An Analytical Comparison of Ethanolysis and Methanolysis Kinetics and the Refined Biodiesel Product

A Major Qualifying Project Submitted to the Faculty of WORCESTER POLYTECHNIC INSTITUTE in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science

Submitted to:

Professor William M. Clark, Advisor-CM, Worcester Polytechnic Institute
Professor Suzanne LePage, Advisor-CE, Worcester Polytechnic Institute

Prepared:

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Presented by:

Melissa Boule, CM
Hannah Gallagher, CM
Torin Zonfrelli, CM/EVE

Abstract

The purpose of this Major Qualifying Project was to determine the viability of replacing the methanolysis Unit Operations II Laboratory experiment with a similar, yet safer, ethanolysis experiment. Furthermore, the heating value and emissions profile of biodiesel from ethanolysis and methanolysis were compared to petroleum diesel to gain more knowledge on the implications of biodiesel. This was done by modifying the existing methodology to utilize ethanol, maintaining a 6:1 molar ratio of alcohol to oil and 0.5 wt% potassium hydroxide catalyst. Methyl-biodiesel and ethyl-biodiesel were refined through a multi-step process and burned in a combustion unit to analyze the emissions concentrations and heating values.

For methanolysis, rate constants were determined, from which an activation energy of 59.9 kJ/mol was calculated. For ethanolysis, rate constants were determined, from which an activation energy of 49.6 kJ/mol was calculated. Both calculated activation energies fell within the ranges provided by literature for the respective transesterification reactions. Additionally, both reaction curves followed the patterns predicted by literature.

On a per mass basis, refined ethyl-biodiesel and refined methyl-biodiesel contained 95% and 94% of the heating value of petroleum diesel, respectively. From an emissions standpoint, both methyl- and ethyl-biodiesels have significantly lower emissions concentrations than petroleum diesel. Furthermore, ethyl-biodiesel has additional emissions benefits over methyl-biodiesel.

From the successful kinetics study using ethanolysis, and the added safety benefits, it was concluded that ethanol is a viable replacement for methanol in the Unit Operations biodiesel experiment. Due to the preliminary indications of its higher heating value and less hazardous emissions compared to methyl-biodiesel, ethyl-biodiesel was recommended to be phased into the biodiesel market.

Executive Summary

Introduction

Considering approximately 75% of human-induced carbon dioxide emissions in the past 20 years are due to fossil fuel combustion, it is clear that people need to reduce their consumption and shift their reliance to resources that are both renewable and less impactful on the environment [1]. The world uses fossils fuels for an average of 71% of our total energy consumption, and combustible renewable sources, such as ethanol and biodiesel, for an average of 20%. However, developed countries like the United States tend to use more fossil fuels (84%) and fewer renewable combustibles (4%) than underdeveloped countries [2], [3]. Biodiesel is a renewable resource that is currently more expensive than diesel, but could significantly decrease the amount of carbon dioxide emissions in the world.

Goals and Objectives

The purpose of this Major Qualifying Project was to determine the viability of replacing the methanolysis Unit Operations II experiment with a similar, yet safer, ethanolysis experiment. Furthermore, the heating value and emissions profile of biodiesel from ethanolysis and methanolysis were studied to gain more knowledge on the implications of biodiesel fuel.

These purposes were achieved by executing the following objectives:

- Compare the experimental data for the kinetics of base-catalyzed transesterification with methanol and ethanol
- Determine if the existing Unit Operations methodology can be applied to ethanolysis
- Update the Unit Operations pre-laboratory exercise as necessary
- Compare the heating value of diesel, and biodiesel from methanolysis and ethanolysis
- Determine which biodiesel emissions would be less hazardous for the environment

Methodology

Alcohol, both methanol and ethanol, and canola oil were reacted in a jacketed glass vessel in a 6:1 alcohol to oil ratio with 0.5 wt% (oil-based) KOH catalyst. Reactor Master (Syrris) software was used to automatically control the reaction and provide a digital log of the experiment. Samples were taken at predetermined time intervals and analyzed at the completion of the 40 minute reaction period. The samples were analyzed using a glycerol enzyme assay and colorimetric plate reader. Monitoring the production of glycerol allowed for the study of the reaction kinetics and determination of the rate constants at various temperatures, and therefore the overall activation energy as defined by the Arrhenius equation.

Both ethyl- and methyl-biodiesel were refined and combusted. The biodiesel product was de-alcoholized in a rotary evaporator, separated from the triglycerides in a separatory funnel, and run through a resin column packed with sodium polystyrene sulphonate to remove impurities. Petroleum diesel, refined methyl-biodiesel, and refined ethyl-biodiesel were combusted. The heating values and emissions were evaluated using a flue gas analyzer, a combustion heater, and a heat exchanger.

Results and Discussion

Transesterification

The averaged methanolysis data followed the predicted "S"-shaped curve, indicating initial mass transfer limitations. It was also confirmed that the methanolysis reaction is kinetically favorable at higher temperatures in that it proceeds faster, producing more glycerol in early time periods.

The rate constants for the methanolysis reaction were determined and the activation energy was calculated to be 59.9 kJ/mol, which agrees with the literature values of 26.8-61.5 kJ/mol for methanolysis at various operating parameters.

The average ethanolysis data followed the predicted curve of an immediate increase in glycerol concentration followed by a plateau. This shape is indicative of little to no mass transfer limitations. Furthermore, it was confirmed that the ethanolysis reaction is also kinetically favorable at higher temperatures. The increase in reaction rate with temperature is not as large with ethanolysis as with methanolysis, but it is still present and can be observed.

The rate constants for the ethanolysis reaction were determined and the activation energy was calculated to be 49.6 kJ/mol, which agrees with the literature values of 3.4-51 kJ/mol for ethanolysis reactions at various operating parameters.

Heating Value and Emissions

The heating values of refined methyl-biodiesel and refined ethyl-biodiesel were compared to the current market standard of petroleum diesel. On a per mass basis, refined ethyl-biodiesel contained 95% of the heating value of petroleum diesel and refined methyl-biodiesel contained 94% of the heating value of petroleum diesel. Not only did ethyl-biodiesel have a higher heating value than methyl-biodiesel, but it also had 59%, 34%, and 35% less carbon monoxide, nitrogen monoxide, and nitrogen oxides, respectively, compared to methyl-biodiesel's 55%, 19%, and 20%.

Conclusions and Recommendations

It was determined that the kinetics of ethanolysis are similar to those of methanolysis, but without mass transfer limitations, which agreed with literature. The Unit Operations methodology allowed for the successful study of the kinetics of ethanolysis as well. It was therefore recommended to utilize ethanol instead of methanol as the alcohol agent in the transesterification Unit Operations experiment due to its less hazardous nature. The Unit Operations pre-laboratory exercise was updated for utilizing ethanol instead of methanol, as well as to provide clarity on experimental objectives. It was also recommended that ethyl-biodiesel be phased into the biodiesel market as an alternative to methyl-biodiesel due to the preliminary indications of its higher heating value and less hazardous emissions.

Acknowledgements

This project could not have been completed without the support from various individuals. We would like to express gratitude to our advisors Professor Don Clark and Professor Suzanne LePage for their continued guidance and support throughout the course of the project. We would also like to thank Worcester Polytechnic Institute for giving us the opportunity to conduct this research, specifically the Chemical Engineering Department for allowing us to use the Unit Operations Laboratory.

Table of Authorship

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1. Introduction

The change in the global climate has been described as being caused primarily by human actions, specifically exponential population growth and overconsumption of natural resources such as fossil fuels [4]. Carbon dioxide concentrations have increased by over 30% since pre-industrial times, with half of this increase since 1965, and the global mean surface temperatures have increased 0.6°C since the late 19th Century (0.2-0.3°C over the past 40 years) [5]. Considering approximately 75% of human-induced carbon dioxide emissions in the past 20 years are due to fossil fuel combustion, it is clear that people need to reduce their consumption and shift their reliance to resources that are both renewable and less impactful on the environment [1]. One such alternative fuel is biodiesel, the consumption of which has increased over 400% since 2010 [6]. Experience with renewable fuels like biodiesel can educate current and future engineering students of their environmental benefits, which may further increase consumption in the future.

The Chemical Engineering and Environmental Engineering Departments at Worcester Polytechnic Institute are accredited by the Accreditation Board for Engineering and Technology, Inc., or ABET. ABET is a non-governmental organization recognized by the Council for Higher Education Accreditation that accredits college and university programs in the disciplines of applied science, computing, engineering, and engineering technology [7]. The WPI Chemical Engineering and Environmental Engineering curricula have defined student outcomes to meet ABET accreditation, including:

- an ability to design and conduct experiments, as well as to analyze and interpret data
- an ability to design a system, component, or process to meet desired needs within realistic constraints such as economic, environmental, social, political, ethical, health and safety, manufacturability, and sustainability
- an ability to use the techniques, skills, and modern engineering tools necessary for engineering practice

The Unit Operations course is a senior-level laboratory practicum in the Chemical Engineering curriculum. The purpose of the Unit Operations class is to apply engineering principles of fundamental chemical engineering theories. Laboratory experiments require practical knowledge of key topics such as fluid mechanics and heat and mass transfer, as well as provide students with an introduction to industrial equipment like packed towers, reactors, and evaporators. The experiments are furthermore designed to meet ABET student outcomes.

One existing Unit Operations experiment is the transesterification of canola oil to produce biodiesel using methanol and a potassium hydroxide catalyst. The reaction kinetics are studied throughout the process to analyze the effects of temperature and determine the activation energy of the reaction. This Major Qualifying Project researches modifying this experiment to utilize ethanol instead of methanol as a significantly less hazardous material. Additionally, there is a Unit Operations experiment being developed that uses a combustion unit and flue gas analyzer to measure the heating content and emissions concentrations of a fuel source. This Major Qualifying Project utilizes this equipment to analyze the environmental implications of biodiesel, while providing additional information to the experiment development team.

Section 2 discusses the history of biodiesel, the safety benefits of ethanol, the details of transesterification and the Unit Operations Experiment, and the effects of biodiesel combustion. Section 3 outlines the methods by which we achieved our goals regarding transesterification and emissions research. Sections 4 and 5 provide the results and conclusions of our research.

2. Background

2.1 History of Biodiesel

The first achievement in the development of biodiesel and the diesel engine was the establishment of the transesterification reaction. E. Duffy and J. Patrick conducted transesterification in 1853 [8], [9]. Transesterification is the process of converting vegetable oils or animal fats into monoalkyl esters, or biodiesel [8]. However, the inception of the diesel engine began four decades later when Dr. Rudolph Diesel published "The Theory and Construction of a Rational Heat Engine" [8], [10]. Dr. Diesel applied Sadi Carnot's theory of compression ratios to the internal combustion engine, and his compression-ignition engine was patented in 1893 and first demonstrated in 1897 [8].

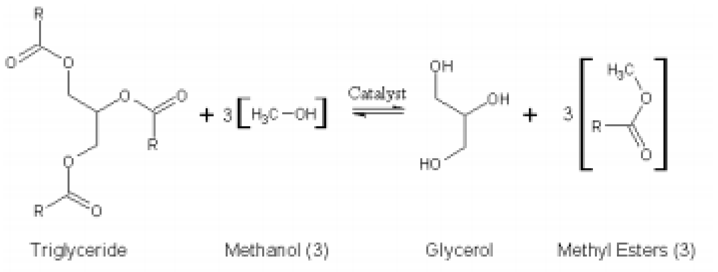
This engine was innovative because it could utilize a variety of fuels, ranging from coal dust to kerosene. This versatility allowed the application of vegetable oils, which were found to have high energy content, and therefore make excellent fuels. This application led to France commissioning the Otto Company to use peanut oil in a diesel engine at the 1900 World's Fair in a hope to enable a domestic fuel made from vegetable oils for African Colonies. Dr. Diesel realized that vegetable oils could also be utilized as a fuel that farmers could produce themselves, and devoted much of his time into researching vegetable oil fuels. At the 1911 World's Fair in Paris, Dr. Diesel demonstrated his diesel engine using peanut oil, stating, "the diesel engine can be fed with vegetable oils and will help considerably in the development of the agriculture of the countries which use it" [8]. However, shortly after Dr. Diesel's death in 1913, petroleum became widely available in multiple forms, including today's modern diesel fuel. Petroleum-based diesel fuel soon became the standard because it was so widely available and affordable, which led to biodiesel falling out of favor. The diesel engine was adapted for the combustion of petroleum-based diesel, essentially eliminating the use of other fuels.

Fuel shortages, and the Second World War, led to price spikes in petroleum products, which temporarily renewed interest in vegetable oils over diesel fuels. However, because the diesel engine had been changed to suit petroleum-based diesel, vegetable oils were too viscous to be used. This sparked research into making vegetable oils less viscous. In 1937, G. Chavanne obtained a patent for using transesterification to transform vegetable oils into a usable biodiesel fuel. This process established by G. Chavanne is what is now used for today's modern biodiesel.

It wasn't until the 1980s that the use of vegetable oils as an alternative fuel to petroleum was proposed. Vegetable oils are advantageous due to their portability, ready availability, renewability, higher heat content, lower sulfur content, lower aromatic content, and biodegradability. Despite this, commercial production did not begin until the late 1990s [8]. In recent years, there has been growing concern with petroleum-based diesel's lack of sustainability and harmful emissions. This has led to a renewed interest in biodiesel because it can be produced sustainably and it possesses a "clean emissions profile"; however, biodiesel has not yet been implemented on a large scale.

2.2 Transesterification

Biodiesel can be produced in a variety of ways, including blending, microemulsions, pyrolysis, and transesterification. Transesterification is currently the most utilized method of producing biodiesel [11]. Also known as alcoholysis, transesterification is the displacement of alcohol from an ester by another alcohol. When methanol is used as the displacing alcohol, the transesterification reaction is called methanolysis, as pictured below:



$$\text{TG (or O)} + 3\text{ M} \rightleftarrows \text{G} + 3\text{ BD}$$

Figure 2-1: Overall Transesterification Reaction with Methanol

The fatty acid esters, in this case methyl esters, are the biodiesel product. A strong acid or base catalyst is needed to accelerate the reaction [12].

Transesterification is used to convert renewable feedstocks such as vegetable oils or animal fats into shorter monoalkyl esters like methyl esters that have properties more similar to those of diesel fuels; this process reduces the molecular weight by a factor of three, reduces the viscosity by a factor of eight approximately, and increases the volatility marginally [13].

As mentioned above, methanol is the most commonly used alcohol for transesterification due to its low cost, availability, and suitable physical and chemical properties [14], [15]. It is, however, extremely toxic and has various safety concerns, further discussed in Section 2.2.6 Safety. As methanolysis has been the primary pathway for transesterification, it has been extensively studied, and there are various papers that discuss the kinetics of the reaction [16].

The use of ethanol in transesterification is increasing for various reasons. Ethanol has higher solubility for vegetable oils than methanol and is less toxic [14], [15]. Ethanol is also renewable as it primarily comes from biomass. Producing ethyl esters rather than methyl esters also improves the renewability of biodiesel as an entirely agricultural fuel, as well as slightly increasing the heat content and cetane number due to the extra carbon atom, and lowering the cloud and pour points which improves cold starts [14], [17]. However, the separation of ethyl esters and glycerol is more difficult than with methyl esters [12]. One of the largest concerns with using ethanol for transesterification is the formation of emulsions. Emulsions form in all transesterification reactions due to the formation of monoglyceride and diglyceride intermediates, which have both polar and nonpolar components. In the case of methanol, emulsions quickly dissipate to form a glycerol rich lower layer and methyl ester rich upper layer. In the case of ethanol, emulsions are more stable due to the larger non-polar group, and thus complicate the separation and purification of esters. However, if the concentration of monoglyceride and diglyceride intermediates are low enough, then the emulsions become unstable as with methanolysis [12]. It is therefore very important that ethanolysis reactions go to near completion so as to minimize the intermediate concentrations.

The transesterification reaction is affected by various variables, including catalyst, temperature, molar ratio of alcohol, and mass transfer.

2.2.1 Catalyst

As mentioned above, a strong acid or base catalyst is needed in the transesterification reaction to accelerate the conversion of triglycerides. Alkaline metal alkoxides and hydroxides are the most effective catalysts, but sodium and potassium hydroxide are frequently used because they are lower in cost and easier to handle [14], [17]. An alkaline catalyst concentration from 0.5-1 wt% yields 94-99% conversion of vegetable oil into esters. Furthermore, an alkali-catalyzed reaction proceeds approximately 4000 times faster than an equal acid-catalyzed reaction, and alkaline catalysts are less corrosive to equipment [13], [18]. However, the base catalyzed reaction is very sensitive to the free fatty acid (FFA) content and research suggests that a FFA content over 3% requires an acid catalyst [12], [17].

2.2.2 Temperature

The rate of the transesterification reaction is strongly influenced by temperature, but will proceed at room temperature [13], [17]. This is indicated by Figure 2-2 below, which demonstrates the temperature dependence of transesterification of sunflower oil with ethanol [14]. The highest yields of esters occurs near the boiling point of the alcohol used (in this case, near the boiling point of ethanol, 78°C).

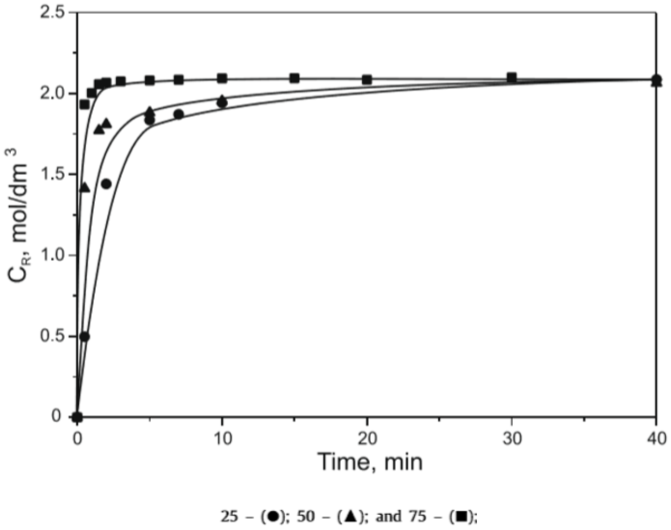


Figure 2-2: Temperature Dependence of Transesterification

2.2.3 Molar Ratio

Figure 2-2 above was determined using a 6:1 molar ratio of alcohol to oil. It is more favorable to shift the transesterification reaction to the right for higher ester yield, and this is achieved primarily by increasing the alcohol to oil ratio. A molar ratio of 6:1 is suggested for maximum conversion, but other literature suggests up to a 9:1 ratio depending on oil and alcohol type [12], [17]. While increasing the molar ratio shifts equilibrium to the right, too large of a molar ratio interferes with the separation of products because there is an increase in glycerol solubility in the alcohol [17].

2.2.4 Mass Transfer Limitations

Both methanol and ethanol are not miscible with triglycerides at ambient temperature, so the mixture is stirred to improve mass transfer and initiate the transesterification reaction. Monoglycerides and diglycerides are miscible with methanol and ethanol, so once the reaction proceeds to the right and a single phase is established, mixing becomes relatively insignificant [13]. These mass transfer limitations can be observed in a plot of methyl ester concentration over time. There is an initial mass transfer controlled region before the reaction kinetics dominate and give way to an equilibrium period. The initial mass transfer controlled region is not observed in production of ethyl esters. Despite this, ethanolysis reactions are still mechanically agitated to ensure proper mass transfer and to encourage representative sampling [14].

2.2.5 Kinetics

The kinetics of the transesterification reaction has been modeled multiple times using various methods, oils, and catalysts at varying concentrations of each. Different research has suggested multiple mechanisms, but in general, second order kinetics for all three reversible reactions provided a satisfactory mechanism [19]. Marjanovic et al suggested irreversible pseudo second order during the initial period and reverse second order close to equilibrium. Richard et al found that a pseudo second order model was more compatible with the ethanolysis of base-catalyzed sunflower oil than first order kinetics. Vicente et al also agrees that the base-catalyzed methanolysis of sunflower oil follows a pseudo second order kinetic model. Other research, however, found transesterification reactions following pseudo first order kinetics, pseudo second order kinetics, and combinations of second order consecutive and fourth order shunt reactions [16]. Some of this research is described in more detail in Table 2-1.

From the overall reaction pictured in Figure 2-1, the proposed transesterification mechanism is:

$$TG + M \leftrightarrow BD + DG \qquad (1)$$
$$DG + M \leftrightarrow BD + MG \qquad (2)$$

$$\mathrm{MG} + \mathrm{M} \leftrightarrow \mathrm{BD} + \mathrm{G} \qquad (3)$$

Modeling the reversible reactions further results in:

$$\begin{gathered}
TG'(t) = -k1\cdot TG(t)\cdot M(t) + k2\cdot BD(t)\cdot DG(t) \\
DG'(t) = k1\cdot TG(t)\cdot M(t) - k2\cdot BD(t)\cdot DG(t) - k3\cdot DG(t)\cdot M(t) + k4\cdot BD(t)\cdot MG(t) \\
MG'(t) = k3\cdot DG(t)\cdot M(t) - k4\cdot BD(t)\cdot MG(t) - k5\cdot MG(t)\cdot M(t)) + k_6\cdot BD(t)\cdot G(t) \\
M'(t) = -k1\cdot TG(t)\cdot M(t) + k2BD(t)\cdot DG(t) - k3\cdot DG(t)\cdot M(t) + k4\cdot BD(t)\cdot MG(t) - k5\cdot MG(t)\cdot M(t)+k6\cdot BD(t)\cdot G(t) \\
BD'(t)= k1\cdot TG(t)\cdot M(t) - k2\cdot BD(t)\cdot DG(t) + k3\cdot DG(t)\cdot M(t) - k4\cdot BD(t)\cdot MG(t) + k5\cdot MG(t)\cdot M(t) - k6\cdot BD(t)\cdot G(t) \\
G'(t) = k5\cdot MG(t)\cdot M(t) - k6\cdot BD(t)\cdot G(t)
\end{gathered}$$

Vicente et. al studied the base-catalyzed methanolysis reaction of sunflower oil and developed a mathematical model that defines the forward and reverse reactions outlined in the equations above. The model was able to determine the individual rate constants at varying operating conditions.

With a working mechanism, the Arrhenius equation is studied as follows:

$$k = Ae^{-E_A/RT}$$

Where k is the rate constant, A is the pre-exponential factor, E_A is the activation energy, R is the gas constant, and T is the absolute temperature in Kelvin. Rearranged:

$$\ln(k) = \ln(A) - \frac{E_A}{R}\left(\frac{1}{T}\right)$$

From this analysis, the activation energy is determined. Table 2-1 below summarizes the results of various transesterification research. An extended version can be found in Appendix A.

Table 2-1: Compilation of Transesterification Kinetic Research

Oil	**Alcohol**	**Catalyst (wt%)**	**Alcohol Ratio**	**Temperature (°C)**	**Kinetic Model**	**E_A**	**Source**
Palm	Methanol	KOH 1.0	6:1	55-65	3 consecutive second order reactions	26.8-61.5	[14]
Sunflower	Methanol	KOH 0.5-1.5	6:1	25-65	three second order reactions	31.0-59.6	[16]
Sunflower	Methanol	KOH 1.0	6:1	10-30	overall irreversible second order, reversible second order in final phase	33.2-53.5	[14]
Sunflower	Ethanol	NaOH 0.75,1.00,1.25	6:1, 9:1, 12:1	25-75	overall irreversible second order, reversible second order in final phase	3.4-43.9	[14]
Sunflower	Ethanol	1.0 EtONa	6:1	30-60	pseudo second order	51	[20]
Palm	Ethanol	1.0 EtONa			irreversible second order	42	[15]

2.2.6 Safety

Both ethanol and methanol are hazardous as an eye and skin irritant as well as when ingested and inhaled; they are also flammable and have similar flash points. Potassium hydroxide is very hazardous in case of skin contact, eye contact, ingestion, and inhalation. In order to protect equipment and operators, personal protective equipment (PPE) such as gloves and safety glasses should be worn at all times. Further, the process should be vented to reduce the chance of inhalation exposure.

While ethanol and methanol both exhibit toxic properties, those of ethanol are significantly less dangerous to human health than methanol. The Emergency Response Planning Guidelines (ERPG) and Acute Exposure Guideline Levels (AEGL) were compared in Table 2-2 below, and are measured in parts per million in air. Level 1 indicates 60 minutes of exposure with no irreversible serious health impacts. Level 2 indicates 60 minutes of exposure with recoverable health impacts and reversible bodily harm. Level 3 indicates 60 minutes of exposure that can cause life threatening or fatal health impacts. Table 2-2 indicates that it requires nearly three times the exposure to ethanol than methanol for Level 1 impacts.

Table 2-2: Toxicity of Ethanol and Methanol

ERPG/AEGL Level	Methanol	Ethanol
1	530 ppm	1800 ppm
2	2100 ppm	3300 ppm
3	7200 ppm	N/A

Furthermore, the acute toxicological data shows that the lethal vapor concentration (LC_{50}) for methanol is 64,000 ppm in 4 hours, while the lethal vapor concentration for ethanol is 20,000 ppm in 8 hours (both tested on rats). The risk of methanol inhalation is also higher than ethanol inhalation because the vapor pressure of methanol is higher than that of ethanol. [21], [22]. The lethal dermal dose (LD_{50}) for methanol is 15,800 mg/kg, while the lethal dermal dose for ethanol is 20,000 mg/kg (both tested on rabbits) [23]. The risk for inhalation or skin contact is much higher than the risk of ingestion when it comes to laboratory applications of methanol and ethanol in transesterification, but these values can be found in Appendix B.

2.3 Unit Operations of Transesterification

The methanolysis of canola oil is currently studied in the Unit Operations Laboratory at Worcester Polytechnic Institute. The experiment analysis includes understanding the complex kinetic model suggested for the transesterification reaction, modeling the reaction as pseudo second order, determining the rate constants and activation energy, and studying the temperature and mass transfer effects on the base-catalyzed reaction. The existing pre-laboratory document can be found in Appendix C.

The first objective of the Unit Operations experiment is to understand the kinetics of transesterification and confirm that the pseudo-second order mechanism is valid. Section 2.2.5 Kinetics above describes the kinetics of transesterification in detail, in particular the Vicente et al mathematical model that is further used in this section.

Assuming second order kinetics, a plot of inverse oil concentration versus time will yield a line with slope k, the reaction constant. With pseudo-second order kinetics, the plot might yield a curve with a linear portion, particularly in the beginning of the reaction where it proceeds the fastest. Using the Vicente et. al mathematical model at 35°C, 6:1 methanol to oil ratio, and 0.5wt% KOH, it was determined that the overall rate constant was 0.7.

A simplified pseudo-second order mechanism results in:

$$\frac{dO}{dt} = -k \cdot [O]^2$$

Using the determined value of the overall rate constant k from the above, the pseudo-second order equation can be solved. A graphical comparison of the Vicente et. al model and the pseudo-second order model, as depicted in Figure 2-3, allows students to determine that the pseudo-second order kinetics model is a valid assumption for this transesterification experiment.

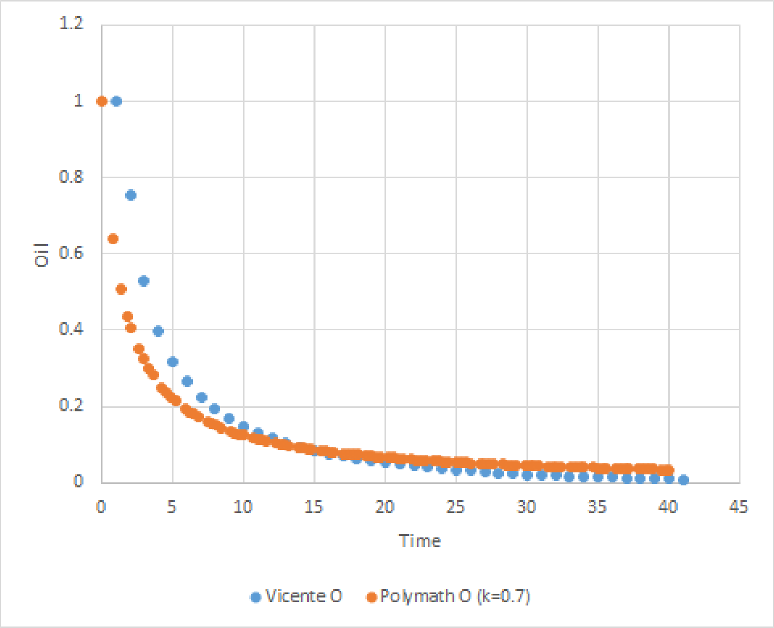


Figure 2-3: Comparison of Vicente Mathematical Model and Pseudo-Second Order Model

The second objective of the Unit Operations experiment is to study the temperature effects of the transesterification reaction. Studying the reaction at multiple temperatures allows an analysis of the Arrhenius equation described in Section 2.2.5 Kinetics.

The third objective of the Unit Operations experiment is to study the mass transfer limitations of the transesterification reaction using methanol. The plot of oil concentration over time should yield an S-shape curve which indicates an initial mass-transfer controlled region followed by a kinetically controlled region, ending with a region near equilibrium [16].

2.3.1 Lab Outcomes

Aside from the aforementioned objectives, the intended outcomes of the lab are learning how to maintain an electronic batch record and to practice proper lab safety. The electronic batch record is kept by utilizing a computer software to execute the experiment and manually inputting procedural comments into the record. The safety aspect is achieved by having students familiarize themselves with the MSDS, wear proper PPE, having the process reactors located in a fume hood, and having the electronic controls located outside of the hood. From this, students should take away a knowledge of the precautions necessary when dealing with caustic and flammable chemicals in unit operations. Furthermore, the enzyme assay used to measure the reaction exposes students to enzyme reactions and practice of micropipetting techniques.

2.4 Combustion of Biodiesel

Biodiesel offers significant greenhouse gas emission benefits over petroleum-based diesel when used to fuel a car. Even with the current move towards higher government regulations on motor vehicle emissions, incorporating biodiesel as a fuel source will positively impact the environment further. Figure 2-4 below shows the change in emissions resulting from the incorporation of biodiesel. Despite the increase in nitrogen oxides, the decrease in other greenhouse gas emissions is much more significant. For example, a 20% biodiesel blend increases nitrogen oxides by less than 2%, yet decreases particulate matter by about 11%, carbon monoxide by about 12%, and hydrocarbons by about 20%. This shows that incorporating biodiesel into fuel sources can have a major impact on the environment.

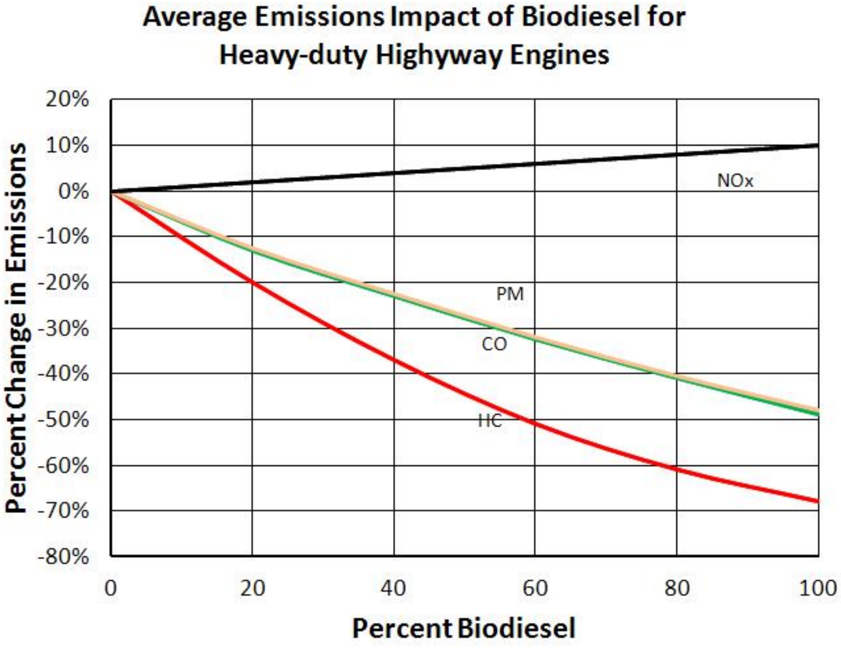


Figure 2-4: Biodiesel Blending Impacts on Emissions [24]

Figure 2-5 below shows the percent reduction of greenhouse gases comparing pure biodiesel (B100) and a 20% biodiesel blend (B20). It stresses the importance of higher blends of biodiesel due to the higher potential for greenhouse gas reduction.

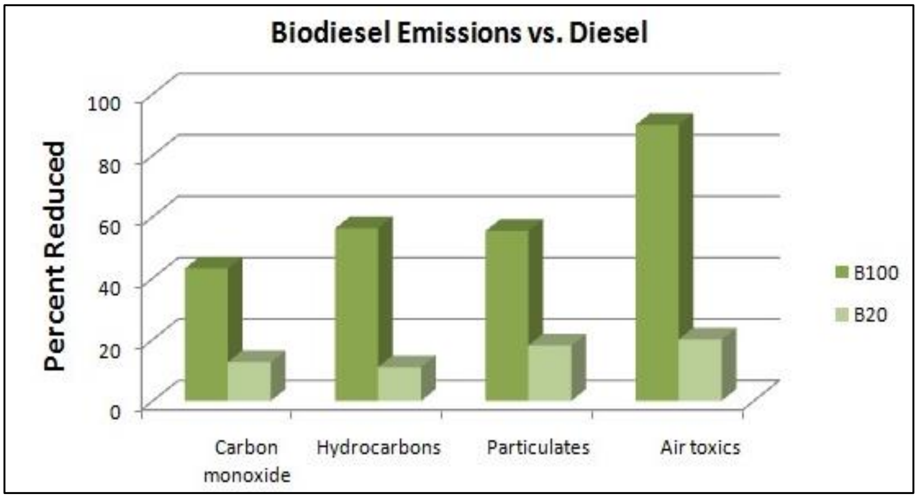


Figure 2-5: Effect of Biodiesel Blending on Greenhouse Gas Reduction [25]

Figures Figure *2-4* and Figure *2-5* are based on using methyl-biodiesel. Producing biodiesel with ethanol has only recently emerged, resulting in very limited studies on the combustion products of ethyl-biodiesel compared to those of methyl-biodiesel. Due to the renewable nature of biodiesel that has been discussed, one can conclude that both methyl- and ethyl-biodiesel would be a more environmentally friendly choice than petroleum-based diesel, but research has shown ethyl-biodiesel might be a more favorable choice. This is due to ethyl-biodiesel being a completely agricultural fuel. Ethyl-biodiesel creates ethyl esters which increase the heat content, cetane number, and have a less negative effect on the environment compared to methyl esters [14], [17].

3. Methodology

3.1 Objectives

The purpose of this Major Qualifying Project was to determine the viability of replacing the methanolysis Unit Operations II experiment with a similar ethanolysis experiment. Furthermore, the heating value and emissions profile of biodiesel from ethanolysis and methanolysis were compared to petroleum diesel to gain more knowledge on the implications of biodiesel fuel.

These purposes were achieved by executing the following objectives:

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- Determine which biodiesel emissions would be less hazardous for the environment

3.2 Summary

Alcohol and canola oil were reacted in a jacketed glass vessel in a 6:1 alcohol to oil ratio with 0.5 wt% (oil-based) KOH catalyst. Reactor Master (Syrris) software was used to automatically control the reaction and provide a digital log of the experiment. Samples were taken at predetermined time intervals and analyzed at the completion of the 40 minute reaction period. The samples were analyzed using a glycerol enzyme assay and colorimetric plate reader.

Both ethyl- and methyl-biodiesel were refined and combusted. The biodiesel product was de-alcoholized in a rotary evaporator, separated from the triglycerides in a separatory funnel, and run through a resin column to remove impurities. The refined biodiesel was combusted and the heating value and emissions were evaluated.

3.3 Biodiesel Production

3.3.1 Equipment

The biodiesel pilot plant consisted of one 250mL and one 500mL jacketed glass vessel inside a fume hood; the vessel temperatures were controlled by circulating heated water baths. The 250mL reactor was the catalyst preparation reactor, where alcohol was measured, heated, and reacted with the potassium hydroxide catalyst. The 500mL reactor was the process reactor, where the oil was measured, heated, and mixed with the alcohol/catalyst solution. The two vessels were connected by a peristaltic pump. Alcohol and oil were provided to the system by separate peristaltic pumps and storage vessels. Each reactor vessel was stirred by a sparkless and brushless overhead electronic stirrer to ensure mixing and encourage representative sampling. Figure 3-1 below demonstrates the reactor system.

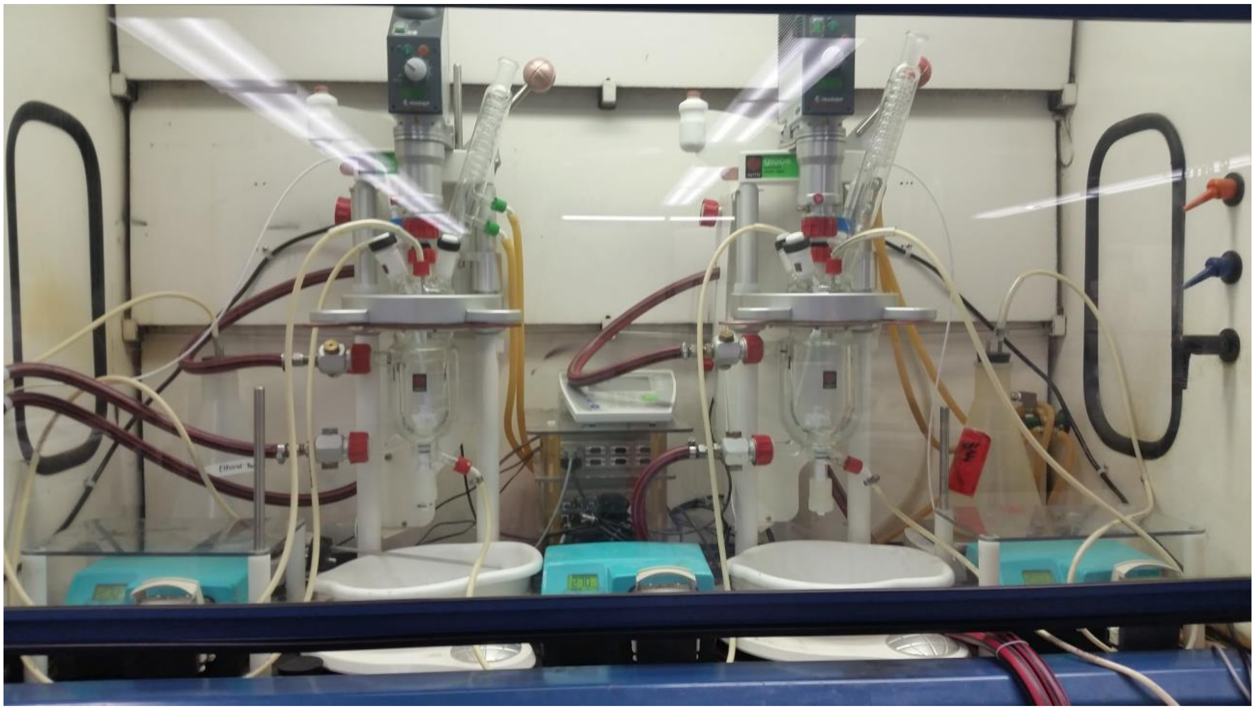

Figure 3-1: Pilot Biodiesel Reactor

3.3.2 Determining Operating Parameters

As discussed in the Section 2, the ideal conditions for transesterification are a 6:1 alcohol to oil ratio and 0.5-1 wt% alkaline catalyst. For conservation of resources and to encourage dissolution, a catalyst concentration of 0.5 wt% (oil-based) was selected. Given the total volume of 500mL, it was determined that 337.4 g (366.8 mL) of oil, 105.1 g (133.2 mL) of ethanol, and 1.687 g of KOH would be required (see Appendix D for calculations). For methanolysis, it was provided that 368 g (400mL) of oil, 78.9g (100 mL) of methanol, and 1.84g of KOH would be required. Even though the optimum operating temperature would be near the boiling point of the alcohol (approximately 78°C for ethanol, 64.7°C for methanol), the experiment was operated at 25°C, 35°C, and 45°C in order to study the temperature dependence of the reaction and calculate the activation energy. Furthermore, since it was shown that both transesterification reactions will proceed at near room-temperature, it was an unnecessary safety hazard to operate at higher temperatures.

