0.00083	0.00083	0.00052	0.00052	0.00023	0.00023	0.34661	0.34661	0.15339	0.15339	30.678	539.847
2700	0.00181	0.00181	0.00089	0.00089	0.0005	0.0005	0.00025	0.00025	0.33474	0.33474	0.16526	0.16526	33.0514	1150.67
2880	0.0018	0.0018	0.0009	0.0009	0.0005	0.0005	0.00025	0.00025	0.3332	0.3332	0.1668	0.1668	33.3602	1396.09
3000	0.00179	0.00179	0.00092	0.00092	0.0005	0.0005	0.00025	0.00025	0.33054	0.33054	0.16946	0.16946	33.8917	#NUM!

Table A.28. Linoleic Acid Conversion at 423 K, 1:1 Molar Ratio in the absence of Catalyst

Time (Mins)	Linoleic Conc (mol/mL)	Ethanol Conc (mol/mL)	Ethyl Lino Conc (mol/mL)	Water Conc (mol/mL)	Linoleic mole mol	Ethanol Mole mol	Ethyl Lino mole mol	Water Mole mol	Linoleic Mole Fraction	Ethanol mole Fraction	Ethyl Lino mole Fraction	Water mole Fraction	Linoleic % Conversn	Y
0	0.0027	0.002703	0	0	0.00075	0.00075	0	0	0.5	0.5	0	0	0	0
5	0.00238	0.002377	0.00033	0.00033	0.00066	0.00066	9E-05	9E-05	0.43983	0.43983	0.06017	0.06017	12.0349	55.458
10	0.00232	0.002324	0.00038	0.00038	0.00064	0.00064	0.00011	0.00011	0.42993	0.42993	0.07007	0.07007	14.0143	67.5738
20	0.00226	0.002265	0.00044	0.00044	0.00063	0.00063	0.00012	0.00012	0.419	0.419	0.081	0.081	16.1996	82.4433
30	0.00207	0.002071	0.00063	0.00063	0.00057	0.00057	0.00018	0.00018	0.38306	0.38306	0.11694	0.11694	23.3889	147.544
60	0.00183	0.00183	0.00087	0.00087	0.00051	0.00051	0.00024	0.00024	0.33852	0.33852	0.16148	0.16148	32.2964	302.705
120	0.00179	0.00179	0.00091	0.00091	0.0005	0.0005	0.00025	0.00025	0.33117	0.33117	0.16883	0.16883	33.7658	346.092
180	0.00171	0.001714	0.00099	0.00099	0.00048	0.00048	0.00027	0.00027	0.31702	0.31702	0.18298	0.18298	36.5953	460.932
300	0.00165	0.001655	0.00105	0.00105	0.00046	0.00046	0.00029	0.00029	0.30615	0.30615	0.19385	0.19385	38.7696	598.765
420	0.00159	0.001591	0.00111	0.00111	0.00044	0.00044	0.00031	0.00031	0.29441	0.29441	0.20559	0.20559	41.1175	859.781
600	0.00148	0.001484	0.00122	0.00122	0.00041	0.00041	0.00034	0.00034	0.27449	0.27449	0.22551	0.22551	45.1027	#NUM!

