A Kinetic Study on Auto-Catalytic Esterification for Reactive Separation of Formic Acid, Acetic Acid, Methanol and Water from Biorefinery Feed

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Acknowledgement

Abstract

Paper and pulping industry uses organic acid as a solvent and produces wastewater that contains formic acid (FA), acetic acid (AA) and methanol (MeOH). The research project is aiming at determining the kinetics of autocatalytic esterification of FA, AA and MeOH in a batch reactor. Different temperature and concentration are applied to see how these factors affect the reaction rate of esterification. However, no experiment about the dependence of FA concentration could be carried out due to the time constraint. The result suggests that a significant impact of temperature on reaction rate that higher temperature would largely increase the reaction rate. Besides, an insufficient feed of AA yields a higher reaction rate. Due to the limited working hours, each experiment can only be carried out for no more than 8 hours, which is far from reaching reaction equilibrium. More variables would be studied in the future.

Content

1. Introduction

2.1. Motivation

As a third largest polluter in the U.S., pulp and paper industry creates huge pollution problem in land, water and air environment. The high usage of water, which is around 20,000 to 60,000 gallon per ton product, [1] makes wastewater a major source of pollutants in pulp and paper industry. These pollutants are responsible for color problems, thermal impacts and the increasing the toxic substances or dirt, such as scum and slime, in water, which is seriously affecting terrestrial ecosystem. Now public pays great attention to the regulation and treatment of these pollutants. [2]

Organic acid, such as formic acid and acetic acid, methanol and ethanol are often use as solvent in Organosolv pulping process [3-4], which is the major characteristics of wastewater[2]. However, formic acid/acetic acid/water mixtures are very hard to separate due to the high boiling point of formic acid azeotrope (107.3˚C) [5] and a complex saddle azeotrope. Several methods like rectify aqueous acetic by using an entrainer to lower boiling point of the mixture [6] or continuous distillation by adding an esterifying agent to obtain formic acid and water at the overhead product with formic ester when acetic acid accumulates in the bottom [7]. However, most methods require catalysts [8] and they are hard to produce highly pure acid. [9] Besides, esterifying and distillate carboxylic acids at the same time or selective esterification while distillation is a new method to reactive separate component in azeotropic mixtures.

Reactive separation in this program is based on esterification of formic acid and acetic acid with methaonl, making it into low boiling esters completely by removing the esters. Here no catalyst is required due to auto-catalytic effect. Because formic acid esterification is faster, there is more methyl formate than methyl acetate, which makes selective removal of formic acid possible. [8-12]

2.2. Previous Work

Catalyst such as Amberlyst 15 and Amberlyst 70 ion exchange resins are wildly used in catalyzing esterification, and the kinetic model with catalyst was well studied. [8,13] Moreover, the auto-catalytic effect of acetic acid and formic acid with some alcohol was studied: the reaction kinetics of the auto-catalytic and catalytic esterification of formic acid with methanol was determined by PÖpken et al; [8] the hydrolysis of methyl and the kinetic model were also studied by Jogunola et al; [10-11] the kinetics study on esterification of acetic with a more complicated alcohol, isomyl alcohol, had been carried out by DUQUE-BERNAL et al, revealing the self-catalytic effect of acetic acid. [12] Nonetheless, the study on auto-catalytic effect of mixed formic acid and acetic acid are limited.

Highly selective product separation and applying chemically altering of the substance properties to avoid distillation limits was proven, making it very promising and realizable. [9] A method for isolating mixed succinic acid and acetic acid with ethanol was experimental studied and computational simulated by Orjuela et al. The flow sheet of the distillation is shown in Figure 2.2.1. The feed was first prereacted in

the Pre-reactor with Amberlyst 15. After 24 hours, the equilibrium of mixed succinic acid and acetic acid with ethyl esters in ethanol could be reached. The distillation column had four reactive sections and two nonreactive sections. Internal packing of Amberlyst 70 was applied in those reactive sections. By adjusting parameters, distillate could contain more than 90% of ethanol and the bottoms product contained a maximum 98.3% of diethyl succinate. [13]

However, much research is required in terms of kinetics and reactive distillation experiments to solve practical problem and for further improvements.

Figure 3.2.1 Pilot plant reactive distillation column
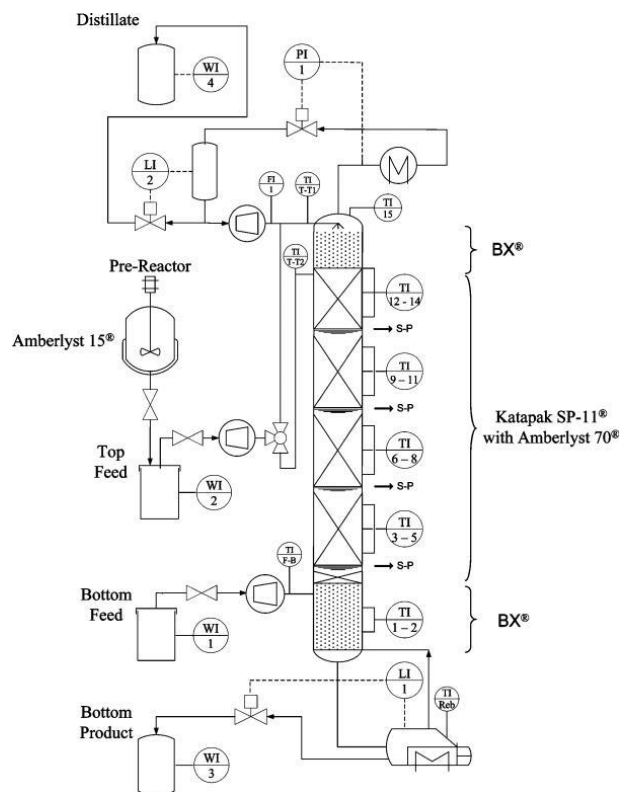
2.3. Objectives

The goal of this project is to determine the kinetic model under different temperature and feed composition of formic acid, acetic acid, methanol and water. The specific objectives are:

1. To determine the effects of temperature on acetic acid esterification at each feed composition.
2. To determine the effects of feed composition on acetic acid esterification at each temperature sets.
3. To determine the effects of temperature on simultaneous acid esterification at each feed composition for the mixed formic acid, acetic acid, methanol and water system.
4. To determine the effects of feed composition on simultaneous acid esterification at each temperature sets for the mixed formic acid, acetic acid, methanol and water system.
5. To derive a kinetic model of simultaneous acid esterification for the mixed formic acid, acetic acid, methanol and water system.

3. Literature Review and Summary for Kinetic Models

3.1. Homogeneously esterification of acetic acid with methanol by autocatalysis of acetic acid [8]

This kinetic model considers one of the esterification occurred in this project, where the self-catalytic effect of acetic acid is considered.

$$MeOH + AA \rightleftharpoons MeOAc + H_2O$$
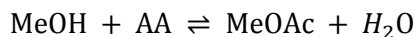
The rate law is expressed as

$$r = a_{HOAc}^{\alpha}(k_1 a_{HOAc} a_{MeOH} - k_{-1} a_{MeOAc} a_{H_2O})$$

where x_i is the mole fraction of component i, a_i the activity that equals to $x_i \times ç_i$, k_1 the rate constant of esterification, k_2 the rate constant of hydrolysis. Both k_1 and k_2 follow Arrhenius law.

α here depends on the catalysis mechanism that equals to 0.5, 1, or other variables. If one assumes the reaction is catalyzed by protons and dissociated acetic acid, it would become

$$K_a = \frac{a_{H^+} a_{AcO^-}}{a_{HOAc}} \approx \frac{x_{H^+}^2}{a_{HOAc}}$$

and yield

$$x_{H^+} \approx \sqrt{a_{HOAc} K_a}$$

Obviously, α is choose to be 0.5 under this assumption. However, if the acetic acid is assumed to be not dissociated, α should be 1.

Under either ideal liquid behavior assumption (γ_i=1.0, which means a_i=x_i) or activity calculation from UNIQUAC equation, parameters are fit to the experimental data. In this model, it is suggested that α=1 and use UNIQUAC to calculate activity.

3.2. Hydrolysis of alkyl formate using formic acid as catalyst (autocatalytic) [10-11]

Alkyl formate hydrolysis is the one of the reversed reactions occured in this project, methyl formate hydrolysis, and ethyl formate hydrolysis.

$$MeOAc + H_2O \rightleftharpoons MeOH + FA$$
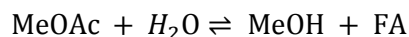
Formic acid is involved in the reaction as well as worked as a catalyst.