3.3.3 Reactor Preparation

Reactor Master software was utilized in operating the reactor system. There was an existing Reactor Master file for the methanolysis reaction, which was edited for the ethanolysis reaction. The file was changed to modify equipment names and adjust the weight parameters of the oil, ethanol, and catalyst. The file was manipulated on a regular basis to adjust for the desired reaction temperature. Temperature manipulation of the file also occurs in the Unit Operations experiment and is the only manipulation required. Figure 3-2 through Figure *3-4* below show the Reactor Master software and the interfaces that are used in the Unit Operations experiment in addition to this research.

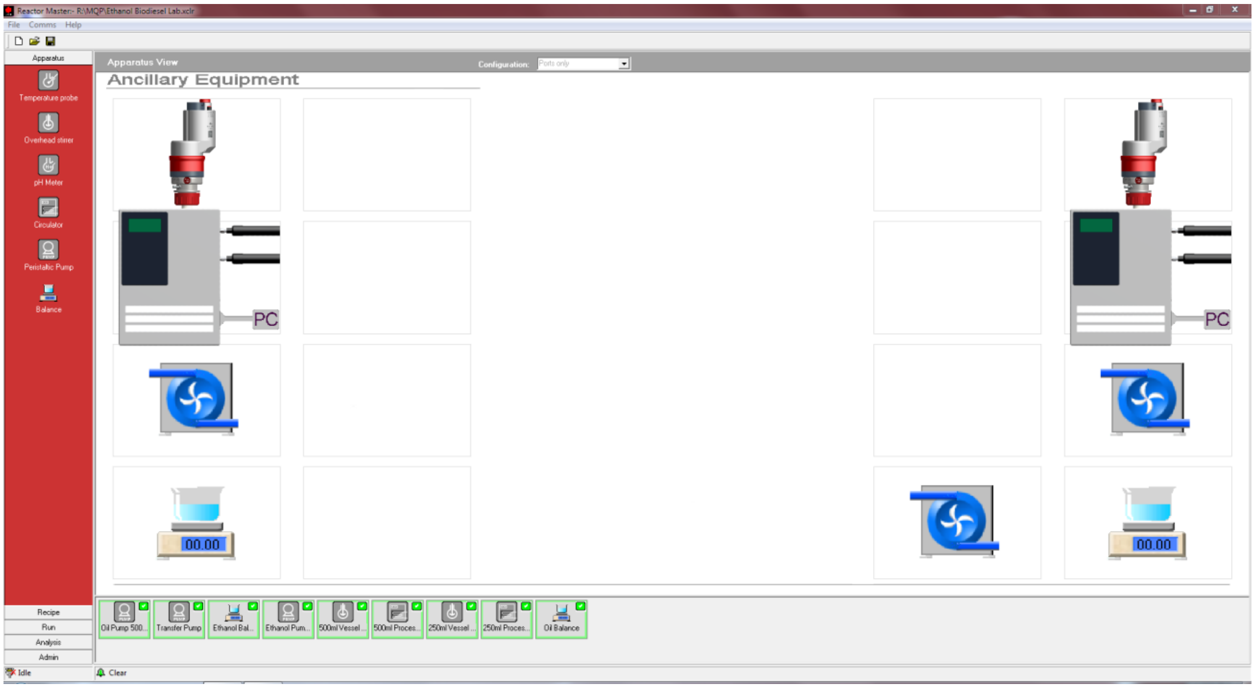

Figure 3-2: ReactorMaster Equipment View

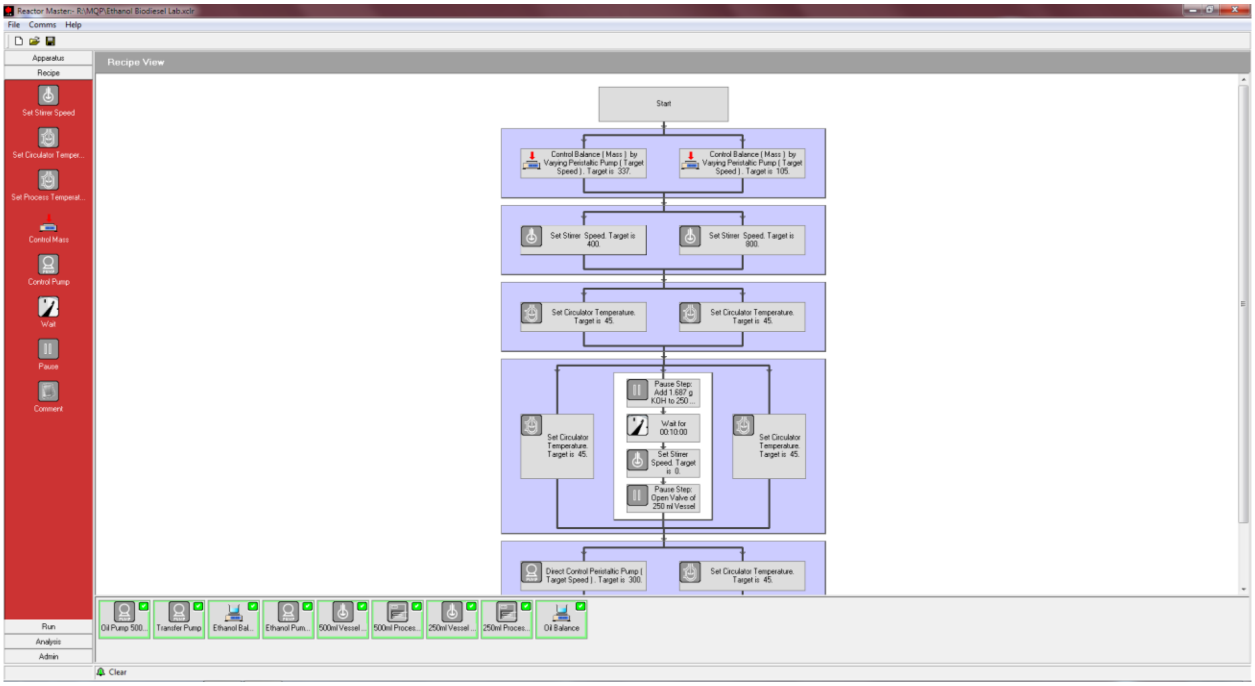

Figure 3-3: ReactorMaster Recipe View

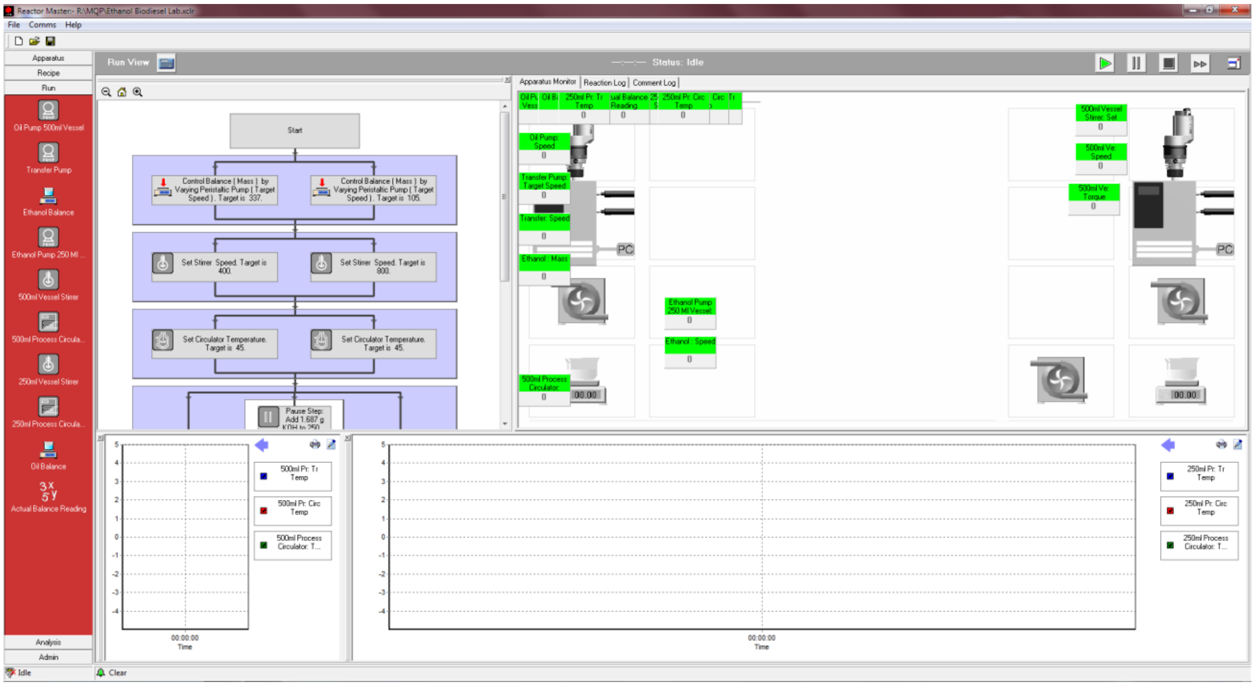

Figure 3-4: ReactorMaster Run View

3.3.4 Sampling and Sample Dilution

The sampling time intervals were determined based on a general understanding of the transesterification reaction. The ethanolysis reaction was not expected to exhibit an initial mass-transfer limited phase; therefore, the rate of the reaction increased quickly from initial contact of the ethanol mixture and oil [14]. At the determined time intervals, 40 µL were withdrawn from the reactor and quenched in 40 mL of chilled distilled water in a 50mL centrifuge tube to achieve a concentration of 1 mM. The sample concentration of millimolar corresponds to a reactor concentration of molar. Due to this, all graphs in this report cite units of molar concentrations of glycerol. The sample was then well mixed in a Lab Line Super-Mixer and chilled for the remainder of the experiment.

3.3.5 Glycerol Assay

The conversion of canola oil to biodiesel was monitored by the production of glycerol. An enzyme assay (BioAssay Systems EnzyChrom(™) Glycerol Assay Kit) was utilized to determine the glycerol concentration at each sample time.

The assay was comprised of a working reagent and sample volumes in a 96 well plate. The working reagent reacted with the glycerol in the sample volumes and produced varying color intensities, which were read by a colorimetric microplate reader.

3.3.5.1 Reagent Preparation

Table 3-1 below outlines the components and their concentrations in the working reagent. The volumes provided are for one sample volume. Each transesterification experiment required 20 volumes of working reagent including four glycerol standard samples.

Table 3-1: Components of Working Reagent Solution

Component	Volume Required for One Sample
Buffer Solution	100 µL
Dye Reagent	1 µL
ATP	1 µL
Enzyme (glycerol kinase, glycerol phosphate oxidase)	2 µL

The glycerol standard was prepared by combining the volumes of glycerol and distilled water listed in Table 3-2 below in separate cuvettes, labeled one, two, three, and four.

Table 3-2: Glycerol Standard Measurements

	Volume of Glycerol Standard	Volume of Distilled Water	Total Volume	Corresponding Glycerol Concentration
Standard 1	10µL	990µL	1000µL	1.0 mM
Standard 2	6µL	994µL	1000µL	0.6 mM
Standard 3	3µL	997µL	1000µL	0.3 mM
Standard 4	0µL	100µL	1000µL	0 mM

3.3.5.2 Plating

The samples were plated on a clear 96-well plate. 10 μL of each standard and sample and 100 μL of working reagent were pipetted into separate wells following Figure 3-5 below. The outside wells of the plate were avoided in order to yield a more accurate reading of each sample.

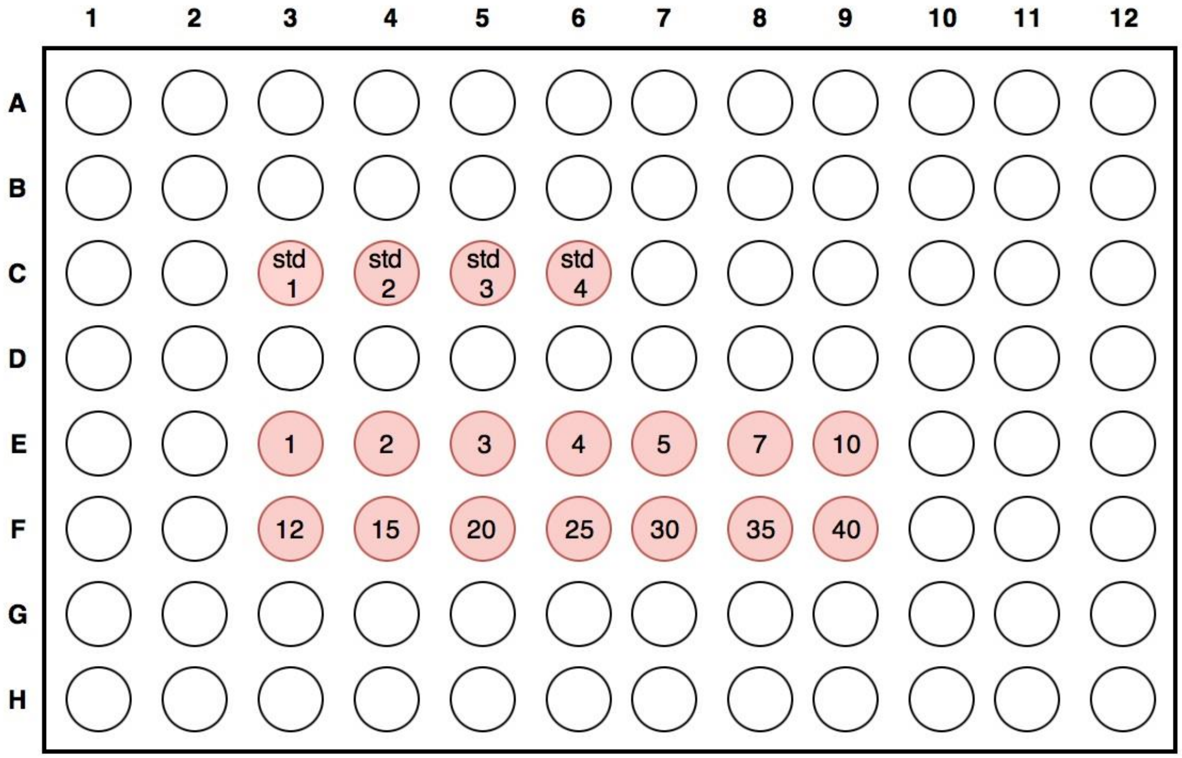

Figure 3-5: 96-well Plating Layout for Glycerol Assay

3.3.6 Gathering and Interpreting Colorimetric Readings

3.3.6.1 Running the Colorimetric Microplate Reader

The Molecular Devices SPECTRAmax 340PC384 SoftMax® Pro 5 microplate reader was utilized to read the absorbance of the microplate and therefore determine the glycerol concentration. The colorimetric microplate reader was read at 570 nm absorbance.

3.3.6.2 Calibration Curves

Calibration curves were created by plotting the adjusted absorbance readings for the assay standards against their predicted molar concentration values. Absorbance readings were adjusted by subtracting the blank standard from the reading.

$$Adjusted\ Absorbance\ Reading\ =\ Reading - Standard\ 4\ (Blank)$$

Table 3-3 and Figure 3-6 below show an example of adjusting absorbance readings and creating a calibration curve.

Table 3-3: Example Calibration Curve Calculation

	Reading	**Adjusted**	**mol/L**
Std 1	1.410	1.410 – 0.073 = 1.337	1.000
Std 2	0.650	0.650 – 0.073 = 0.577	0.600
Std 3	0.472	0.472 – 0.073 = 0.399	0.300
Std 4	0.073	0.073-0.073 = 0.000	0.000
Slope			1.3703

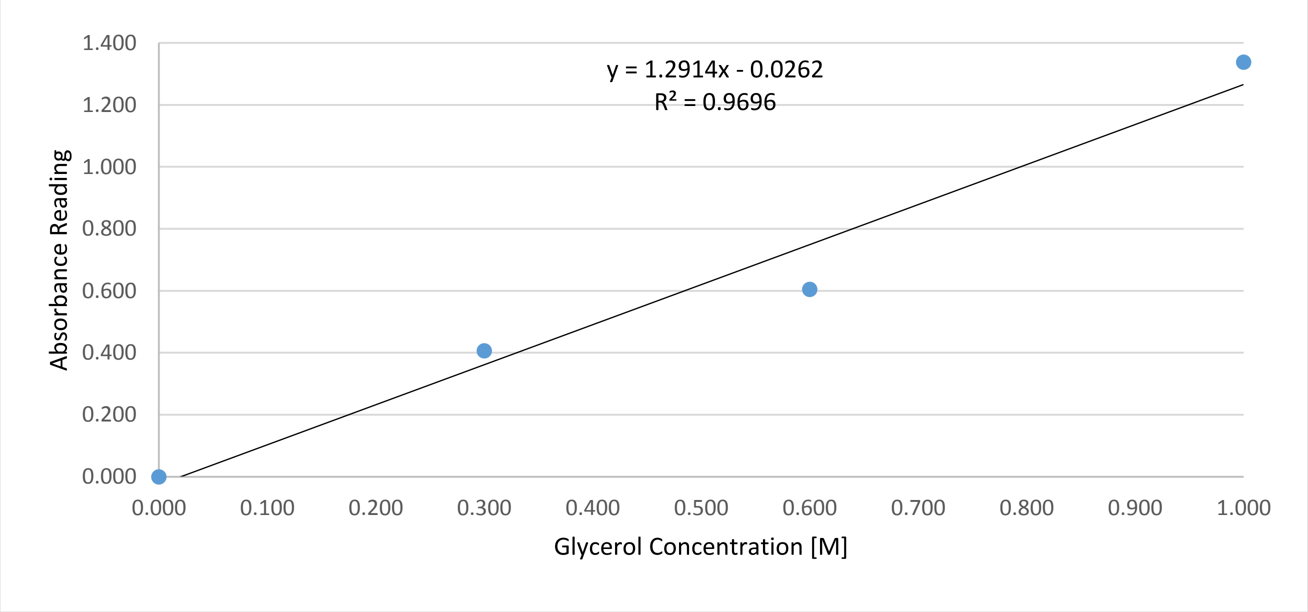

Figure 3-6: Example Calibration Curve Calculation

The ideal slope of a calibration curve is 1.2 [26].

3.3.6.3 Absorption Readings

Similar to calibration curves, the absorption readings were adjusted based on Standard 4. In order to determine the molar concentration of glycerol, the adjusted reading was divided by the slope of the calibration curve. Table 3-4 below shows a sample calculation.

Table 3-4: Example Absorbance Calculation

Time	Reading	Adjusted	Slope	Glycerol Concentration
1	0.079	0.079 – 0.073 = 0.006	1.3703	0.006/1.3703 = 0.004 M

3.4 Refining

3.4.1 Rotary Evaporator

Creating functional biodiesel requires further processing after transesterification with methanol or ethanol. In addition to the glycerol byproduct, the product of transesterification has many unwanted compounds like potassium hydroxide, water, triglycerides, soap, and methanol or ethanol. The first step to creating refined biodiesel is evaporating the alcohol using a rotary evaporator. Rotary evaporators are used to remove solvents from mixtures by using a heated water bath, a vacuum, and a condenser. The unrefined biodiesel was inserted into the flask and diagonally clipped into the rotary evaporator. The flask was then lowered and spun into the heated water bath. The water temperature depended on the boiling point of the alcohol that was being removed; methanol removal was completed at 65°C and ethanol removal was completed at 78°C. The vacuum-sealed condenser, filled with dry ice, collected the evaporated alcohol, and condensed it into a removable flask to be later recycled. The total process ran for twenty minutes.

Figure 3-7: Rotary Evaporator

3.4.2 Separation and Resin Column

After the unrefined de-alcoholized biodiesel was cooled, it was placed into a separatory funnel to separate the biodiesel into two phases, a top biodiesel-rich phase and a bottom glycerol-rich phase. The glycerol-rich phase was slowly drained from the funnel to ensure maximum removal of glycerol and minimal removal of biodiesel.

Figure 3-8: Biodiesel Settling in Separatory Funnel

The glycerol-rich phase was disposed of and the biodiesel was moved into a beaker which fed into the resin column to be refined. The resin was a DWR10 dry ion-exchanger designed to remove salts, soap, potassium hydroxide, glycerin, water, and unreacted oil. The resin consisted of small spherical amber-colored bead packing made from sodium polystyrene sulphonate [27] (see Appendix B for MSDS). The column filled one-third with resin packing. After reading previous MQP reports, the suggested flow rate of biodiesel through the resin was 30 mL/hr [28]. This allowed for sufficient ion exchange between the contaminants and the packing to remove contaminants from the biodiesel. The product from the resin column was processed and refined biodiesel, which can be combusted.

Figure 3-9: Resin Column refining dealcoholized biodiesel

3.5 Combustion

Petroleum-based diesel, ethyl-biodiesel, and methyl-biodiesel were burned in a combustion unit to measure the exhaust emissions with a flue gas analyzer. The flue gas analyzer, Testo-340, analyzed O_2, CO, NO, and NO_X to determine whether methyl-biodiesel or ethyl-biodiesel was less hazardous for the environment. The emissions of petroleum-based diesel were also measured in order to ascertain a baseline emissions reading for comparison with biodiesel emissions.

The combustion unit consisted of a heater that burned fuels to produce a constant flame, and a subsequent heat exchanger. To ensure that the heater produced the same amount of energy during every run, the cooling water entering and leaving the heat exchanger had a constant temperature rise of 10°F. Several thermocouples were set up throughout the experiment to indicate when the combustion unit was at steady state. Once at steady state, the initial weight of the fuel was taken, and then the process was run for ten minutes. At the conclusion of the ten minutes, the fuel was reweighed to calculate the amount of fuel consumed, and therefore required to power the heater. The heating values for all three fuels were measured and compared to each other.

3.6 Determining Rate Constant

Given that the transesterification reaction is pseudo second order, the value of the rate constant, k, can be defined as the slope of the linear line resulting in a plot of the inverse oil concentration over time. Figure 3-10 shows this plot using the pseudo-second order kinetics model of the methanolysis of sunflower oil [16]. The linear trend for a pseudo-second order model may only occur for a portion of the reaction, particularly the beginning, where the reaction is proceeding the quickest.

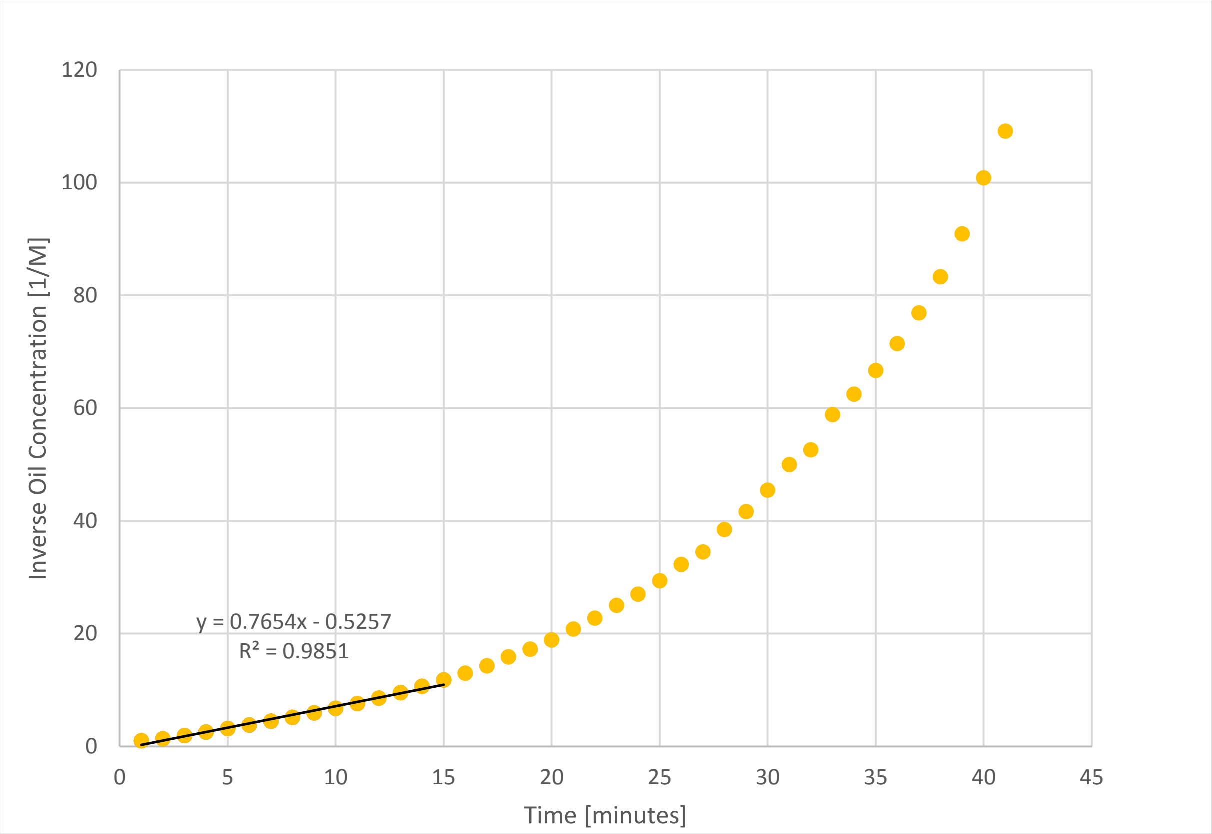

Figure 3-10: Estimate of Rate Constant for Methanolysis of Sunflower Oil at 35°C, 6:1, 0.5 wt% catalyst (Vicente et al, 2005)

3.7 Determining Activation Energy

In order to analyze the temperature dependence of the overall reaction, the Arrhenius equation was applied.

$$k = Ae^{-E_A/RT}$$

Where k is the rate constant, A is the pre-exponential factor, E_A is the activation energy, R is the gas constant, and T is the absolute temperature in Kelvin. Rearranged:

$$\ln(k) = \ln(A) - \frac{E_A}{R}\left(\frac{1}{T}\right)$$

Hence, the Arrhenius plot of ln(k) vs 1/T yields a slope of E_A/R.

3.8 Gathering Data on Methanolysis

The initial phases of this research involved performing the transesterification as outlined above with methanol (6:1 methanol to oil ratio and 0.5 wt% KOH catalyst). The purpose of this was to become familiar with the equipment, procedure, and gather data more fitting to our experimental procedure. Further methanolysis data was gathered from Unit Operations II experiments completed during the Fall 2015 course offering. This data was analyzed following the same methodologies as for ethanolysis data in order to determine if the reaction kinetics were comparable and if ethanolysis could replace methanolysis in the Unit Operations II Laboratory class.

4. Results and Discussion

4.1 Methanolysis

From the methanolysis experiments completed during this research and those completed in the Unit Operations II class, 16 runs were analyzed; eight at 25°C, five at 35°C, and three at 45°C. The data from these experiments can be found in Appendix E.

4.1.1 Glycerol Assay Overshoot

It was observed during analysis of the glycerol assay that the readings exceeded the maximum stoichiometric concentration of glycerol. Assuming 100% conversion, the maximum molar concentration of glycerol during methanolysis is 0.829M (See Appendix F). Using the calculated calibration curves, the average maximum reading was 1.057M, 0.228M over the maximum value (see Figure 4-1). Using an ideal calibration curve of 1.2, the average maximum glycerol concentration was 1.360M, 0.531M over the maximum value (see Figure 4-2). This overshoot can be explained by the tendency for glycerol to separate into a lower phase during later reaction times. Non-representative sampling could result in high glycerol concentrations. Furthermore, this overshoot was considered to be included in the error range of the glycerol assay, as the reaction curve followed the predicted "S" shape curve.

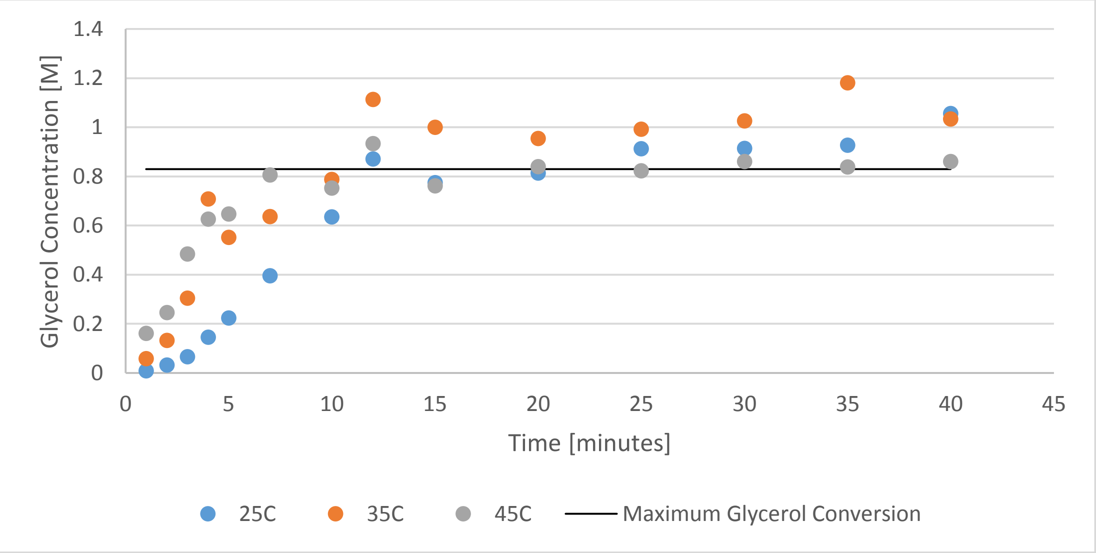

Figure 4-1: Averaged Methanolysis Data

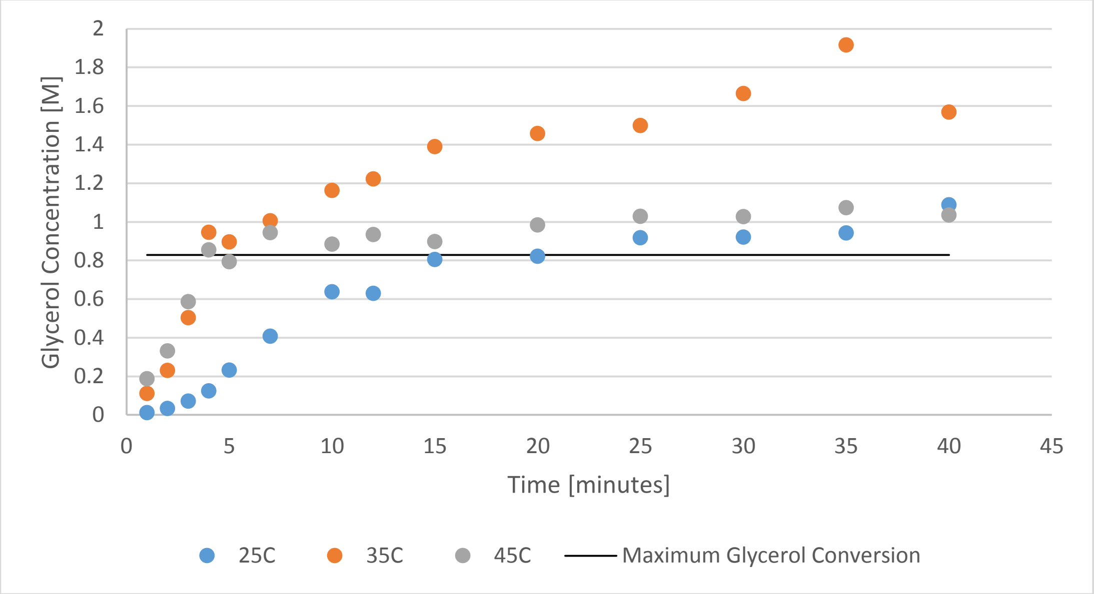

Figure 4-2: Averaged Ideal Methanolysis Data

You can also see from Figure 4-1 Figure 4-2 that the temperature trends are consistent with literature. That is, the transesterification reaction is kinetically favorable at higher temperatures, indicated by the higher glycerol concentrations at lower times.

4.1.2 Rate Constants and Activation Energy

As described in Section 3, the rate constants for each temperature were determined by the plot of the inverse oil concentration versus time (see Appendix G).

Table 4-1: Calculated Methanolysis Rate Constants

Temperature	Rate Constant, k
25°C	0.2371
35°C	0.8575
45°C	1.073

Also described in Section 3, the activation energy for the methanolysis reaction was determined by a plot of the Arrhenius equation, shown in Figure 4-3. The Arrhenius plot should follow a linear trend, which Figure 4-3 models with a R^2 value of 0.8714. The activation energy was found to be 59.9 kJ/mol, which agrees with the literature values of 26.8-61.5 kJ/mol for methanolysis at various operating parameters, as described in Table 2-1. Detailed calculations can be found in Appendix H.

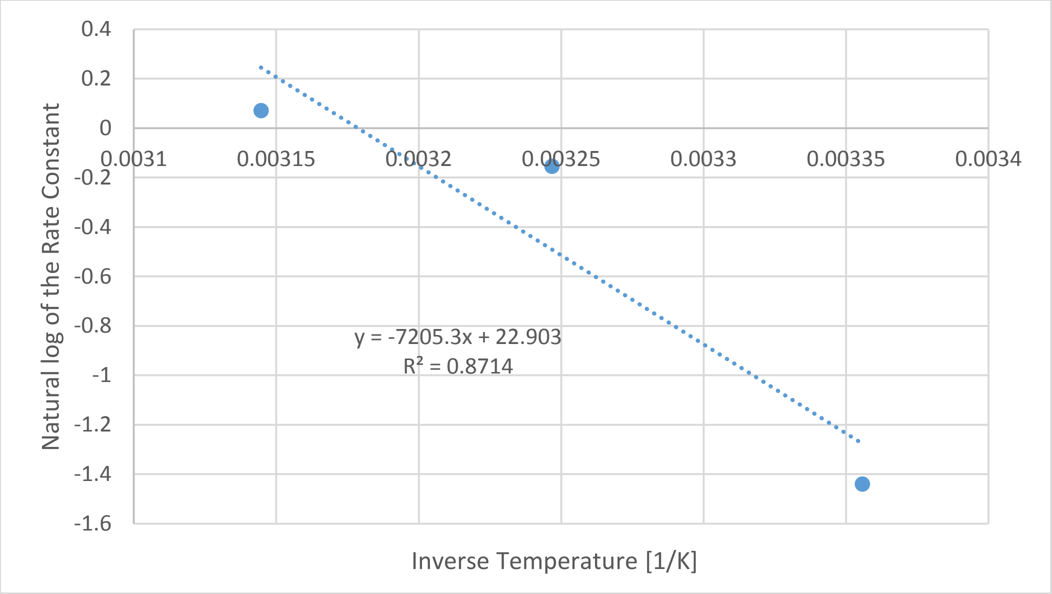

Figure 4-3: Arrhenius Plot to Determine the Methanolysis Activation Energy

4.2 Ethanolysis

From the ethanolysis experiments completed during this research, 12 runs were analyzed; four at 25 °C, four at 35 °C, and four at 45 °C. The data from these experiments can be found in Appendix I.

4.2.1 Glycerol Assay Overshoot

As with methanolysis, it was observed during the analysis of the glycerol assay that the readings exceeded the maximum stoichiometric glycerol concentration. Assuming 100% conversion, the maximum molar glycerol concentration during ethanolysis is 0.76M (see Appendix F). Using the calculated calibration curves, the average maximum reading was 0.708M, 0.053M under the maximum value (see Figure 4-4). Using an ideal calibration curve of 1.2, the average maximum glycerol concentration was 0.924M, 0.163M over the maximum value (see Figure 4-5). Depending on the calculation method, this undershoot or overshoot can be considered well within the error margin of the glycerol assay. When compared to the overshoot for methanolysis, it is significantly lower. At the completion of the ethanolysis experiments, it was observed that the glycerol-rich bottom phase was smaller than that formed by methanolysis. This can be translated to more representative sampling at later reaction times during ethanolysis experiments. The shape of the reaction curve is also as predicted for ethanolysis. It was predicted that no mass transfer limitations would be observed, which would be indicated by an immediate increase in glycerol concentration. Methanolysis does have mass transfer limitations, which is indicated by the “S”-shaped curve, where there is an initial period of slow increase in glycerol concentration. Figure 4-4Figure 4-5 show no initial period of slow increase, indicative of mass transfer limitations, therefore agreeing with literature.