Table A.29. Linoleic Acid Conversion at 473 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	
(Mins)	Conc	Conc	Conc	Conc	mole	Mole	mole	Mole	Mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.0027	0.0027	0	0	0.00075	0.00075	0	0	0.5	0.5	0	0	0	0
5	0.00214	0.00214	0.00056	0.00056	0.00059	0.00059	0.00016	0.00016	0.39627	0.39627	0.10373	0.10373	20.7469	118.01
10	0.00198	0.00198	0.00072	0.00072	0.00055	0.00055	0.0002	0.0002	0.36613	0.36613	0.13387	0.13387	26.7745	185.394
20	0.00194	0.00194	0.00077	0.00077	0.00054	0.00054	0.00021	0.00021	0.35822	0.35822	0.14178	0.14178	28.3566	208.707
30	0.00196	0.00196	0.00074	0.00074	0.00055	0.00055	0.0002	0.0002	0.3635	0.3635	0.1365	0.1365	27.3002	192.807
60	0.00177	0.00177	0.00093	0.00093	0.00049	0.00049	0.00026	0.00026	0.32816	0.32816	0.17184	0.17184	34.3672	336.674
120	0.00161	0.00161	0.00109	0.00109	0.00045	0.00045	0.0003	0.0003	0.29784	0.29784	0.20216	0.20216	40.4327	619.644
180	0.00161	0.00161	0.00109	0.00109	0.00045	0.00045	0.0003	0.0003	0.29766	0.29766	0.20234	0.20234	40.4689	622.408
300	0.00154	0.00154	0.00116	0.00116	0.00043	0.00043	0.00032	0.00032	0.28501	0.28501	0.21499	0.21499	42.9986	893.61
420	0.0015	0.0015	0.0012	0.0012	0.00042	0.00042	0.00033	0.00033	0.27728	0.27728	0.22272	0.22272	44.5447	1215.73
600	0.00143	0.00143	0.00127	0.00127	0.0004	0.0004	0.00035	0.00035	0.26499	0.26499	0.23501	0.23501	47.0013	#NUM!

Table A.30. Linoleic Acid Conversion at 523 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	
(Mins)	Conc	Conc	Conc	Conc	mole	Mole	mole	Mole	Mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.0027	0.0027	0	0	0.00075	0.00075	0	0	0.5	0.5	0	0	0	0
2	0.00192	0.00192	0.00078	0.00078	0.00053	0.00053	0.00022	0.00022	0.35553	0.35553	0.14447	0.14447	28.8946	259.501
3	0.00188	0.00188	0.00082	0.00082	0.00052	0.00052	0.00023	0.00023	0.34764	0.34764	0.15236	0.15236	30.4729	304.422
5	0.00185	0.00185	0.00086	0.00086	0.00051	0.00051	0.00024	0.00024	0.3418	0.3418	0.1582	0.1582	31.6398	345.535
10	0.00179	0.00179	0.00091	0.00091	0.0005	0.0005	0.00025	0.00025	0.33173	0.33173	0.16827	0.16827	33.653	440.804
20	0.00176	0.00176	0.00094	0.00094	0.00049	0.00049	0.00026	0.00026	0.32562	0.32562	0.17438	0.17438	34.8755	522.717
30	0.00171	0.00171	0.001	0.001	0.00047	0.00047	0.00028	0.00028	0.31573	0.31573	0.18427	0.18427	36.8537	733.656
60	0.00171	0.00171	0.001	0.001	0.00047	0.00047	0.00028	0.00028	0.31567	0.31567	0.18433	0.18433	36.8664	735.529
120	0.00167	0.00167	0.00103	0.00103	0.00046	0.00046	0.00029	0.00029	0.30933	0.30933	0.19067	0.19067	38.1331	990.958
180	0.00163	0.00163	0.00107	0.00107	0.00045	0.00045	0.0003	0.0003	0.30233	0.30233	0.19767	0.19767	39.534	1771.98
300	0.00163	0.00163	0.00108	0.00108	0.00045	0.00045	0.0003	0.0003	0.30071	0.30071	0.19929	0.19929	39.8576	2485.08
420	0.00162	0.00162	0.00108	0.00108	0.00045	0.00045	0.0003	0.0003	0.30024	0.30024	0.19976	0.19976	39.9527	3153.14
600	0.00161	0.00161	0.0011	0.0011	0.00045	0.00045	0.0003	0.0003	0.29707	0.29707	0.20293	0.20293	40.5857	#NUM!