The rate law is presented as

$$r = f(C_{MeOAc}C_{H_2O} - \frac{1}{K_C}C_{MeOH}C_{FA})$$

where K_C is the equilibrium constant based on concentration, C_i is the concentration that $C_i = n_i/m_i$ (mol/kg), f is a function that includes the autocatalytic effect

$$f = k° + k'C_c$$

$k°$ (due to the dissociation of water) and k' (due to the autocatalytic reaction) are the rate constant also follow Arrhenius law.

Different from the first model, this model use concentration rather than activity since the system is assumed as an ideal, pure-liquid phase system (gas volume<0.5%). However, activities would be considered when accounting for the deviation from the ideal mixture.

The kinetic model above is developed by Jogunola's group in 2011 [9]. In 2012, their group improve the model. Because the unanalyzed rate constant k is negligible comparing to that of catalytic hydrolysis, the rate law is presented as

$$r = kC_{H^+}(C_{MeOAc}C_{H_2O} - \frac{1}{K_C}C_{MeOH}C_{FA})$$

As a relatively weak acid, proton concentration is considered to be $C_{H^+} = \sqrt{K_d C_{FA}}$. If developing a rate equation follows the first model, the exponent α would be equal to 0.5:

$$r = k'C_{FA}^{0.5}(C_{MeOAc}C_{H_2O} - \frac{1}{K_C}C_{MeOH}C_{FA})$$

3.3. Homogeneous esterification of acetic acid with isoamyl alcohol by autocatalysis of acetic acid [12]

The reaction of acetic acid with isoamyl alcohol is shown below:

$$CH_3COOH + (CH_3)_2CHCH_2CH_2OH \rightleftharpoons CH_3COOCH_2CH_2CH(CH_3)_2 + H_2O$$
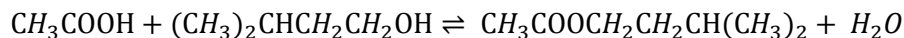
Isoamyl alcohol is not included in this project, and the autocatalytic effect depends chiefly on formic acid when formic acid and acetic acid both exist. However, the effects of autocatalysis are similar in both researches.

The kinetic model in this research:

$$r = k_1 a_{ROH}^\alpha(a_{HOAc}a_{ROH} - \frac{a_{ROAc}a_{H_2O}}{K_{eq}(T)})$$

which is very similar to model 1 since

$$K_{eq}(T) = \frac{k_1}{k_{-1}}$$

It discusses 36 kinetic models for this reaction. The activity a is considered under either ideal liquid condition or non-ideal condition. And it further includes NRTL activity coefficient model. Exponent α is considered under 4 conditions: no autocatalysis (0), autocatalysis by undissociated acid (1.0), autocatalysis by dissociated acid (0.5) and as an adjustable parameter. Three ways of calculating equilibrium constant is also presented: from Wyczesany's theory, from Van't Hoff's equation and as an adjustable variable.

The result shows that the most fitted value of α is slightly above theoretical value of undissociated acid (1.0).

3.4. Summary
All these models follow a parallel kinetic equation that can be presented as

$$r = a_{Acid}^{\alpha}(k_1 a_A a_B - k_{-1} a_C a_D)$$

If it is esterification, A = acid, B = alcohol, C = ester, D = H_2O. If it is hydrolysis, A = ester, B = H_2O, C = acid, D = alcohol. The chief inconsistence exists in the value of exponent α.

Acetic acid works as catalyst in both first and third model, and the exponent α is chosen to be 1 or around 1, which suggests acetic acid would possible be undissociated in the mixture of organic acids, alcohols and water. Formic acid dominates the catalytic effect in the second model, the exponent is chosen to be 0.5. It may suggest that formic acid would dissociate in the mixture. In this project, the environment of esterification is a mixture of formic acid, acetic acid, methanol and a small amount of water, therefore the kinetic model in this experiment could possibly refer to the kinetic models mentioned above.

4. Experimental

4.1. Overview

The reaction is carried out in a three-necked flask (500mL) with magnetically stirring. The temperature under the control of thermocouple is retain to be constant, the range is from 40˚C to 70˚C. See Figure 4.1.1 for the equipment used. Due to the time constraint, only objective 1 and 2 are partially carried out. Namely, esterification of acetic acid with methanol, and the molar ratios of acetic acid to methanol are 1:1 and 1:0.65, see Table 4.1.2. Usually, the experiments would last 6-8 hours due to the limited working hours. Samples would be taken every 20 minutes and be analyzed by GC using both FID detector and TCD detector.
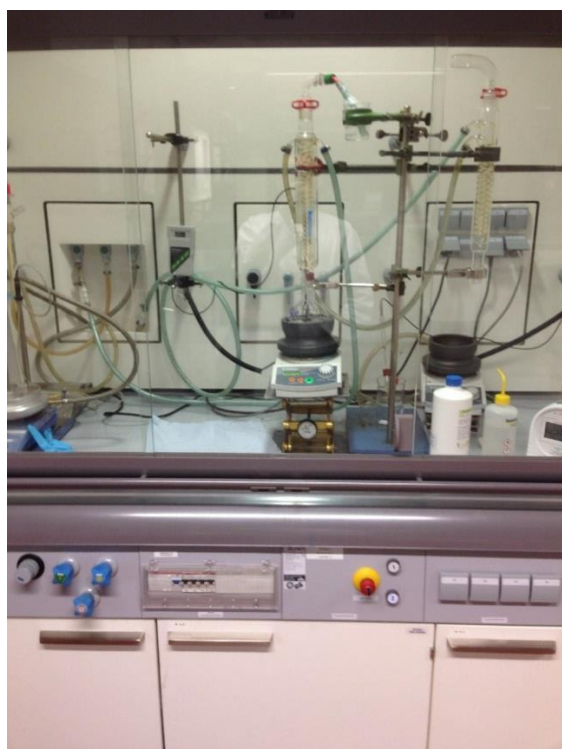
Figure 4.1.1 Experiment equipment

Table 4.1.2 Experiment Sheet with Actual Feed Data and Temperature

Set	Exp.	AA/g	FA/g	MeOH/g	Water/g	Molar Concentration	Temp. /˚C
A: 1:1	K16	179.92	0	95.97	0	50.0% AA / 50.0% MeOH	40
	K17	180.42	0	96.09	0	50.1% AA / 49.9% MeOH	50
	K18	181.13	0	96.27	0	50.1% AA / 49.9% MeOH	60
	K19	179.82	0	96.13	0	49.9% AA / 50.1% MeOH	70
B:1:0.65	K20	201.45	0	69.59	0	60.7% AA / 39.3% MeOH	40
	K21	200.10	0	69.33	0	60.6% AA / 39.4% MeOH	50
	K22	200.40	0	69.41	0	60.6% AA / 39.4% MeOH	60
	K23	200.39	0	69.59	0	60.6% AA / 39.4% MeOH	70

4.2. Experimental procedures

1. Acetic acid (>99%) is heated to 5-10˚C higher than the desired temperature in a three necked flask, since the temperature would drop when adding cold methanol. How much higher depends on the amount of acid and the desired temperature.
2. The magnetic stirrer speed is set to around 400 rpm, turning on cooling water.
3. After reaching the intended temperature, adding the methanol (>99%) at ambient temperature into the flask. The temperature changes are noted, and have to be adjusted when reaching either too high or too low.
4. Starting timing after adding the methanol. Mixing required a few minutes, therefore take the first sample after well mixed (around 2mins).
5. Samples of approximately 1mL should be taken by syringes every 20 minutes and putting into GC vials. To stop the reaction of samples, they should be cooled down immediately by burying GC vials in ice.
6. To avoid reaction under low temperature, samples should also be sent to the GC immediately, and the GC is supposed to get ready for the new samples in a short time.
7. The experiment should run for more than 6 hours. And each set should be carried out at least twice.

4.3. Data Analysis

Calibration

To quantitative analyze the concentration of each chemical component in the samples by GC, several calibration curves of standards need to be graphed. The components and weights of standards and the volume injected are presented in Table 4.3.1. Each set will be injected and measured three times. Actual weights of standards were used in the calculation and graphing. GC stores the samples in a cooling jacket at 5˚C, and density of standards are measured at 5˚C by density meter.