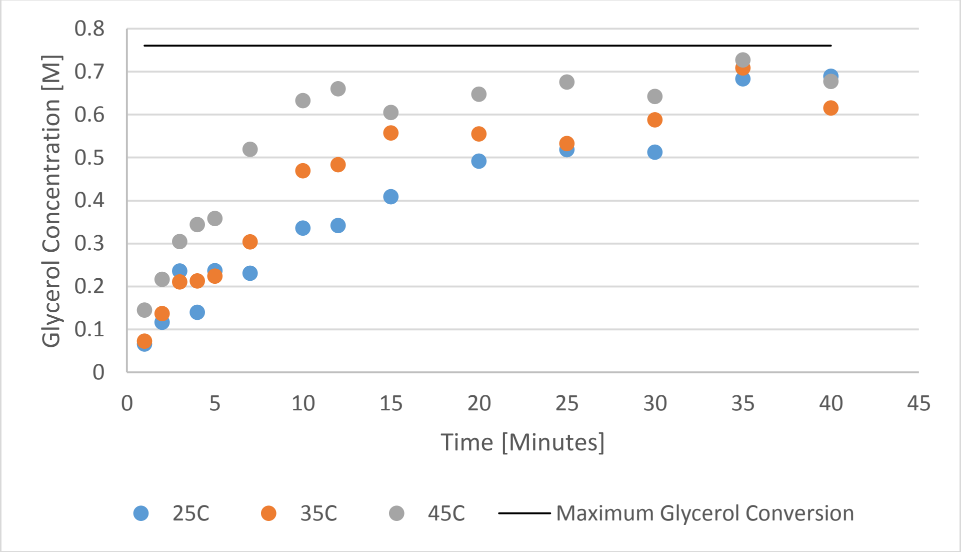

Figure 4-4: Averaged Ethanolysis Data

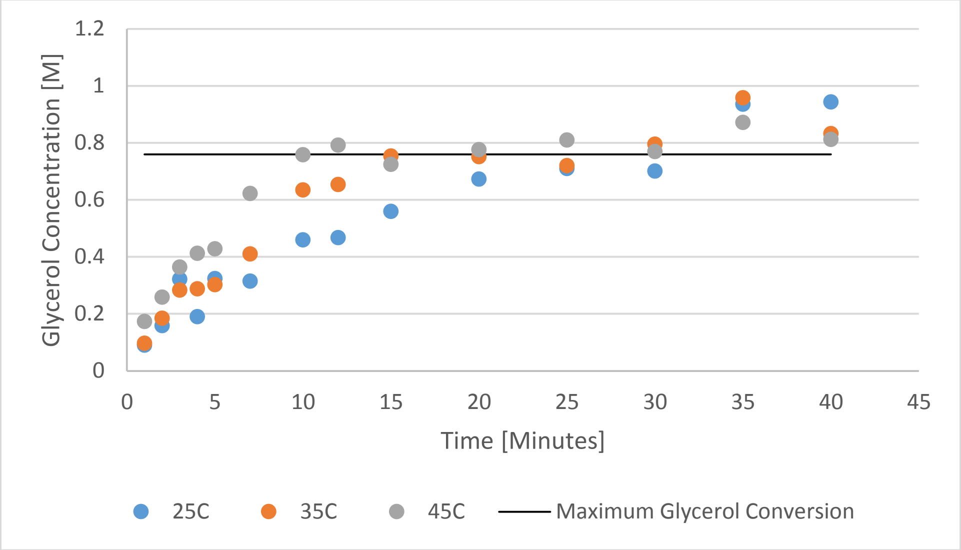

Figure 4-5: Averaged Ideal Ethanolysis Data

As with methanolysis, the ethanolysis reaction is also kinetically favorable at higher temperatures. The increase in reaction rate is not as large with ethanolysis as with methanolysis, but it is still present.

4.2.2 Rate Constants and Activation Energy

The calculated rate constants for the ethanolysis reaction are summarized in Table 4-2 (see Appendix J). The Arrhenius plot used to determine the activation energy can be found in Figure 4-6. The plot should follow a linear trend, which Figure 4-6 models with a R^2 value of 0.8680. The activation energy was determined to be 49.6 kJ/mol. This activation energy agrees with the literature values of 3.4-51 kJ/mol for ethanolysis at various operating parameters, as described in Table 2-1. Detailed calculations can be found in Appendix K.

Table 4-2: Calculated Ethanolysis Rate Constants

Temperature	Rate Constant, k
25°C	0.116
35°C	0.3253
45°C	0.3891

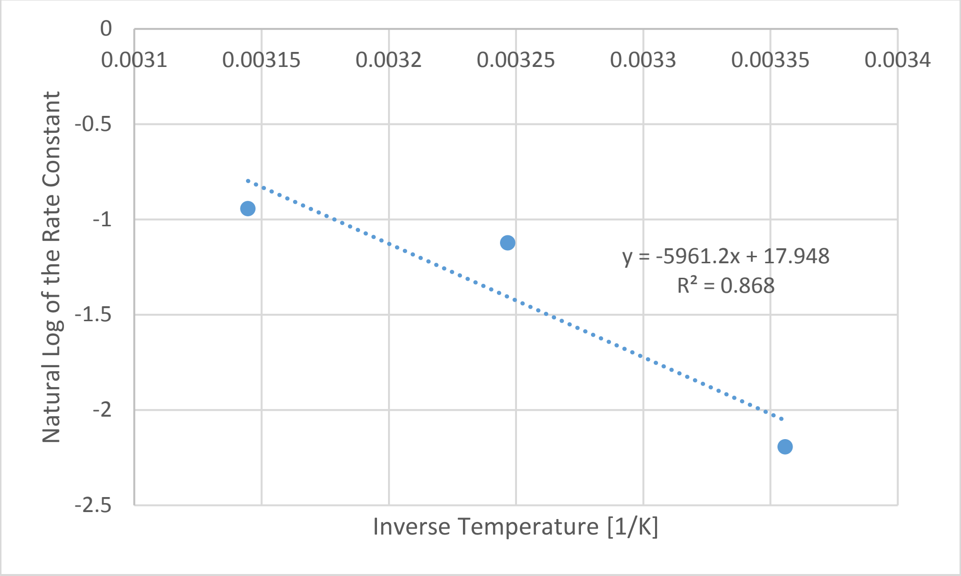

Figure 4-6: Arrhenius Plot to Determine the Ethanolysis Activation Energy

4.3 Emissions Analysis

The heating values and emissions of refined methyl-biodiesel and refined ethyl-biodiesel were compared to petroleum-based diesel to show the potential impacts biodiesel could have on a global scale.

Table 4-3 below shows that refined ethyl-biodiesel and refined methyl-biodiesel contained 95% and 93.6% of the heating value of petroleum-based diesel on a per mass basis, respectively. Literature states that methyl-biodiesel contains 92% of the heating value of petroleum-based diesel [29]. This difference was most likely because the scale that was used measured in increments of 0.005 kg, which is less accurate than increments of 0.001 kg. Also, due to time restrictions, only one run for each fuel was tested. More tests would increase the accuracy of the data.

During each ten minute trial, a flue gas analyzer was inserted into the exhaust pipe to read the emissions of the fuel being analyzed. Table 4-4 shows that both biodiesel fuels had a decrease in all emissions compared to petroleum-based diesel. These results follow literature except for the nitrogen oxide concentrations. A 2015 MQP reported similar results when investigating the emissions of different methyl-biodiesel/petroleum-based diesel mixtures [30]. This is most likely due to the different heat content of each fuel. Both biodiesels burn at a lower temperature than petroleum-based diesel, resulting in a lower stack temperature. Because nitrogen oxide formation increases as the combustion temperature increases, the lower stack temperature could explain why the biodiesel fuels had a lower concentration of nitrogen oxides. More tests would have to be run in order to accurately show the difference between biodiesel fuel and petroleum-based diesel fuel emissions. However, the flue gas analyzer can still compare methyl-biodiesel to ethyl-biodiesel because they have similar stack temperatures. Ethyl-biodiesel had 2.7%, 12%, and 11% less carbon monoxide, nitrogen monoxide, and nitrogen oxides, respectively compared to methyl-biodiesel.

Table 4-3: Heating Value Comparison of Biodiesel

Fuel	Initial Weight	Final Weight	∆Weight	%Efficient	Stack Temperature
Petroleum Diesel	3.335	3.045	0.290	100	349.8
Methyl-Biodiesel	3.115	2.805	0.310	93.6	310.9
Ethyl-Biodiesel	2.475	2.170	0.305	95.0	315.1

Table 4-4: Emissions Concentrations by Fuel Type

Emissions	Petroleum Diesel [ppm]	Methyl-Biodiesel [ppm]	Ethyl-Biodiesel (ppm)
CO	116	75	73
NO	51	43	38
NO_X	54	45	40
SO_2	0	0	0

5. Conclusions and Recommendations

5.1 Transesterification

As previously mentioned, the production of glycerol occurred as predicted for both methanolysis and ethanolysis. Furthermore, the activation energies of both reactions agreed with literature. This shows that the existing Unit Operations methodology, including the glycerol enzyme assay, can be applied to ethanolysis. **It is therefore recommended that the Unit Operations experiment utilize ethanol instead of methanol as the alcohol agent for transesterification.** To support this recommendation, an updated ReactorMaster file for use during the experiment, as well as an updated pre-laboratory exercise (Appendix L), were created for use in the ethanolysis experiment. The updated pre-laboratory exercise continues to use the Vicente mathematical model because the overall reaction kinetics and the activation energies of both transesterification reactions agree with literature, confirming the reaction mechanism.

5.2 Emissions Concentrations and Heating Value Analysis

From the analysis of emissions concentrations using the flue gas analyzer, both ethyl-biodiesel and methyl-biodiesel had significantly less emissions concentrations than petroleum-based diesel. Moreover, ethyl-biodiesel had additional emissions benefits over methyl-biodiesel. The concentrations of NOx in both biodiesels were observed to decrease compared to petroleum-based diesel, whereas literature suggests they increase in comparison. Due to the fact that NO_X emissions increase at higher temperatures, it was concluded that the most plausible explanation for the discrepancy with literature resulted from petroleum-based diesel burning at a higher temperature than biodiesel, as observed in the combustion unit. **It is therefore recommended that further experiments be developed to test the effect of temperature on emissions concentrations for each fuel type.**

The refined ethyl-biodiesel and refined methyl-biodiesel contained 95% and 94% of the heating value of petroleum-based diesel on a per mass basis, respectively. However, due to time restrictions, only one run for each fuel was performed. **It is therefore recommended that more tests be performed to increase the accuracy of the heating values for each fuel. Nonetheless,**

it is also recommended that ethyl-biodiesel be phased into the biodiesel market due to the similar heating values and emissions concentrations to methyl-biodiesel. Economically, methyl-biodiesel remains less expensive to produce and refine, but the environmental and safety benefits of ethyl-biodiesel may outweigh the cost difference.

6. References

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7. Appendices

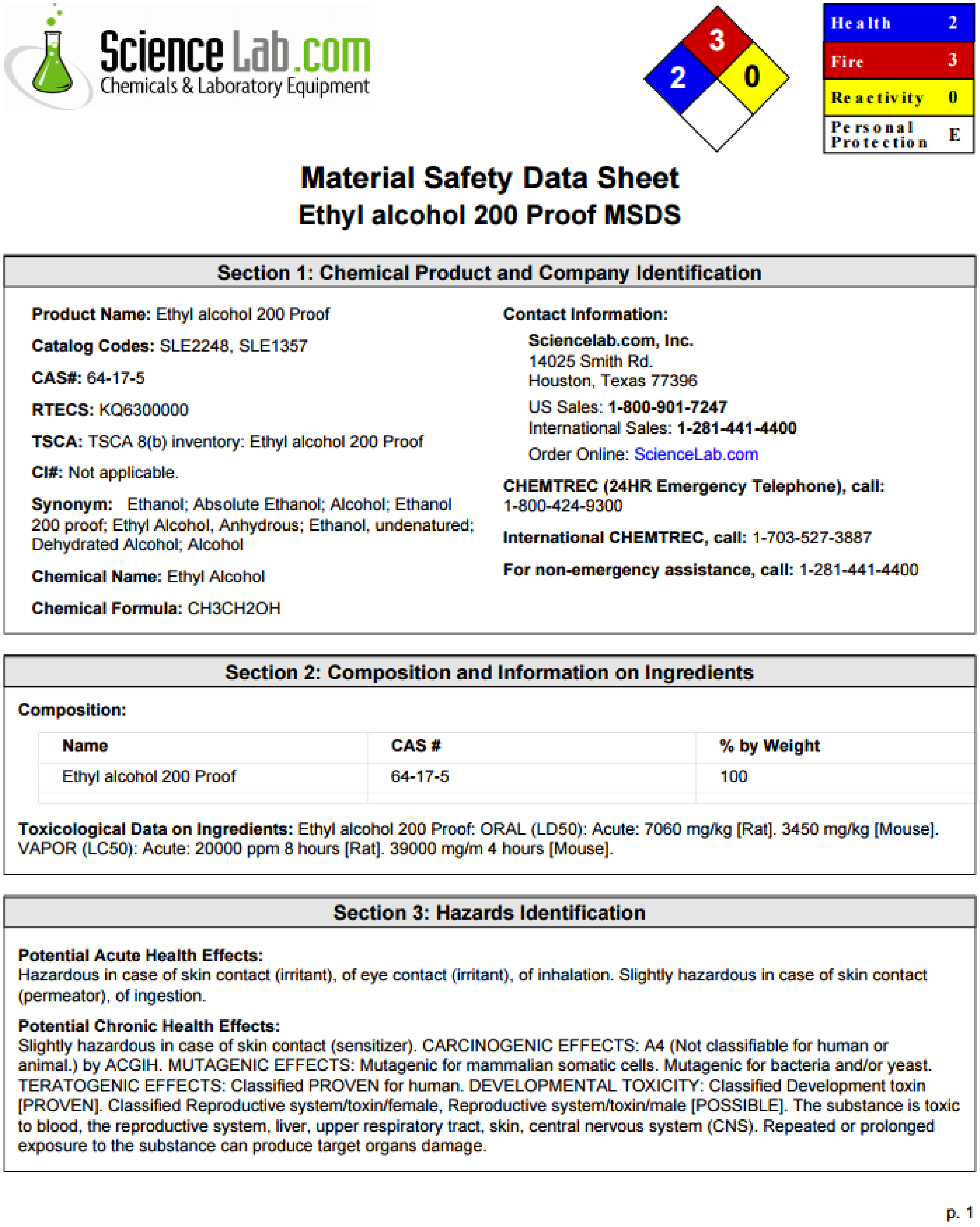
A. Summary of Transesterification Research

Table A-1: Summary of Transesterification Research

Oil	**Alcohol**	**Catalyst (wt%)**	**Ratio**	**Temperature (°C)**	**Kinetic Model**	**E_A (kJ/mol)**	**Source**
Palm	Methanol	KOH 1.0	6:1	55-65	three consecutive reversible second order reactions	26.8-61.5	[14]
Soybean	Methanol	NaOCH3 0.5	6:1	20-60	combination of consecutive second order and fourth order shunt reactions	56.8-83.8	[14]
Soybean	Methanol	NaOH 0.2	6	30-70	three consecutive reversible second order reactions	21.7-83.1	[14]
Brassica carinata oil	Methanol	KOH 0.5-1.5	6	25-65	three consecutive reversible second order reactions	12.0-104.8	[14]
Sunflower	Methanol	KOH 0.5-1.5	6	25-65	three consecutive reversible second order reactions	31.0-59.6	[16]
Sunflower	Methanol	KOH 1.0	6	10-30	Overall irreversible second order reactions, reversible second order reaction in final phase	33.2-53.5	[14]
Sunflower	Ethanol	NaOH 0.75,1.00,1.25	6,9,12	25-75	Overall irreversible second order reactions, reversible second order reaction in final phase	3.4-43.9	[14]

Sunflower	Ethanol	1.0 EtONa	6	30-60	pseudo second order	51	[20]
Palm	Ethanol	1.0 EtONa			Irreversible second order	42	[15]
Sunflower	Ethanol	NaOH 0.10	6,12,24	50		48.7-53.9	[31]
Cottonseed	Ethanol	2.0 NaOH			First order	-	[15]
Canola	Ethanol	2 Mg2CoAl			First order	60.5	[15]
Castor	Ethanol	1 NaOH			First order	70.6	[15]

B. Material Safety Data Sheets for Ethanol, Methanol, Potassium Hydroxide, and Sodium Polystyrene Sulphonate



Health	2
Fire	3
Reactivity	0
Personal Protection	E

Material Safety Data Sheet
Ethyl alcohol 200 Proof MSDS

Section 1: Chemical Product and Company Identification

Product Name: Ethyl alcohol 200 Proof

Catalog Codes: SLE2248, SLE1357

CAS#: 64-17-5

RTECS: KQ6300000

TSCA: TSCA 8(b) inventory: Ethyl alcohol 200 Proof

CI#: Not applicable.

Synonym: Ethanol; Absolute Ethanol; Alcohol; Ethanol 200 proof; Ethyl Alcohol, Anhydrous; Ethanol, undenatured; Dehydrated Alcohol; Alcohol

Chemical Name: Ethyl Alcohol

Chemical Formula: CH3CH2OH

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Ethyl alcohol 200 Proof	64-17-5	100

Toxicological Data on Ingredients: Ethyl alcohol 200 Proof: ORAL (LD50): Acute: 7060 mg/kg [Rat]. 3450 mg/kg [Mouse]. VAPOR (LC50): Acute: 20000 ppm 8 hours [Rat]. 39000 mg/m 4 hours [Mouse].

Section 3: Hazards Identification

Potential Acute Health Effects:
Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation. Slightly hazardous in case of skin contact (permeator), of ingestion.

Potential Chronic Health Effects:
Slightly hazardous in case of skin contact (sensitizer). CARCINOGENIC EFFECTS: A4 (Not classifiable for human or animal.) by ACGIH. MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. Mutagenic for bacteria and/or yeast. TERATOGENIC EFFECTS: Classified PROVEN for human. DEVELOPMENTAL TOXICITY: Classified Development toxin [PROVEN]. Classified Reproductive system/toxin/female, Reproductive system/toxin/male [POSSIBLE]. The substance is toxic to blood, the reproductive system, liver, upper respiratory tract, skin, central nervous system (CNS). Repeated or prolonged exposure to the substance can produce target organs damage.

p. 1

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Cold water may be used. Get medical attention.

Skin Contact:
In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Cold water may be used.Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek medical attention.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention if symptoms appear.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek medical attention.

Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: Flammable.

Auto-Ignition Temperature: 363°C (685.4°F)

Flash Points: CLOSED CUP: 12.78°C (55°F). OPEN CUP: 17.78°C (64°F) (Cleveland).

Flammable Limits: LOWER: 3.3% UPPER: 19%

Products of Combustion: These products are carbon oxides (CO, CO2).

Fire Hazards in Presence of Various Substances:
Highly flammable in presence of open flames and sparks, of heat. Slightly flammable to flammable in presence of oxidizing materials.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Slightly explosive in presence of open flames and sparks, of heat, of oxidizing materials, of acids.

Fire Fighting Media and Instructions:
Flammable liquid, soluble or dispersed in water. SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use alcohol foam, water spray or fog.

Special Remarks on Fire Hazards:
Containers should be grounded. CAUTION: MAY BURN WITH NEAR INVISIBLE FLAME Vapor may travel considerable distance to source of ignition and flash back. May form explosive mixtures with air. Contact with Bromine pentafluoride is likely to cause fire or explosion. Ethanol ignites on contact with chromyl chloride. Ethanol ignites on contact with iodine heptafluoride gas. It ignites than explodes upon contact with nitrosyl perchlorate. Additon of platinum black catalyst caused ignition.

Special Remarks on Explosion Hazards:
Ethanol has an explosive reaction with the oxidized coating around potassium metal. Ethanol ignites and then explodes on contact with acetic anhydride + sodium hydrosulfate (ignites and may explode), disulfuric acid + nitric acid, phosphorous(III) oxide platinum, potassium-tert-butoxide+ acids. Ethanol forms explosive products in reaction with the following compound :

ammonia + silver nitrate (forms silver nitride and silver fulminate), iodine + phosphorus (forms ethane iodide), magnesium perchlorate (forms ethyl perchlorate), mercuric nitrate, nitric acid + silver (forms silver fulminate) silver nitrate (forms ethyl nitrate) silver(I) oxide + ammonia or hydrazine (forms silver nitride and silver fulminate), sodium (evolves hydrogen gas). Sodium Hydrazide + alcohol can produce an explosion. Alcohols should not be mixed with mercuric nitrate, as explosive mercuric fulminate may be formed. May form explosive mixture with manganese perchlorate + 2,2-dimethoxypropane. Addition of alcohols to highly concentrate hydrogen peroxide forms powerful explosives. Explodes on contact with calcium hypochlorite

Section 6: Accidental Release Measures

Small Spill:
Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container.

Large Spill:
Flammable liquid. Keep away from heat. Keep away from sources of ignition. Stop leak if without risk. Absorb with DRY earth, sand or other non-combustible material. Do not touch spilled material. Prevent entry into sewers, basements or confined areas; dike if needed. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:
Keep locked up.. Keep away from heat. Keep away from sources of ignition. Ground all equipment containing material. Do not ingest. Do not breathe gas/fumes/ vapor/spray. Wear suitable protective clothing. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as oxidizing agents, acids, alkalis, moisture.

Storage:
Store in a segregated and approved area. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame). Do not store above 23°C (73.4°F).

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective threshold limit value. Ensure that eyewash stations and safety showers are proximal to the work-station location.

Personal Protection:
Splash goggles. Lab coat. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Gloves. Use a respirator if the exposure limit is exceeded.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Vapor respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:
TWA: 1900 (mg/m3) from OSHA (PEL) [United States] TWA: 1000 (ppm) from OSHA (PEL) [United States] TWA: 1900 (mg/m3) from NIOSH [United States] TWA: 1000 (ppm) from NIOSH [United States] TWA: 1000 (ppm) [United Kingdom (UK)] TWA: 1920 (mg/m3) [United Kingdom (UK)] TWA: 1000 STEL: 1250 (ppm) [Canada]Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Liquid. (Liquid.)

Odor:

Mild to strong, rather pleasant; like wine or whiskey. Alcohol-like; Ethereal, vinous.

Taste: Pungent. Burning.

Molecular Weight: 46.07 g/mole

Color: Colorless. Clear

pH (1% soln/water): Not available.

Boiling Point: 78.5°C (173.3°F)

Melting Point: -114.1°C (-173.4°F)

Critical Temperature: 243°C (469.4°F)

Specific Gravity: 0.789 (Water = 1)

Vapor Pressure: 5.7 kPa (@ 20°C)

Vapor Density: 1.59 (Air = 1)

Volatility: Not available.

Odor Threshold: 100 ppm

Water/Oil Dist. Coeff.: The product is more soluble in water; log(oil/water) = -0.3

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water, methanol, diethyl ether, acetone.

Solubility:
Easily soluble in cold water, hot water. Soluble in methanol, diethyl ether, acetone.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Incompatible materials, heat, sources of ignition.

Incompatibility with various substances: Reactive with oxidizing agents, acids, alkalis.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity:
Ethanol rapidly absorbs moisture from the air. Can react vigorously with oxiders. The following oxidants have been demonstrated to undergo vigorous/explosive reaction with ethanol: barium perchlorate, bromine pentafluoride, calcium hypochlorite, chloryl perchlorate, chromium trioxide, chromyl chloride, dioxygen difluoride, disulfuryl difluoride, fluorine nitrate, hydrogen peroxide, iodine heptafluoride, nitric acid nitrosyl perchlorate, perchloric acid permanganic acid, peroxodisulfuric acid, potassium dioxide, potassium perchlorate, potassium permanganate, ruthenium(VIII) oxide, silver perchlorate, silver peroxide, uranium hexafluoride, uranyl perchlorate. Ethanol reacts violently/expodes with the following compounds: acetyl bromide (evolves hydrogen bromide) acetyl chloride, aluminum, sesquibromide ethylate, ammonium hydroxide & silver oxide, chlorate, chromic anhydride, cyanuric acid + water, dichloromethane + sulfuric acid + nitrate (or) nitrite, hydrogen peroxide + sulfuric acid, iodine + methanol + mercuric oxide, manganese perchlorate + 2,2-dimethoxy propane, perchlorates, permanganates + sulfuric acid, potassium superoxide, potassium tert-butoxide, silver & nitric acid, silver perchlorate, sodium hydrazide, sulfuric acid + sodium dichromate, tetrachlorisilane + water. Ethanol is also incompatible with platinium, and sodium. No really safe conditions exist under which ethyl alcohol and chlorine oxides can be handled. Reacts vigorously with acetyl chloride

Special Remarks on Corrosivity: Not available.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Dermal contact. Eye contact. Inhalation. Ingestion.

Toxicity to Animals:
WARNING: THE LC50 VALUES HEREUNDER ARE ESTIMATED ON THE BASIS OF A 4-HOUR EXPOSURE. Acute oral toxicity (LD50): 3450 mg/kg [Mouse]. Acute toxicity of the vapor (LC50): 39000 mg/m3 4 hours [Mouse].

Chronic Effects on Humans:
CARCINOGENIC EFFECTS: A4 (Not classifiable for human or animal.) by ACGIH. MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. Mutagenic for bacteria and/or yeast. TERATOGENIC EFFECTS: Classified PROVEN for human. DEVELOPMENTAL TOXICITY: Classified Development toxin [PROVEN]. Classified Reproductive system/toxin/female, Reproductive system/toxin/male [POSSIBLE]. Causes damage to the following organs: blood, the reproductive system, liver, upper respiratory tract, skin, central nervous system (CNS).

Other Toxic Effects on Humans:
Hazardous in case of skin contact (irritant), of inhalation. Slightly hazardous in case of skin contact (permeator), of ingestion.

Special Remarks on Toxicity to Animals:
Lowest Published Dose/Conc: LDL[Human] - Route: Oral; Dose: 1400 mg/kg LDL[Human child] - Route: Oral; Dose: 2000 mg/kg LDL[Rabbit] - Route: Skin; Dose: 20000 mg/kg

Special Remarks on Chronic Effects on Humans:
May affect genetic material (mutagenic) Causes adverse reproductive effects and birth defects (teratogenic) , based on moderate to heavy consumption. May cause cancer based on animal data. Human: passes through the placenta, excreted in maternal milk.

Special Remarks on other Toxic Effects on Humans:
Acute potential health effects: Skin: causes skin irritation Eyes: causes eye irritation Ingestion: May cause gastrointestinal tract irritation with nausea, vomiting, diarrhea, and alterations in gastric secretions. May affect behavior/central nervous system (central nervous system depression - amnesia, headache, muscular incoordination, excitation, mild euphoria, slurred speech, drowsiness, staggaring gait, fatigue, changes in mood/personality, excessive talking, dizziness, ataxia, somnolence, coma/narcosis, hallucinations, distorted perceptions, general anesthetic), peripherial nervous system (spastic paralysis)vision (diplopia). Moderately toxic and narcotic in high concentrations. May also affect metabolism, blood, liver, respiration (dyspnea), and endocrine system. May affect respiratory tract, cardiovascular(cardiac arrhythmias, hypotension), and urinary systems. Inhalation: May cause irritation of the respiratory tract and affect behavior/central nervous system with symptoms similar to ingestion. Chronic Potential Health Effects: Skin: Prolonged or repeated skin contact may casue dermatitis, an allergic reaction. Ingestion: Prolonged or repeated ingestion will have similiar effects as acute ingestion. It may also affect the brain.

Section 12: Ecological Information

Ecotoxicity: Ecotoxicity in water (LC50): 14000 mg/l 96 hours [Rainbow trout]. 11200 mg/l 24 hours [fingerling trout].

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The product itself and its products of degradation are not toxic.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:
Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: CLASS 3: Flammable liquid.

Identification: : Ethanol UNNA: 1170 PG: II

Special Provisions for Transport: Not available.

Section 15: Other Regulatory Information

Federal and State Regulations:
California prop. 65: This product contains the following ingredients for which the State of California has found to cause cancer, birth defects or other reproductive harm, which would require a warning under the statute: Ethyl alcohol 200 Proof (in alcoholic beverages) California prop. 65: This product contains the following ingredients for which the State of California has found to cause birth defects which would require a warning under the statute: Ethyl alcohol 200 Proof (in alcoholic beverages) Connecticut hazardous material survey.: Ethyl alcohol 200 Proof Illinois toxic substances disclosure to employee act: Ethyl alcohol 200 Proof Rhode Island RTK hazardous substances: Ethyl alcohol 200 Proof Pennsylvania RTK: Ethyl alcohol 200 Proof Florida: Ethyl alcohol 200 Proof Minnesota: Ethyl alcohol 200 Proof Massachusetts RTK: Ethyl alcohol 200 Proof Massachusetts spill list: Ethyl alcohol 200 Proof New Jersey: Ethyl alcohol 200 Proof Tennessee: Ethyl alcohol 200 Proof California - Directors List of Hazardous Substances (8 CCR 339): Ethyl alcohol 200 Proof TSCA 8(b) inventory: Ethyl alcohol 200 Proof

Other Regulations:
OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200). EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada):
CLASS B-2: Flammable liquid with a flash point lower than 37.8°C (100°F). CLASS D-2A: Material causing other toxic effects (VERY TOXIC).

DSCL (EEC):
R11- Highly flammable. S7- Keep container tightly closed. S16- Keep away from sources of ignition - No smoking.

HMIS (U.S.A.):

Health Hazard: 2

Fire Hazard: 3

Reactivity: 0

Personal Protection: E

National Fire Protection Association (U.S.A.):

Health: 2

Flammability: 3

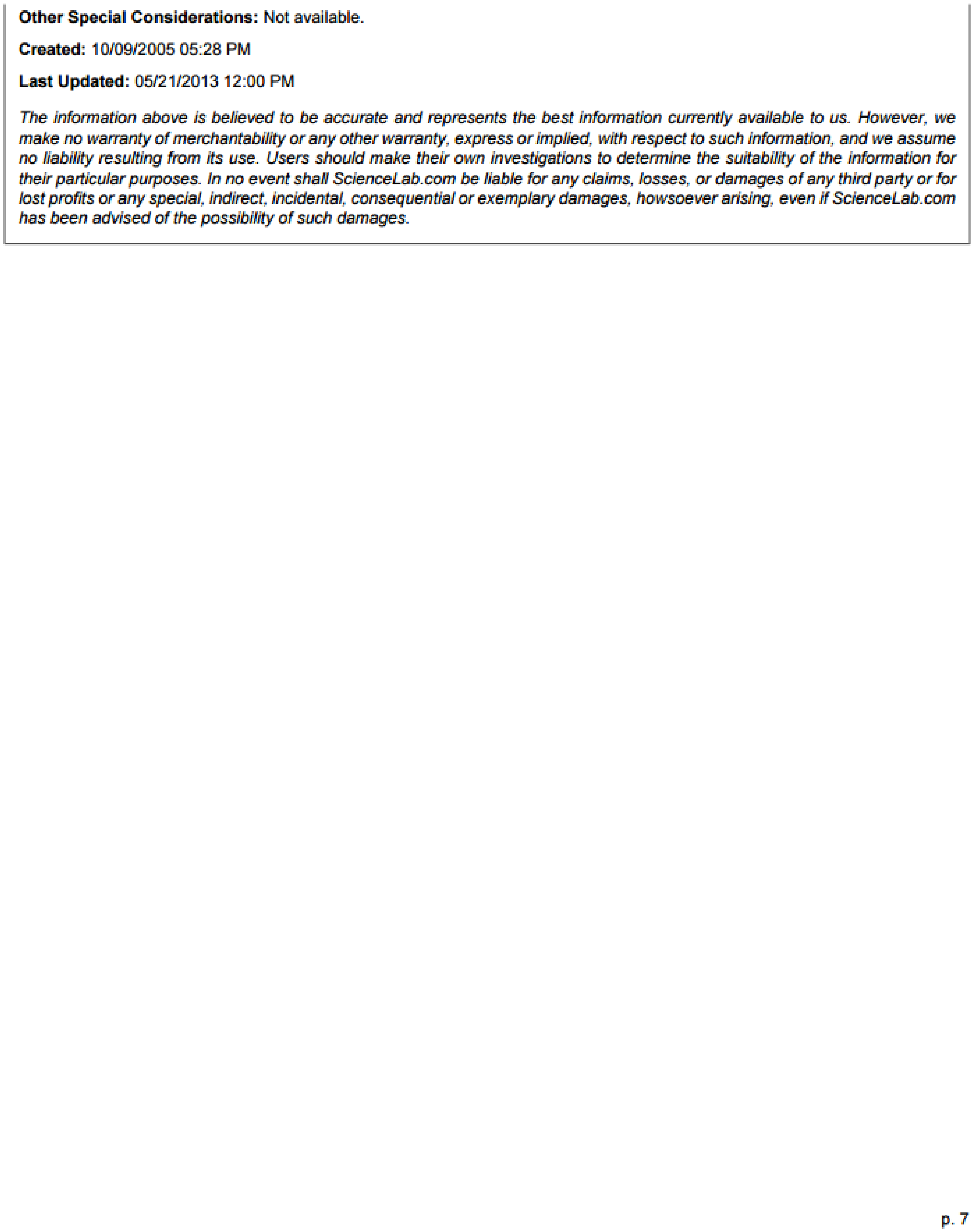
Reactivity: 0

Specific hazard:

Protective Equipment:
Gloves. Lab coat. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Splash goggles.

Section 16: Other Information

References:
-SAX, N.I. Dangerous Properties of Indutrial Materials. Toronto, Van Nostrand Reinold, 6e ed. 1984. -Material safety data sheet emitted by: la Commission de la Santé et de la Sécurité du Travail du Québec. -Hawley, G.G.. The Condensed Chemical Dictionary, 11e ed., New York N.Y., Van Nostrand Reinold, 1987. -The Sigma-Aldrich Library of Chemical Safety Data, Edition II. HSDB, RTECS, and LOLI databases.



Other Special Considerations: Not available.

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SYNDEL LABORATORIES LTD.
An *Aquatic Life Sciences* Company
SYNDEL

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MATERIAL SAFETY DATA SHEET

ETHYL ALCOHOL (DENATURED)

New TMS Sizes
2008 Catalogue
Aquaculture Products
Spawning Products
International Agents
What's New
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In the USA contact:

WESTERN CHEMICAL INC.
Product Purity & Environmental Stewardship

Section I - IDENTIFICATION

PRODUCT: Ethyl alcohol (denatured)

SYNONYMS: Denatured ethanol

CHEMICAL FORMULA: C_2H_5OH

CHEMICAL ABSTRACT NO.: Mixture

PRODUCT CODE NO.: 12902

Section II - HAZARDOUS INGREDIENTS

COMPOSITION	%	CAS #	TLV	HAZARD
Ethyl alcohol	82.9	000064175	1000 ppm	Flammable
Ethyl acetate	0.2	141-78-6	400 ppm	Flammable
Methyl alcohol	16.4	000067561	200 ppm	Flammable, poisonous
Methyl ethyl ketone	0.5	000078933	200 ppm	Flammable

Section III - HEALTH & FIRST AID INFORMATION

INHALATION: Irritating to upper respiratory tract. Remove patient to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Seek medical attention immediately

INGESTION: Poisonous, may damage central nervous system and internal organs and cause blindness. DO NOT induce vomiting. Have conscious person drink several glasses of water or milk. Never give anything by mouth to an unconscious person. Lower the head so that vomit will not re-enter the mouth and throat. Seek medical attention immediately.

EYE CONTACT: Irritating, can cause colour blindness. Check for and remove any contact lenses. Rinse eyes for at least 20 minutes with cold water. Seel medical attention immediately.

SKIN CONTACT: Only hazardous with prolonged contact. Wash immediately with plenty of water for at least 20 minutes. Thoroughly clean contaminated clothing and shoes before re-use. Seek medical attention.

OTHER HEALTH INFORMATION:
Potential Acute health effects: Very hazardous in case of eye contact (irritant), ingestion or inhalation. hazardous in case of skin contact (permeator). Slightly hazardous in case of skin contact (irritant). Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering and itching.
Potential Chronic health effects:
Carcinogenic effects: Classified A4 by ACGIH (for ethyl alcohol) - (Not Classifiable for human or animal)
Mutagenic effects: Not available
Teratogenic effects: Not available
Developmental toxicity: Not available
This substance is toxic to the liver. Repeated or prolonged exposure can produce target organs damage. Repeated exposure to a highly toxic material may produce general deterioration of health by an accumulation in one or many organs.
LC_{50}/LD_{50}:

Ethyl Alcohol	LD_{50} Acute	Oral	7060 mg/kg	Rat
			3450 mg/kg	Mouse
		Dermal	20000 mg/kg	Rabbit
Methanol	LD_{50} Acute	Oral	5628 mg/kg	Rat
			7300 mg/kg	Mouse
		Dermal	15800 mg/kg	Rabbit
	LC_{50} Acute	Vapour	64000 ppm-4 hours	Rat
Methyl ethyl ketone	LD_{50}Acute	Oral	2737 mg/kg	Rat
			4050 mg/kg	Mouse
		Dermal	6480 mg/kg	Rabbit (RTECS)
			13000 mg/kg	Rabbit
	LC_{50} Acute	Vapour	23500 mg/m3-8 hours	Rat
Ethyl acetate	LD_{50} Acute	Oral	5620 mg/kg	Rat
			4100 mg/kg	Mouse
	LC_{50} Acute	Vapour	22627 ppm-4 hours	Rate

OTHER TOXICOLOGICAL INFORMATION:
Routes of entry: Dermal, Eye, Inhalation, Ingestion
Toxicity to Animals: Ethyl alcohol LD50 3450 mg/kg acute oral (Mouse)
Methanol LD50 15800 mg/kg acute dermal (Rabbit)
Remarks: Repeated or prolonged exposure may lead to dermatitis, erythema and scaling. Long term repeated exposure to ethanol may result in development of progressive liver injury with fibrosis.

Section IV - PHYSICAL DATA

BOILING POINT: 75°C (167°F)

VAPOUR DENSITY (AIR=1): Ethyl alcohol: 1.6; Methyl alcohol: 1.1. Weighted average 1.51

SOLUBILITY IN WATER: partially to completely miscible

APPEARANCE AND COLOUR: colourless liquid, alcohol with an alcohol-like odour

SPECIFIC GRAVITY (WATER=1): 0.79

VAPOUR PRESSURE (@20°C): 12.9 kPa

ODOUR THRESHOLD: Highest known value is 2000 ppm (methanol). Weighted average = 413.8 ppm

Section V - FIRE AND EXPLOSION HAZARDS

FLASH POINT & METHODS USED: 12°C (53.6°F) - closed cup

FLAMMABLE LIMITS IN AIR; % BY VOL. LOWER: Ethyl alcohol: 4.3%; Methyl alcohol: 6%

FLAMMABLE LIMITS IN AIR; % BY VOL. UPPER: Ethyl alcohol: 19%; Methyl alcohol: 36.5%

SPECIAL FIRE FIGHTING PROCEDURES & PRECAUTIONS: Flammable liquid soluble or dispersed in water. For Small Fire - use dry chemical powder. For Large Fire - use alcohol foam, water spray or foam. Cool containing vessels with water jet in order to prevent pressure build-up, autoignition or explosion. Vapours from this product may travel or be moved by air currents and ignited by pilot lights or other flames, sparks, heaters, electrical equipment, static discharges or other ignition sources.