Table A.31. Linoleic Acid Conversion at 573 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	
(Mins)	Conc	Conc	Conc	Conc	mole	Mole	mole	Mole	Mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.0027	0.0027	0	0	0.00075	0.00075	0	0	0.5	0.5	0	0	0	0
0.33333	0.00204	0.00204	0.00066	0.00066	0.00057	0.00057	0.00018	0.00018	0.37729	0.37729	0.12271	0.12271	24.5418	189.761
0.66667	0.00202	0.00202	0.00068	0.00068	0.00056	0.00056	0.00019	0.00019	0.37398	0.37398	0.12602	0.12602	25.2039	202.698
1	0.00201	0.00201	0.00069	0.00069	0.00056	0.00056	0.00019	0.00019	0.37234	0.37234	0.12766	0.12766	25.5313	209.528
1.33333	0.00196	0.00196	0.00074	0.00074	0.00054	0.00054	0.00021	0.00021	0.36237	0.36237	0.13763	0.13763	27.5266	258.973
1.66667	0.00191	0.00191	0.00079	0.00079	0.00053	0.00053	0.00022	0.00022	0.35416	0.35416	0.14584	0.14584	29.1686	313.749
2	0.00188	0.00188	0.00082	0.00082	0.00052	0.00052	0.00023	0.00023	0.34767	0.34767	0.15233	0.15233	30.4654	371.203
3	0.00185	0.00185	0.00086	0.00086	0.00051	0.00051	0.00024	0.00024	0.3418	0.3418	0.1582	0.1582	31.6398	440.238
5	0.0018	0.0018	0.0009	0.0009	0.0005	0.0005	0.00025	0.00025	0.33353	0.33353	0.16647	0.16647	33.2933	586.208
10	0.0018	0.0018	0.0009	0.0009	0.0005	0.0005	0.00025	0.00025	0.33302	0.33302	0.16698	0.16698	33.396	598.266
20	0.00179	0.00179	0.00091	0.00091	0.0005	0.0005	0.00025	0.00025	0.33173	0.33173	0.16827	0.16827	33.653	630.622
30	0.00179	0.00179	0.00091	0.00091	0.0005	0.0005	0.00025	0.00025	0.33113	0.33113	0.16887	0.16887	33.7741	647.076
60	0.00176	0.00176	0.00094	0.00094	0.00049	0.00049	0.00026	0.00026	0.32642	0.32642	0.17358	0.17358	34.7168	812.409
90	0.00175	0.00175	0.00095	0.00095	0.00049	0.00049	0.00026	0.00026	0.3244	0.3244	0.1756	0.1756	35.1207	914.302
120	0.00175	0.00175	0.00096	0.00096	0.00048	0.00048	0.00027	0.00027	0.32331	0.32331	0.17669	0.17669	35.3383	982.061
180	0.00171	0.00171	0.00099	0.00099	0.00047	0.00047	0.00028	0.00028	0.31639	0.31639	0.18361	0.18361	36.7226	2558.47

Table A.32. Linoleic Acid Conversion at 623 K, 1:1 Molar Ratio in the absence of Catalyst