Table 4.3.1 Calibration Standards

Names	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
Components & weights	Water 2g Methanol 2g Methyl acetate 2g Acetic acid 2g	Methyl formate 2g Formic acid 2g Methyl acetate 2g Acetic acid 2g	Water 4g Formic acid 0.4g Acetic acid 0.4g	Methanol 4g Methyl formate 0.4g Methyl acetate 0.4g	Water 0.4g Methanol 0.4g Methyl acetate 2g Acetic acid 2g
Volume injected (µL)	0.2, 0.4, 0.6, 0.8	0.2, 0.4, 0.6, 0.8	0.2	0.2	0.2

The mass of each component being injected into the GC can be calculate by the equation:

$$m_i = W_i \times \rho_{sample} \times V \times purity_i$$

Where $m_i = mass\ of\ component\ i\ injected\ into\ GC$

$$W_i = mass\ farction\ of\ component\ i = \frac{mass\ of\ component\ i\ in\ standard}{total\ mass\ of\ that\ standard}$$

$$\rho_{sample} = density\ of\ the\ samples\ at\ 5°C$$

$$V = volumes\ injected$$

$$purity_i = purity\ of\ component\ i$$

FID (Flame Ionization Detector) is used for methanol, methyl formate, methyl acetate and acetic acid. TCD (Thermal Conductivity Detector) is used for water and formic acid. The signal vs. retention time would be responded by GC Real Time Analysis. At each retention time of the species injected, peak area is chosen. The mass of each species is correlated to the peak area, then fitted to a second order polynomial, examples are shown in Figure 4.3.2 and Figure 4.3.3. The results would not be chosen if the deviation is great than 3%. The calibration should be repeated every four weeks to guarantee the accuracy.
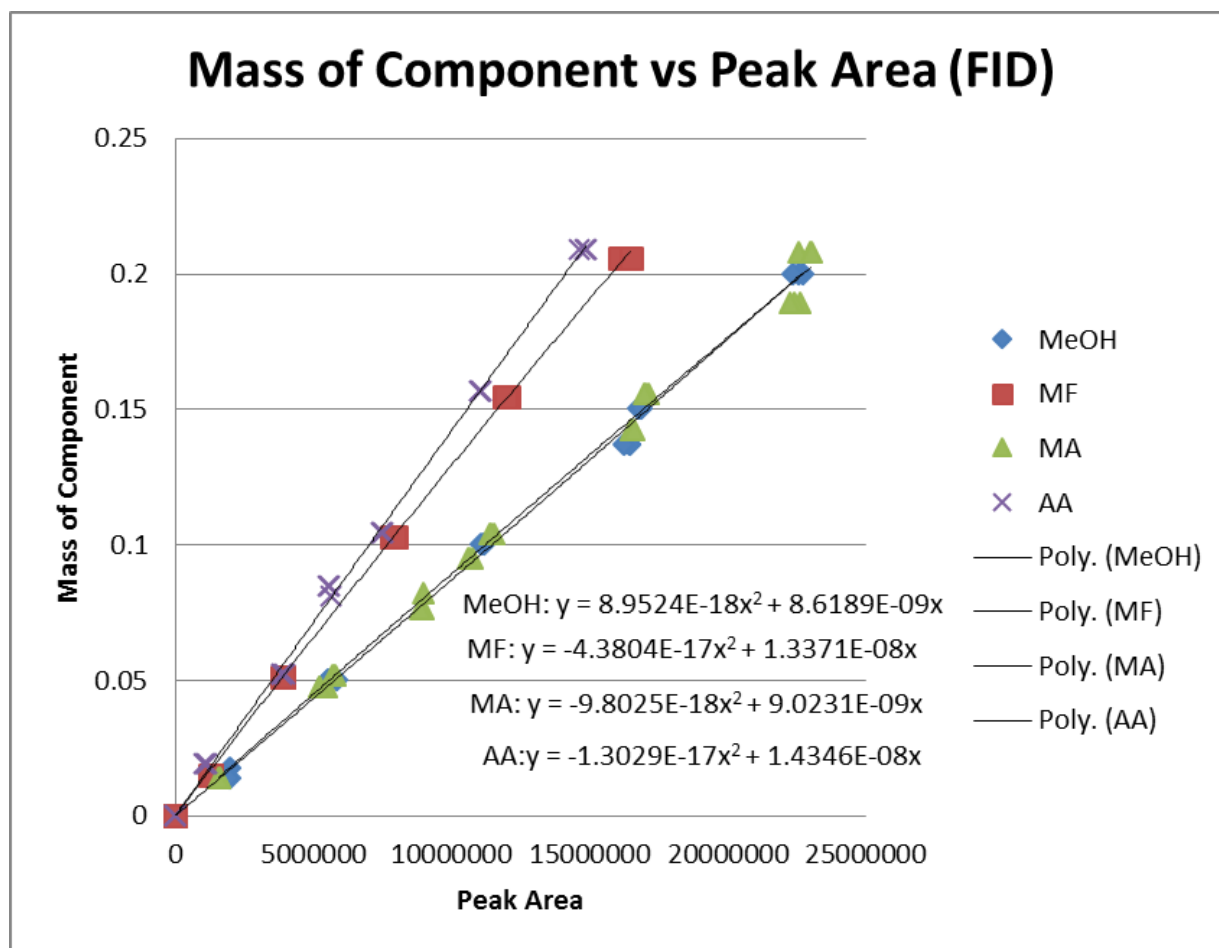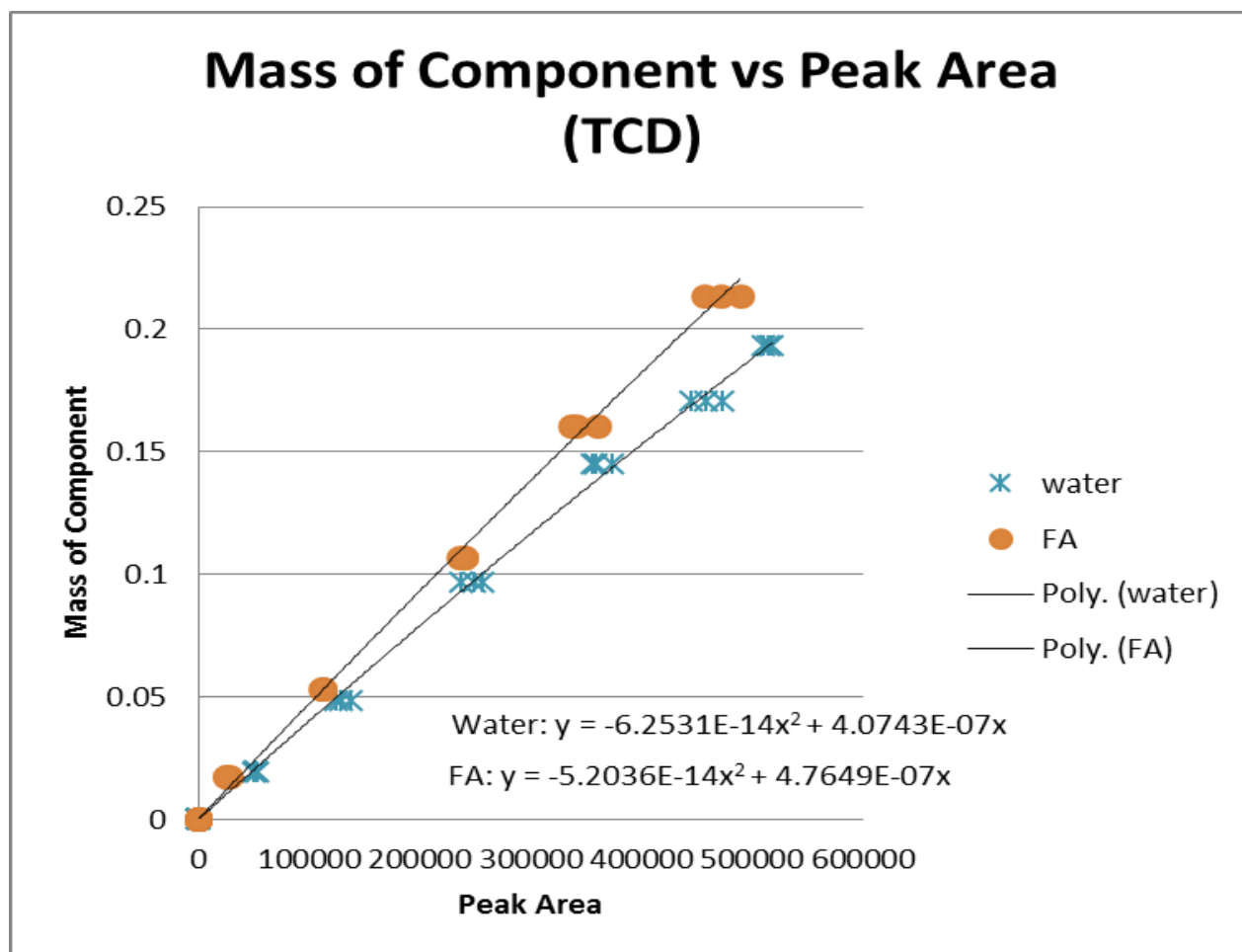
Figure 4.3.2 FID Calibration Curve, 07/28/2014