FIRE HAZARD: Flammable in presence of open flames and sparks. Slightly flammable to flammable in the presence of oxidizing materials.

EXPLOSION HAZARDS: Explosive in presence of open flames and sparks.

UNUSUAL FIRE & EXPLOSION HAZARDS: none

AUTO-IGNITION TEMPERATURE: Lowest known value is 363°C (685.4°F) - Ethyl alcohol

Section VI - REACTIVITY

STABILITY: stable

HAZARDOUS POLYMERIZATION: will not occur

CONDITIONS & MATERIALS TO AVOID: heat, sparks, other sources of ignition

HAZARDOUS DECOMPOSITION PRODUCTS: Carbon dioxide

Section VII - EMPLOYEE PROTECTION

CONTROL MEASURES: In case of spill, shut off all sources of ignition. Small spills may be run to waste with plenty of water. Large spills should be transferred to a salvage container. Seek the advice of a professional chemical disposal service. Contact local authorities if spill has entered surface drains or sewers.

RESPIRATORY PROTECTION: Use organic vapour cartridge or self contained breathing apparatus if handling large quantities (use self contained breathing appartatus if concentration is above 1000 ppm).

PROTECTIVE CLOTHING: Wear protective gloves (neoprene, rubber or butyl gloves are recommended).

EYE PROTECTION: Wear approved safety goggles if splashing is likely. Ensure that eyewash station and safety showers are available.

EXPOSURE LIMITS:

Ethyl Acetate	TWA 400 ppm from ACGIH (TLV) (US) TWA 1440 ppm from ACGIH (TLV) (US)
Ethyl Alcohol	TWA 1000 ppm from ACGIH (TLV) (US) TWA 1000 ppm from OSHA (PEL) (US) TWA 1900 mg/m3 from ACGIH (TLV) (US) TWA 1880 mg/m3 from OSHA (PEL) (US)
Methanol	TWA 200 ppm from ACGIH (TLV) (US) SKIN TWA 260 ppm from ACGIH (TLV) (US) SKIN
Methyl Ethyl Ketone	TWA 590 STEL 885 mg/m3 from ACGIH (TLV) (US) TWA 200 STEL 300 ppm from ACGIH (TLV) (US)

Consult local authorities for acceptable exposure limits.

Section VIII - ENVIRONMENTAL PROTECTION

ENVIRONMENTAL PRECAUTIONS: Use with adequate ventilation, local exhaust is acceptable. When transferring between metal containers, ground both vessels.

SPILL OR LEAK PRECAUTIONS: Shut off all possible sources of ignition. Wear protective gloves, use respirator if large quantities are involved of if working in a poorly ventilated area

WASTE DISPOSAL: Small amounts can be run to waste with plenty of water. Large amounts should be disposed of in an incineration facility equipped with an afterburner and scrubber. Consult local, provincial and federal regulations.

Section IX - REGULATORY CONTROLS

DEPT. OF TRANSPORTATION: Regulated under Transport of Dangerous Goods

DOT CLASSIFICATION: Class 3.2 (6.1) UN: 1986

DOT PROPER SHIPPING NAME: Alcohols, Toxic NOS (Ethanol solutions)

OTHER DOT INFORMATION: Packing group II

WHMIS CLASSIFICATION: B2, D1A, D2B

OTHER REGULATORY REQUIREMENT: none

Section X - PRECAUTIONS: HANDLING, STORAGE & USAGE

Store in a cool place away from any possible source of ignition, use only in adequately ventilated areas and ensure against static electricity.

PREPARED BY: MSDS Department **DATE:** Update January 10, 2008

Syndel Laboratories Ltd.
958 Chatsworth Road
Qualicum Beach, BC
Canada V9K 1V5
Tel: (250) 752-5256 or (800) 663-2282
FAX: (250) 752-5188
e-mail: info@syndel.com

Website updated - May 20, 2008

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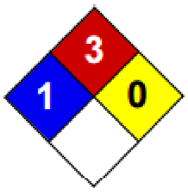

Health	2
Fire	3
Reactivity	0
Personal Protection	H

Material Safety Data Sheet
Methyl alcohol MSDS

Section 1: Chemical Product and Company Identification

Product Name: Methyl alcohol

Catalog Codes: SLM3064, SLM3952

CAS#: 67-56-1

RTECS: PC1400000

TSCA: TSCA 8(b) inventory: Methyl alcohol

CI#: Not applicable.

Synonym: Wood alcohol, Methanol; Methylol; Wood Spirit; Carbinol

Chemical Name: Methanol

Chemical Formula: CH3OH

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Methyl alcohol	67-56-1	100

Toxicological Data on Ingredients: Methyl alcohol: ORAL (LD50): Acute: 5628 mg/kg [Rat]. DERMAL (LD50): Acute: 15800 mg/kg [Rabbit]. VAPOR (LC50): Acute: 64000 ppm 4 hours [Rat].

Section 3: Hazards Identification

Potential Acute Health Effects:
Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator). Severe over-exposure can result in death.

Potential Chronic Health Effects:
Slightly hazardous in case of skin contact (sensitizer). CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. Mutagenic for bacteria and/or yeast. TERATOGENIC EFFECTS: Classified POSSIBLE for human. DEVELOPMENTAL TOXICITY: Not available. The substance is toxic to eyes. The substance may be toxic to blood, kidneys, liver, brain, peripheral nervous system, upper respiratory tract, skin, central nervous system (CNS), optic nerve. Repeated or prolonged exposure to the substance can produce target organs damage. Repeated exposure to a highly toxic material may produce general deterioration of health by an accumulation in one or many human organs.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Cold water may be used. Get medical attention.

Skin Contact:
In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used.Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

Ingestion:
If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: Flammable.

Auto-Ignition Temperature: 464°C (867.2°F)

Flash Points: CLOSED CUP: 12°C (53.6°F). OPEN CUP: 16°C (60.8°F).

Flammable Limits: LOWER: 6% UPPER: 36.5%

Products of Combustion: These products are carbon oxides (CO, CO2).

Fire Hazards in Presence of Various Substances:
Highly flammable in presence of open flames and sparks, of heat. Non-flammable in presence of shocks.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Explosive in presence of open flames and sparks, of heat.

Fire Fighting Media and Instructions:
Flammable liquid, soluble or dispersed in water. SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use alcohol foam, water spray or fog.

Special Remarks on Fire Hazards:
Explosive in the form of vapor when exposed to heat or flame. Vapor may travel considerable distance to source of ignition and flash back. When heated to decomposition, it emits acrid smoke and irritating fumes. CAUTION: MAY BURN WITH NEAR INVISIBLE FLAME

Special Remarks on Explosion Hazards:
Forms an explosive mixture with air due to its low flash point. Explosive when mixed with Choroform + sodium methoxide and diethyl zinc. It boils violently and explodes.

Section 6: Accidental Release Measures

Small Spill:
Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container.

Large Spill:
Flammable liquid. Poisonous liquid. Keep away from heat. Keep away from sources of ignition. Stop leak if without risk. Absorb with DRY earth, sand or other non-combustible material. Do not get water inside container. Do not touch spilled material. Use water spray to reduce vapors. Prevent entry into sewers, basements or confined areas; dike if needed. Call for assistance on disposal. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:
Keep locked up.. Keep away from heat. Keep away from sources of ignition. Ground all equipment containing material. Do not ingest. Do not breathe gas/fumes/ vapor/spray. Wear suitable protective clothing. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as oxidizing agents, metals, acids.

Storage:
Store in a segregated and approved area. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective threshold limit value. Ensure that eyewash stations and safety showers are proximal to the work-station location.

Personal Protection:
Splash goggles. Lab coat. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Vapor respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:
TWA: 200 from OSHA (PEL) [United States] TWA: 200 STEL: 250 (ppm) from ACGIH (TLV) [United States] [1999] STEL: 250 from NIOSH [United States] TWA: 200 STEL: 250 (ppm) from NIOSH SKIN TWA: 200 STEL: 250 (ppm) [Canada] Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Liquid.

Odor: Alcohol like. Pungent when crude.

Taste: Not available.

Molecular Weight: 32.04 g/mole

Color: Colorless.

pH (1% soln/water): Not available.

Boiling Point: 64.5°C (148.1°F)

Melting Point: -97.8°C (-144°F)

Critical Temperature: 240°C (464°F)

Specific Gravity: 0.7915 (Water = 1)

Vapor Pressure: 12.3 kPa (@ 20°C)

Vapor Density: 1.11 (Air = 1)

Volatility: Not available.

Odor Threshold: 100 ppm

Water/Oil Dist. Coeff.: The product is more soluble in water; log(oil/water) = -0.8

Ionicity (in Water): Non-ionic.

Dispersion Properties: See solubility in water.

Solubility: Easily soluble in cold water, hot water.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Heat, ingnition sources, incompatible materials

Incompatibility with various substances: Reactive with oxidizing agents, metals, acids.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity:
Can react vigorously with oxidizers. Violent reaction with alkyl aluminum salts, acetyl bromide, chloroform + sodium methoxide, chromic anhydride, cyanuirc chlorite, lead perchlorate, phosphorous trioxide, nitric acid. Exothermic reaction with sodium hydroxide + chloroform. Incompatible with beryllium dihydride, metals (potassium and magnesium), oxidants (barium perchlorate, bromine, sodium hypochlorite, chlorine, hydrogen peroxide), potassium tert-butoxide, carbon tetrachloride, alkali metals, metals (aluminum, potassium magnesium, zinc), and dichlormethane. Rapid autocatalytic dissolution of aluminum, magnesium or zinc in 9:1 methanol + carbon tetrachloride - sufficiently vigorous to be rated as potentially hazardous. May attack some plastics, rubber, and coatings.

Special Remarks on Corrosivity: Not available.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Eye contact. Inhalation. Ingestion.

Toxicity to Animals:
WARNING: THE LC50 VALUES HEREUNDER ARE ESTIMATED ON THE BASIS OF A 4-HOUR EXPOSURE. Acute oral toxicity (LD50): 5628 mg/kg [Rat]. Acute dermal toxicity (LD50): 15800 mg/kg [Rabbit]. Acute toxicity of the vapor (LC50): 64000 4 hours [Rat].

Chronic Effects on Humans:
MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. Mutagenic for bacteria and/or yeast. TERATOGENIC EFFECTS: Classified POSSIBLE for human. Causes damage to the following organs: eyes. May cause damage to the following organs: blood, kidneys, liver, brain, peripheral nervous system, upper respiratory tract, skin, central nervous system (CNS), optic nerve.

Other Toxic Effects on Humans:
Hazardous in case of skin contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator).

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans:

Passes through the placental barrier. May affect genetic material. May cause birth defects and adverse reproductive effects(paternal and maternal effects and fetotoxicity) based on animal studies.

Special Remarks on other Toxic Effects on Humans:

Section 12: Ecological Information

Ecotoxicity: Ecotoxicity in water (LC50): 29400 mg/l 96 hours [Fathead Minnow].

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are less toxic than the product itself.

Special Remarks on the Products of Biodegradation:
Methanol in water is rapidly biodegraded and volatilized. Aquatic hydrolysis, oxidation, photolysis, adsorption to sediment, and bioconcentration are not significant fate processes. The half-life of methanol in surfact water ranges from 24 hrs. to 168 hrs. Based on its vapor pressure, methanol exists almost entirely in the vapor phase in the ambient atmosphere. It is degraded by reaction with photochemically produced hydroxyl radicals and has an estimated half-life of 17.8 days. Methanol is physically removed from air by rain due to its solubility. Methanol can react with NO2 in pollulted to form methyl nitrate. The half-life of methanol in air ranges from 71 hrs. (3 days) to 713 hrs. (29.7 days) based on photooxidation half-life in air.

Section 13: Disposal Considerations

Waste Disposal:
Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: CLASS 3: Flammable liquid.

Identification: : Methyl alcohol UNNA: 1230 PG: II

Special Provisions for Transport: Not available.

Section 15: Other Regulatory Information

Federal and State Regulations:
Connecticut hazardous material survey.: Methyl alcohol Illinois toxic substances disclosure to employee act: Methyl alcohol Illinois chemical safety act: Methyl alcohol New York release reporting list: Methyl alcohol Rhode Island RTK hazardous substances: Methyl alcohol Pennsylvania RTK: Methyl alcohol Minnesota: Methyl alcohol Massachusetts RTK: Methyl alcohol Massachusetts spill list: Methyl alcohol New Jersey: Methyl alcohol New Jersey spill list: Methyl alcohol Louisiana spill reporting: Methyl alcohol California Directors List of Hazardous Substances (8CCR 339): Methyl alcohol Tennesse Hazardous Right to Know : Methyl alcohol TSCA 8(b) inventory: Methyl alcohol SARA 313 toxic chemical notification and release reporting: Methyl alcohol CERCLA: Hazardous substances.: Methyl alcohol: 5000 lbs. (2268 kg)

Other Regulations:
OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200). EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada):
CLASS B-2: Flammable liquid with a flash point lower than 37.8°C (100°F). CLASS D-1B: Material causing immediate and serious toxic effects (TOXIC). CLASS D-2A: Material causing other toxic effects (VERY TOXIC). Class D-2B: Material causing other toxic effects (TOXIC).

DSCL (EEC):
R11- Highly flammable. R23/24/25- Toxic by inhalation, in contact with skin and if swallowed. R39- Danger of very serious irreversible effects. R39/23/24/25- Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed. S7- Keep container tightly closed. S16- Keep away from sources of ignition - No smoking. S36/37- Wear suitable protective clothing and gloves. S45- In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

HMIS (U.S.A.):

Health Hazard: 2

Fire Hazard: 3

Reactivity: 0

Personal Protection: h

National Fire Protection Association (U.S.A.):

Health: 1

Flammability: 3

Reactivity: 0

Specific hazard:

Protective Equipment:
Gloves. Lab coat. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Splash goggles.

Section 16: Other Information

References:
-SAX, N.I. Dangerous Properties of Indutrial Materials. Toronto, Van Nostrand Reinold, 6e ed. 1984. -Material safety data sheet emitted by: la Commission de la SantÃ© et de la SÃ©curitÃ© du Travail du QuÃ©bec. -Hawley, G.G.. The Condensed Chemical Dictionary, 11e ed., New York N.Y., Van Nostrand Reinold, 1987. LOLI, HSDB, RTECS, HAZARDTEXT, REPROTOX databases

Other Special Considerations: Not available.

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Last Updated: 05/21/2013 12:00 PM

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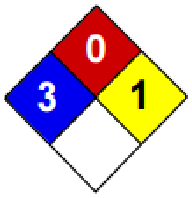

Health	3
Fire	0
Reactivity	2
Personal Protection	J

Material Safety Data Sheet
Potassium hydroxide MSDS

Section 1: Chemical Product and Company Identification

Product Name: Potassium hydroxide

Catalog Codes: SLP4096, SLP3085, SLP4900, SLP2071

CAS#: 1310-58-3

RTECS: TT2100000

TSCA: TSCA 8(b) inventory: Potassium hydroxide

CI#: Not available.

Synonym:

Chemical Name: Potassium Hydroxide

Chemical Formula: KOH

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Potassium hydroxide	1310-58-3	100

Toxicological Data on Ingredients: Potassium hydroxide: ORAL (LD50): Acute: 273 mg/kg [Rat].

Section 3: Hazards Identification

Potential Acute Health Effects:
Very hazardous in case of skin contact (corrosive, irritant), of eye contact (irritant, corrosive), of ingestion, of inhalation. The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to upper respiratory tract, skin, eyes. Repeated or prolonged exposure to the substance can produce target organs damage. Repeated exposure of the eyes to a low level of dust can produce eye irritation. Repeated skin exposure can produce local skin destruction, or dermatitis. Repeated inhalation of dust can produce varying degree of respiratory irritation or lung damage.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

Skin Contact:
In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used.Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: Non-flammable.

Auto-Ignition Temperature: Not applicable.

Flash Points: Not applicable.

Flammable Limits: Not applicable.

Products of Combustion: Not available.

Fire Hazards in Presence of Various Substances: metals, acids

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions: Not applicable.

Special Remarks on Fire Hazards:
Violent reaction or ignition under appropriate conditions with acids, alcohols, p-bis(1,3-dibromoethyl) benzene, cyclopentadiene, germanium, hyponitrous acid, maleic anhydride, nitroalkanes, 2-nitrophenol, potassium peroxodisulfate, sugars, 2,2,3,3-tetrafluoropropanol, thorium dicarbide. Molten ortho -nitrophenol reacts violently with potassium hydroxide. When potassium hydroxide and tetrachloroethane are heated, a spontaneously flammable gas, chloroacetylene, is formed. When phosphorus is boiled in a solution of potassium hydroxide, phosphine gas is evolved which is spontaneously flammable. 1,2-Dichloroethylene and Potassium hydroxide reaction produces chloroacetylene which is spontaneously flammable in air. Potassium Persulfate and a little Potassium hydroxide and water will ignite. When wet, attacks metals such as aluminum, tin, lead, and zinc, producing flammable hydrogen gas.

Special Remarks on Explosion Hazards:

Potentially explosive reaction with bromoform + crown ethers, chlorine dioxide, nitrobenzene, nitromethane, nitrogen trichloride, peroxidized tetrahydrofuran, 2,4,6-trinitrotoluene. Reaction with ammonium hexachloroplatiate(2-) + heat forms heat sensitive explosive product. Potassium hydroxide will cause explosive decomposition of maleic anhydride. Detonation will occur when potassiuim hydroxide is mixed with n-methyl-nitroso urea and methylene chloride. Nitrogen trichloride explodes on contact with potassium hydroxide.

Section 6: Accidental Release Measures

Small Spill:
Use appropriate tools to put the spilled solid in a convenient waste disposal container. If necessary: Neutralize the residue with a dilute solution of acetic acid.

Large Spill:
Corrosive solid. Stop leak if without risk. Do not get water inside container. Do not touch spilled material. Use water spray to reduce vapors. Prevent entry into sewers, basements or confined areas; dike if needed. Call for assistance on disposal. Neutralize the residue with a dilute solution of acetic acid. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:
Keep container dry. Do not ingest. Do not breathe dust. Never add water to this product. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as organic materials, metals, acids, moisture.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area. Do not store above 23°C (73.4°F).

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection:
Splash goggles. Synthetic apron. Vapor and dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Vapor and dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:
CEIL: 2 (mg/m3) from OSHA (PEL) [United States] CEIL: 2 (mg/m3) from ACGIH (TLV) [United States] Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (Solid pellets.)

Odor: Odorless.

Taste: Not available.

Molecular Weight: 56.11 g/mole

Color: White.

pH (1% soln/water): 13 [Basic.]

Boiling Point: Decomposition temperature: 1384°C (2523.2°F)

Melting Point: 380°C (716°F)

Critical Temperature: Not available.

Specific Gravity: 2.044 (Water = 1)

Vapor Pressure: Not applicable.

Vapor Density: Not available.

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water.

Solubility:
Easily soluble in cold water, hot water. Insoluble in diethyl ether.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Incompatible materials, dust generation, exposure to moist air or water.

Incompatibility with various substances:
Highly reactive with acids. Reactive with organic materials, metals, moisture.

Corrosivity:
Extremely corrosive in presence of aluminum, brass, and zinc. Slightly corrosive in presence of copper, of stainless steel(304). Non-corrosive in presence of stainless steel(316).

Special Remarks on Reactivity:
Hygroscopic (absorbs moisture from air). When dissolved in water or alcohol or when the solution is treated with acid, much heat is generated. Reacts violently with acids, halogens, halogenated hydrocarbons, maleic anhydride, organic anhydrides, isocyanates, alkylene oxides, epichlorhydrin, aldehydes, alcohols, gylcols, phenols, cresols, caprolactum solution. Also incompatible with nitro compounds (nitrobenzene, nitromethane, nitrogen trichloride), organic materials, acid anhydrides, acid chlorides, magnesium, peroxidized tetrahydrofuran, chlorine dioxide, maleic dicarbide, sugars. When wet attacks metals such as aluminum, tin, lead, and zinc.

Special Remarks on Corrosivity:
When wet, attacks metals such as aluminum, tin, lead, and zinc, producing flammable hydrogen gas. Severe corrosive effect on brass and bronze.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Inhalation. Ingestion.

Toxicity to Animals: Acute oral toxicity (LD50): 273 mg/kg [Rat].

Chronic Effects on Humans:

MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. May cause damage to the following organs: upper respiratory tract, skin, eyes.

Other Toxic Effects on Humans:
Extremely hazardous in case of inhalation (lung corrosive). Very hazardous in case of skin contact (corrosive, irritant), of eye contact (corrosive), of ingestion, .

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: May affect genetic material based on animal data.

Special Remarks on other Toxic Effects on Humans:
Acute Potential Health Effects: Skin: Causes severe skin irritation and burns. Eyes: Causes severe eye irritation and burns. May cause irreversible eye injury. Inhalation: Causes severe irritation and burns of the respiratory tract and mucous membranes. Irritation may lead to chemical pneumonitis Ingestion: Harmful if swallowed. May cause severe and permanent damage to the digestive tract. Causes severe irritation and burns of the gastrointestinal (digestive) tract with abdominal pain, vomiting and possible death. May cause perforation of the digestive tract. Chronic Potential Health Effects: Chronic contact with dilute solutions of potassium hydroxide can cause dermatitis. Inhalation can produce chronic productive cough, and shortness of breath.

Section 12: Ecological Information

Ecotoxicity: Ecotoxicity in water (LC50): 80 mg/l 24 hours [Mosquito Fish].

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are less toxic than the product itself.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:
Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Class 8: Corrosive material

Identification: : Potassium hydroxide, solid UNNA: 1813 PG: II

Special Provisions for Transport: Not available.

Section 15: Other Regulatory Information

Federal and State Regulations:
New York release reporting list: Potassium hydroxide Pennsylvania RTK: Potassium hydroxide Florida: Potassium hydroxide Minnesota: Potassium hydroxide Massachusetts RTK: Potassium hydroxide New Jersey: Potassium hydroxide California Director's List of Hazardous Substances: Potassium hydroxide TSCA 8(b) inventory: Potassium hydroxide CERCLA: Hazardous substances.: Potassium hydroxide: 1000 lbs. (453.6 kg)

Other Regulations:
OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200). EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada):
CLASS D-1B: Material causing immediate and serious toxic effects (TOXIC). CLASS E: Corrosive solid.

DSCL (EEC):

HMIS (U.S.A.):

Health Hazard: 3

Fire Hazard: 0

Reactivity: 2

Personal Protection: j

National Fire Protection Association (U.S.A.):

Health: 3

Flammability: 0

Reactivity: 1

Specific hazard:

Protective Equipment:
Gloves. Synthetic apron. Vapor and dust respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Splash goggles.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

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MATERIAL SAFETY DATA SHEET

1. Identification of substance and of the company

1.1 Identification of the substance:	DudaLite DW-R10 DryWash Resin
1.2 Use of substance:	Purification of biodiesel
1.3 Name of manufacturer:	Duda Diesel 7055 Greenbrier Road Bldg A Madison, AL 35756 Tel: 256-340-4866 Fax: 866-568-3412
Responsible person:	Brian Duda
Email:	support@dudadiesel.com
1.4 Emergency telephone:	256-340-4866

2. Hazards identification

Emergency overview

- Physical state: amber, light brown, dark brown, gold, black solid bead
- Odor: Not applicable
- Contact with eyes: may cause temporary eye irritation
- Contact with skin: may be slightly irritating to skin
-

Low hazard for usual industrial or commercial handling by trained personnel

OSHA regulatory status: This product is not hazardous according to OSHA 29CFR 1910.1200

Potential health effects

Inhalation: limited inhalation hazard at normal work temperatures
Eye contact: may cause temporary eye irritation
Skin contact: may be slightly irritating to skin
Ingestion: under normal conditions of intended use, this material does not pose a risk to health. However, ingestion may cause irritation and malaise
Chronic health effects: no other specific acute or chronic health impact noted.
Target organs: eye/skin
Potential physical/chemical effects: This product is a combustible per NFPA

Environmental effects: The environmental hazard of this product is considered limited

3. Composition/information on ingredients

3.1

Ingredient	Concentration	CAS Number	R Phrases	Symbol
Sodium polystyrene sulphonate	98-99%	69011-22-9	–	–
Water	1-2%	7732-18-5	_	_

4. First aid measures

Inhalation: no specific first aid measures noted

Eye contact: any material that contacts the eye should be washed out immediately with water. If possible, remove any contact lenses. Get medical attention if discomfort continues.
Skin contact: Wash skin with soap and water.
Ingestion: immediately rinse mouth and drink plenty of water (200-300ml). Get medical attention if irritation persists.

5. Fire-fighting measures

Flammable properties- NFPA rating fire=1

Extinguishing media: extinguish with foam, carbon dioxide, dry powder or water fog.

Unsuitable extinguishing media: not applicable

Special fire fighting procedures: self contained breathing apparatus and full protective clothing must be worn in case of fire

Unusual fire and explosion hazards: Not available

Hazardous combustion products: Monomers, residual organics, carbon and sulfur oxides

Protective measures: Selection of respiratory protection for fire-fighting: follow the general fire precautions indicated in the workplace.

6. Accidental release measures

Personal precautions:
Keep people away
Spillage causes slippery surfaces
Environmental precautions
Do not allow to enter public sewers and water courses.
Methods of cleaning up:
Sweep up as much as possible and transfer to plastic containers for recovery and disposal.

7. Handling and storage

7.1 Handling

Avoid contact with eyes and prolonged skin contact. See section 8 of the MSDS for Personal protective equipment.

7.2 Storage

Store at temperatures above zero degrees C
Store at temperatures below forty degrees C
Keep in original container
Keep container tightly closed to prevent the absorption of water
Store away from incompatible materials

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8. Exposure controls/personal protection

8.1. Exposure limits: no exposure limits noted for substances

8.2 Exposure Controls: provide adequate ventilation

8.2.1 Occupational exposure controls

Respiratory protection: if engineering controls do not maintain airborne concentrations below recommended exposure limits (where applicable) or to an acceptable level (in countries where exposure limits have not been established), an approved respirator must be worn. In the United States of America, if respirators are used, a program must be instituted to assure compliance with OSHA standard 63 FR 1152, January 8, 1998. Respirator type: High efficiency particulate respirator

- –Eye protection: Risk of contact- wear approved safety goggles
- – Hand protection: Risk of contact – Wear protective gloves. Suitable gloves can be recommended by the glove supplier.
- Skin protection: Risk of contact- use skin protection. It is a good industrial hygiene practice to minimize skin contact.

8.2.2. Hygiene measures

-always observe goo personal hygiene measures, such as washing after handling the material before eating drinking and/or smoking. Routinely wash work clothing and protective equipment to remove contaminants.

8.2.3 Environmental exposure controls

- environmental manager must be informed of all major spillages.

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9. 9. Physical and chemical properties

9.1 Appearance: Gold, amber, light brown, dark brown, black and green beads
Odor: odorless
Odor threshold: Not available
Physical state: Solid (bead)
pH: neutral aqueous slurry
Melting point: not available
Freezing point: not available
Boiling point: not available
Flash point: not available
Evaporation rate: not available
Flammability (solid, gas): not available
Flammability limit –
    Upper flammability limit: not available.
    Lower flammability limit: not available
Vapor pressure: not available
Vapor density (air = 1): not available
Specific Gravity: 1.15 to 1.35
Solubility in water: insoluble
Solubility (other): not available
Partition coefficient (n0octanol/water): not available
Auto ignition temperature: not available
Decomposition temperature: not available

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10. Stability and reactivity

10.1 Conditions to avoid

Considered stable under normal conditions
Avoid heat

10.2 Materials to avoid

Incompatible with strong oxidizing substances. Contact with strong oxidizers, especially nitric acid, may produce low molecular weight organics that may form explosive mixtures.

10.3 Hazardous decomposition products

At elevated temperatures: Benzene compounds, carbon oxides, styrene, sulfur oxides

10.4 Possibility of hazardous reactions: not available

11. Toxicological information

Acute toxicity: no evidence of acute toxicity
Carcinogenicity: no evidence of carcinogenic effects
Teratogenicity: no evidence of reproductive effects
Mutagenicity: no evidence of mutagenic effects

12. Ecological information

12.1 Ecotoxicity- no data available
12.2 Mobility- The product is insoluble in water and will sediment in water systems
12.3 Persistence and degradability: The product is not readily biodegradable
12.4 Bio-accumulative potential: potential to bio-accumulate is low
12.5 Other adverse effects: no data available

13. Disposal considerations

General information: Dispose of waste and residues in accordance with local authority requirements
Disposal method: no specific disposal method required
Container: Since emptied containers retain product residue, follow label warnings even after container is emptied

14.Transport information

-DOT- not regulated
-TDG – not regulated
-IATA – not regulated
-IMDG- not regulated

15.Regulatory information

Canadian controlled Products Regulations- This product has been classified according to the hazard criteria of the Canadian Controlled Products Regulations Section 33 and the MSDS contains all required information

WHMIS Classification- This is not a WHMIS controlled product

Mexican Dangerous Statement – This product is not dangerous according to Mexican regulations

Applicable International laws and regulations: This substance meets OECD polymer definition and is therefore exempt from REACH registration

Inventory Status – This product or all components are listed or exempt from listing on the following inventory: TSCA, DSL

US Regulations
CERCLA Hazardous Substance List (40 CFR 302.4): not regulated

SARA Title III
-Section 302 Extremely Hazardous Substances (40 CFR 355, Appendix A): Not Not regulated
Section 311/312 (40 CFR 370): Acute (Immediate) Chronic (delayed) Fire reactive Pressure Generating
Section 313 Toxic Release Inventory (40C CFR 372): Not regulated

Clean Air Act (CAA) Sections 112(R) Accidental Release Prevention (40 CFR 68.130) – not regulated
Clean Water Act Section 311 Hazardous Substances (40 CFR 117.3)- not regulated

Drug Enforcement Act – not regulated

TSCA

TSCA Section 4(a) Final Test Rules & Testing Consent Orders: Not regulated
TSCA Section 5(a)(2) Final Significant Use Rules (SNURs) (40CFR 721, Subpt. E): not regulated
TSCA Section 5(e) PMN – Substance Consent Orders: not regulated
TSCA Section 12(b) Export Notification (40 CFR 707, Subpt. D): not regulated

State Regulations

- California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65): not regulated
- Massachusetts Right-To-Know List: not regulated
- Michigan Critical Materials List: not regulated
- Minnesota Hazardous Substances List: not regulated
- New Jersey Right-To-Know List: not regulated
- Pennsylvania Right-To-Know List: not regulated
- Rhode Island Right-To-Know List: not regulated

16. Other information

Hazard Ratings
NFPA

Health hazard- 1 ; Fire hazard- 1 ; Instability – 0; Special Hazard – 0
Hazard rating 0- minimal; 1- slight; 2 – moderate; 3 – serious; 4 – severe
NFPA Label colored diamond code: Blue – health; Red – Flammability; Yellow – instability; White – Special hazards

HMIS – Health hazard – 1; Flammability – 1; Physical Hazard – 0; Personal Protection –
Hazard rating: 0 – minimal; 1 – slight; 2 – moderate; 3 – serious; 4 – Severe
HMIS Label colored bar code: Blue – Health; Red – Flammability; Orange – Physical Hazards; White – Special

Relevant R phrases: none

Note:
The information provided in this material safety data sheet is based on current knowledge about he product and current legal requirements and standards. It relates specifically to health, safety and environmental requirements and standards. It may not identify all hazards associated with the product or its uses or misuses. It does not signify any warranty with regard to the properties of the product, and only applies when the product is used for the purposes indicated in section 1. This product is not sold as suitable for other purposes and such other usage may cause risks not mentioned in the safety data sheet.

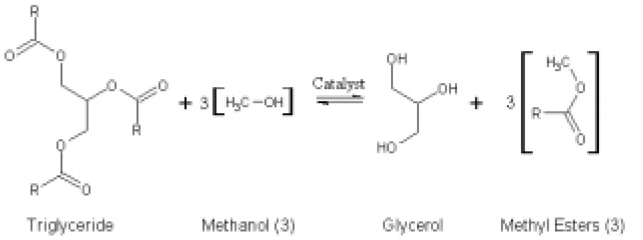
Date of Revision November 1, 2011

C. Existing Pre-laboratory Exercise

Biodiesel Reaction Safety and Kinetics

Renewable fuels such as ethanol and biodiesel are becoming increasingly popular alternatives to petroleum based fuels. In this laboratory exercise, you will study temperature and mass transfer effects on the base-catalyzed transesterification reaction used to produce biodiesel from vegetable oil. In addition to studying the fundamental chemical engineering principles required to optimize the reaction, you will study the safety requirements for this process and gain experience with following a standard operating procedure and maintaining an electronic batch record.

The overall reaction for production of biodiesel from vegetable oil is shown in Figure 1.



$$\text{TG (or O)} + 3\,\text{M} \rightleftarrows \text{G} + 3\,\text{BD}$$

Figure 1. Overall biodiesel production reaction [1].

Vegetable oil is primarily composed of triglycerides with long chain aliphatic R groups of the form $CH_3(CH_2)_7CH{=}CH(CH_2)_7$, but different types of oils have different amounts of saturated and unsaturated fats of various types in the R groups [2]. The methyl esters, also called fatty acid methyl esters (FAMEs), are the biodiesel product we seek. The reaction can be either base-catalyzed or acid-catalyzed. Vegetable oil can be burned directly but is not a good engine fuel due to its high viscosity. Transesterification converts the high viscosity oil into 3 biodiesel molecules with viscosity and other properties similar to those of petroleum diesel fuel [3].

The apparent simplicity of the process along with the readily available supply of waste vegetable oil from deep fry food preparation has given rise to a large number of small scale and “home brew” processors who usually use potassium hydroxide as catalyst. As you will learn in this laboratory experiment, this base-catalyzed biodiesel process is neither particularly simple nor particularly safe. Methanol is both poisonous and highly flammable. KOH is caustic and when mixed with methanol forms an extremely dangerous potassium methoxide solution. Your first objective for the pre-lab exercise will be to obtain and read the MSDS information for KOH, methanol, and potassium methoxide. You will need to write a brief discussion of the safety precautions required for handling and processing these materials and the safeguards we have included in the lab. Your second objective for the pre-lab will be to locate (on the web or elsewhere) a report of an accident involving a fire with this process. You will need to write a brief summary of the accident and a discussion of what could have been done to prevent it.

We have converted a 5 ft wide fume hood into a mini biodiesel pilot plant. Our computer controlled reactor system consists of a 250 ml jacketed glass catalyst preparation reactor and a 500 ml jacketed glass process reactor connected to feed and product vessels and each other via peristaltic pumps [4]. Sparkless and brushless overhead electronic stirrers are used to control and monitor the stirrer rpms and torque in each reactor. A constant temperature is maintained with a separate temperature bath circulating water through the jacket of each reactor. A third circulating temperature bath is used to circulate chilled water through condensers attached to each reactor vessel to minimize evaporation losses at elevated process temperatures. Using a computer control panel outside of the hood to operate the process gives it the feel of a larger scale industrial process and minimizes some of the dangers from the hazardous and flammable materials involved.

For a typical experiment, methanol and vegetable oil are introduced into the catalyst prep reactor and process reactor, respectively, by computer controlled gravimetric dosing from feed vessels on electronic balances working together with the peristaltic pumps. Once both reactors reach the target temperature, solid KOH catalyst is manually added and dissolved in the catalyst prep reactor. The process reaction is initiated by pumping the contents of the catalyst prep reactor into the process reactor. Samples are withdrawn from the process reactor at regular intervals and analyzed for glycerol content via an enzymatic assay to follow the reaction progress [5]. At the end of the experiment all samples can be analyzed at once using a 96 well plate reader at a wavelength of 570 nm. The reactor system is washed with acetone and allowed to air dry between experimental runs. The ReactorMaster software [4] that controls the process also collects data on each piece of equipment, allows for pauses to insert comments, and effectively keeps an electronic batch record of everything that happens in each experimental run. You will be required to input comments into the batch record indicating that you have either performed or witnessed various aspects of the standard operating procedure as is often required in the bioprocess industry.

As noted above, the biodiesel production process is more complex than it may seem from looking at Figure 1. It has been observed that the production process depends on the type of oil used, the water and free fatty acid content of the oil, the type and amount of catalyst, the alcohol to oil ratio, and operating conditions such as temperature, pressure, and mixing rate [6, 7]. The reaction is believed to involve multiple steps as indicated in Figure 2 where it can be seen that triglyceride (TG) is first attacked by the methoxide ion CH_3O- (present in the basic KOH/methanol solution) to produce one biodiesel (BD) and a di-glyceride (DG). The DG is next converted to a second BD and a mono-glyceride (MG). Finally, in a third reaction step, the MG is converted to a third BD and glycerol (G). Each of these reactions can be considered reversible, giving rise to a forward and a reverse rate constant for each of the three reactions. Side reactions that produce soap (via saponification) instead of biodiesel often occur, especially if water is present in the mixture, but we will neglect side reactions in our analysis. To complicate matters further, methanol and oil are essentially insoluble in one another requiring good stirring to bring them into contact. The reaction mixture begins as two phases, then goes to one phase, and finally back to two phases because the glycerol and biodiesel are also essentially insoluble in one another. This has caused many researchers to believe that the reaction cannot be properly modeled without understanding the phase behavior and droplet size changes that occur during the course of the reaction [8, 9]. Others have shown that in cases with sufficient stirring, experimental data can be modeled using only the reversible reactions shown in Figure 2.

$$\mathrm{TG + M \rightleftarrows BD + DG} \qquad (1)$$

$$\mathrm{DG + M \rightleftarrows BD + MG} \qquad (2)$$

$$\mathrm{MG + M \rightleftarrows BD + G} \qquad (3)$$

Figure 2. Multiple step biodiesel reaction mechanism.