Time	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	Ethanol	Ethyl Lino	Water	Linoleic	
(Mins)	Conc	Conc	Conc	Conc	mole	Mole	mole	Mole	Mole	mole	mole	mole	%	
	(mol/mL)	(mol/mL)	(mol/mL)	(mol/mL)	mol	mol	mol	mol	Fraction	Fraction	Fraction	Fraction	Conversn	Y
0	0.0027	0.0027	0	0	0.00075	0.00075	0	0	0.5	0.5	0	0	0	0
0.16667	0.00221	0.00221	0.00049	0.00049	0.00061	0.00061	0.00014	0.00014	0.40893	0.40893	0.09107	0.09107	18.2148	112.929
0.33333	0.00203	0.00203	0.00068	0.00068	0.00056	0.00056	0.00019	0.00019	0.37509	0.37509	0.12491	0.12491	24.9814	243.944
0.66667	0.00201	0.00201	0.00069	0.00069	0.00056	0.00056	0.00019	0.00019	0.37216	0.37216	0.12784	0.12784	25.5685	264.22
1	0.00196	0.00196	0.00074	0.00074	0.00054	0.00054	0.00021	0.00021	0.36333	0.36333	0.13667	0.13667	27.3336	345.028
2	0.00187	0.00187	0.00083	0.00083	0.00052	0.00052	0.00023	0.00023	0.3468	0.3468	0.1532	0.1532	30.639	716.193
3	0.00186	0.00186	0.00085	0.00085	0.00052	0.00052	0.00023	0.00023	0.34338	0.34338	0.15662	0.15662	31.3236	922.876
5	0.00185	0.00185	0.00085	0.00085	0.00051	0.00051	0.00024	0.00024	0.34255	0.34255	0.15745	0.15745	31.4893	995.711
10	0.00185	0.00185	0.00086	0.00086	0.00051	0.00051	0.00024	0.00024	0.34162	0.34162	0.15838	0.15838	31.6756	1096.52
20	0.00184	0.00184	0.00086	0.00086	0.00051	0.00051	0.00024	0.00024	0.34124	0.34124	0.15876	0.15876	31.7526	1146.24
30	0.00184	0.00184	0.00087	0.00087	0.00051	0.00051	0.00024	0.00024	0.33994	0.33994	0.16006	0.16006	32.012	1370.91
60	0.00183	0.00183	0.00088	0.00088	0.00051	0.00051	0.00024	0.00024	0.33809	0.33809	0.16191	0.16191	32.3815	2232.82
90	0.00183	0.00183	0.00088	0.00088	0.00051	0.00051	0.00024	0.00024	0.33809	0.33809	0.16191	0.16191	32.3827	2240.28
120	0.00183	0.00183	0.00088	0.00088	0.00051	0.00051	0.00024	0.00024	0.33793	0.33793	0.16207	0.16207	32.415	2483.09
180	0.00183	0.00183	0.00088	0.00088	0.00051	0.00051	0.00024	0.00024	0.33786	0.33786	0.16214	0.16214	32.4277	2620.92

A.4. Estimation of Parameter for Thermodynamic properties

The temperature functions for heat capacities, residual enthalpy change, and residual entropy change according the corresponding equation of state are obtained as follows:

The liquid heat capacities (Cp_{liq}) for acetic acid, ethanol, and ethyl acetate were estimated using the residual heat capacity (C^r_p) equation, calculated with the corresponding states method.[84]

$$C^r_P = \frac{C_{P_{liq}} - C^{ig}_p}{R} = 1.586 + \frac{0.49}{1-T_r} + \omega * \left[4.2775 + \frac{6.3(1-T_r)^{1/3}}{T_r} + \frac{0.4355}{1-T_r} \right] \qquad (A15)$$

Where the ideal gas heat capacity (C^{ig}_p) was calculated from the correlation equation

$$\frac{C_p}{R} = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \qquad (A16)$$

Table A.33. Constants for Heat Capacity [84]

Compound	a_0	$a_1 \times 10^3$	$a_2 \times 10^5$	$a_3 \times 10^8$	$a_4 \times 10^{11}$
Ethanol	4.396	0.628	5.546	-7.024	2.685
Water	4.395	-4.186	1.405	-1.564	0.632
Acetic Acid	4.375	-2.397	6.757	-8.764	3.478
Ethyl Acetate	10.228	-14.948	13.033	-15.736	5.999

$$\int_{T_2}^{T_1} C^{ig}_P dT = R\left[a_0 (T_1 - T_2) + \frac{a_1}{2}(T_1^2 - T_2^2) + \frac{a_2}{3}(T_1^3 - T_2^3) + \frac{a_3}{4}(T_1^4 - T_2^4) + \frac{a_4}{5}(T_1^5 - T_2^5) \right] \qquad (A17)$$

$$\int_{T_1}^{T_2} C^{ig}_p dT = R\left[a_0 (T_2 - T_1) + \frac{a_1}{2}(T_2^2 - T_1^2) + \frac{a_2}{3}(T_2^3 - T_1^3) + \frac{a_3}{4}(T_2^4 - T_1^4) + \frac{a_4}{5}(T_2^5 - T_1^5) \right] \qquad (A18)$$

$$\int_{T_2}^{T_1} C_p^{ig}\frac{dT}{T} = R\left[a_0 \ln\frac{T_1}{T_2} + a_1\left(T_1 - T_2\right) + \frac{a_2}{2}(T_1^2 - T_2^2) + \frac{a_3}{3}(T_1^3 - T_2^3) + \frac{a_4}{4}(T_1^4 - T_2^4)\right] \qquad (A19)$$

$$\int_{T_1}^{T_2} C_p^{ig} dT = R\left[a_0 \ln\frac{T_2}{T_1} + a_1\left(T_2 - T_1\right) + \frac{a_2}{2}(T_2^2 - T_1^2) + \frac{a_3}{3}(T_2^3 - T_1^3) + \frac{a_4}{4}(T_2^4 - T_1^4)\right] \qquad (A20)$$