Mass of Component vs Peak Area (FID)

MeOH: y = 8.9524E-18x^2 + 8.6189E-09x

MF: y = -4.3804E-17x^2 + 1.3371E-08x

MA: y = -9.8025E-18x^2 + 9.0231E-09x

AA: y = -1.3029E-17x^2 + 1.4346E-08x

Figure 4.3.3 TCD calibration Curve, 07/28/2014

Mass of Component vs Peak Area (TCD)

Water: y = -6.2531E-14x² + 4.0743E-07x

FA: y = -5.2036E-14x² + 4.7649E-07x

Experiment Samples Analysis

All the samples would be injected into the GC at a volume of 0.3 μL, and the corresponded peak area would be chosen. Peak area would be applied to the calibration curve, and the mass of each component injected would be calculated. The mass of each component would be further transferred to molar concentration:

$$X_i = \frac{m_i/MW_i}{\frac{m_{AA}}{MW_{AA}} + \frac{m_{MeOH}}{MW_{MeOH}} + \frac{m_{MA}}{MW_{MA}} + \frac{m_{Water}}{MW_{water}}}$$

The molar concentration is plotted verse time, see 5. Result & Discussion.

5. Results & Discussion

5.1. Overview

Overall, the reaction rate of acetic acid and methanol esterification is observed under various temperatures and feed ratio. It shows that a higher temperature leads to a higher reaction rate. Besides, a different feed ratio would also affect, not as significantly as temperature, the reaction rate. Basically, 1:1 ratio of feed AA:MeOH is slightly slower than 1:0.65 ratio of feed AA:MeOH. Duration of 3 days is required for 1:1 ratio of the methyl acetate esterification to reach equilibrium at 60˚C, and at 40˚C, the duration is 34 days. [12] In this project, all the experiments are carried out around 6-8 hours, which is far from the equilibrium.

The detail result and discussion would be presented below. The first part discusses the temperature effect on methyl acetate esterification, while the second part discusses the concentration effect.

5.2. Temperature effects

The molar fraction of 1:1 ratio experiments at different temperature is plotted by component in Figure 4.2.1-4. The axis of graph is adjusted to the same scale, and the fluctuation can be explained by the accuracy of GC. The first two graphs are highly similar, which are the reactants. It can be seen that the reaction is uncompleted since the reactants are largely remained.

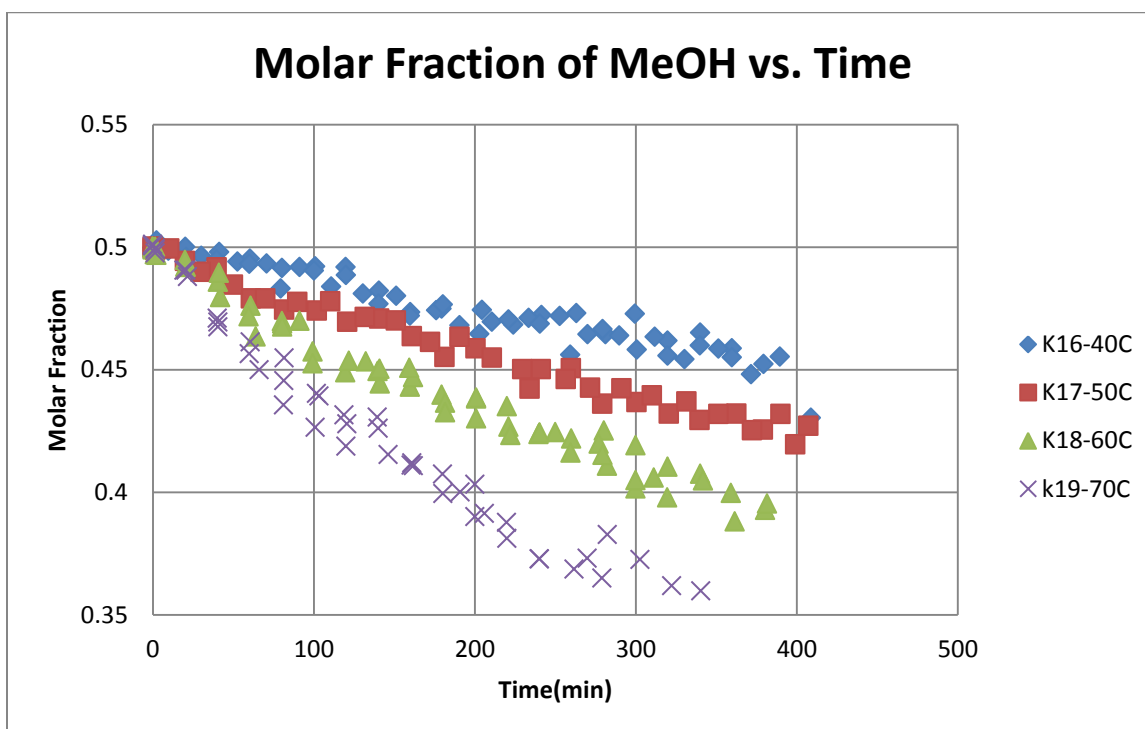Figure 4.2.1 Molar Fraction of MeOH vs. Time
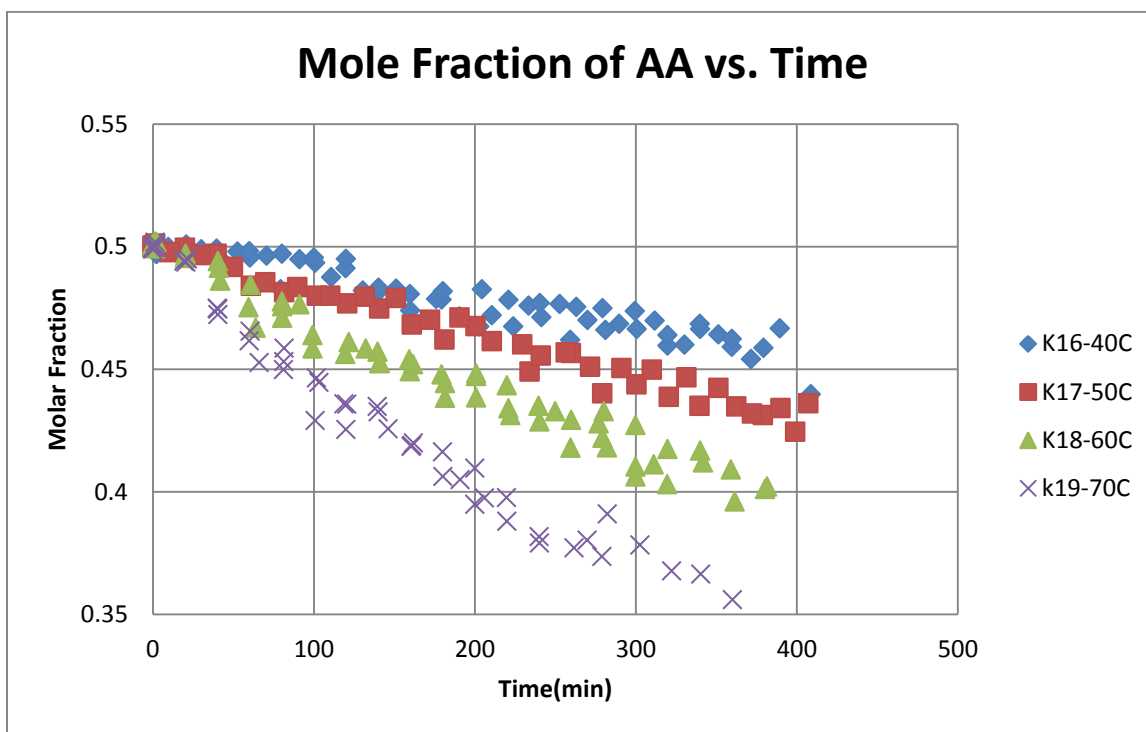
Figure 4.2.2 Mole Fraction of AA vs. Time