For example, Vicente et al [10] studied base-catalyzed transesterification of sunflower oil with 6:1 mole ratio of methanol to oil and stirring rates that they believed were sufficient to avoid mass transfer limitations. They varied the KOH catalyst concentration and the process temperature and measured the concentration of TG, DG, MG, BD, M, and G with time during the reaction. Assuming that the forward rate constants for reactions 1, 2, and 3 are given by k1, k3, and k5, while the reverse rate constants for the three reactions are given by k2, k4, and k6, they found the values of the rate constants that fit their data according to the mathematical model shown in Figure 3.

$$TG(0) = TGo \qquad M(0) = Mo \qquad DG(0) = 0 \qquad MG(0) = 0 \qquad BD(0) = 0 \qquad G(0) = Go$$

$$TG'(t) = -k1 \cdot TG(t) \cdot M(t) + k2 \cdot BD(t) \cdot DG(t)$$

$$DG'(t) = k1 \cdot TG(t) \cdot M(t) - k2 \cdot BD(t) \cdot DG(t) - k3 \cdot DG(t) \cdot M(t) + k4 \cdot BD(t) \cdot MG(t)$$

$$MG'(t) = k3 \cdot DG(t) \cdot M(t) - k4 \cdot BD(t) \cdot MG(t) - k5 \cdot MG(t) \cdot M(t)$$

$$M'(t) = -k1 \cdot TG(t) \cdot M(t) + k2 \cdot BD(t) \cdot DG(t) - k3 \cdot DG(t) \cdot M(t) + k4 \cdot BD(t) \cdot MG(t) - k5 \cdot MG(t) \cdot M(t)$$

$$BD'(t) = k1 \cdot TG(t) \cdot M(t) - k2 \cdot BD(t) \cdot DG(t) + k3 \cdot DG(t) \cdot M(t) - k4 \cdot BD(t) \cdot MG(t) + k5 \cdot MG(t) \cdot M(t)$$

$$G'(t) = k5 \cdot MG(t) \cdot M(t)$$

Figure 3. Mathematical model equations for multistep biodiesel reaction shown in Figure 2.

Note that in the mathematical model, the symbol TG'(t) represents the time derivative of the triglyceride concentration, dTG(t)/dt. At 35 °C and 0.5 weight percent KOH (on a percent weight of oil basis) they found the following rate constants with units of L/(mol min): k1 = 0.20, k2 = 0.98, k3 = 1.67, k4 = 2.18, k5 = 0.27, and k6 = 0.01 (sufficiently small that it has been omitted in the model). A Mathcad file that solves this model is available on the course website for your use.

In your experiments you will use canola oil rather than sunflower oil and will only be able to follow overall reaction conversion by following the glycerol concentration with time. It will, therefore, be difficult, if not impossible, to fit all six rate constants to your data. Some researchers have suggested that it is advantageous to consider the reaction in three stages: a brief initial mixing/mass transfer limited stage, an irreversible chemical reaction controlled stage, and a reversible equilibrium reaction controlled stage near the end [11]. These authors have further suggested that the pseudo 2nd order reaction:

$$O'(t) = dO(t)/dt = -k\,O(t)^2 \qquad (4)$$

provides an approximate model for the overall reaction shown in Figure 1, at least in the middle stage.

You will want to test this hypothesis using the Mathcad model of the reaction at 35 °C. That is, use the multistep model results for concentration with time to test if a 2nd order model could fit those results and determine the pseudo 2nd order rate constant, k. You should consult a chemical reaction engineering text for information on how to fit reaction data to a 2nd order model. Note that in the 2nd order model for oil (O) of Equation 4 there is no accounting for DG or MG, and the oil concentration, O, is used instead of TG. To compare results of this simple model to those of the multistep Mathcad model that solves the equations in Figure 3, you will need to follow total oil, O = TG + DG + MG, as indicated in the multistep Mathcad model.

For your lab exercise and final report, you will want to assume a pseudo 2nd order overall reaction and study the temperature dependence and evaluate an activation energy for canola oil conversion to BD with 0.5 weight % KOH and 6:1 methanol to oil ratio. You will also want to discuss mass transfer limitations of the reaction. For the pre-lab you should explain how you will study the T dependence, evaluate the activation energy, and study the mass transfer limitations. Densities and molecular weights for reactants and products are given in Table 1.

Table 1. Densities and molecular weights of canola biodiesel reactants and products [12].

component	density (g/ml)	molecular weight (g/mol)
canola oil	0.92	887.3
methanol	0.792	32.0
glycerol	1.26	92.1
biodiesel	0.88	297.1

Summary of deliverables for your pre-lab report:

1) Locate, copy, and read the MSDS for methanol, KOH, and potassium methoxide.

2) Write a brief discussion of the safety precautions needed in handling and processing these materials and include a brief discussion of the safeguards we have included to conduct this reaction safely.

3) Locate (on the web or elsewhere) a report of an accident involving a fire in biodiesel production. Write a brief summary of the accident and a discussion of what could have been done to prevent it.

4) Use the data generated in the Mathcad file that solves the multistep biodiesel reaction mathematical model to test the validity of using a pseudo 2nd order rate equation for sunflower oil at 35 °C, 0.5 weight % KOH, and 6:1 methanol to oil ratio. Report the pseudo 2nd order rate constant.

5) Explain how you will study the T dependence and evaluate the activation energy for a pseudo 2nd order rate equation using canola oil in the lab.

6) Explain how you will investigate mass transfer limitations of the tranesterification reaction in the lab.

References

1. http://upload.wikimedia.org/wikipedia/commons/7/72/Generic_Biodiesel_Reaction1.gif

2. http://www.scientificpsychic.com/fitness/fattyacids1.html

3. Van Gerpen, J., Biodiesel processing and production, Fuel Processing Technology, 86, 1097-1107, (2005).

4. http://syrris.com/batch-products/globe-chemical-reactor

5. http://www.bioassaysys.com/file_dir/EGLY.pdf

6. Freedman, B., Butterfield, R. O., and Pryde, E. H., Transesterification kinetics of soybean oil, J. Am. Oil Chem. Soc., 63, 1375-1380 (1986).

7. Noureddini, H. and Zhu, D., Kinetics of transesterification of soybean oil, J. Am. Oil Chem. Soc., 74, 1457-1463 (1997).

8. Gunvachai, K., Hassan, M. G., Shama, G., and Hellgardt, K., A new solubility model to describe biodiesel formation kinetics, Trans. IChemE, Part B, 85(B5), 383-389, (2007).

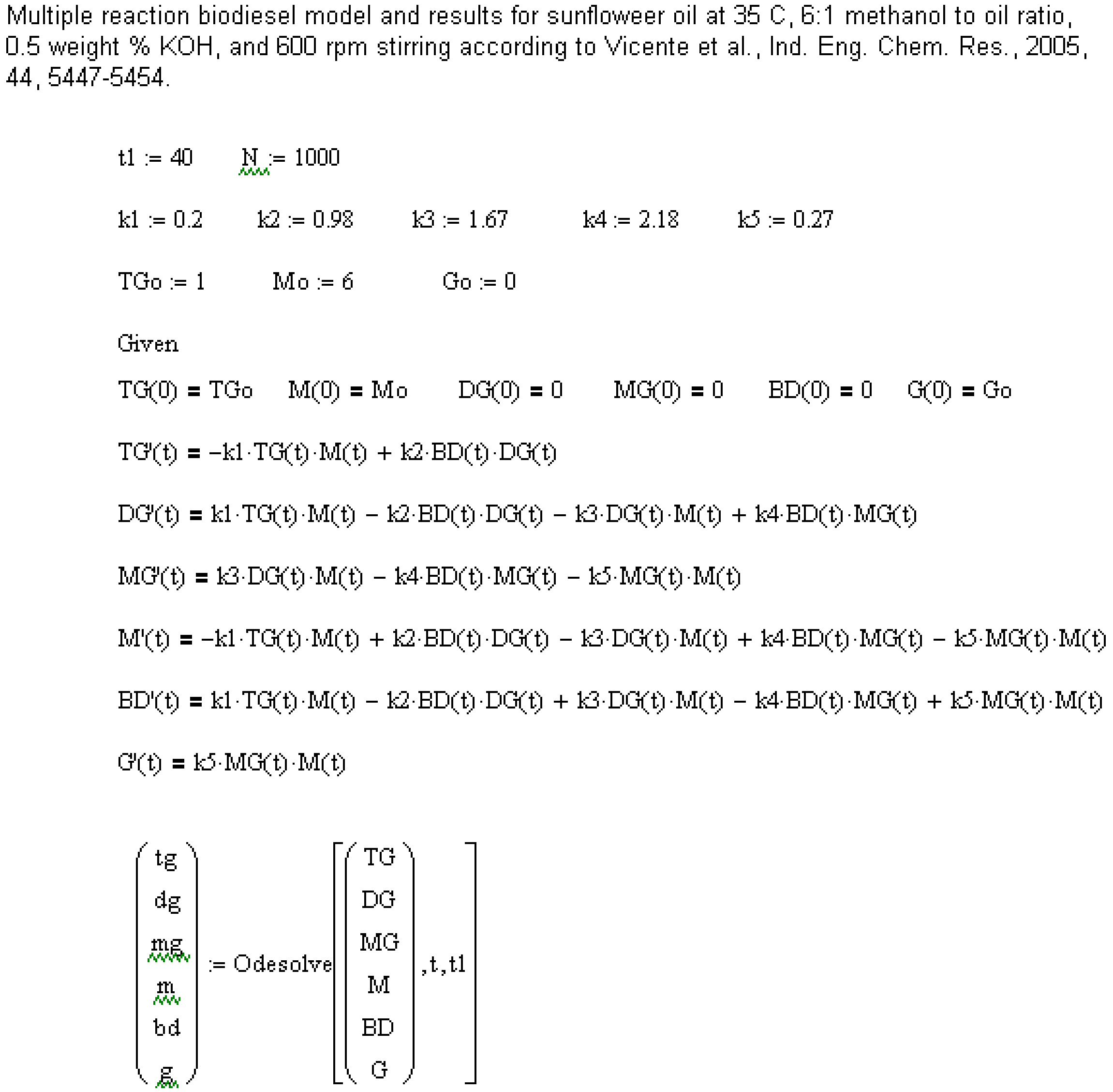
9. Slinn, M. and Kendall, K., Developing the reaction kinetics for a biodiesel reactor, Bioresource Technology, 100, 2324-2327, (2009).

10. Vicente, G., Martinez, M., Aracil, J., and Esteban, A., Kinetics of sunflower oil methanolysis, Ind. Eng. Chem. Res., 44, 5447-5454, (2005).

11. Stamenkovic, O. S., Todorovic, Z. B., Lazic, M. L., Veljkovic, V. B., and Skala, D. U., Kinetics of sunflower oil methanolysis at low temperatures, Bioresource Technology, 99 (2008) 1131-1140, (2008).

12. He, B. B., Singh, A. P., and Thompson, J. C., Experimental optimization of a continuous-flow reactive distillation reactor for biodiesel production, Trans. ASAE, 48, 2237-2243, (2005).

Mathcad Model



Multiple reaction biodiesel model and results for sunfloweer oil at 35 C, 6:1 methanol to oil ratio, 0.5 weight % KOH, and 600 rpm stirring according to Vicente et al., Ind. Eng. Chem. Res., 2005, 44, 5447-5454.

$t1 := 40 \qquad N := 1000$

$k1 := 0.2 \qquad k2 := 0.98 \qquad k3 := 1.67 \qquad k4 := 2.18 \qquad k5 := 0.27$

$TGo := 1 \qquad Mo := 6 \qquad Go := 0$

Given

$TG(0) = TGo \qquad M(0) = Mo \qquad DG(0) = 0 \qquad MG(0) = 0 \qquad BD(0) = 0 \qquad G(0) = Go$

$TG'(t) = -k1 \cdot TG(t) \cdot M(t) + k2 \cdot BD(t) \cdot DG(t)$

$DG'(t) = k1 \cdot TG(t) \cdot M(t) - k2 \cdot BD(t) \cdot DG(t) - k3 \cdot DG(t) \cdot M(t) + k4 \cdot BD(t) \cdot MG(t)$

$MG'(t) = k3 \cdot DG(t) \cdot M(t) - k4 \cdot BD(t) \cdot MG(t) - k5 \cdot MG(t) \cdot M(t)$

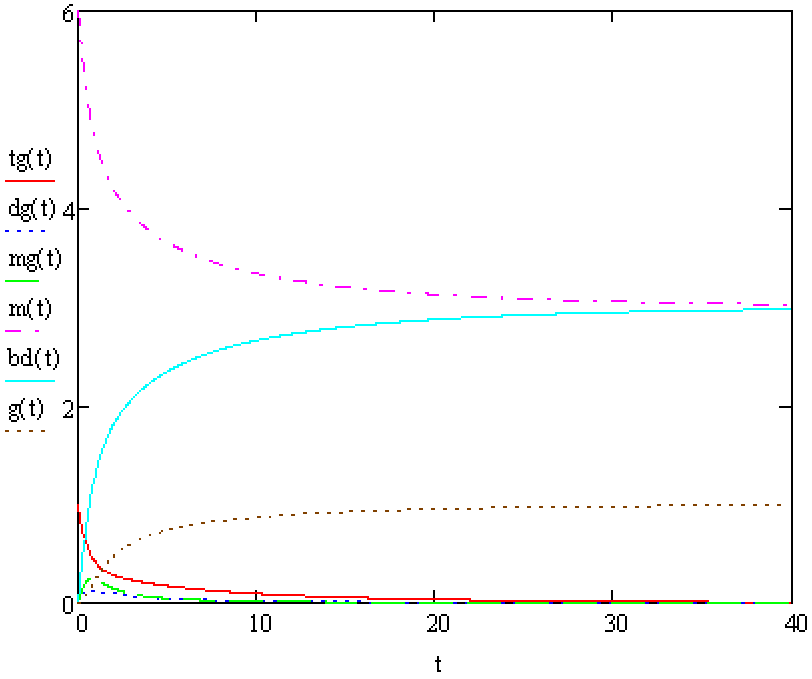
$M'(t) = -k1 \cdot TG(t) \cdot M(t) + k2 \cdot BD(t) \cdot DG(t) - k3 \cdot DG(t) \cdot M(t) + k4 \cdot BD(t) \cdot MG(t) - k5 \cdot MG(t) \cdot M(t)$

$BD'(t) = k1 \cdot TG(t) \cdot M(t) - k2 \cdot BD(t) \cdot DG(t) + k3 \cdot DG(t) \cdot M(t) - k4 \cdot BD(t) \cdot MG(t) + k5 \cdot MG(t) \cdot M(t)$

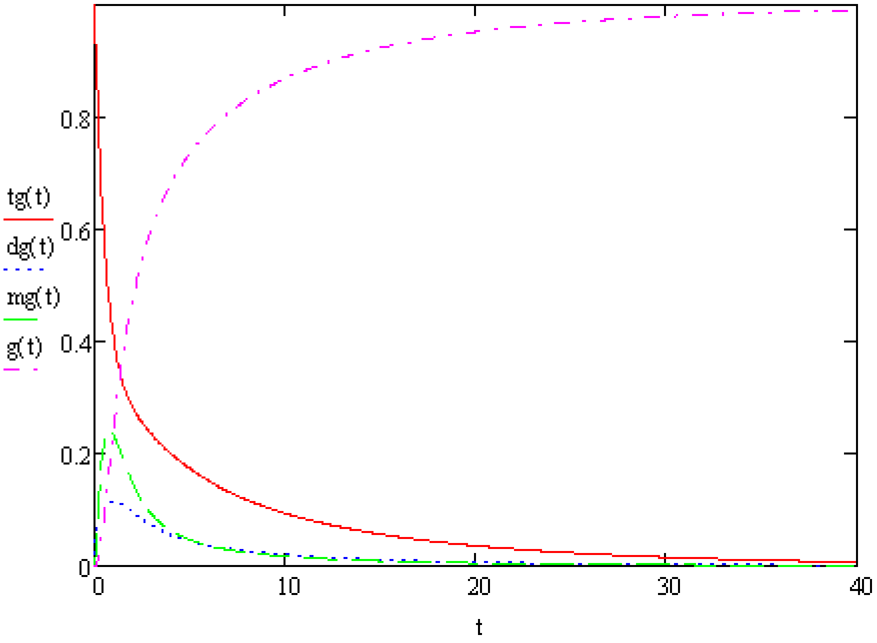
$G'(t) = k5 \cdot MG(t) \cdot M(t)$

$$\begin{pmatrix} tg \\ dg \\ mg \\ m \\ bd \\ g \end{pmatrix} := \text{Odesolve}\left[\begin{pmatrix} TG \\ DG \\ MG \\ M \\ BD \\ G \end{pmatrix}, t, t1\right]$$

Concentration (mol/L) versus time (min) results

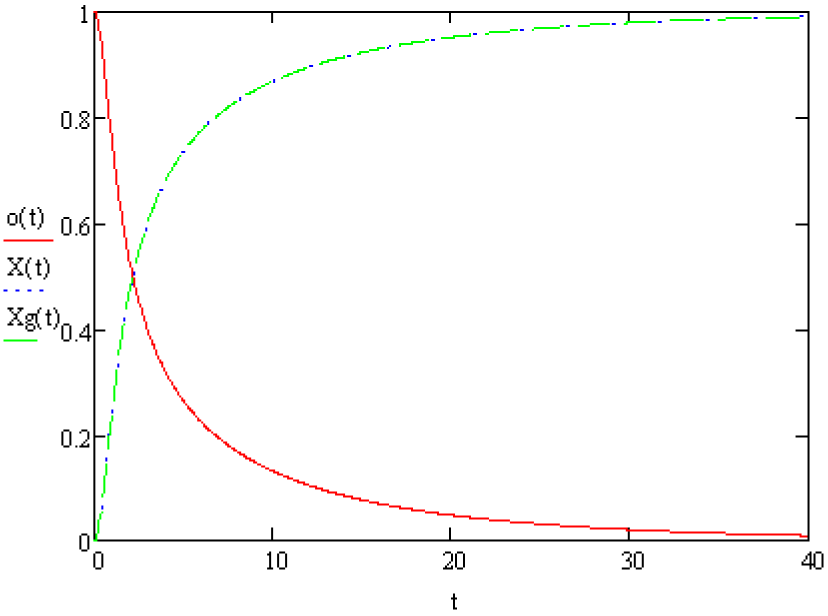


A closer look at lower concentration components, mol/L versus time (min)



Total oil $o(t) := tg(t) + dg(t) + mg(t)$

Conversion based on oil and glycerol $X(t) := \frac{(TGo - o(t))}{TGo}$ $Xg(t) := \frac{g(t) - Go}{TGo - Go}$



Results in tabular form:

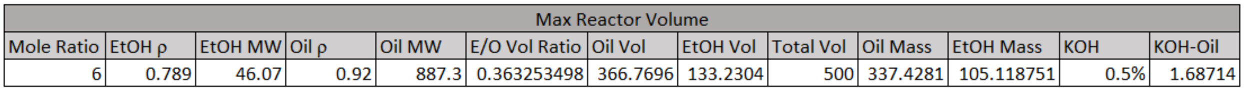
$t := 0, 1 .. 40$

tg(t) =	o(t) =	bd(t) =	g(t) =	m(t) =	X(t) =
1	1	0	0	6	0
0.408	0.754	1.316	0.246	4.684	0.246
0.283	0.528	1.81	0.472	4.19	0.472
0.234	0.399	2.061	0.601	3.939	0.601
0.2	0.319	2.225	0.681	3.775	0.681
0.173	0.265	2.344	0.735	3.656	0.735
0.151	0.225	2.436	0.775	3.564	0.775
0.133	0.194	2.509	0.806	3.491	0.806
0.118	0.169	2.569	0.831	3.431	0.831
0.105	0.148	2.618	0.852	3.382	0.852
0.094	0.132	2.66	0.868	3.34	0.868
0.085	0.117	2.696	0.883	3.304	0.883
0.076	0.105	2.727	0.895	3.273	0.895
0.069	0.094	2.754	0.906	3.246	0.906
0.063	0.085	2.777	0.915	3.223	0.915
...	...	...	...	...	...

D. Balance Calculations

The operating conditions were determined on a volumetric basis allowing for a total volume of oil and ethanol of 500 mL.

Table D-1: Balance Calculation Summary Table



Max Reactor Volume												
Mole Ratio	EtOH ρ	EtOH MW	Oil ρ	Oil MW	E/O Vol Ratio	Oil Vol	EtOH Vol	Total Vol	Oil Mass	EtOH Mass	KOH	KOH-Oil
6	0.789	46.07	0.92	887.3	0.363253498	366.7696	133.2304	500	337.4281	105.118751	0.5%	1.68714

$$\frac{6\ mol\ EtOH}{1\ mol\ oil} * \frac{46.07\ g\ EtOH}{mol\ EtOH} * \frac{1\ mol\ oil}{887.3\ g\ oil} * \frac{0.92\ g\ oil}{mL\ oil} * \frac{mL\ EtOH}{0.789\ g\ EtOH} = \frac{254.306\ mL\ EtOH}{700.0797\ mL\ oil}$$

$$\frac{254.3064\ mL\ EtOH}{700.0797\ mL\ oil} = \frac{x\ mL\ EtOH}{y\ mL\ oil}$$

$$x + y = 500\ mL$$

$$x = 133.23\ mL\ EtOH, y = 366.77\ mL\ oil$$

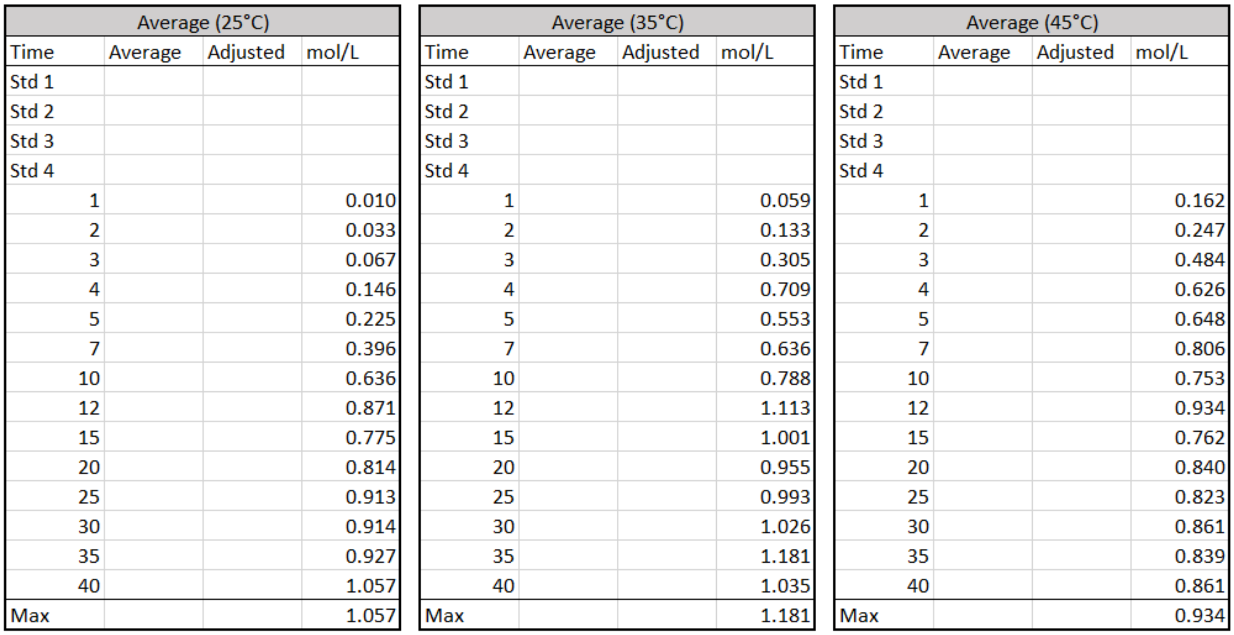
$$133.23\ mL\ EtOH * \frac{0.789\ g\ EtOH}{mL\ EtOH} = 105.12\ g\ EtOH$$

$$366.77\ mL\ oil * \frac{887.3\ g\ oil}{mL\ oil} = 337.43\ g\ oil$$

E. Methanolysis Summary

Averaged

Table E-1: Averaged Calculated Methanolysis Glycerol Concentration by Temperature

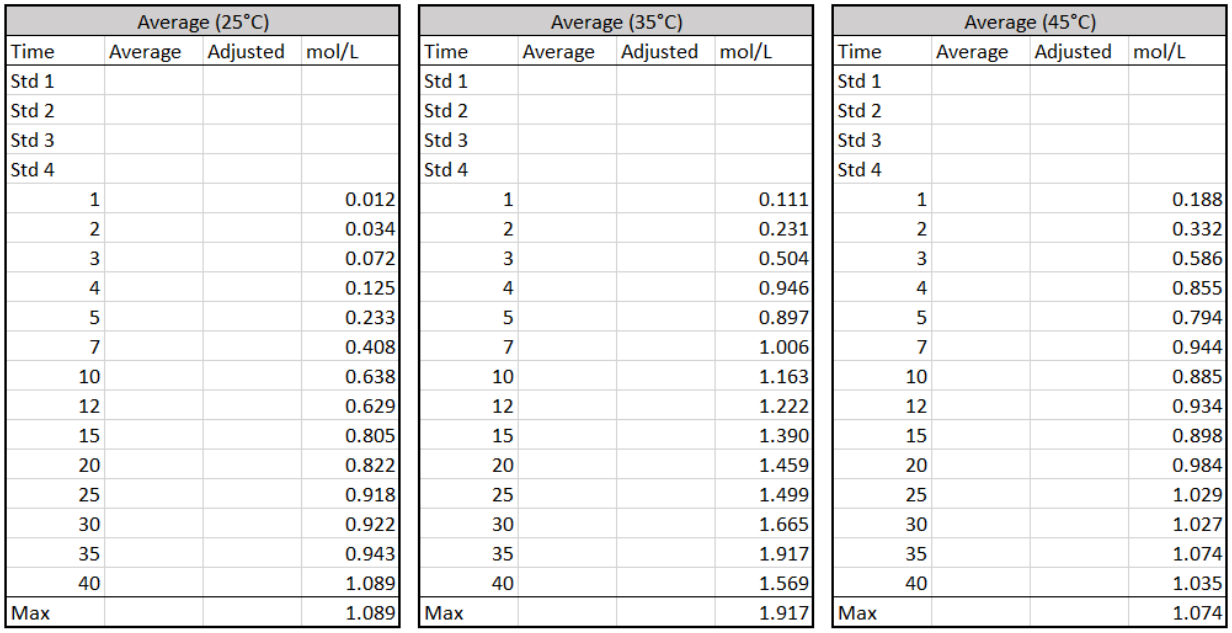


Average (25°C)			
Time	Average	Adjusted	mol/L
Std 1			
Std 2			
Std 3			
Std 4			
1			0.010
2			0.033
3			0.067
4			0.146
5			0.225
7			0.396
10			0.636
12			0.871
15			0.775
20			0.814
25			0.913
30			0.914
35			0.927
40			1.057
Max			1.057

Average (35°C)			
Time	Average	Adjusted	mol/L
Std 1			
Std 2			
Std 3			
Std 4			
1			0.059
2			0.133
3			0.305
4			0.709
5			0.553
7			0.636
10			0.788
12			1.113
15			1.001
20			0.955
25			0.993
30			1.026
35			1.181
40			1.035
Max			1.181

Average (45°C)			
Time	Average	Adjusted	mol/L
Std 1			
Std 2			
Std 3			
Std 4			
1			0.162
2			0.247
3			0.484
4			0.626
5			0.648
7			0.806
10			0.753
12			0.934
15			0.762
20			0.840
25			0.823
30			0.861
35			0.839
40			0.861
Max			0.934

Table E-2 - Averaged Ideal Methanolysis Glycerol Concentration by Temperature



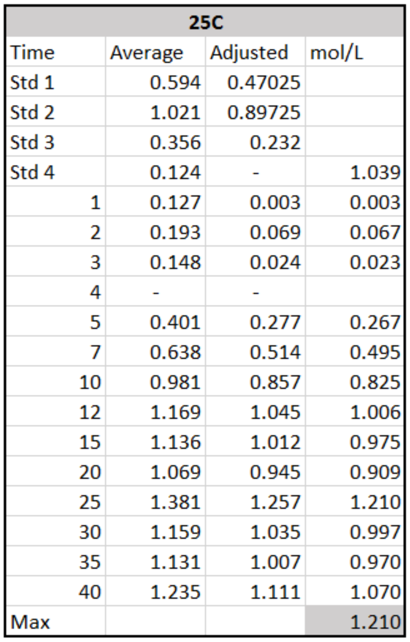
Average (25°C)			
Time	Average	Adjusted	mol/L
Std 1			
Std 2			
Std 3			
Std 4			
1			0.012
2			0.034
3			0.072
4			0.125
5			0.233
7			0.408
10			0.638
12			0.629
15			0.805
20			0.822
25			0.918
30			0.922
35			0.943
40			1.089
Max			1.089

Average (35°C)			
Time	Average	Adjusted	mol/L
Std 1			
Std 2			
Std 3			
Std 4			
1			0.111
2			0.231
3			0.504
4			0.946
5			0.897
7			1.006
10			1.163
12			1.222
15			1.390
20			1.459
25			1.499
30			1.665
35			1.917
40			1.569
Max			1.917

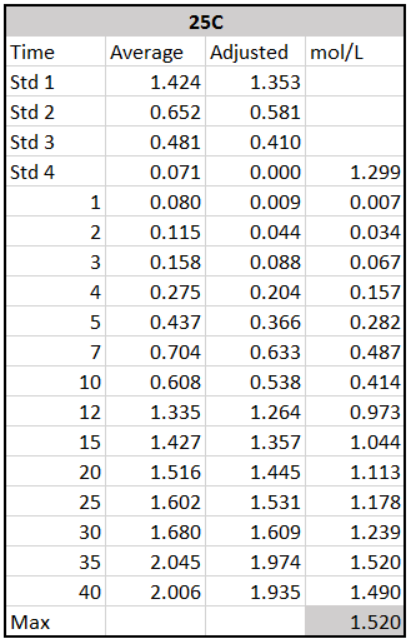
Average (45°C)			
Time	Average	Adjusted	mol/L
Std 1			
Std 2			
Std 3			
Std 4			
1			0.188
2			0.332
3			0.586
4			0.855
5			0.794
7			0.944
10			0.885
12			0.934
15			0.898
20			0.984
25			1.029
30			1.027
35			1.074
40			1.035
Max			1.074

25°C

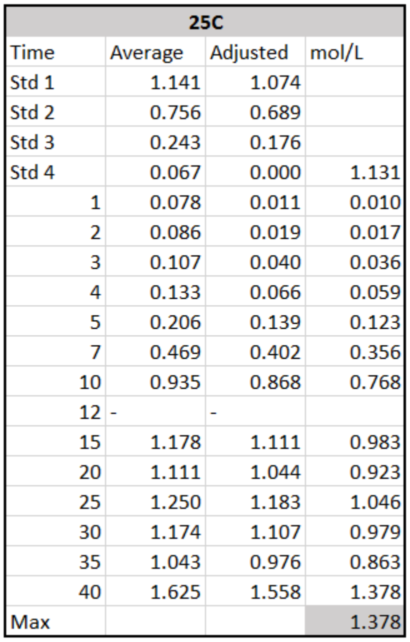
Table E-3: Data for Methanolysis at 25°C Using Calculated Calibration Curves



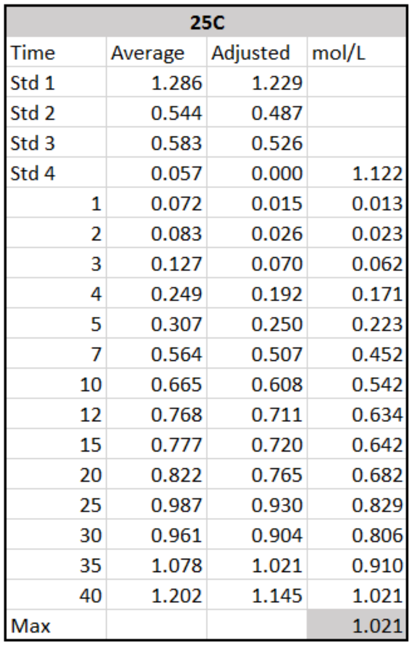
25C			
Time	Average	Adjusted	mol/L
Std 1	0.594	0.47025	
Std 2	1.021	0.89725	
Std 3	0.356	0.232	
Std 4	0.124	-	1.039
1	0.127	0.003	0.003
2	0.193	0.069	0.067
3	0.148	0.024	0.023
4	-	-	
5	0.401	0.277	0.267
7	0.638	0.514	0.495
10	0.981	0.857	0.825
12	1.169	1.045	1.006
15	1.136	1.012	0.975
20	1.069	0.945	0.909
25	1.381	1.257	1.210
30	1.159	1.035	0.997
35	1.131	1.007	0.970
40	1.235	1.111	1.070
Max			1.210



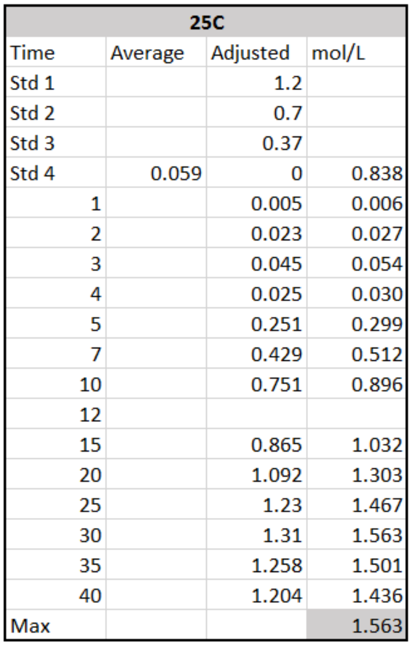
25C			
Time	Average	Adjusted	mol/L
Std 1	1.424	1.353	
Std 2	0.652	0.581	
Std 3	0.481	0.410	
Std 4	0.071	0.000	1.299
1	0.080	0.009	0.007
2	0.115	0.044	0.034
3	0.158	0.088	0.067
4	0.275	0.204	0.157
5	0.437	0.366	0.282
7	0.704	0.633	0.487
10	0.608	0.538	0.414
12	1.335	1.264	0.973
15	1.427	1.357	1.044
20	1.516	1.445	1.113
25	1.602	1.531	1.178
30	1.680	1.609	1.239
35	2.045	1.974	1.520
40	2.006	1.935	1.490
Max			1.520



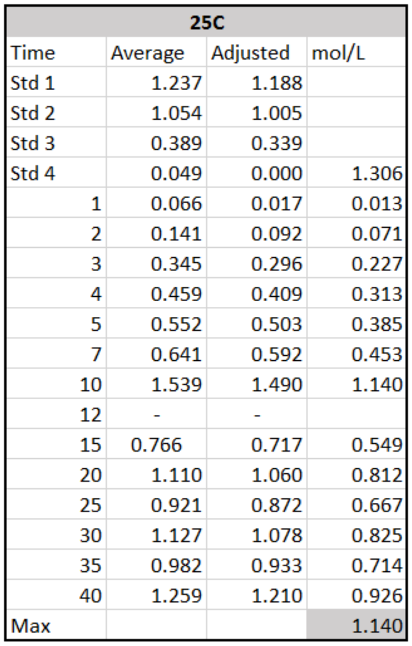
25C			
Time	Average	Adjusted	mol/L
Std 1	1.141	1.074	
Std 2	0.756	0.689	
Std 3	0.243	0.176	
Std 4	0.067	0.000	1.131
1	0.078	0.011	0.010
2	0.086	0.019	0.017
3	0.107	0.040	0.036
4	0.133	0.066	0.059
5	0.206	0.139	0.123
7	0.469	0.402	0.356
10	0.935	0.868	0.768
12	-	-	
15	1.178	1.111	0.983
20	1.111	1.044	0.923
25	1.250	1.183	1.046
30	1.174	1.107	0.979
35	1.043	0.976	0.863
40	1.625	1.558	1.378
Max			1.378



25C			
Time	Average	Adjusted	mol/L
Std 1	1.286	1.229	
Std 2	0.544	0.487	
Std 3	0.583	0.526	
Std 4	0.057	0.000	1.122
1	0.072	0.015	0.013
2	0.083	0.026	0.023
3	0.127	0.070	0.062
4	0.249	0.192	0.171
5	0.307	0.250	0.223
7	0.564	0.507	0.452
10	0.665	0.608	0.542
12	0.768	0.711	0.634
15	0.777	0.720	0.642
20	0.822	0.765	0.682
25	0.987	0.930	0.829
30	0.961	0.904	0.806
35	1.078	1.021	0.910
40	1.202	1.145	1.021
Max			1.021



25C			
Time	Average	Adjusted	mol/L
Std 1		1.2	
Std 2		0.7	
Std 3		0.37	
Std 4	0.059	0	0.838
1		0.005	0.006
2		0.023	0.027
3		0.045	0.054
4		0.025	0.030
5		0.251	0.299
7		0.429	0.512
10		0.751	0.896
12			
15		0.865	1.032
20		1.092	1.303
25		1.23	1.467
30		1.31	1.563
35		1.258	1.501
40		1.204	1.436
Max			1.563



25C			
Time	Average	Adjusted	mol/L
Std 1	1.237	1.188	
Std 2	1.054	1.005	
Std 3	0.389	0.339	
Std 4	0.049	0.000	1.306
1	0.066	0.017	0.013
2	0.141	0.092	0.071
3	0.345	0.296	0.227
4	0.459	0.409	0.313
5	0.552	0.503	0.385
7	0.641	0.592	0.453
10	1.539	1.490	1.140
12	-	-	
15	0.766	0.717	0.549
20	1.110	1.060	0.812
25	0.921	0.872	0.667
30	1.127	1.078	0.825
35	0.982	0.933	0.714
40	1.259	1.210	0.926
Max			1.140