Table A.34. Estimated C_pdT and C_pdT/T Values for IGTC Thermodynamic Path

Temp (K)	Acetic Acid C_pdT (J/mol)	Ethanol C_pdT (J/mol)	Ethyl Acetate C_pdT (J/mol)	Acetic Acid C_pdT (J/mol.K)	Ethanol C_pdT (J/mol)	Ethyl Acetate C_pdT (J/mol)
373	5181	5324	9170	14	14	25
423	9118	9346	16032	22	22	38
473	13434	13741	23496	28	29	50
523	18111	18496	31543	35	35	60

Table A.35. Estimated C_{pliq}dT and C_{pliq}dT/T Values for LTC Thermodynamic Path

Temp (K)	Acetic Acid C_{pliq}dT (J/mol)	Ethanol C_{pliq}dT (J/mol)	Ethyl Acetate C_{pliq}dT (J/mol)	Acetic Acid C_{pliq}dT/T (J/mol.K)	Ethanol C_{pliq}dT/T (J/mol.K)	Ethyl Acetate C_{pliq}dT/T (J/mol.K)
373	5229	5388	9217	14	14	24.711287
423	9169	9421	16088	22	22	38.032946
473	13492	13859	23579	28	29	49.849315
523	18188	18169	40943	35	35	78.284444

The Lee/Kesler correlation values calculated with Lee-Kesler calculator found at http://www.macatea.com/wshop/lk/ was used to estimate the residual properties (H^R and S^R) acetic acid, ethanol, and ethyl acetate at respective reduced pressures and reduced temperatures. With the same reduced pressures and reduced temperatures, the compressibility factor (Z) was also estimated.

$$\frac{H^R}{RT_c} = \frac{\left(H^R\right)^0}{RT_c} + \omega * \frac{\left(H^R\right)^1}{RT_c} \tag{A21}$$

$$\frac{S^R}{R} = \frac{\left(S^R\right)^0}{R} + \omega * \frac{\left(S^R\right)^1}{R} \tag{A22}$$

Where $\frac{\left(H^R\right)^0}{RT_c}$, $\frac{\left(H^R\right)^1}{RT_c}$, $\frac{\left(S^R\right)^0}{R}$, $\frac{\left(S^R\right)^1}{R}$, and ω were estimated from three parameter corresponding state correlation developed by Lee and Kesler

Table A.36. Estimated Residual Properties for IGTC Thermodynamic Path

Temp (K)	Acetic Acid H^R (J/mol)	Ethanol H^R (J/mol)	Ethyl Acetate H^R (J/mol)	Acetic Acid S^R (J/mol.K)	Ethanol S^R (J/mol.K)	Ethyl Acetate S^R (J/mol.K)
373	-49263	-597	-18974	-96	-1.2	-84
423	-44132	-1337	-17818	-77	-2.4	-83
473	-38610	-2932	-11495	-64	-5	-74
523	-35121	-5757	-7521	-50	-9	-59

Table A.37. Estimated Residual Properties for LTC Thermodynamic Path

Temp (K)	Acetic Acid H^R (J/mol)	Ethanol H^R (J/mol)	Ethyl Acetate H^R (J/mol)	Acetic Acid S^R (J/mol.K)	Ethanol S^R (J/mol.K)	Ethyl Acetate S^R (J/mol.K)
373	-36631	-34201	-35722	-124	-141	-86
423	-36608	-34185	-35261	-125	-128	-85
473	-36553	-34150	-35193	-117	-123	-77
523	-36438	-34077	-35042	-116	-114	-71