Figure 4.2.3 shows the molar fraction of water, where a large fluctuation is observed. The reason is the water cannot be detected by FID since it cannot be combusted, and TCD does not have a good accuracy for a small amount of water. Figure 4.2.4 is the product methyl acetate, which shows a clear trend. All of graphs are consist to some extents, therefore the figure of methyl acetate would be used to represent the whole reaction.
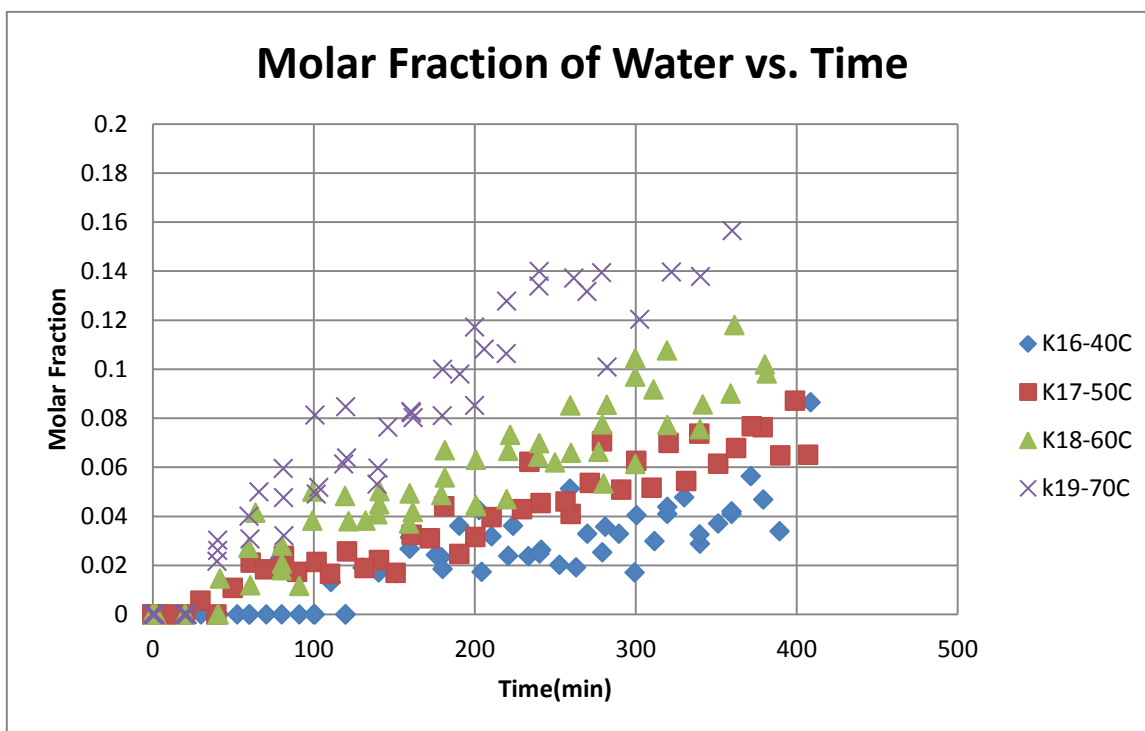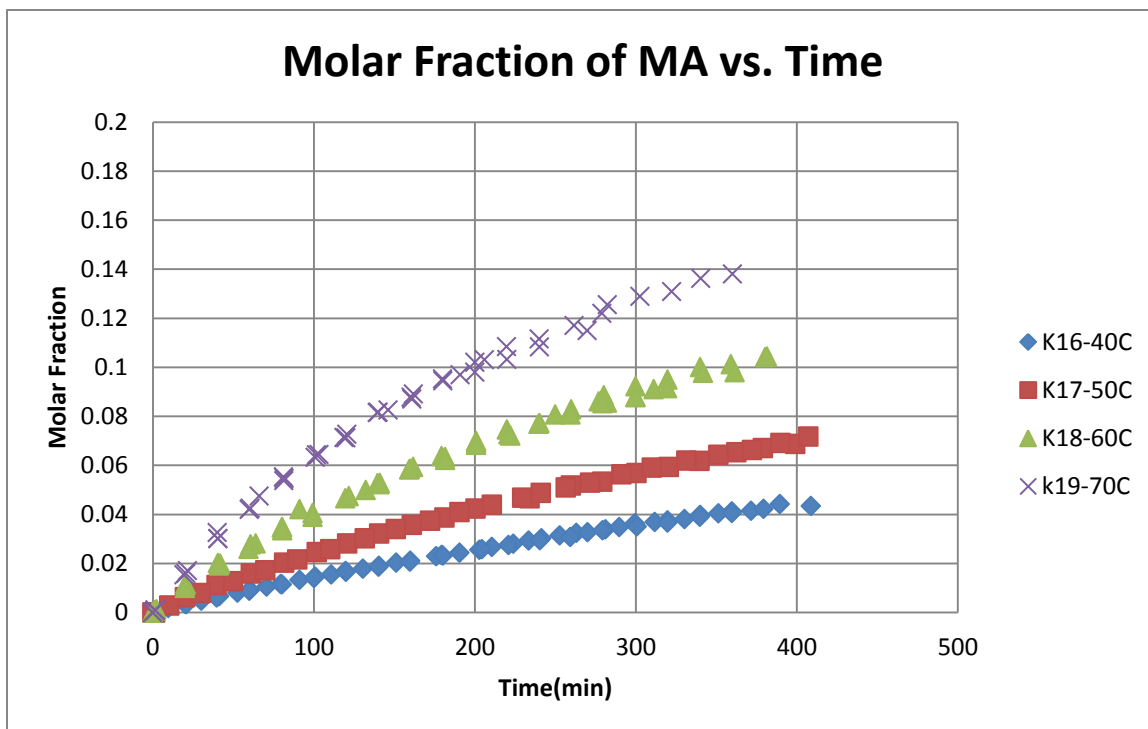
Figure 4.2.3 Molar Fraction of Water vs. Time

Molar Fraction of Water vs. Time

Legend: K16-40C, K17-50C, K18-60C, k19-70C

X-axis: Time(min); Y-axis: Molar Fraction

Figure 4.2.4 Molar Fraction of MA vs. Time

Molar Fraction of MA vs. Time

Legend: K16-40C, K17-50C, K18-60C, k19-70C

X-axis: Time(min); Y-axis: Molar Fraction

The temperature effects are significant in Figure 4.2.4 that the higher temperature, the more product would be produced at fixed time, or says the faster reaction goes. By around 400 minutes, a rise of 10 ˚C would result in a rise of 3-4% of methyl acetate produced.

The molar fraction of 1:0.65 ratio experiments at different temperature are plotted by component in Figure 4.2.5-8. Similarly, the axis is adjusted to the same scale as Figure 4.2.1-4, and there are fluctuations in both reactants and products.