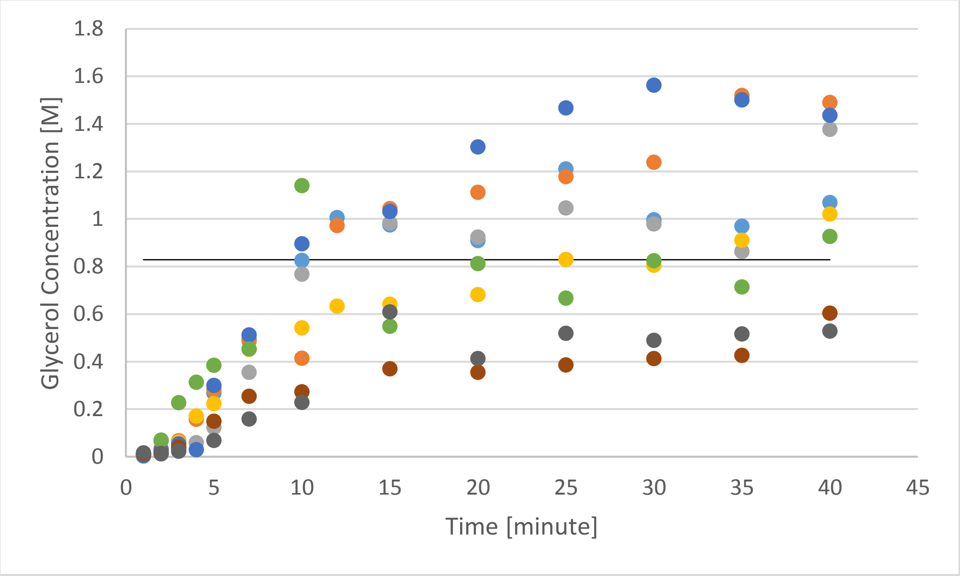


Figure E-1 - Methanolysis at 25°C Using Calculated Calibration Curves

35°C

Table E-4: Data for Methanolysis at 35°C Using Calculated Calibration Curves

35C			
Time	Average	Adjusted	mol/L
Std 1	1.226	1.149	
Std 2	0.970	0.893	
Std 3	0.514	0.438	
Std 4	0.077	-	1.166
1	0.210	0.133	0.114
2	0.289	0.212	0.182
3	0.681	0.605	0.518
4	1.212	1.136	0.974
5	1.153	1.076	0.923
7	1.284	1.207	1.035
10	1.473	1.396	1.197
12	1.544	1.467	1.258
15	1.744	1.668	1.430
20	1.827	1.750	1.501
25	1.876	1.799	1.543
30	2.075	1.998	1.713
35	2.377	2.300	1.973
40	1.960	1.883	1.615
Max			1.973

35C			
Time	Average	Adjusted	mol/L
Std 1	1.458	1.390	
Std 2	0.965	0.897	
Std 3	0.498	0.431	
Std 4	0.068	0.000	1.400
1	0.128	0.061	0.043
2	0.345	0.278	0.198
3	0.634	0.566	0.404
4	0.847	0.779	0.557
5	0.880	0.812	0.580
7	1.210	1.143	0.816
10	1.397	1.329	0.949
12	1.423	1.355	0.968
15	1.520	1.453	1.038
20	1.540	1.473	1.052
25	1.776	1.709	1.220
30	1.623	1.555	1.111
35	1.700	1.633	1.166
40	1.462	1.394	0.996
Max			1.220

35C			
Time	Average	Adjusted	mol/L
Std 1		1.2	
Std 2		0.7	
Std 3		0.37	
Std 4	0.059	-0.004	0.838
1	0.088	0.092	0.110
2	0.151	0.155	0.185
3	0.350	0.354	0.422
4	0.496	0.500	0.596
5	0.574	0.578	0.689
7	0.670	0.674	0.804
10	0.844	0.848	1.012
12			
15	1.116	1.120	1.336
20	1.045	1.049	1.251
25	0.908	0.912	1.088
30	0.940	0.944	1.126
35	1.310	1.314	1.567
40	1.068	1.072	1.279
Max			1.567

35C			
Time	Average	Adjusted	mol/L
Std 1	1.747	1.660	
Std 2	0.742	0.654	
Std 3	0.542	0.455	
Std 4	0.088	0.000	1.595
1	0.103	0.016	0.010
2	0.228	0.140	0.088
3	0.340	0.252	0.158
4			
5	0.888	0.800	0.501
7	0.673	0.585	0.367
10	0.968	0.881	0.552
12			
15	1.030	0.942	0.590
20	0.975	0.887	0.556
25	1.034	0.946	0.593
30	1.190	1.103	0.691
35	1.180	1.093	0.685
40	1.291	1.204	0.754
Max			0.754

35C			
Time	Average	Adjusted	mol/L
Std 1	1.973	1.910	
Std 2	1.138	1.075	
Std 3	0.586	0.523	
Std 4	0.063		1.910
1	0.102	0.039	0.016
2	0.277	0.214	0.012
3	0.519	0.456	0.024
4			
5	1.144	1.081	0.069
7	0.869	0.806	0.159
10	1.106	1.043	0.228
12			
15	1.027	0.964	0.609
20	0.857	0.794	0.413
25	1.281	1.218	0.519
30	1.114	1.051	0.489
35	1.212	1.149	0.516
40	1.145	1.082	0.529
Max			0.609

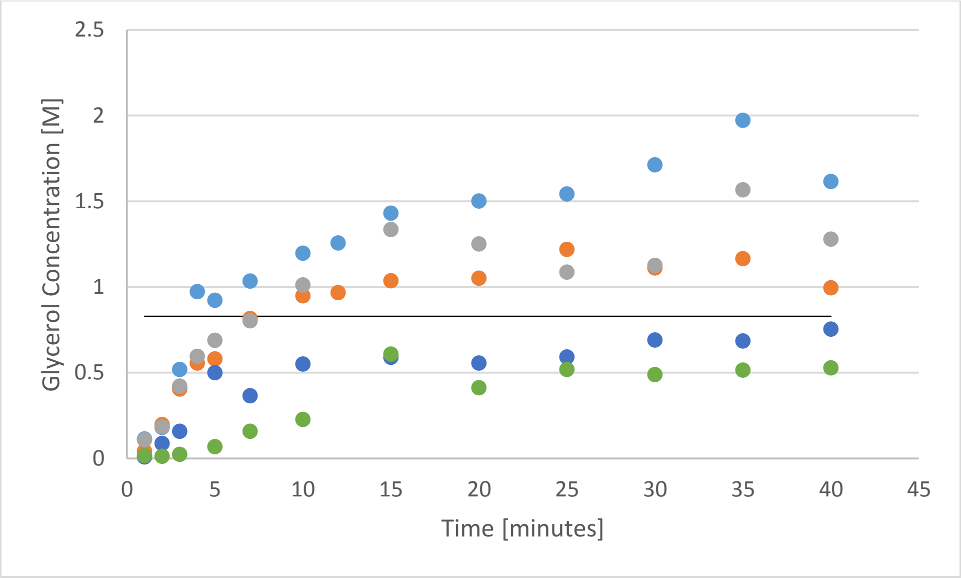


Figure E-2 - Methanolysis at 35°C Using Calculated Calibration Curves

45°C

Table E-5: Data for Methanolysis at 45°C Using Calculated Calibration Curves

45C			
Time	Average	Adjusted	mol/L
Std 1			
Std 2			
Std 3			
Std 4	0.077	-	1.211
1	0.47	0.393	0.324
2	-	-	
3	0.793	0.716	0.591
4	-	-	
5	0.921	0.844	0.697
7.5	1.262	1.185	0.978
10	1.086	1.009	0.833
12	-	-	
15	1.12	1.043	0.861
20	1.11	1.033	0.853
25	-	-	
30	1.142	1.065	0.879
35	-	-	
40	1.387	1.31	1.081
Max			1.081

45C			
Time	Average	Adjusted	mol/L
Std 1	1.141	1.074	
Std 2	0.756	0.689	
Std 3	0.243	0.176	
Std 4	0.067	0	2.068
1	0.283	0.216	0.105
2	0.553	0.486	0.235
3	0.928	0.861	0.417
4	1.379	1.312	0.635
5	1.298	1.231	0.595
7	1.223	1.156	0.559
10	1.174	1.107	0.535
12	-	-	
15	1.209	1.142	0.552
20	1.279	1.212	0.586
25	1.245	1.178	0.570
30	1.466	1.399	0.677
35	1.410	1.343	0.650
40	1.529	1.462	0.707
Max			0.707

45C			
Time	Average	Adjusted	mol/L
Std 1	0.91	0.86	
Std 2	1.206	1.156	
Std 3	0.171	0.121	
Std 4	0.05	0	1.050
1	0.109	0.059	0.056
2	0.321	0.271	0.258
3	0.517	0.467	0.445
4	0.698	0.648	0.617
5	0.734	0.684	0.651
7	0.975	0.925	0.881
10	0.986	0.936	0.892
12	1.031	0.981	0.934
15	0.967	0.917	0.873
20	1.185	1.135	1.081
25	1.180	1.130	1.076
30	1.128	1.078	1.027
35	1.130	1.080	1.029
40	0.885	0.835	0.795
Max			1.081

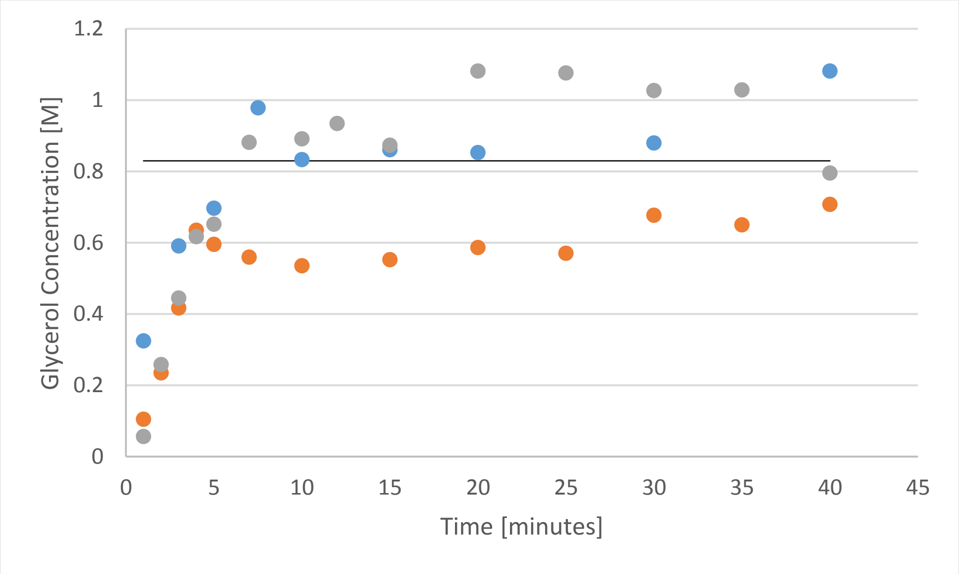
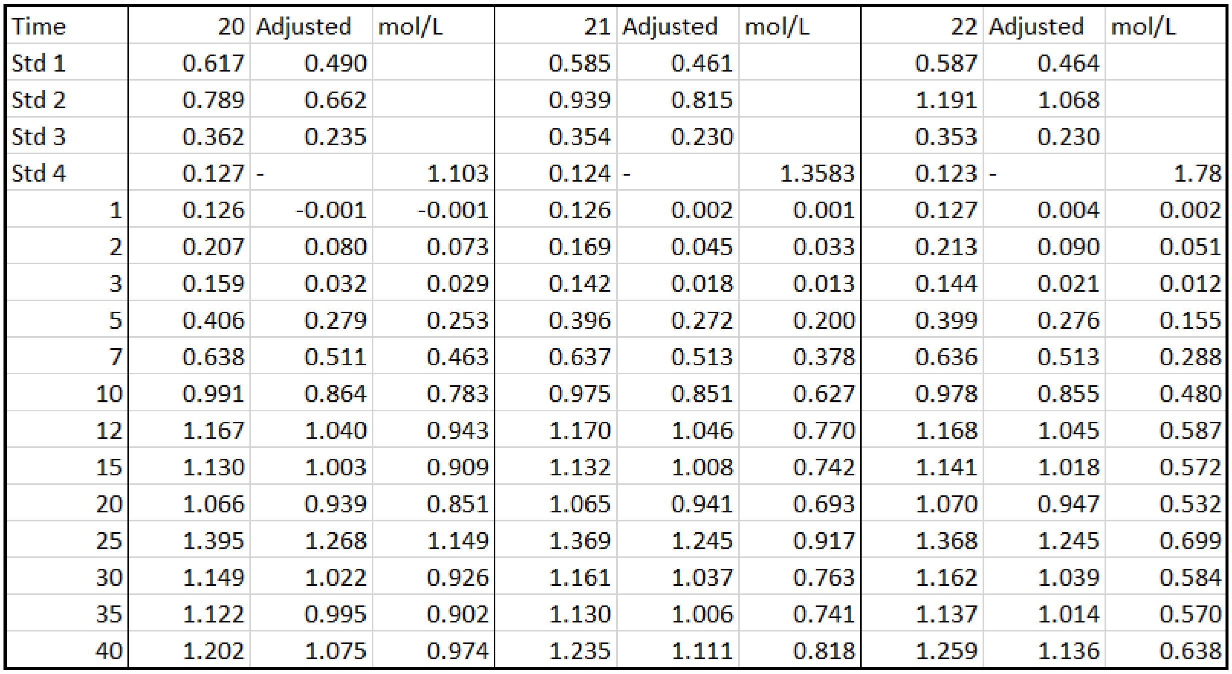


Figure E-3 - Methanolysis at 45°C Using Calculated Calibration Curves

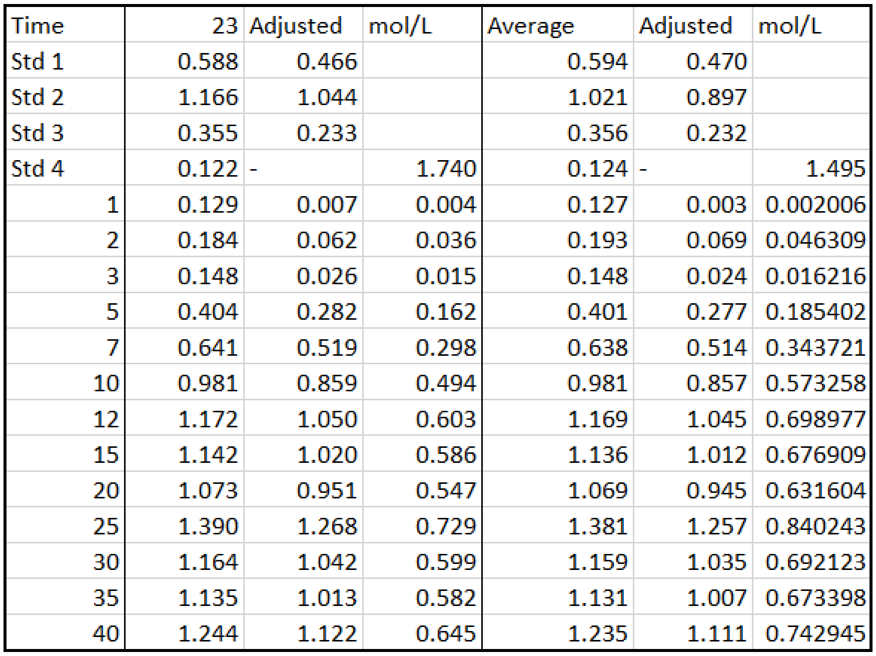
Experiment – 9/27/15

Calculated

Table E-6: Data for Methanolysis at 25°C Using Calculated Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	0.617	0.490		0.585	0.461		0.587	0.464	
Std 2	0.789	0.662		0.939	0.815		1.191	1.068	
Std 3	0.362	0.235		0.354	0.230		0.353	0.230	
Std 4	0.127	-	1.103	0.124	-	1.3583	0.123	-	1.78
1	0.126	-0.001	-0.001	0.126	0.002	0.001	0.127	0.004	0.002
2	0.207	0.080	0.073	0.169	0.045	0.033	0.213	0.090	0.051
3	0.159	0.032	0.029	0.142	0.018	0.013	0.144	0.021	0.012
5	0.406	0.279	0.253	0.396	0.272	0.200	0.399	0.276	0.155
7	0.638	0.511	0.463	0.637	0.513	0.378	0.636	0.513	0.288
10	0.991	0.864	0.783	0.975	0.851	0.627	0.978	0.855	0.480
12	1.167	1.040	0.943	1.170	1.046	0.770	1.168	1.045	0.587
15	1.130	1.003	0.909	1.132	1.008	0.742	1.141	1.018	0.572
20	1.066	0.939	0.851	1.065	0.941	0.693	1.070	0.947	0.532
25	1.395	1.268	1.149	1.369	1.245	0.917	1.368	1.245	0.699
30	1.149	1.022	0.926	1.161	1.037	0.763	1.162	1.039	0.584
35	1.122	0.995	0.902	1.130	1.006	0.741	1.137	1.014	0.570
40	1.202	1.075	0.974	1.235	1.111	0.818	1.259	1.136	0.638



Time	23	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	0.588	0.466		0.594	0.470	
Std 2	1.166	1.044		1.021	0.897	
Std 3	0.355	0.233		0.356	0.232	
Std 4	0.122	-	1.740	0.124	-	1.495
1	0.129	0.007	0.004	0.127	0.003	0.002006
2	0.184	0.062	0.036	0.193	0.069	0.046309
3	0.148	0.026	0.015	0.148	0.024	0.016216
5	0.404	0.282	0.162	0.401	0.277	0.185402
7	0.641	0.519	0.298	0.638	0.514	0.343721
10	0.981	0.859	0.494	0.981	0.857	0.573258
12	1.172	1.050	0.603	1.169	1.045	0.698977
15	1.142	1.020	0.586	1.136	1.012	0.676909
20	1.073	0.951	0.547	1.069	0.945	0.631604
25	1.390	1.268	0.729	1.381	1.257	0.840243
30	1.164	1.042	0.599	1.159	1.035	0.692123
35	1.135	1.013	0.582	1.131	1.007	0.673398
40	1.244	1.122	0.645	1.235	1.111	0.742945

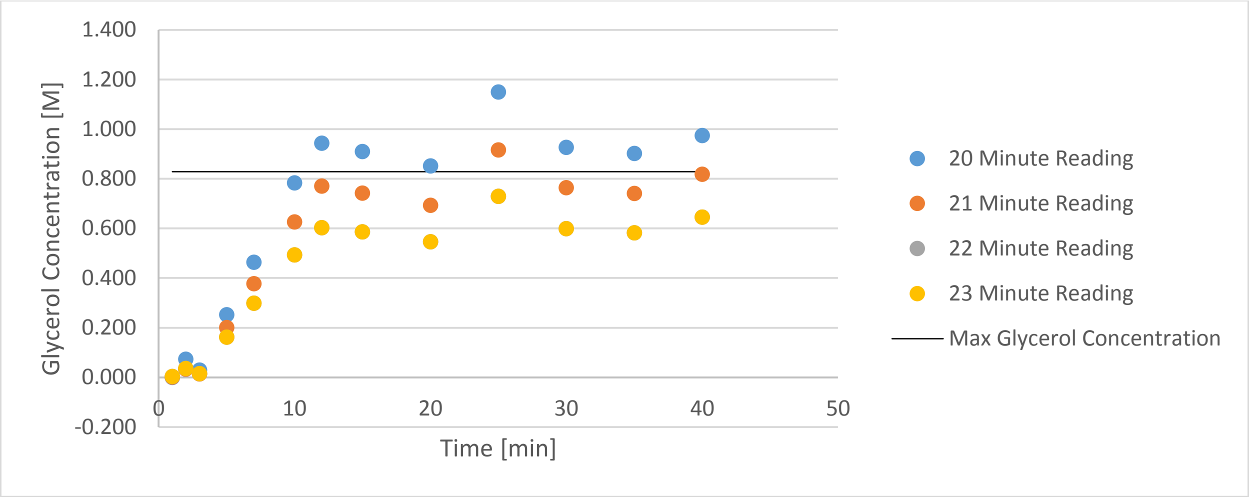


Figure E-4: Methanolysis at 25°C Using Calculated Calibration Curves

Ideal

Table E-7: Data for Methanolysis at 25°C Using Ideal Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	0.617	0.490		0.585	0.461		0.587	0.464		0.588	0.466	
Std 2	0.789	0.662		0.939	0.815		1.191	1.068		1.166	1.044	
Std 3	0.362	0.235		0.354	0.230		0.353	0.230		0.355	0.233	
Std 4	0.127	-	1.200	0.124	-	1.200	0.123	-	1.200	0.122	-	1.200
1	0.126	-0.001	-0.001	0.126	0.002	0.002	0.127	0.004	0.003	0.129	0.007	0.006
2	0.207	0.080	0.067	0.169	0.045	0.038	0.213	0.090	0.075	0.184	0.062	0.052
3	0.159	0.032	0.027	0.142	0.018	0.015	0.144	0.021	0.018	0.148	0.026	0.022
5	0.406	0.279	0.233	0.396	0.272	0.227	0.399	0.276	0.230	0.404	0.282	0.235
7	0.638	0.511	0.426	0.637	0.513	0.428	0.636	0.513	0.428	0.641	0.519	0.433
10	0.991	0.864	0.720	0.975	0.851	0.709	0.978	0.855	0.713	0.981	0.859	0.716
12	1.167	1.040	0.867	1.170	1.046	0.872	1.168	1.045	0.871	1.172	1.050	0.875
15	1.130	1.003	0.836	1.132	1.008	0.840	1.141	1.018	0.848	1.142	1.020	0.850
20	1.066	0.939	0.783	1.065	0.941	0.784	1.070	0.947	0.789	1.073	0.951	0.793
25	1.395	1.268	1.057	1.369	1.245	1.038	1.368	1.245	1.038	1.390	1.268	1.057
30	1.149	1.022	0.852	1.161	1.037	0.864	1.162	1.039	0.866	1.164	1.042	0.868
35	1.122	0.995	0.829	1.130	1.006	0.838	1.137	1.014	0.845	1.135	1.013	0.844
40	1.202	1.075	0.896	1.235	1.111	0.926	1.259	1.136	0.947	1.244	1.122	0.935

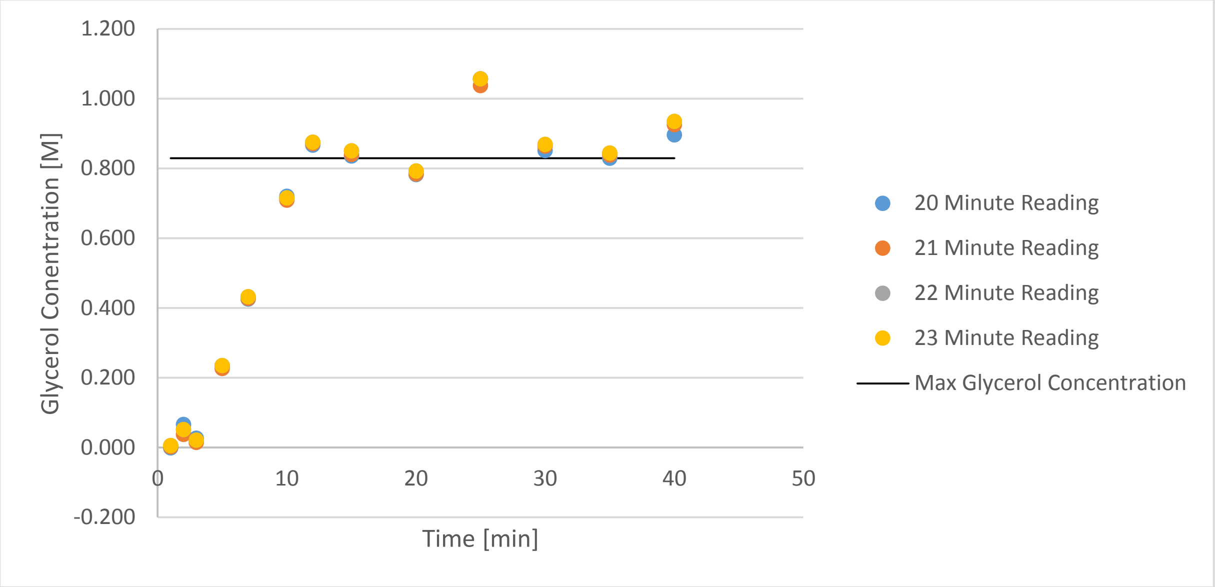


Figure E-5: Methanolysis at 25°C Using Calculated Calibration Curves

Calibration Curves

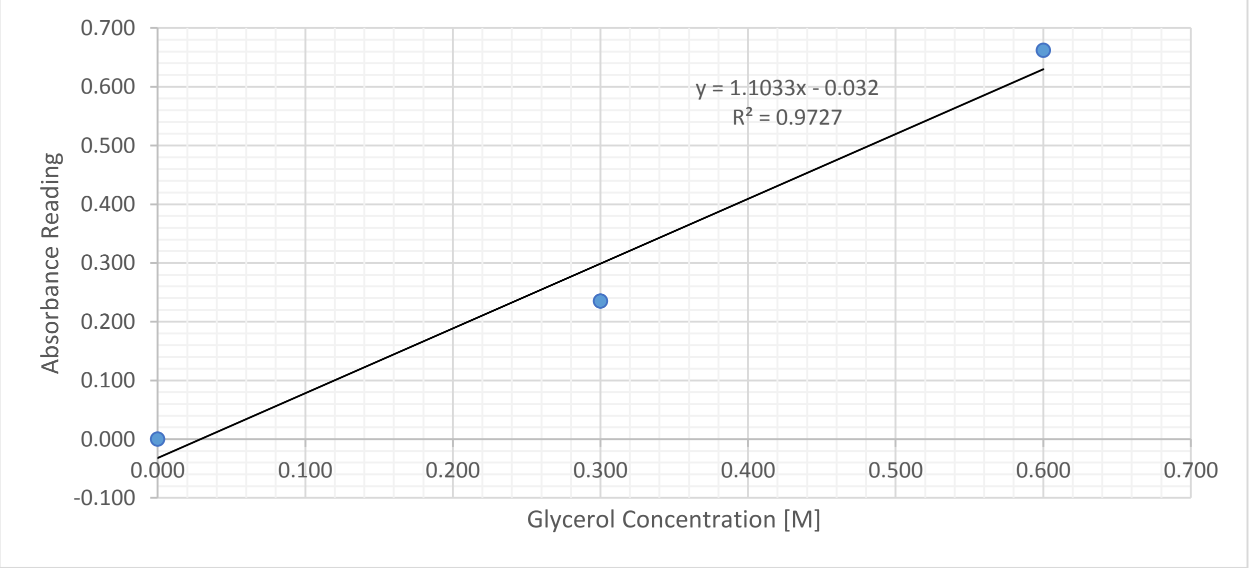


Figure E-6: Calculated Calibration Curve at 20 Minute Reading

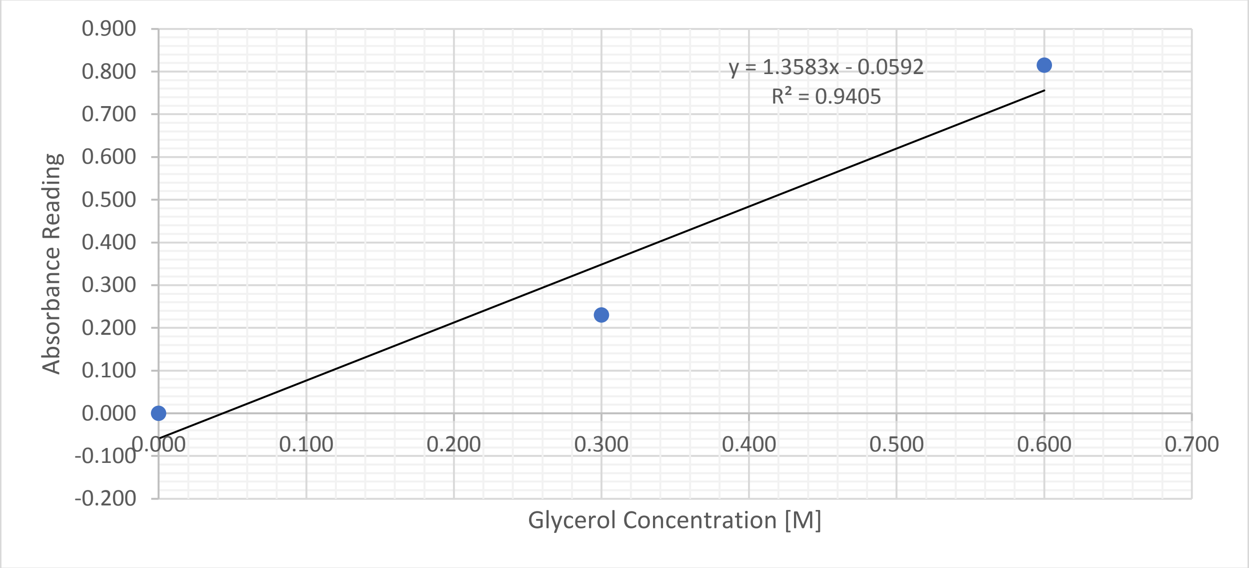


Figure E-7: Calculated Calibration Curve at 21 Minute Reading

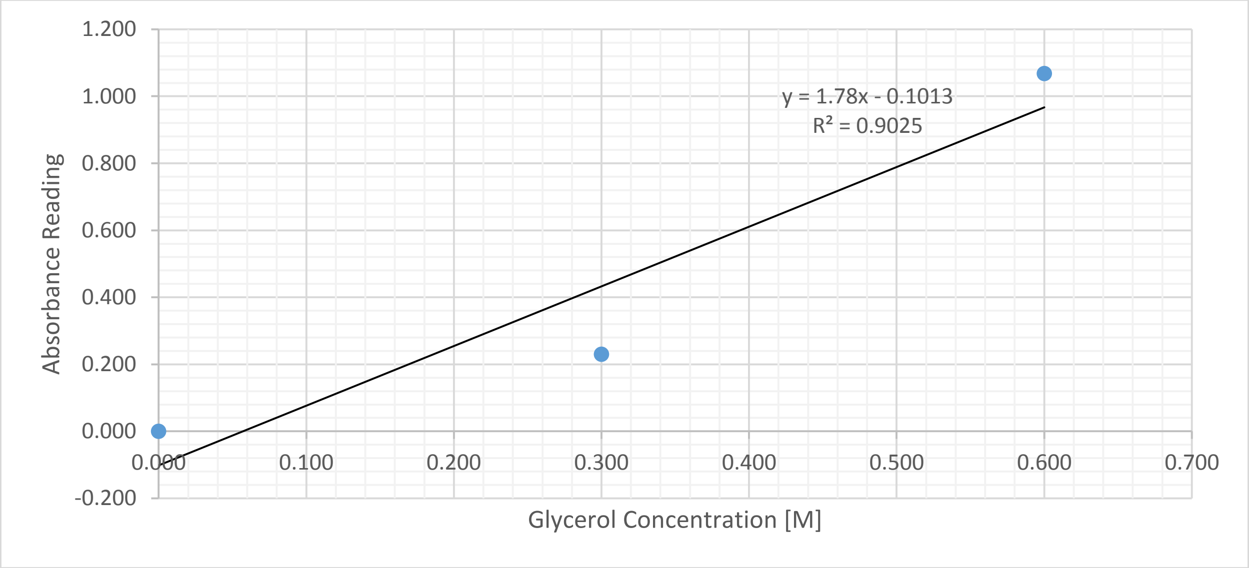


Figure E-8: Calculated Calibration Curve at 22 Minute Reading

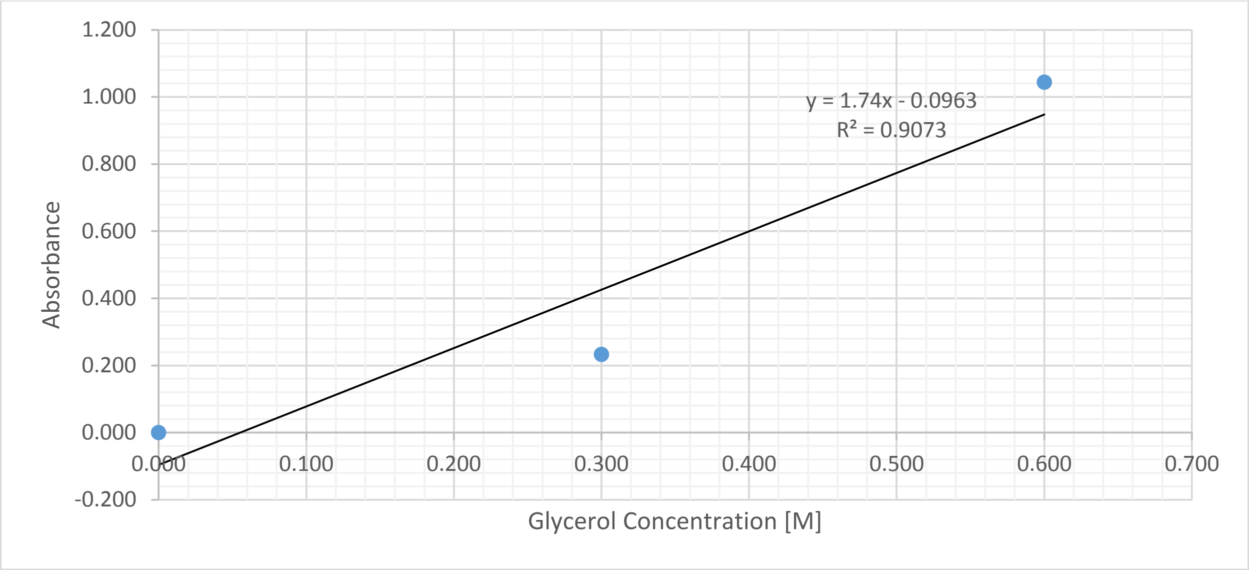


Figure E-9: Calculated Calibration Curve at 23 Minute Reading

Experiment – 10/4/15

Calculated

Table E-8: Data for Methanolysis at 35°C Using Calculated Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	1.221	1.145		1.226	1.149		1.228	1.151	
Std 2	0.966	0.890		0.969	0.892		0.972	0.895	
Std 3	0.512	0.436		0.513	0.436		0.515	0.438	
Std 4	0.076	-	1.162	0.077	-	1.166	0.077	-	1.168
1	0.207	0.131	0.113	0.210	0.133	0.114	0.211	0.134	0.115
2	0.285	0.209	0.180	0.288	0.211	0.181	0.290	0.213	0.182
3	0.679	0.603	0.519	0.681	0.604	0.518	0.680	0.603	0.516
4	1.222	1.146	0.986	1.217	1.140	0.978	1.203	1.126	0.964
5	1.146	1.070	0.921	1.154	1.077	0.924	1.154	1.077	0.922
7	1.281	1.205	1.037	1.283	1.206	1.034	1.286	1.209	1.035
10	1.465	1.389	1.196	1.473	1.396	1.197	1.477	1.400	1.199
12	1.545	1.469	1.264	1.522	1.445	1.239	1.546	1.469	1.258
15	1.752	1.676	1.443	1.758	1.681	1.442	1.738	1.661	1.422
20	1.826	1.750	1.506	1.834	1.757	1.507	1.829	1.752	1.500
25	1.878	1.802	1.551	1.881	1.804	1.547	1.880	1.803	1.544
30	2.077	2.001	1.722	2.082	2.005	1.719	2.077	2.000	1.712
35	2.378	2.302	1.981	2.379	2.302	1.974	2.378	2.301	1.970
40	1.961	1.885	1.622	1.959	1.882	1.614	1.961	1.884	1.613

Time	23	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	1.229	1.152		1.226	1.149	
Std 2	0.972	0.895		0.970	0.893	
Std 3	0.517	0.440		0.514	0.438	
Std 4	0.077	-	1.168	0.077	-	1.166
1	0.212	0.135	0.116	0.210	0.133	0.114272
2	0.291	0.214	0.183	0.289	0.212	0.181592
3	0.685	0.608	0.520	0.681	0.605	0.518406
4	1.207	1.130	0.967	1.212	1.136	0.97378
5	1.157	1.080	0.924	1.153	1.076	0.922754
7	1.285	1.208	1.034	1.284	1.207	1.035096
10	1.476	1.399	1.197	1.473	1.396	1.197179
12	1.561	1.484	1.270	1.544	1.467	1.257852
15	1.729	1.652	1.414	1.744	1.668	1.430011
20	1.819	1.742	1.491	1.827	1.750	1.500975
25	1.863	1.786	1.529	1.876	1.799	1.542568
30	2.063	1.986	1.700	2.075	1.998	1.71344
35	2.373	2.296	1.965	2.377	2.300	1.972643
40	1.959	1.882	1.611	1.960	1.883	1.615033

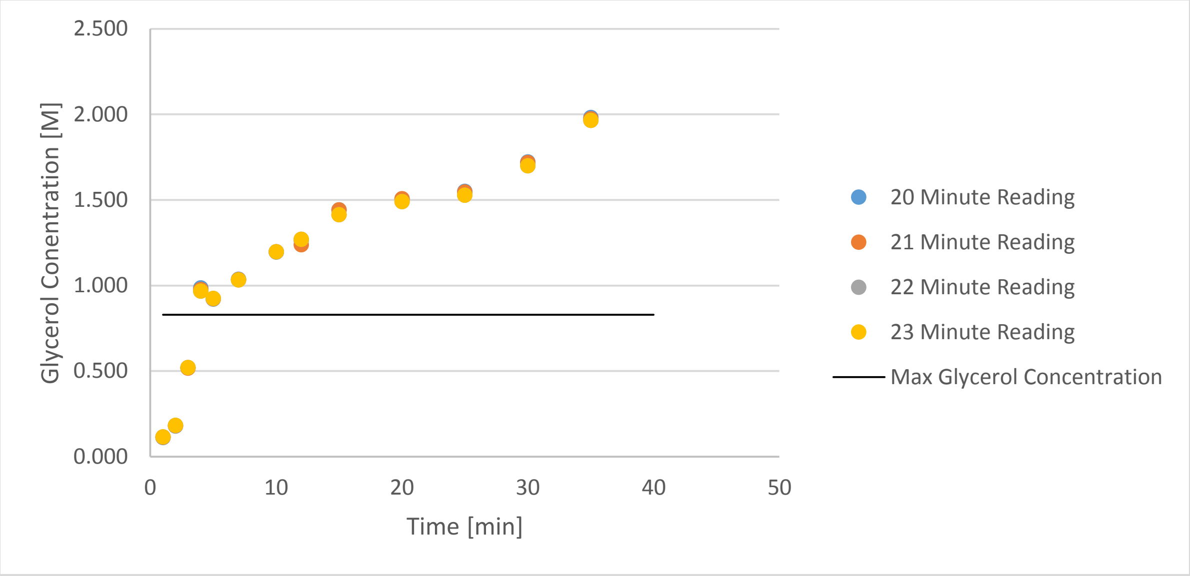


Figure E-10: Methanolysis at 35°C Using Calculated Calibration Curves

Ideal

Table E-9: Data for Methanolysis at 35°C Using Ideal Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	1.221	1.145		1.226	1.149		1.228	1.151		1.229	1.152	
Std 2	0.966	0.890		0.969	0.892		0.972	0.895		0.972	0.895	
Std 3	0.512	0.436		0.513	0.436		0.515	0.438		0.517	0.440	
Std 4	0.076	-	1.200	0.077	-	1.200	0.077	-	1.200	0.077	-	1.200
1	0.207	0.131	0.109	0.210	0.133	0.111	0.211	0.134	0.112	0.212	0.135	0.113
2	0.285	0.209	0.174	0.288	0.211	0.176	0.290	0.213	0.178	0.291	0.214	0.178
3	0.679	0.603	0.503	0.681	0.604	0.503	0.680	0.603	0.503	0.685	0.608	0.507
4	1.222	1.146	0.955	1.217	1.140	0.950	1.203	1.126	0.938	1.207	1.130	0.942
5	1.146	1.070	0.892	1.154	1.077	0.898	1.154	1.077	0.898	1.157	1.080	0.900
7	1.281	1.205	1.004	1.283	1.206	1.005	1.286	1.209	1.008	1.285	1.208	1.007
10	1.465	1.389	1.158	1.473	1.396	1.163	1.477	1.400	1.167	1.476	1.399	1.166
12	1.545	1.469	1.224	1.522	1.445	1.204	1.546	1.469	1.224	1.561	1.484	1.237
15	1.752	1.676	1.397	1.758	1.681	1.401	1.738	1.661	1.384	1.729	1.652	1.377
20	1.826	1.750	1.458	1.834	1.757	1.464	1.829	1.752	1.460	1.819	1.742	1.452
25	1.878	1.802	1.502	1.881	1.804	1.503	1.880	1.803	1.503	1.863	1.786	1.488
30	2.077	2.001	1.668	2.082	2.005	1.671	2.077	2.000	1.667	2.063	1.986	1.655
35	2.378	2.302	1.918	2.379	2.302	1.918	2.378	2.301	1.918	2.373	2.296	1.913
40	1.961	1.885	1.571	1.959	1.882	1.568	1.961	1.884	1.570	1.959	1.882	1.568