Pressure Estimation

The pressures at different temperatures were estimated from the summation of the partial pressure equation below:

$$P = \sum X_i P_i \tag{A23}$$

Where the vapor pressure (P_i) for acetic acid, ethanol, and ethyl acetate were deduced from reduced vapor pressure equation below: [85]

$$P_i = \ln P_r^s = f^0 + \omega * f^1 \tag{A24}$$

$$f^0 = 5.92714 - \frac{6.09648}{T_r} - 1.28862 * \ln T_r + 0.169347 * T_r^6 \tag{A25}$$

$$f^1 = 15.2518 - \frac{15.6875}{T_r} - 13.4721 * \ln T_r + 0.43577 * T_r^6 \tag{A26}$$

$$P_i = P^s = P_r^s * P_c \tag{A27}$$

Water Vapor Pressure

The vapor pressure of water at different temperatures was estimated with five term parameter equation developed by Wagner.[84]

$$\ln P_{vp_r} = \frac{\left(a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6\right)}{T_r} \qquad (A28)$$

$$\tau = 1 - T_r \qquad (A29)$$

Where $\tau = 1 - T_r$, $T_r = T/T_c$, $P_{vpr} = P_{vp}/Pc$, T_c is the critical temperature, P_{vp} is the vapor pressure, P_c is the critical saturated pressure, a, b, c, and d, are constants for specific substance. Wagner's equation has been found to be satisfactorily with high accuracy for large number of substances, including water in the entire range from the triple point to the critical point. Values of the constants for many substances are given by Poling, Prausnitz, and O' Connell.[84] Below are the constant values for water along with the applicable temperature and pressure range.

Table A.38. Vapor Pressure Correlation Parameters for water.[84]

A	B	c	D	Temp range (K)	Pressure Range (bar)
-7.77224	1.45684	-2.71942	-1.41336	273.20 - 647.30	0.01 – 221

On the basis of the above Equation, the vapor pressure at a given temperature was calculated.

Table A.39. Calculated Water Vapor Pressure

Temp	Temp					
°C	K	T_r	T	$\ln P_{vpr}$	P_{vpr}	P_{vp}
100	373	0.6	0.4	-5.4	0.0046	1.00
150	423	0.65	0.35	-3.8	0.022	4.7
200	473	0.7	0.3	-2.7	0.070	15
250	523	0.8	0.2	-1.7	0.2	40

Partial Pressure

The partial pressure (X_iP_i) at reaction temperature for was calculated for acetic acid, ethanol, ethyl acetate, and water by multiplying the mole fraction of individual substance (X_i) at equilibrium constant with its vapor pressure (P_i). The partial pressure of nitrogen gas in the reactor at different temperatures are calculated with the ideal gas equation ($Pv=ZRT$), where the compressibility factor (Z) were estimated with the use of three-parameter corresponding states) correlation developed by Lee and Kesler. The Lee/Kesler calculator found at http://www.macatea.com/wshop/lk/ was applied to the calculation. Partial pressure calculated for other substance in the reactor was used as initial pressure for the calculator. Values for the calculated total pressure with reaction temperatures are shown in Table A.40. The pressure increases with increasing temperature.

Table A.40. Estimated Pressure

Temp (K)	Acetic Acid partial Pressure (bar)	Ethanol partial Pressure (bar)	Ethyl Acetate partial Pressure (bar)	Water partial Pressure (bar)	Nitrogen partial Pressure (bar)	Total Pressure (bar)
373	0.18	0.76	0.33	0.16	0.79	2.2
423	0.65	2.4	1.7	1.1	0.89	6.7
473	1.6	5.9	5.3	4.6	1.0	18
523	3.4	12	13	13	1.1	43

Table A.41. Molar properties of formation at 298 K [84, 85]

Properties	Acetic Acid	Ethanol	Ethyl Acetate	Water	Hydrogen	Oxygen
$\Delta H_i(T_0)$ (kJ/mol)	-484	-277	-479	-286	0	0
$\Delta G_i(T_0)$ (kJ/mol)	-390	-175	-311	-237	0	0
$\Delta S_i(T_0)$ (J/(mol.K)	-314	-344	-564	-163	0	0