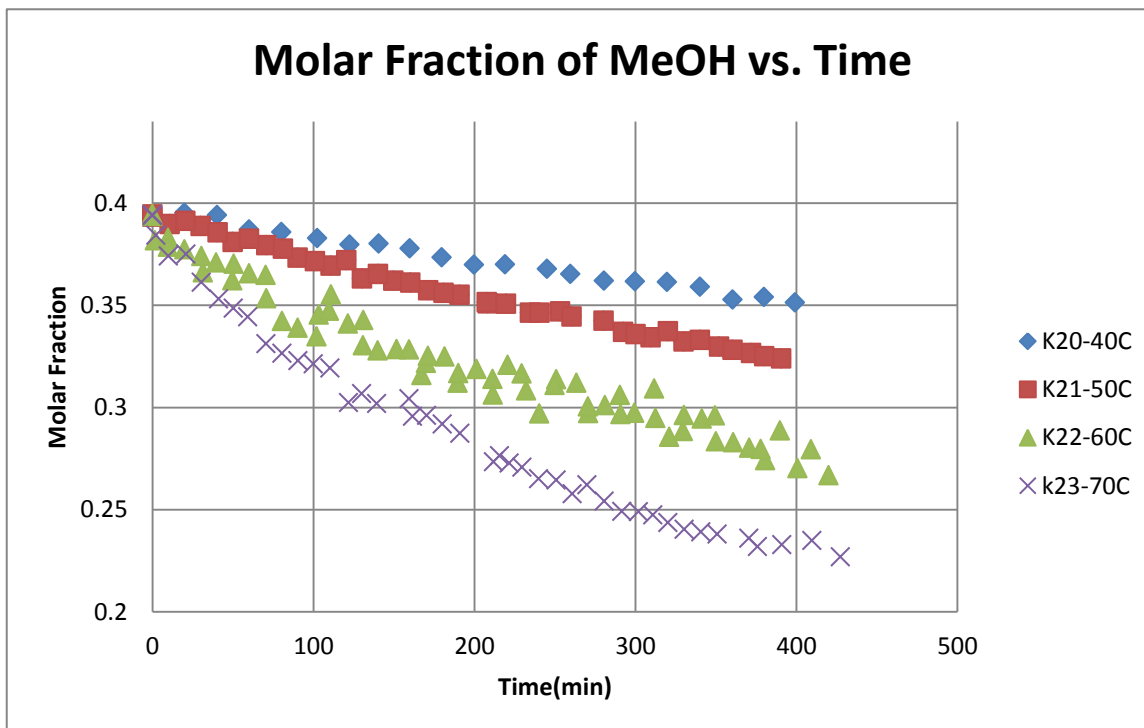Figure 4.2.5 Molar Fraction of MeOH vs. Time
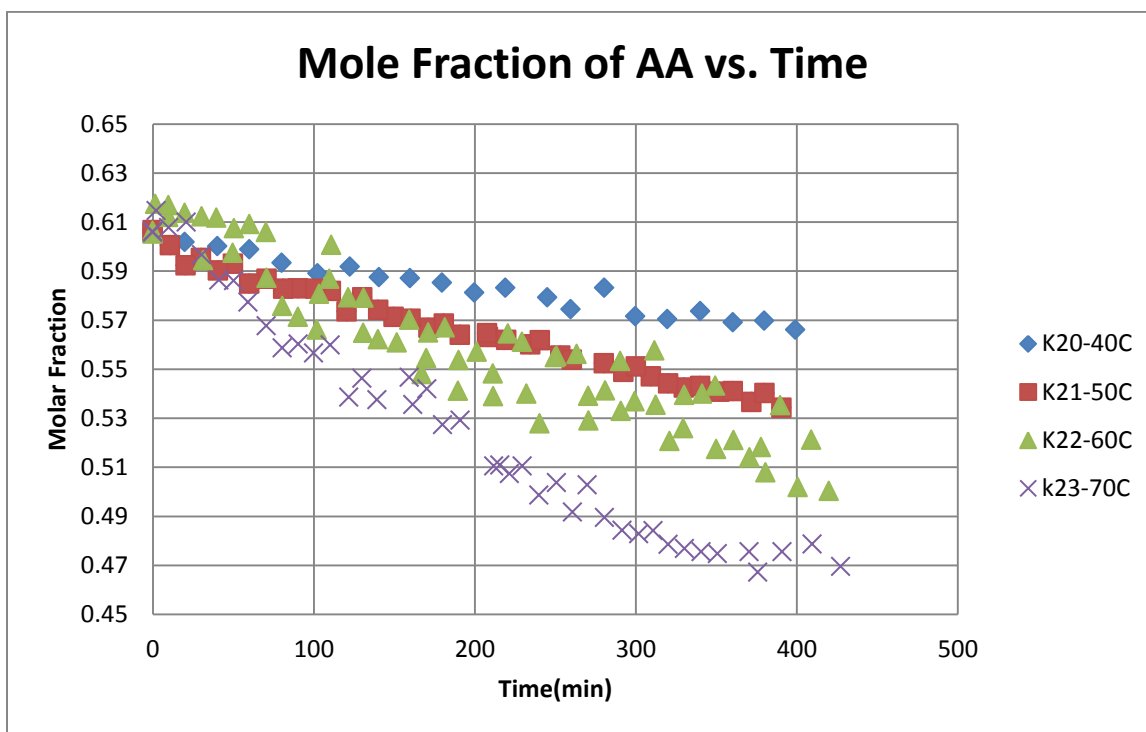
Figure 4.2.6 Mole Fraction of AA vs. Time

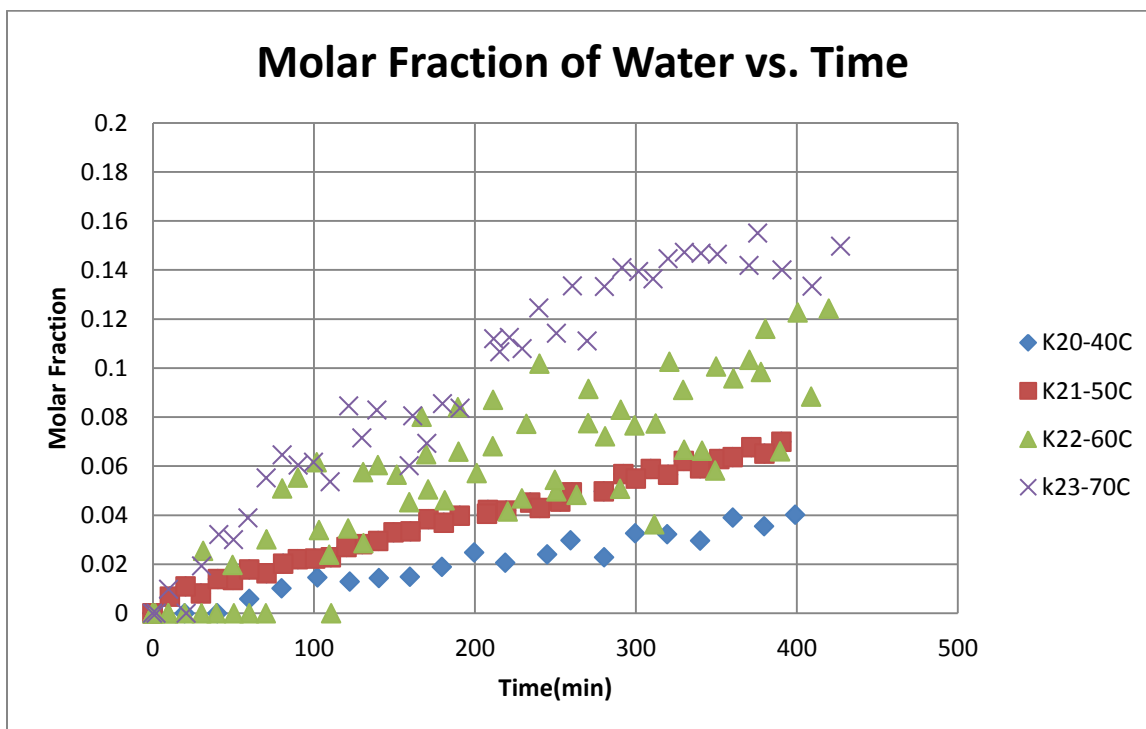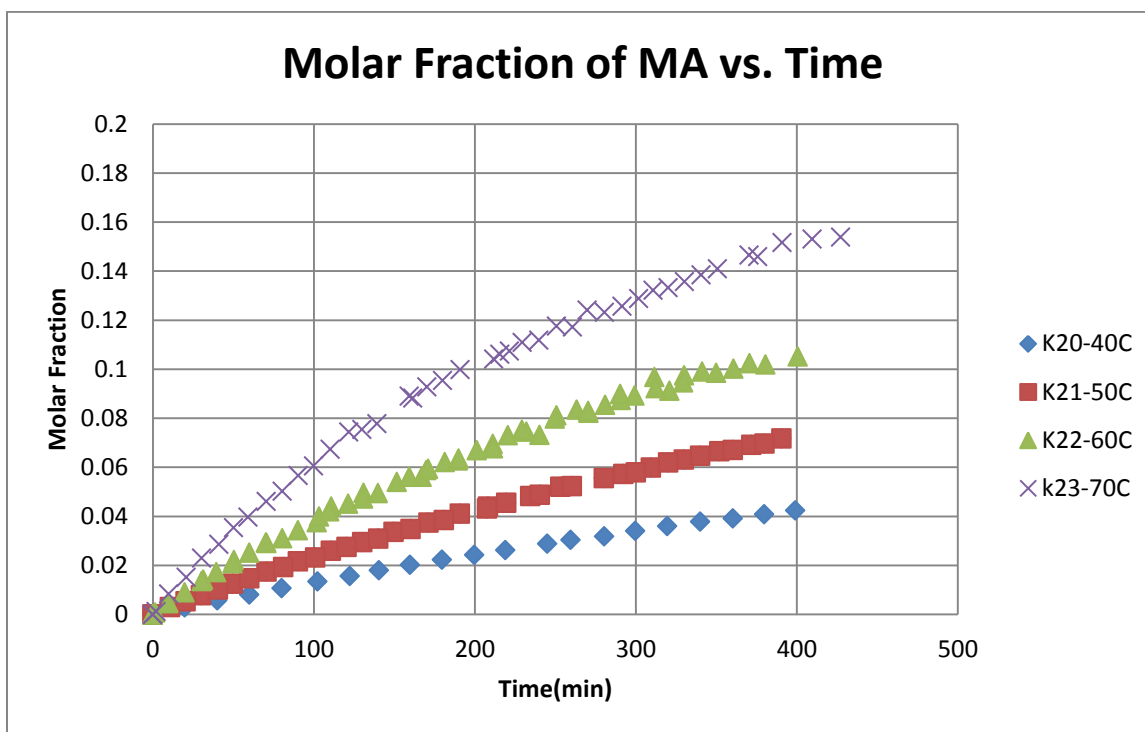Figure 4.2.7 Molar Fraction of Water vs. Time