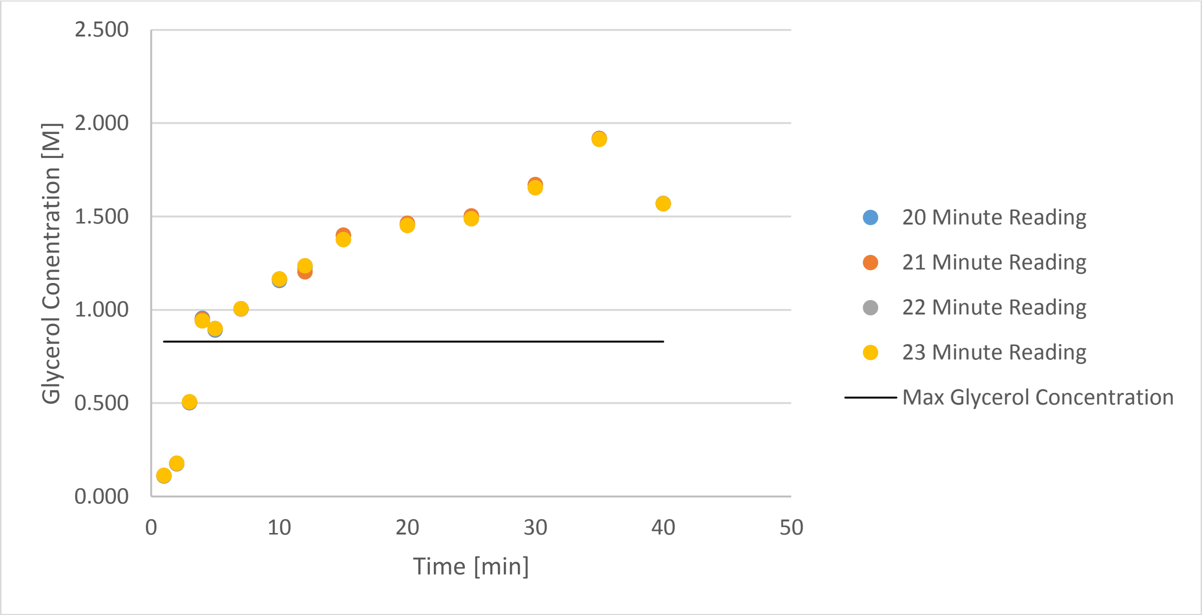


Figure E-11: Methanolysis at 35°C Using Ideal Calibration Curves

Calibration Curves

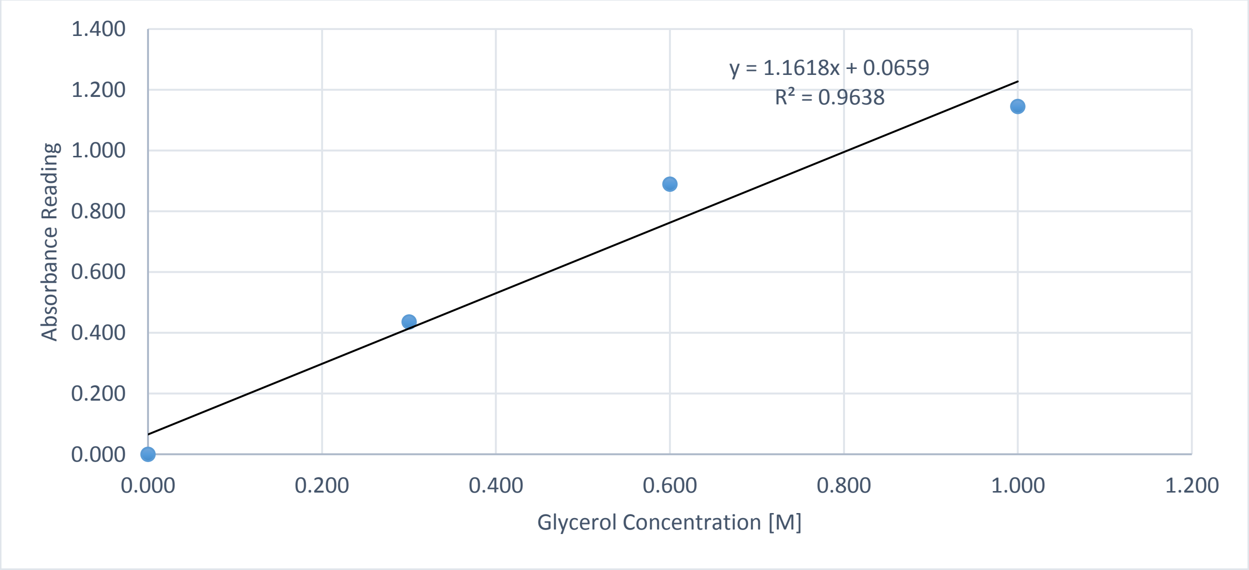


Figure E-12: Calculated Calibration Curve at 20 Minute Reading

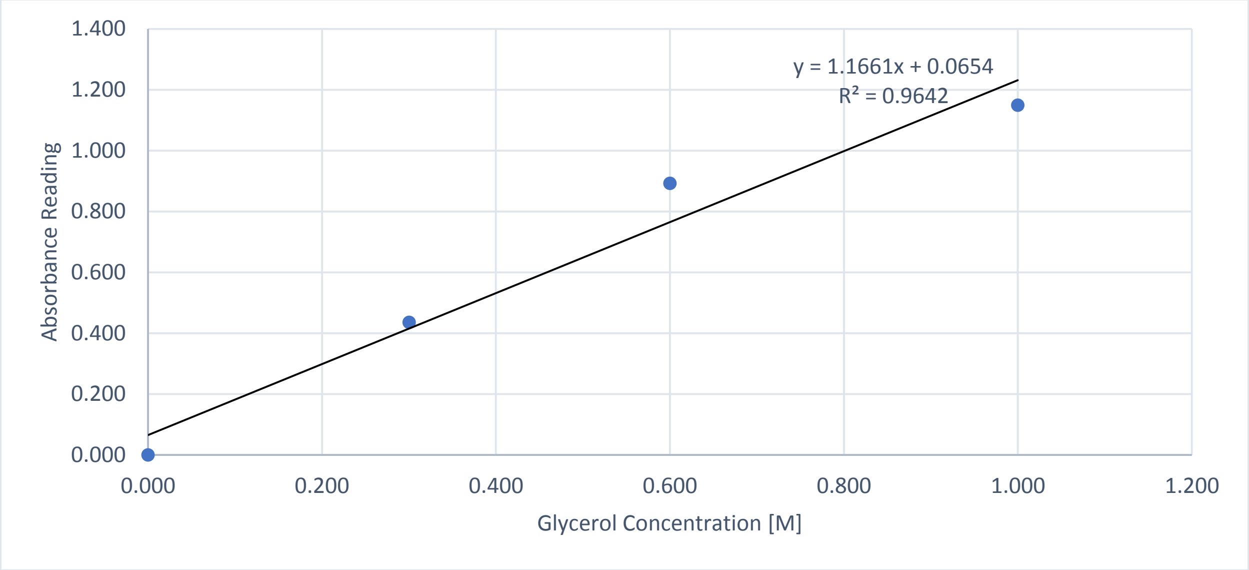


Figure E-13: Calculated Calibration Curve at 21 Minute Reading

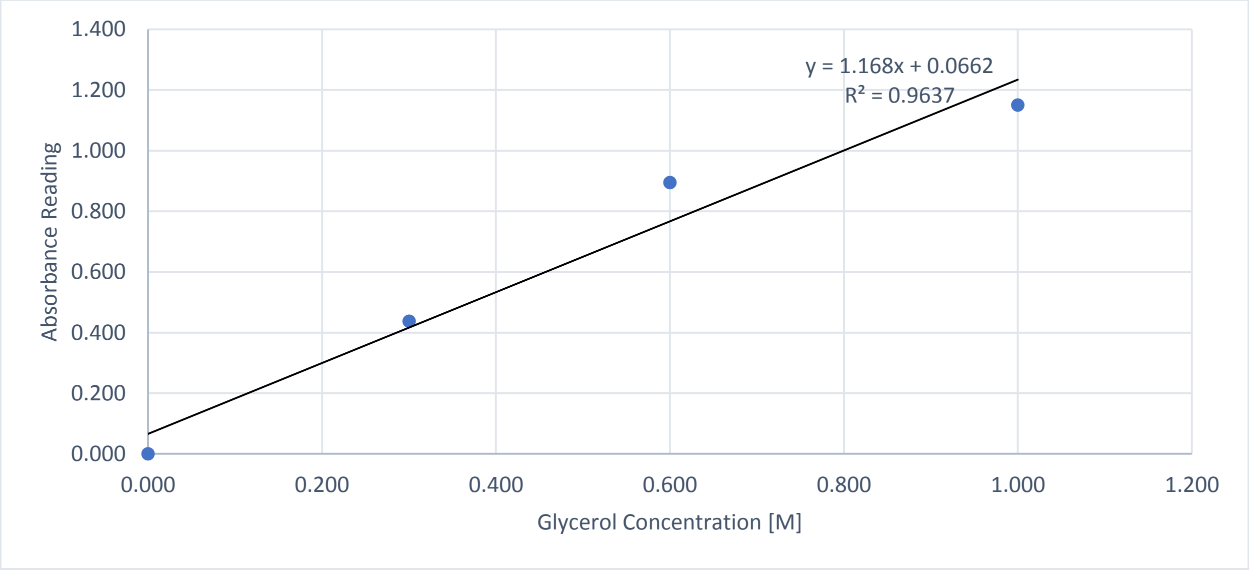


Figure E-14: Calculated Calibration Curve at 22 Minute Reading

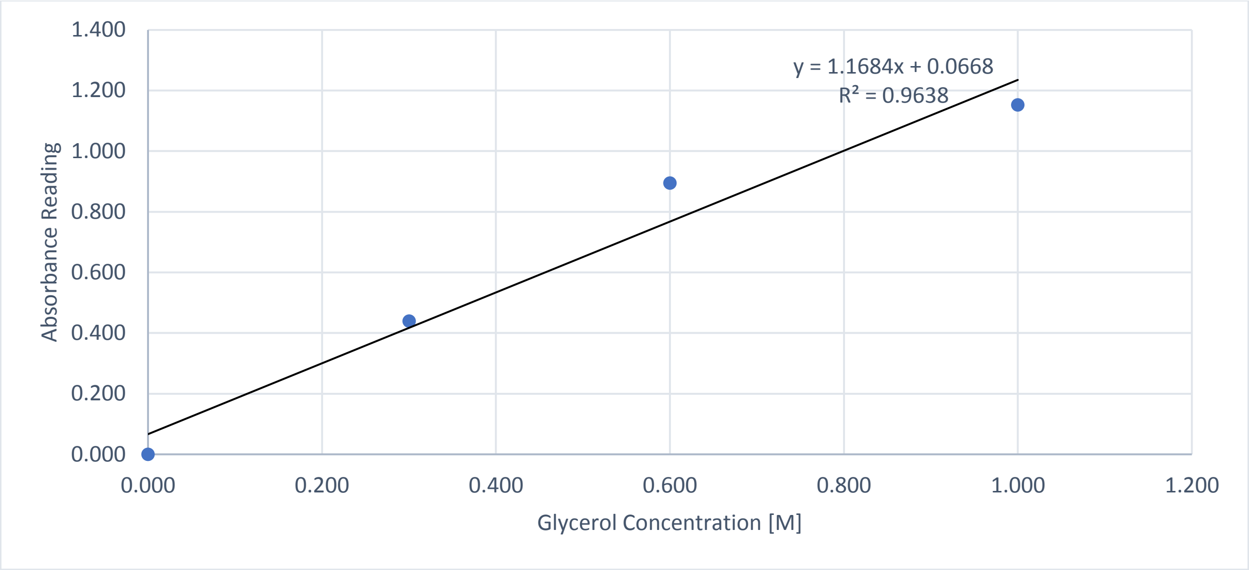


Figure E-15: Calculated Calibration Curve at 23 Minute Reading

F. Molar Conversion Calculations

Methanol

Initial Oil:

$$400\, mL\ Oil * \frac{0.92\ g}{mL} = 368\ g\ Oil$$

$$368\ g\ Oil * \frac{mol\ Oil}{887.3\ g\ Oil} = 0.415\ mol\ Oil$$

$$\frac{0.415 mol\ Oil}{500\ mL} = 0.829\ M\ Oil$$

Catalyst:

$$368\ g\ Oil * 0.005 = 1.84\ g\ catalyst\ (KOH)$$

Ethanol

Initial Oil:

Given 366.8 mL of oil:

$$366.8\, mL\ Oil * \frac{0.92\ g}{mL} = 337.4\ g\ Oil$$

$$337.4\ g\ Oil * \frac{mol\ Oil}{887.3\ g\ Oil} = 0.380\ mol\ Oil$$

$$\frac{0.380\ mol\ Oil}{500\ mL} = 0.761\ M\ Oil$$

Catalyst:

$$337.4\ g\ Oil * 0.005 = 1.687\ g\ catalyst\ (KOH)$$

G. Calculations for Determining Methanolysis Rate Constants

25C AVERAGE			
Time	mol/L		
Std 1			
Std 2			
Std 3			
Std 4		O	1/O
1	0.0123	0.8167	1.22444
2	0.059706	0.769294	1.299893
3	0.08289	0.74611	1.340285
4	0.126136	0.702864	1.42275
5	0.344171	0.484829	2.062583
7	0.611284	0.217716	4.59314
10	0.984767	-0.15577	-6.41985
12	1.376399	-0.5474	-1.82682
15	1.17788	-0.34888	-2.86632
20	1.193824	-0.36482	-2.74105
25	1.404335	-0.57534	-1.73812
30	1.332209	-0.50321	-1.98725
35	1.334013	-0.50501	-1.98015
40	1.524928	-0.69593	-1.43693

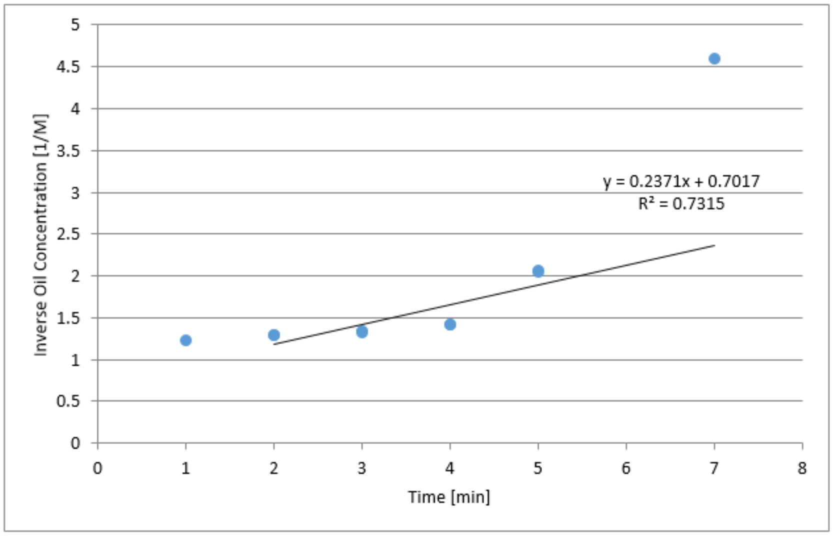


Figure G-1: Calculations for Methanolysis at 25°C

35C AVERAGE			
Time	mol/L		
Std 1			
Std 2			
Std 3			
Std 4		O	1/O
1	0.062538	0.766462	1.304696
2	0.138531	0.690469	1.448291
3	0.322152	0.506848	1.972978
4	0.769148	0.059852	16.70788
5	0.577472	0.251528	3.975701
7	0.668783	0.160217	6.241535
10	0.822833	0.006167	162.1534
12	1.232917	-0.40392	-2.47576
15	1.043543	-0.21454	-4.66107
20	1.00078	-0.17178	-5.8214
25	1.04025	-0.21125	-4.73373
30	1.077206	-0.24821	-4.02891
35	1.241683	-0.41268	-2.42317
40	1.080471	-0.25147	-3.9766

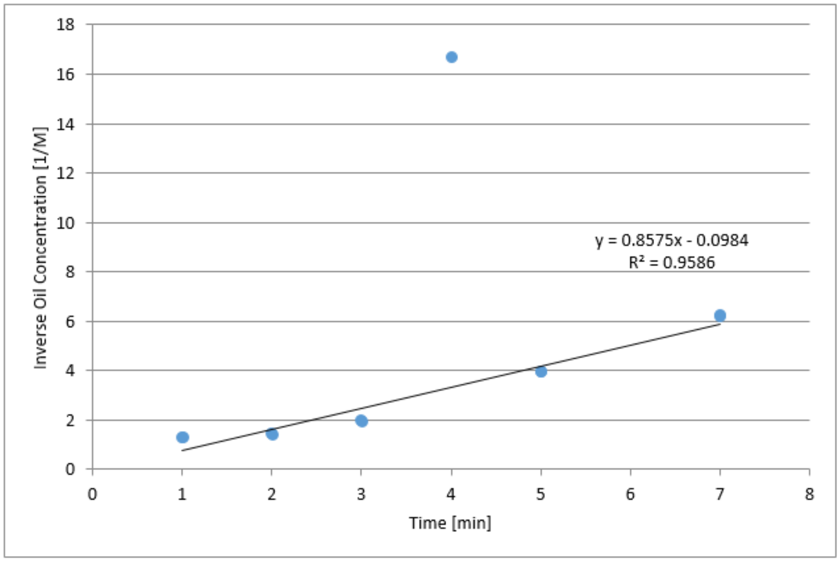
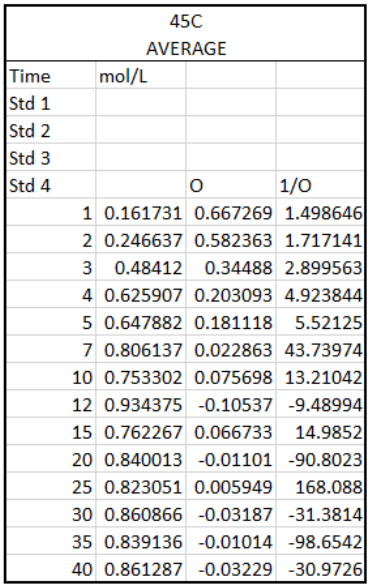


Figure G-2: Calculations for Methanolysis at 35°C



45C
AVERAGE

Time	mol/L		
Std 1			
Std 2			
Std 3			
Std 4		O	1/O
1	0.161731	0.667269	1.498646
2	0.246637	0.582363	1.717141
3	0.48412	0.34488	2.899563
4	0.625907	0.203093	4.923844
5	0.647882	0.181118	5.52125
7	0.806137	0.022863	43.73974
10	0.753302	0.075698	13.21042
12	0.934375	-0.10537	-9.48994
15	0.762267	0.066733	14.9852
20	0.840013	-0.01101	-90.8023
25	0.823051	0.005949	168.088
30	0.860866	-0.03187	-31.3814
35	0.839136	-0.01014	-98.6542
40	0.861287	-0.03229	-30.9726

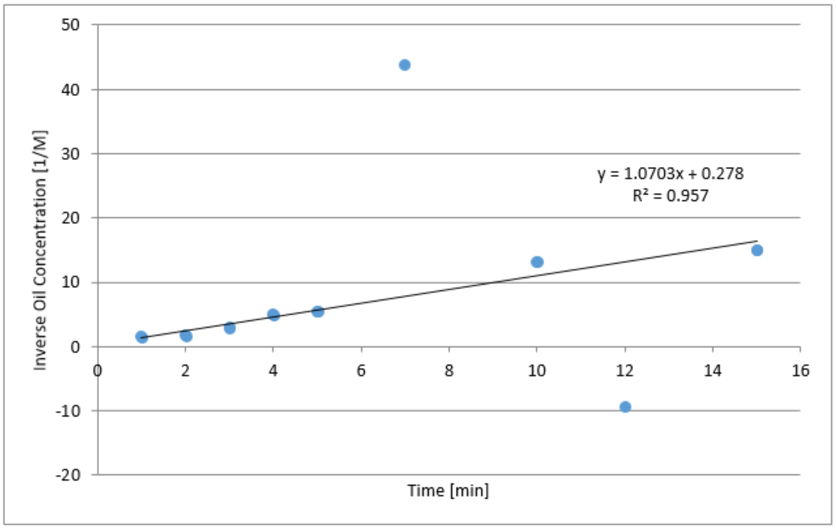
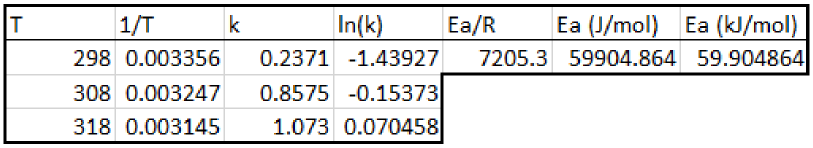


Figure G-3: Calculations for Methanolysis at 45°C

H. Calculations for Determining Methanolysis Activation Energy

Table H-1: Summary of Methanolysis Activation Energy Calculations



T	1/T	k	ln(k)	Ea/R	Ea (J/mol)	Ea (kJ/mol)
298	0.003356	0.2371	-1.43927	7205.3	59904.864	59.904864
308	0.003247	0.8575	-0.15373			
318	0.003145	1.073	0.070458			

$$\ln(k) = \ln(A) - \frac{E_A}{R}\left(\frac{1}{T}\right)$$

$$R = 8.314\ J/mol \cdot K$$

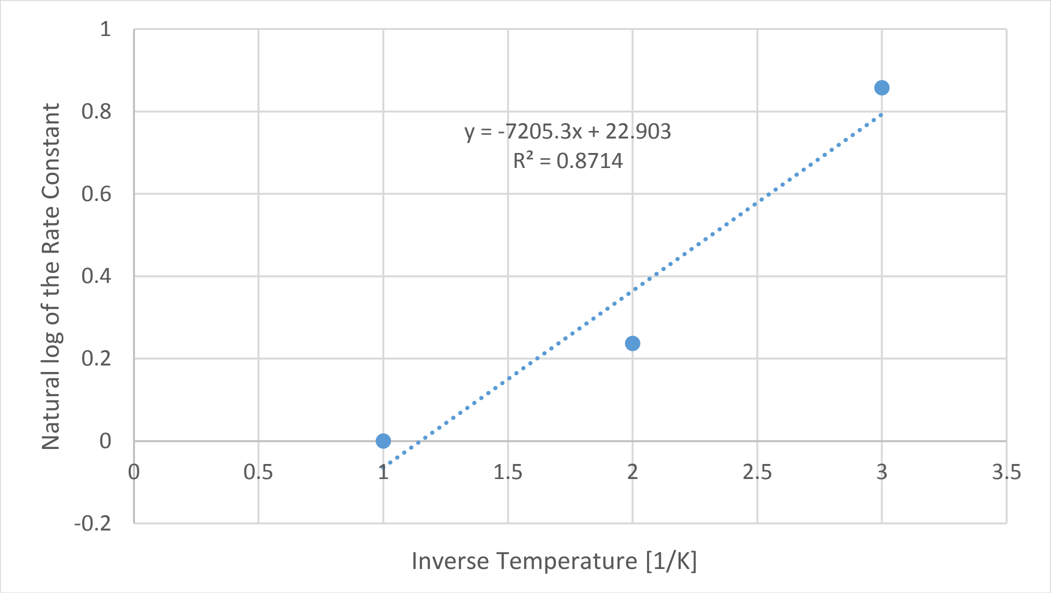


Figure H-1: Methanolysis Arrhenius Plot

I. Ethanolysis Summary

Averaged

Table I-1 - Averaged Calculated Ethanolysis Glycerol Concentration

AVERAGE (25C)			
Time	Average	Adjusted	mol/L
Std 1	1.835	1.677	
Std 2	1.412	1.255	
Std 3	0.945	0.788	
Std 4	0.157	0.000	1.643
1	0.265	0.108	0.066
2	0.348	0.191	0.116
3	0.544	0.387	0.235
4	0.386	0.228	0.139
5	0.545	0.388	0.236
7	0.535	0.378	0.230
10	0.708	0.551	0.335
12	0.718	0.561	0.342
15	0.828	0.671	0.408
20	0.965	0.808	0.492
25	1.009	0.852	0.519
30	0.999	0.841	0.512
35	1.280	1.123	0.683
40	1.289	1.132	0.689
Max			0.689

AVERAGE (35C)			
Time	Average	Adjusted	mol/L
Std 1	1.827	1.734	
Std 2	1.394	1.301	
Std 3	1.091	0.998	
Std 4	0.093	0.000	1.641
1	0.211	0.118	0.072
2	0.317	0.224	0.137
3	0.437	0.344	0.210
4	0.442	0.349	0.213
5	0.460	0.367	0.224
7	0.591	0.498	0.304
10	0.863	0.770	0.469
12	0.886	0.793	0.483
15	1.007	0.914	0.557
20	1.004	0.911	0.555
25	0.967	0.874	0.533
30	1.057	0.964	0.588
35	1.255	1.162	0.708
40	1.102	1.009	0.615
Max			0.708

AVERAGE (45C)			
Time	Average	Adjusted	mol/L
Std 1	1.543	1.474	
Std 2	1.015	0.947	
Std 3	0.666	0.598	
Std 4	0.068	0.000	1.439
1	0.276	0.208	0.145
2	0.379	0.311	0.216
3	0.506	0.438	0.304
4	0.563	0.495	0.344
5	0.583	0.515	0.358
7	0.816	0.747	0.519
10	0.978	0.910	0.632
12	1.018	0.950	0.660
15	0.938	0.870	0.605
20	1.000	0.931	0.647
25	1.041	0.972	0.676
30	0.992	0.924	0.642
35	1.114	1.046	0.727
40	1.043	0.975	0.677
Max			0.727

Table I-2 - Averaged Ideal Ethanolysis Glycerol Concentration

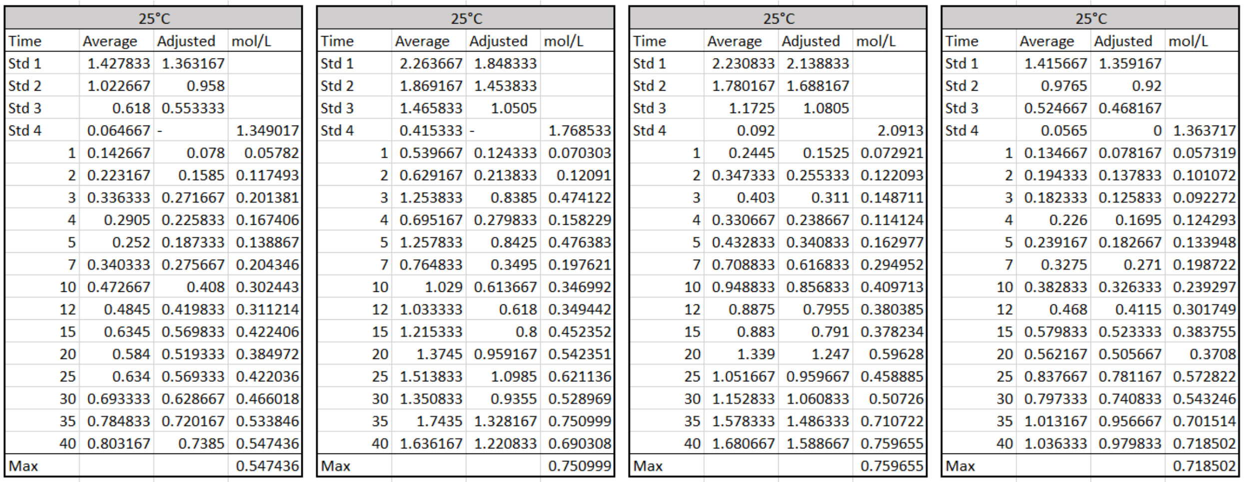
AVERAGE (25C)			
Time	Average	Adjusted	mol/L
Std 1	1.835	1.677	
Std 2	1.412	1.255	
Std 3	0.945	0.788	
Std 4	0.157	0.000	1.2
1	0.265	0.108	0.090
2	0.348	0.191	0.159
3	0.544	0.387	0.322
4	0.386	0.228	0.190
5	0.545	0.388	0.324
7	0.535	0.378	0.315
10	0.708	0.551	0.459
12	0.718	0.561	0.468
15	0.828	0.671	0.559
20	0.965	0.808	0.673
25	1.009	0.852	0.710
30	0.999	0.841	0.701
35	1.280	1.123	0.936
40	1.289	1.132	0.943
Max			0.943

AVERAGE (35C)			
Time	Average	Adjusted	mol/L
Std 1	1.827	1.734	
Std 2	1.394	1.301	
Std 3	1.091	0.998	
Std 4	0.093	0.000	1.2
1	0.211	0.118	0.098
2	0.317	0.224	0.185
3	0.437	0.344	0.284
4	0.442	0.349	0.288
5	0.460	0.367	0.303
7	0.591	0.498	0.411
10	0.863	0.770	0.635
12	0.886	0.793	0.654
15	1.007	0.914	0.754
20	1.004	0.911	0.751
25	0.967	0.874	0.721
30	1.057	0.964	0.795
35	1.255	1.162	0.958
40	1.102	1.009	0.832
Max			0.958

AVERAGE (45C)			
Time	Average	Adjusted	mol/L
Std 1	1.543	1.474	
Std 2	1.015	0.947	
Std 3	0.666	0.598	
Std 4	0.068	0.000	1.2
1	0.276	0.208	0.173
2	0.379	0.311	0.259
3	0.506	0.438	0.365
4	0.563	0.495	0.412
5	0.583	0.515	0.429
7	0.816	0.747	0.623
10	0.978	0.910	0.758
12	1.018	0.950	0.792
15	0.938	0.870	0.725
20	1.000	0.931	0.776
25	1.041	0.972	0.810
30	0.992	0.924	0.770
35	1.114	1.046	0.872
40	1.043	0.975	0.812
Max			0.872

25°C

Table I-3: Ethanolysis at 25°C Using Calculated Calibration Curves



25°C			
Time	Average	Adjusted	mol/L
Std 1	1.427833	1.363167	
Std 2	1.022667	0.958	
Std 3	0.618	0.553333	
Std 4	0.064667	-	1.349017
1	0.142667	0.078	0.05782
2	0.223167	0.1585	0.117493
3	0.336333	0.271667	0.201381
4	0.2905	0.225833	0.167406
5	0.252	0.187333	0.138867
7	0.340333	0.275667	0.204346
10	0.472667	0.408	0.302443
12	0.4845	0.419833	0.311214
15	0.6345	0.569833	0.422406
20	0.584	0.519333	0.384972
25	0.634	0.569333	0.422036
30	0.693333	0.628667	0.466018
35	0.784833	0.720167	0.533846
40	0.803167	0.7385	0.547436
Max			0.547436

25°C			
Time	Average	Adjusted	mol/L
Std 1	2.263667	1.848333	
Std 2	1.869167	1.453833	
Std 3	1.465833	1.0505	
Std 4	0.415333	-	1.768533
1	0.539667	0.124333	0.070303
2	0.629167	0.213833	0.12091
3	1.253833	0.8385	0.474122
4	0.695167	0.279833	0.158229
5	1.257833	0.8425	0.476383
7	0.764833	0.3495	0.197621
10	1.029	0.613667	0.346992
12	1.033333	0.618	0.349442
15	1.215333	0.8	0.452352
20	1.3745	0.959167	0.542351
25	1.513833	1.0985	0.621136
30	1.350833	0.9355	0.528969
35	1.7435	1.328167	0.750999
40	1.636167	1.220833	0.690308
Max			0.750999

25°C			
Time	Average	Adjusted	mol/L
Std 1	2.230833	2.138833	
Std 2	1.780167	1.688167	
Std 3	1.1725	1.0805	
Std 4	0.092		2.0913
1	0.2445	0.1525	0.072921
2	0.347333	0.255333	0.122093
3	0.403	0.311	0.148711
4	0.330667	0.238667	0.114124
5	0.432833	0.340833	0.162977
7	0.708833	0.616833	0.294952
10	0.948833	0.856833	0.409713
12	0.8875	0.7955	0.380385
15	0.883	0.791	0.378234
20	1.339	1.247	0.59628
25	1.051667	0.959667	0.458885
30	1.152833	1.060833	0.50726
35	1.578333	1.486333	0.710722
40	1.680667	1.588667	0.759655
Max			0.759655

25°C			
Time	Average	Adjusted	mol/L
Std 1	1.415667	1.359167	
Std 2	0.9765	0.92	
Std 3	0.524667	0.468167	
Std 4	0.0565	0	1.363717
1	0.134667	0.078167	0.057319
2	0.194333	0.137833	0.101072
3	0.182333	0.125833	0.092272
4	0.226	0.1695	0.124293
5	0.239167	0.182667	0.133948
7	0.3275	0.271	0.198722
10	0.382833	0.326333	0.239297
12	0.468	0.4115	0.301749
15	0.579833	0.523333	0.383755
20	0.562167	0.505667	0.3708
25	0.837667	0.781167	0.572822
30	0.797333	0.740833	0.543246
35	1.013167	0.956667	0.701514
40	1.036333	0.979833	0.718502
Max			0.718502

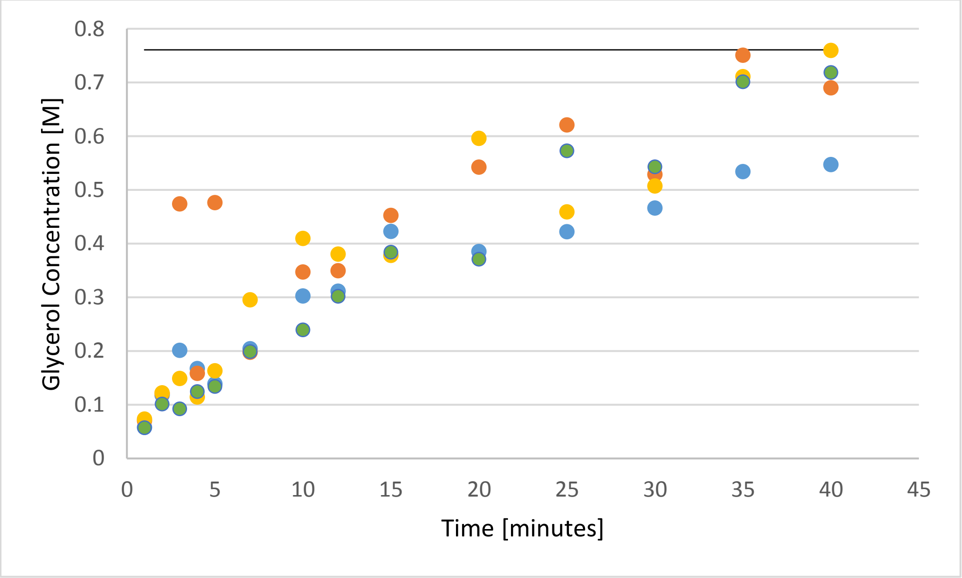


Figure I-1 - Ethanolysis at 25°C Using Calculated Calibration Curves

35°C

Table I-4: Ethanolysis at 35°C Using Calculated Calibration Curves

35°C			
Time	Average	Adjusted	mol/L
Std 1	2.703167	2.492667	
Std 2	2.708833	2.498333	
Std 3	2.6045	2.394	
Std 4	0.2105	-	2.195417
1	0.3375	0.127	0.057848
2	0.513167	0.302667	0.137863
3	0.786333	0.575833	0.262289
4	0.558333	0.347833	0.158436
5	0.5805	0.37	0.168533
7	0.76	0.5495	0.250294
10	1.004333	0.793833	0.361587
12	1.3745	1.164	0.530195
15	1.568333	1.357833	0.618485
20	1.156167	0.945667	0.430746
25	1.202667	0.992167	0.451926
30	1.263333	1.052833	0.47956
35	1.509	1.2985	0.591459
40	1.3395	1.129	0.514253
Max			0.618485

35°C			
Time	Average	Adjusted	mol/L
Std 1	1.4605	1.416	
Std 2	0.933	0.8885	
Std 3	0.5885	0.544	
Std 4	0.0445	0	1.3868
1	0.159833	0.115333	0.083165
2	0.218333	0.173833	0.125349
3	0.301333	0.256833	0.185199
4	0.388667	0.344167	0.248173
5	0.3235	0.279	0.201183
7	0.482833	0.438333	0.316075
10	1.037	0.9925	0.715676
12	0.593	0.5485	0.395515
15	0.709	0.6645	0.479161
20	0.829667	0.785167	0.566172
25	0.855	0.8105	0.584439
30	0.774333	0.729833	0.526272
35	1.023833	0.979333	0.706182
40	0.92	0.8755	0.631309
Max			0.715676