Figure 4.2.8 Molar Fraction of MA vs. Time

3.3. Concentration effects

The molar fraction vs. reaction time of methyl acetate for each temperature is plotted in Figure 4.3.1-4. Due to the fluctuation, there is a unclear trend and a large amount of overlap at the first half of time period, therefore water is not selected for analysis. The reactants acetic acid and formic acid are not selected because the starting points are different.

Figure 4.3.1 Molar Fraction of MA vs. Time at 40 ˚C

Molar Fraction of MA vs. Time

Legend:
× K16-40C/1:1
◆ K20-40C/1:0.65

Axes: Molar Fraction (y) from 0 to 0.05; Time(min) (x) from 0 to 500

Figure 4.3.2 Molar Fraction of MA vs. Time at 50 ˚C

Molar Fraction of MA vs. Time

Legend:
■ K17-50C/1:1
● K21-50C/1:0.65

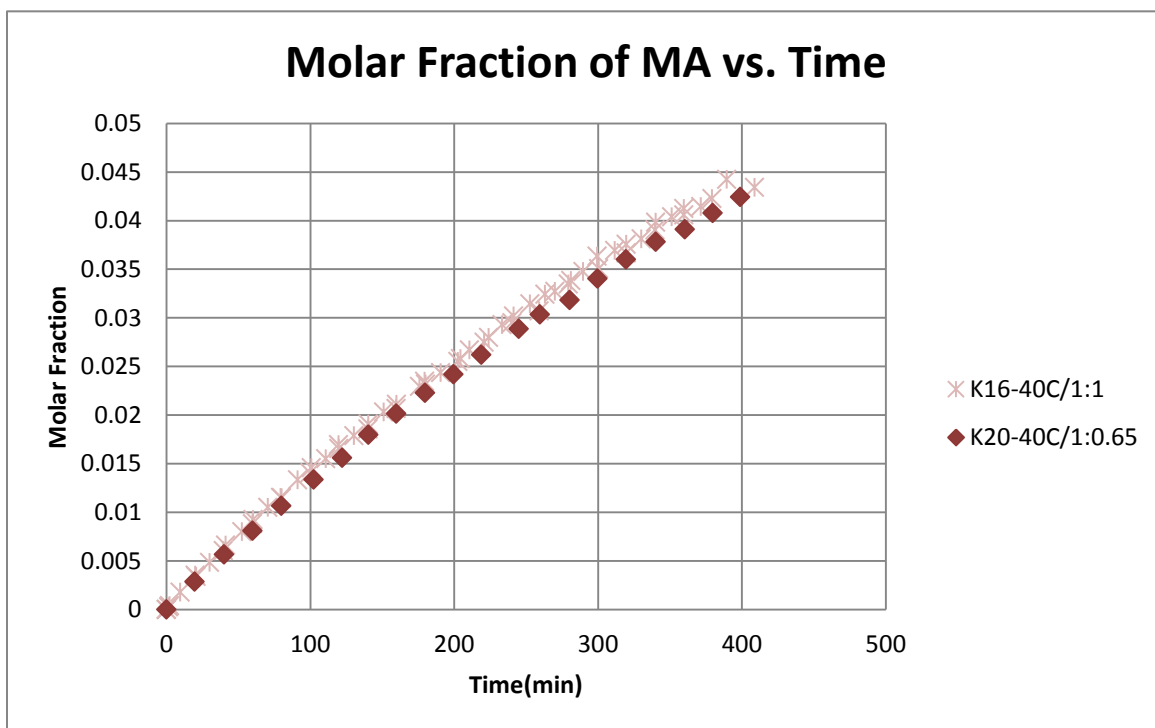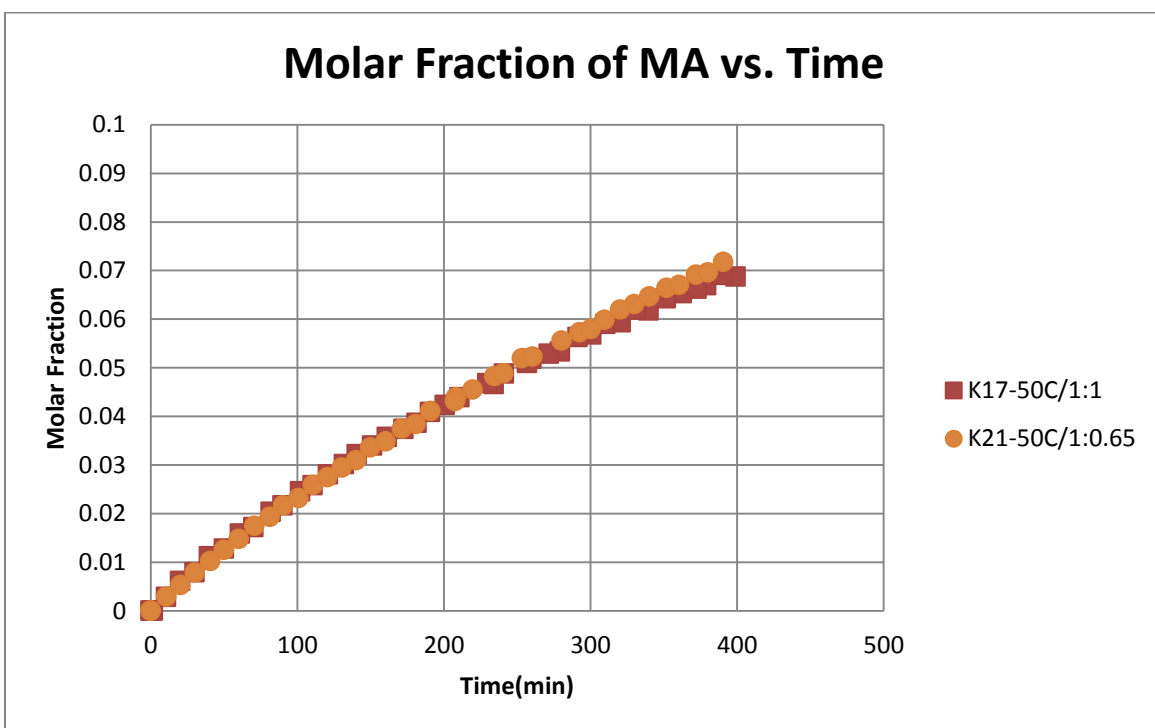Axes: Molar Fraction (y) from 0 to 0.1; Time(min) (x) from 0 to 500

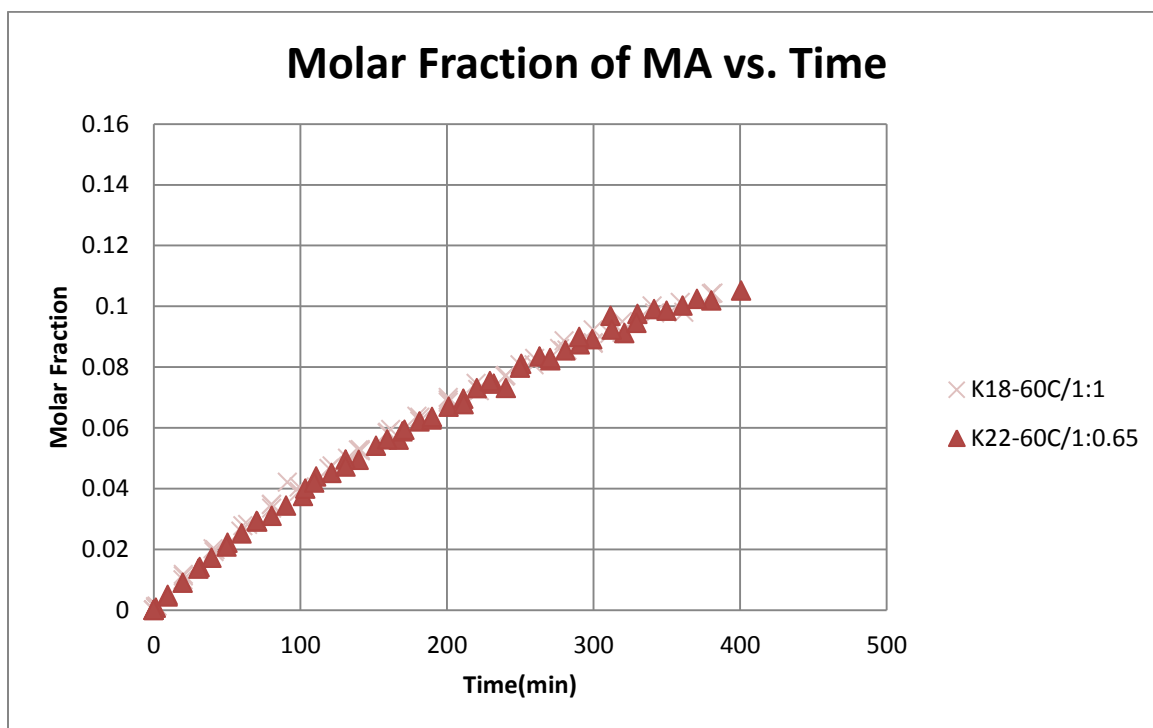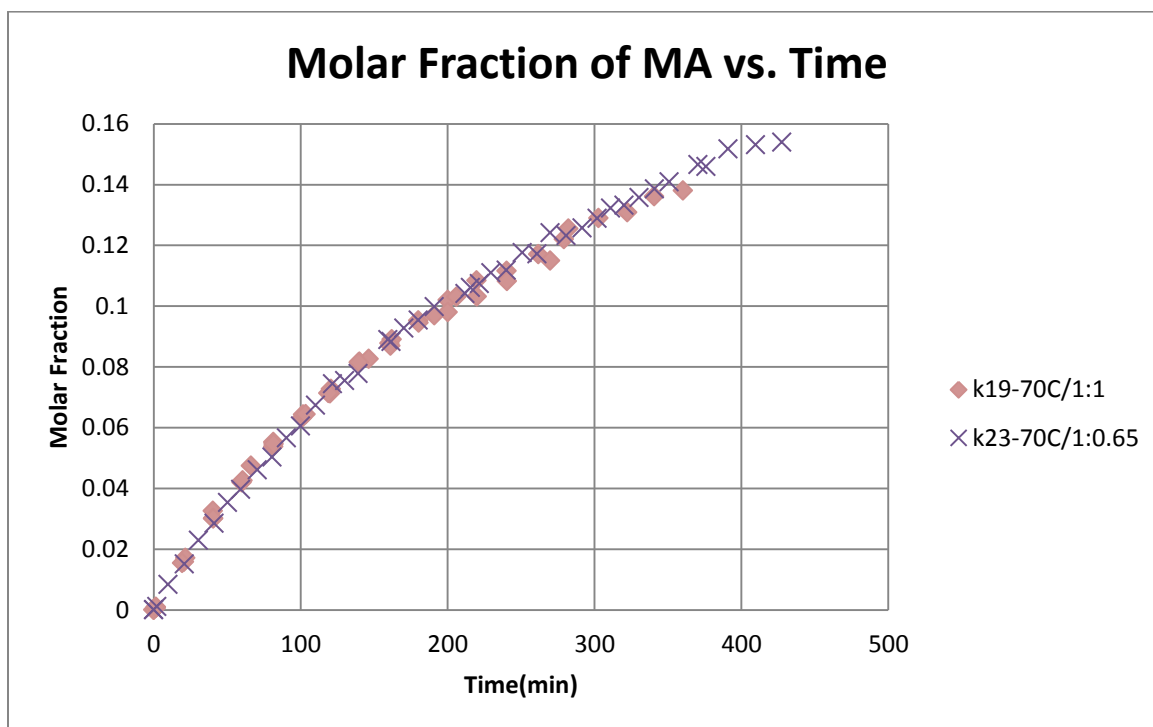Figure 4.3.2 Molar Fraction of MA vs. Time at 60 ˚C

Figure 4.3.2 Molar Fraction of MA vs. Time at 70 ˚C

The y axis is adjusted to represent the trend through the whole timeline while the scale of y axis is set to be as small as possible. Figure 4.3.1 may show that the reaction of 1 to 1 ratio outweighs the reaction of 1 to 0.65 ratio by a small amount at 40˚C. On the contrary, figure 4.3.2 may indicate that 1 to 0.65 ratio exceed 1 to 1 ratio after 250 minutes, which is also not remarkable. Overall, at the same temperature, all the trend lines are nearly overlap, therefore no significant concentration effects could be found the data. This matches results from the esterification of Acetic Acid with Isoamyl Alcohol, which also observed a non-remarkable concentration effect on the reaction rate. [8]

4. Error analysis

During the project, some factors may have influence on the experiments and results.

Processing and waiting time

There are two major factors that may impact the time accuracy. Firstly, it takes a few minutes to move the sample from reactor to GC vials, and then the sample in the GC vials would be cooled down by the ice surrounded. The reaction does not stop during this process. Nonetheless, time of moving samples is usually around 1 minute that the impact on the overall accuracy is limited. Secondly, the reaction does not stop even after being cooled down, therefore a long waiting time may result in inaccuracy. The ice could cool the samples to a temperature from 2 to 8 ˚C, and the GC stores the samples at 5 ˚C. The reaction would slowly go on at the low ambient temperature such that samples should immediately move to GC, and GC should also start immediately. For experiment K18-02, GC started to measure samples one hour after the first sample was taken. Besides, for the experiment K19-02, samples NO.11-13 were measured after NO. 14. Even though the result suggested a consistence, the processing time and waiting time should be minimized.

Calibration

The calibration requires a deviation of less than 3% for both TCD and FID, which is hard to achieve for small amount components. Thus, the calibrations in this project contain some data with larger deviation. Also, the density measurements and GC measurements for standards were not carried out at the same day. Although all standard solutions were sealed and stored in the refrigerator, error might occur.

Other factors

AT experiment K19-02, the cooling water for GC was not turning on. At experiment K21-01, the thermal conductivity detector yielded a result graph with large fluctuation, resulting in water could not be determined. The result of K21-01 was dropped.

6. Suggested Future Work

First of all, due to the time constraint, limited cases were studied during the 3 months project. All the experiments in this project were in the absence of formic acid. More experiments should be carried out under different compositions of the feed system consisted formic acid, acetic acid, methanol and water. A longer experiment may be carried out to reach the equilibrium. A mathematical kinetic model should further determined for the simultaneous esterification.

Besides, though the solutions of high purity for kinetic study promise a precise result, experiment should be conducted under more practical conditions. A real wastewater from pulp and paper industry is suggested. In Organosolv pulping process, solvents could include other components such as acetone, ethanol, butanol, ethylene glycol and a larger amount of water. [4] Resin acids and many other components would also be in the wastewater. [3] The real conditions could possibly provide a more complicated solution for reactive distillation, therefore experiments are suggested to be carried out under more complicated and practical conditions to determine there are any other possible effects.

Moreover, the reactive distillation should be further studied under both experimental conditions and practical conditions. Computational simulations are suggested to study for purpose of applying in industry.

7. Reference

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