35°C			
Time	Average	Adjusted	mol/L
Std 1	1.681	1.625	
Std 2	1.024	0.968	
Std 3	0.552	0.496	
Std 4	0.056		1.6207
1	0.145	0.089	0.054915
2	0.235	0.179	0.110446
3	0.27	0.214	0.132042
4	0.381	0.325	0.200531
5	0.48	0.424	0.261615
7	0.498	0.442	0.272722
10	0.609	0.553	0.341211
12	0.863	0.807	0.497933
15	0.715	0.659	0.406614
20	0.953	0.897	0.553465
25	0.937	0.881	0.543592
30	1.009	0.953	0.588018
35	1.279	1.223	0.754612
40	0.994	0.938	0.578762
Max			0.754612

35°C			
Time	Average	Adjusted	mol/L
Std 1	1.462	1.401	
Std 2	0.91	0.849	
Std 3	0.617	0.556	
Std 4	0.061	0	1.3593
1	0.203	0.142	0.104466
2	0.303	0.247	0.181711
3	0.392	0.336	0.247186
4	0.44	0.384	0.282498
5	0.457	0.401	0.295005
7	0.623	0.567	0.417126
10	0.801	0.745	0.548076
12	0.714	0.658	0.484073
15	1.034	0.978	0.719488
20	1.076	1.02	0.750386
25	0.872	0.816	0.600309
30	1.183	1.127	0.829103
35	1.208	1.152	0.847495
40	1.155	1.099	0.808504
Max			0.847495

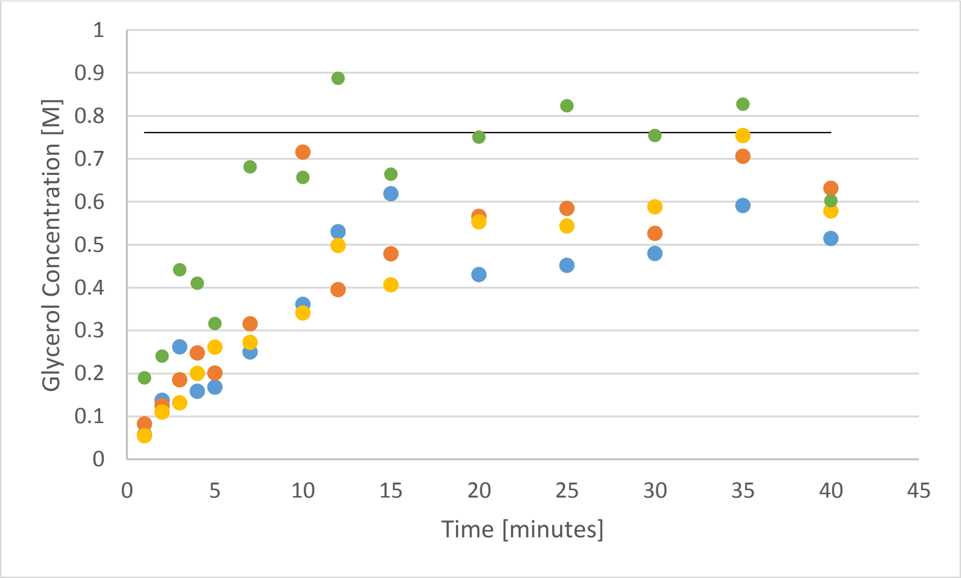


Figure I-2 - Ethanolysis at 35°C Using Calculated Calibration Curves

45°C

Table I-5: Ethanolysis at 45°C Using Calculated Calibration Curves

45°C			
Time	Average	Adjusted	mol/L
Std 1	1.409333	1.339833	
Std 2	0.674833	0.605333	
Std 3	0.4765	0.407	
Std 4	0.0695	-	1.2929
1	0.2245	0.155	0.119886
2	0.308333	0.238833	0.184727
3	0.333667	0.264167	0.204321
4	0.524	0.4545	0.351535
5	0.573333	0.503833	0.389692
7	0.572	0.5025	0.388661
10	1.112833	1.043333	0.806971
12	0.964833	0.895333	0.6925
15	0.902333	0.832833	0.644159
20	0.926167	0.856667	0.662593
25	1.009333	0.939833	0.726919
30	0.960167	0.890667	0.688891
35	1.210667	1.141167	0.882641
40	1.0665	0.997	0.771135
Max			0.882641

45°C			
Time	Average	Adjusted	mol/L
Std 1	1.8185	1.72925	
Std 2	1.3835	1.29425	
Std 3	0.8535	0.76425	
Std 4	0.08925		1.7094
1	0.32875	0.2395	0.140108
2	0.51875	0.4295	0.251258
3	0.6485	0.55925	0.327162
4	0.6545	0.56525	0.330672
5	0.805	0.71575	0.418714
7	0.89975	0.8105	0.474143
10	1.05075	0.9615	0.562478
12	1.17975	1.0905	0.637943
15	1.0885	0.99925	0.584562
20	1.1735	1.08425	0.634287
25	1.253	1.16375	0.680794
30	1.14675	1.0575	0.618638
35	1.2115	1.12225	0.656517
40	1.313	1.22375	0.715894
Max			0.715894

45°C			
Time	Average	Adjusted	mol/L
Std 1	1.496	1.4335	
Std 2	1.02725	0.96475	
Std 3	0.77825	0.71575	
Std 4	0.0625		1.366075
1	0.2365	0.174	0.127372
2	0.30375	0.24125	0.176601
3	0.37675	0.31425	0.230039
4	0.453	0.3905	0.285855
5	0.462	0.3995	0.292444
7	0.79325	0.73075	0.534927
10	0.78625	0.72375	0.529803
12	0.6455	0.583	0.42677
15	0.78875	0.72625	0.531633
20	0.8055	0.743	0.543894
25	0.705	0.6425	0.470326
30	0.763	0.7005	0.512783
35	0.83425	0.77175	0.56494
40	0.904	0.8415	0.615998
Max			0.615998

45°C			
Time	Average	Adjusted	mol/L
Std 1	1.447333	1.395333	
Std 2	0.974333	0.922333	
Std 3	0.555667	0.503667	
Std 4	0.052	0	1.3876
1	0.315667	0.263667	0.190016
2	0.385667	0.333667	0.240463
3	0.665	0.613	0.44177
4	0.621667	0.569667	0.410541
5	0.491667	0.439667	0.316854
7	0.997667	0.945667	0.681512
10	0.963	0.911	0.656529
12	1.283333	1.231333	0.887383
15	0.973667	0.921667	0.664216
20	1.093333	1.041333	0.750456
25	1.195	1.143	0.823724
30	1.098667	1.046667	0.7543
35	1.200333	1.148333	0.827568
40	0.888	0.836	0.602479
Max			0.887383

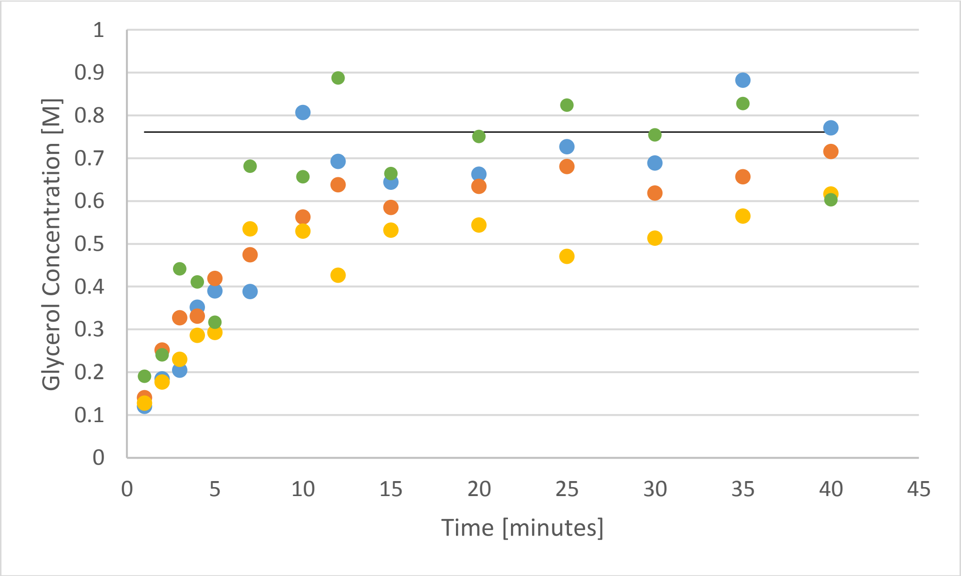
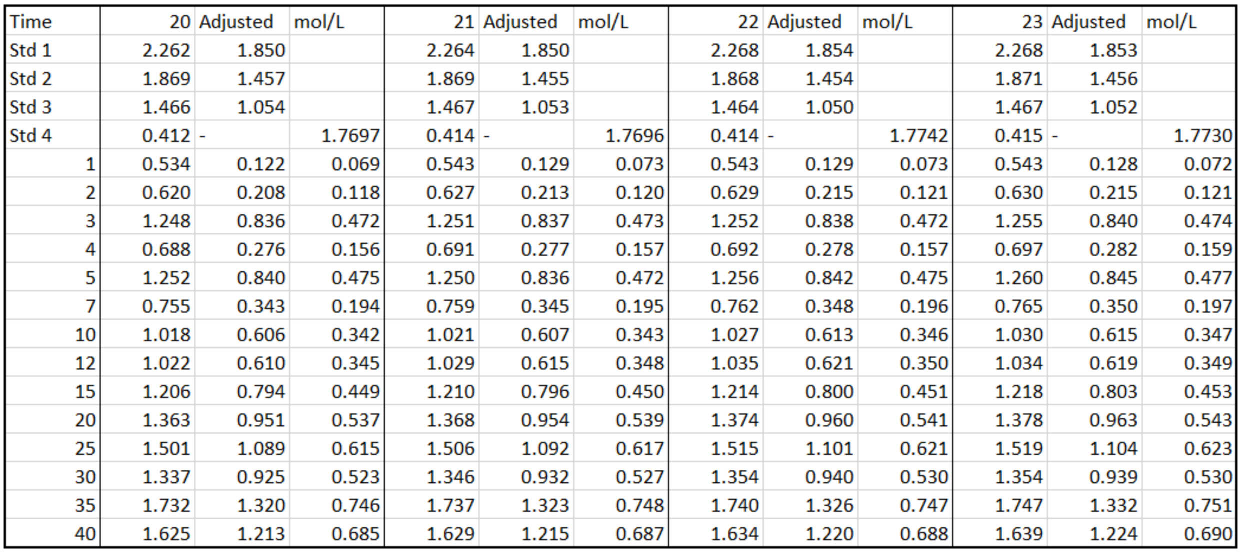


Figure I-3 - Ethanolysis at 45°C Using Calculated Calibration Curves

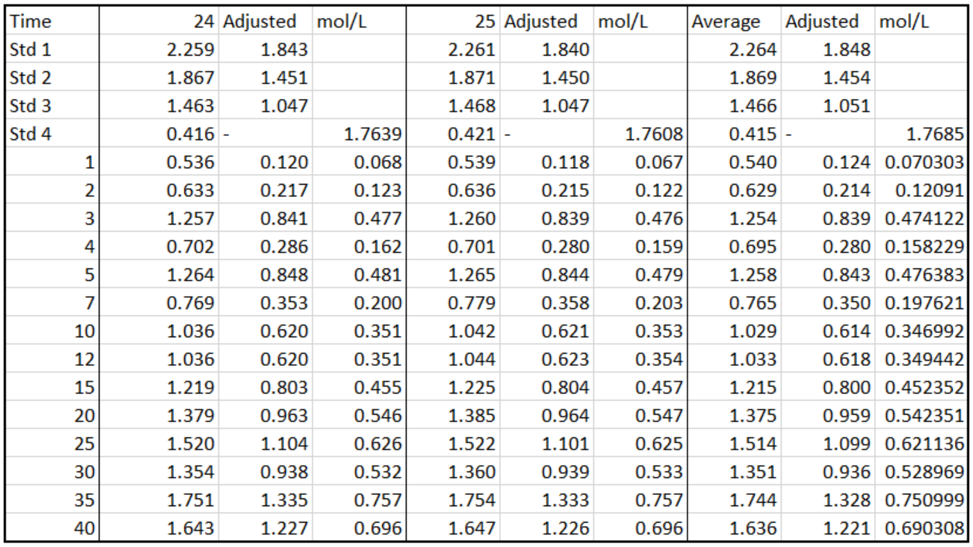
Experiment – 12/6/15

Calculated

Table I-6: Ethanolysis at 25°C Using Calculated Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	2.262	1.850		2.264	1.850		2.268	1.854		2.268	1.853	
Std 2	1.869	1.457		1.869	1.455		1.868	1.454		1.871	1.456	
Std 3	1.466	1.054		1.467	1.053		1.464	1.050		1.467	1.052	
Std 4	0.412	-	1.7697	0.414	-	1.7696	0.414	-	1.7742	0.415	-	1.7730
1	0.534	0.122	0.069	0.543	0.129	0.073	0.543	0.129	0.073	0.543	0.128	0.072
2	0.620	0.208	0.118	0.627	0.213	0.120	0.629	0.215	0.121	0.630	0.215	0.121
3	1.248	0.836	0.472	1.251	0.837	0.473	1.252	0.838	0.472	1.255	0.840	0.474
4	0.688	0.276	0.156	0.691	0.277	0.157	0.692	0.278	0.157	0.697	0.282	0.159
5	1.252	0.840	0.475	1.250	0.836	0.472	1.256	0.842	0.475	1.260	0.845	0.477
7	0.755	0.343	0.194	0.759	0.345	0.195	0.762	0.348	0.196	0.765	0.350	0.197
10	1.018	0.606	0.342	1.021	0.607	0.343	1.027	0.613	0.346	1.030	0.615	0.347
12	1.022	0.610	0.345	1.029	0.615	0.348	1.035	0.621	0.350	1.034	0.619	0.349
15	1.206	0.794	0.449	1.210	0.796	0.450	1.214	0.800	0.451	1.218	0.803	0.453
20	1.363	0.951	0.537	1.368	0.954	0.539	1.374	0.960	0.541	1.378	0.963	0.543
25	1.501	1.089	0.615	1.506	1.092	0.617	1.515	1.101	0.621	1.519	1.104	0.623
30	1.337	0.925	0.523	1.346	0.932	0.527	1.354	0.940	0.530	1.354	0.939	0.530
35	1.732	1.320	0.746	1.737	1.323	0.748	1.740	1.326	0.747	1.747	1.332	0.751
40	1.625	1.213	0.685	1.629	1.215	0.687	1.634	1.220	0.688	1.639	1.224	0.690



Time	24	Adjusted	mol/L	25	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	2.259	1.843		2.261	1.840		2.264	1.848	
Std 2	1.867	1.451		1.871	1.450		1.869	1.454	
Std 3	1.463	1.047		1.468	1.047		1.466	1.051	
Std 4	0.416	-	1.7639	0.421	-	1.7608	0.415	-	1.7685
1	0.536	0.120	0.068	0.539	0.118	0.067	0.540	0.124	0.070303
2	0.633	0.217	0.123	0.636	0.215	0.122	0.629	0.214	0.12091
3	1.257	0.841	0.477	1.260	0.839	0.476	1.254	0.839	0.474122
4	0.702	0.286	0.162	0.701	0.280	0.159	0.695	0.280	0.158229
5	1.264	0.848	0.481	1.265	0.844	0.479	1.258	0.843	0.476383
7	0.769	0.353	0.200	0.779	0.358	0.203	0.765	0.350	0.197621
10	1.036	0.620	0.351	1.042	0.621	0.353	1.029	0.614	0.346992
12	1.036	0.620	0.351	1.044	0.623	0.354	1.033	0.618	0.349442
15	1.219	0.803	0.455	1.225	0.804	0.457	1.215	0.800	0.452352
20	1.379	0.963	0.546	1.385	0.964	0.547	1.375	0.959	0.542351
25	1.520	1.104	0.626	1.522	1.101	0.625	1.514	1.099	0.621136
30	1.354	0.938	0.532	1.360	0.939	0.533	1.351	0.936	0.528969
35	1.751	1.335	0.757	1.754	1.333	0.757	1.744	1.328	0.750999
40	1.643	1.227	0.696	1.647	1.226	0.696	1.636	1.221	0.690308

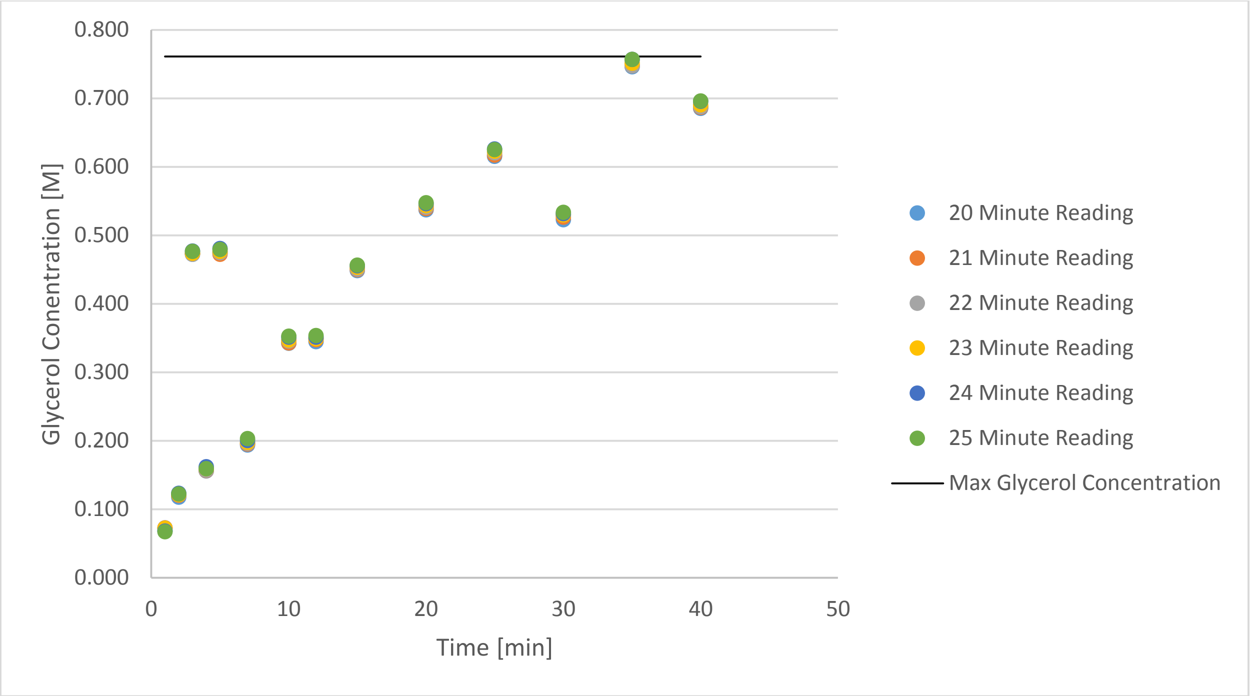
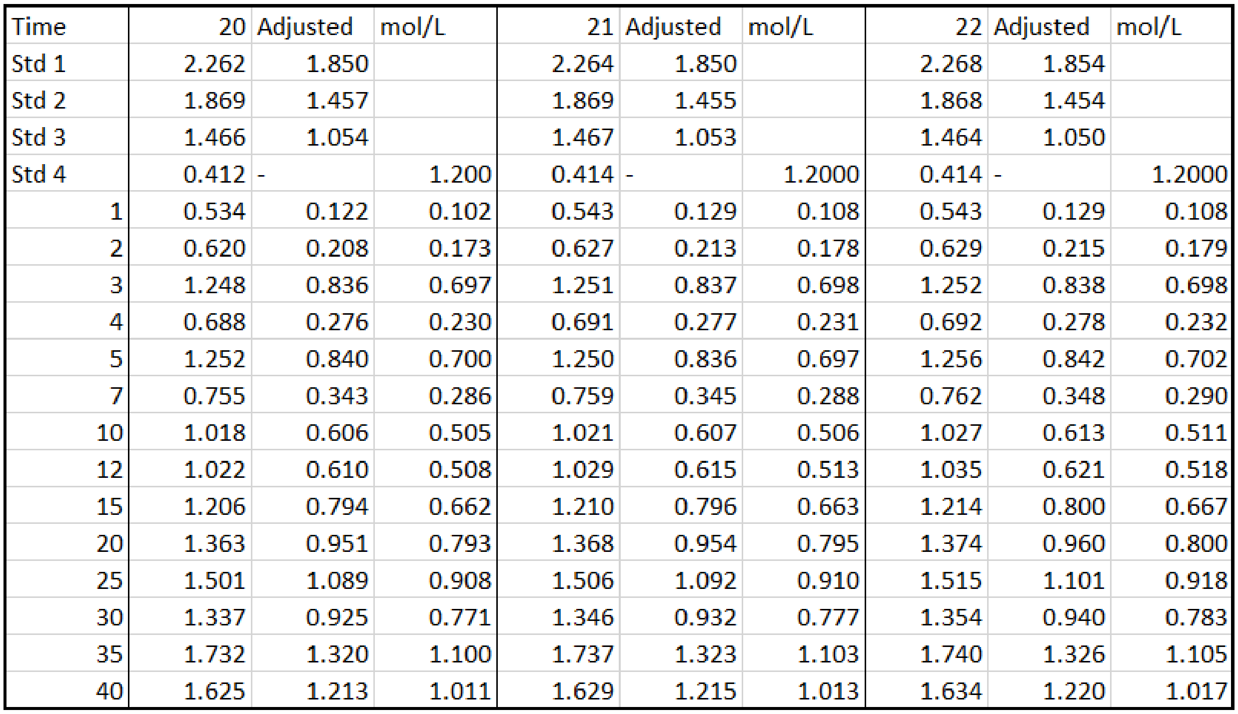


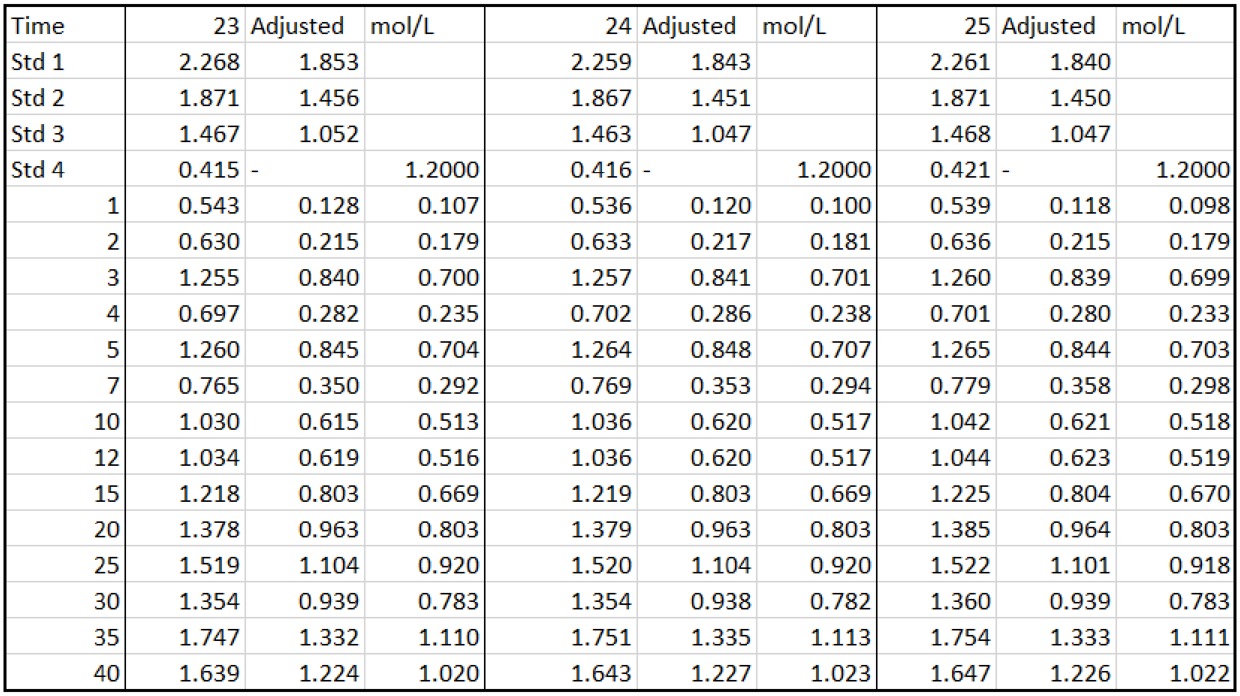
Figure I-4: Ethanolysis at 25°C Using Calculated Calibration Curves

Ideal

Table I-7: Ethanolysis at 25°C Using Ideal Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	2.262	1.850		2.264	1.850		2.268	1.854	
Std 2	1.869	1.457		1.869	1.455		1.868	1.454	
Std 3	1.466	1.054		1.467	1.053		1.464	1.050	
Std 4	0.412	-	1.200	0.414	-	1.2000	0.414	-	1.2000
1	0.534	0.122	0.102	0.543	0.129	0.108	0.543	0.129	0.108
2	0.620	0.208	0.173	0.627	0.213	0.178	0.629	0.215	0.179
3	1.248	0.836	0.697	1.251	0.837	0.698	1.252	0.838	0.698
4	0.688	0.276	0.230	0.691	0.277	0.231	0.692	0.278	0.232
5	1.252	0.840	0.700	1.250	0.836	0.697	1.256	0.842	0.702
7	0.755	0.343	0.286	0.759	0.345	0.288	0.762	0.348	0.290
10	1.018	0.606	0.505	1.021	0.607	0.506	1.027	0.613	0.511
12	1.022	0.610	0.508	1.029	0.615	0.513	1.035	0.621	0.518
15	1.206	0.794	0.662	1.210	0.796	0.663	1.214	0.800	0.667
20	1.363	0.951	0.793	1.368	0.954	0.795	1.374	0.960	0.800
25	1.501	1.089	0.908	1.506	1.092	0.910	1.515	1.101	0.918
30	1.337	0.925	0.771	1.346	0.932	0.777	1.354	0.940	0.783
35	1.732	1.320	1.100	1.737	1.323	1.103	1.740	1.326	1.105
40	1.625	1.213	1.011	1.629	1.215	1.013	1.634	1.220	1.017



Time	23	Adjusted	mol/L	24	Adjusted	mol/L	25	Adjusted	mol/L
Std 1	2.268	1.853		2.259	1.843		2.261	1.840	
Std 2	1.871	1.456		1.867	1.451		1.871	1.450	
Std 3	1.467	1.052		1.463	1.047		1.468	1.047	
Std 4	0.415	-	1.2000	0.416	-	1.2000	0.421	-	1.2000
1	0.543	0.128	0.107	0.536	0.120	0.100	0.539	0.118	0.098
2	0.630	0.215	0.179	0.633	0.217	0.181	0.636	0.215	0.179
3	1.255	0.840	0.700	1.257	0.841	0.701	1.260	0.839	0.699
4	0.697	0.282	0.235	0.702	0.286	0.238	0.701	0.280	0.233
5	1.260	0.845	0.704	1.264	0.848	0.707	1.265	0.844	0.703
7	0.765	0.350	0.292	0.769	0.353	0.294	0.779	0.358	0.298
10	1.030	0.615	0.513	1.036	0.620	0.517	1.042	0.621	0.518
12	1.034	0.619	0.516	1.036	0.620	0.517	1.044	0.623	0.519
15	1.218	0.803	0.669	1.219	0.803	0.669	1.225	0.804	0.670
20	1.378	0.963	0.803	1.379	0.963	0.803	1.385	0.964	0.803
25	1.519	1.104	0.920	1.520	1.104	0.920	1.522	1.101	0.918
30	1.354	0.939	0.783	1.354	0.938	0.782	1.360	0.939	0.783
35	1.747	1.332	1.110	1.751	1.335	1.113	1.754	1.333	1.111
40	1.639	1.224	1.020	1.643	1.227	1.023	1.647	1.226	1.022

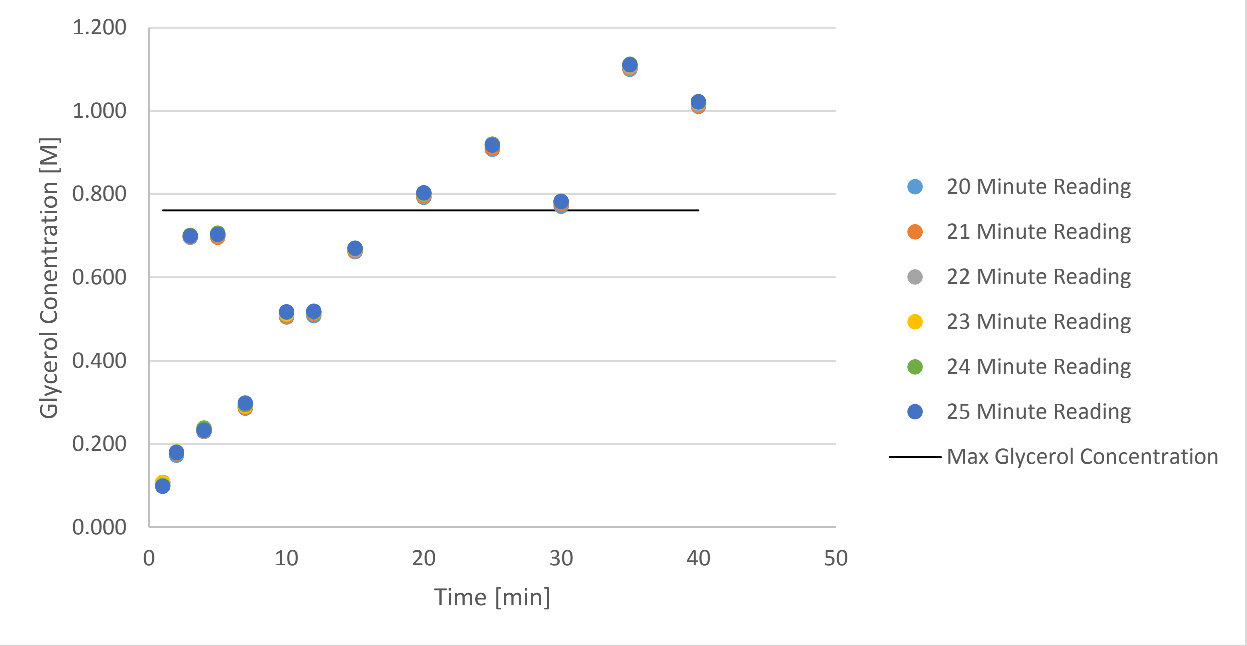


Figure I-5: Ethanolysis at 25°C Using Ideal Calibration Curves

Calibration Curves

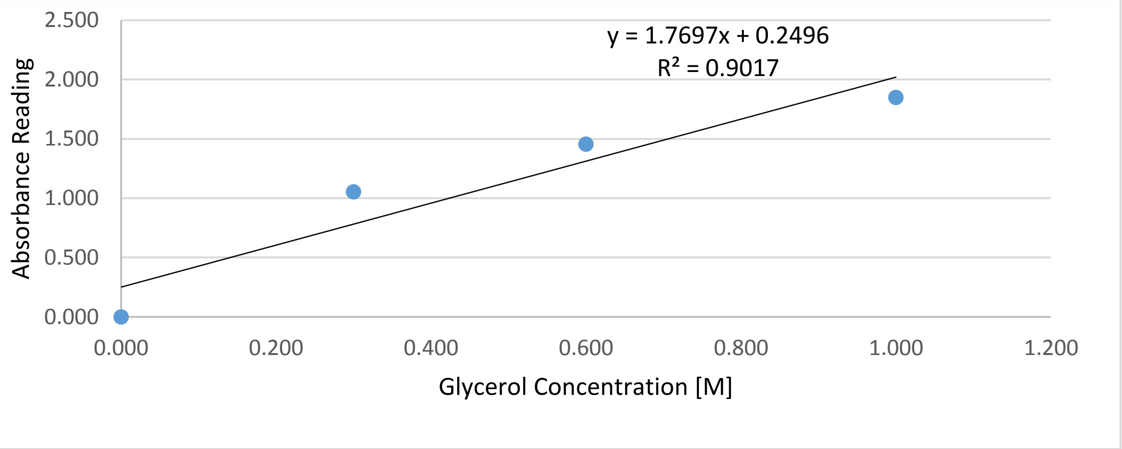


Figure I-6: Calibration Curve at 20 Minute Reading

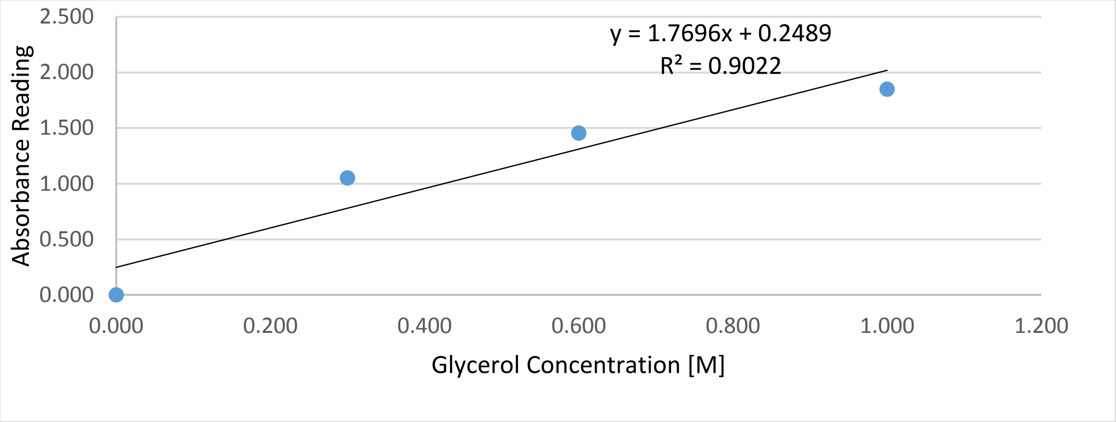


Figure I-7: Calibration Curve at 21 Minute Reading

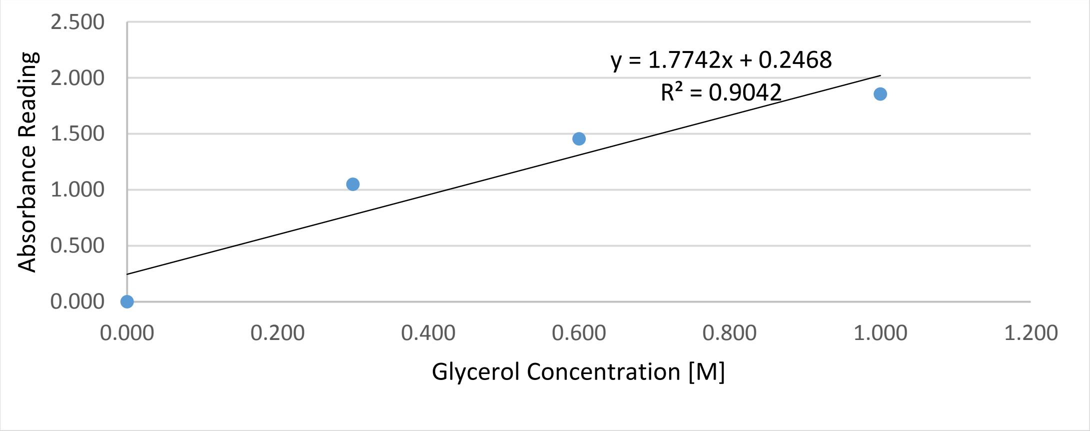


Figure I-8: Calibration Curve at 22 Minute Reading

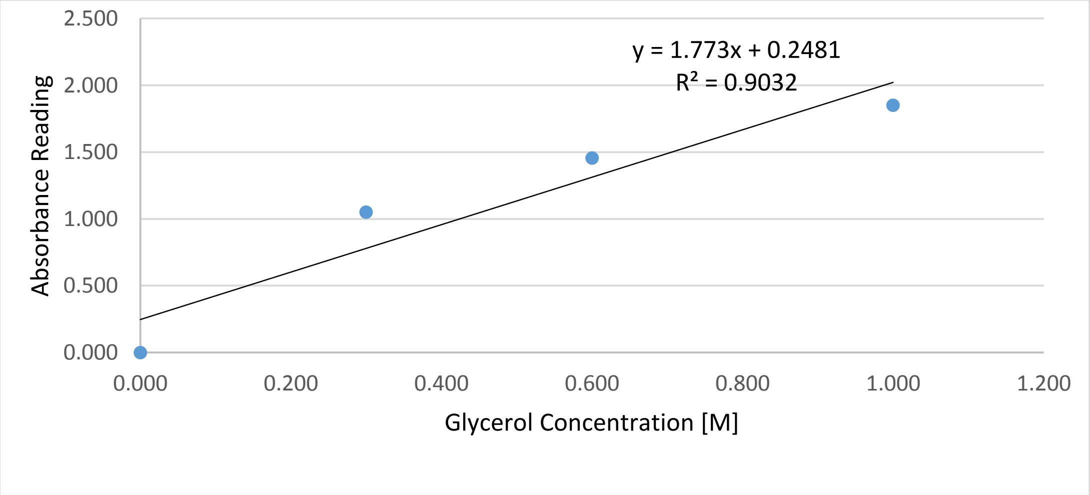


Figure I-9: Calibration Curve at 23 Minute Reading

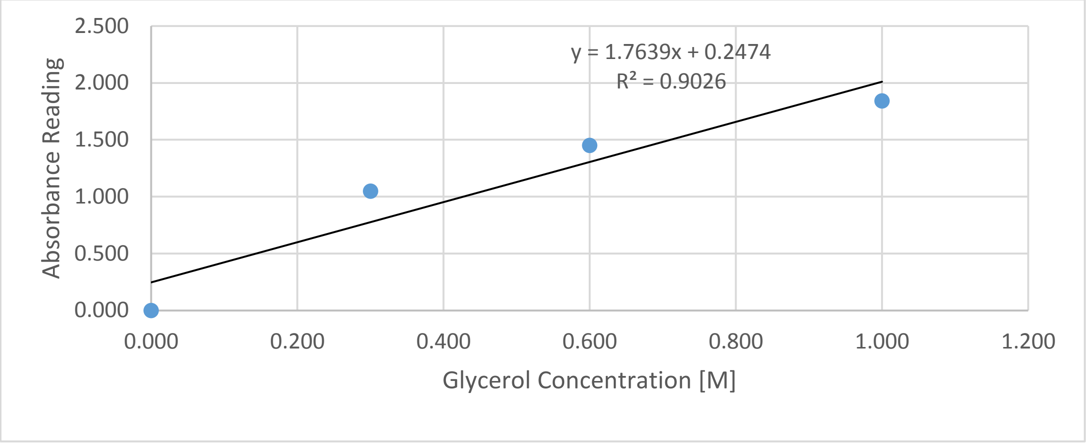


Figure I-10: Calibration Curve at 24 Minute Reading

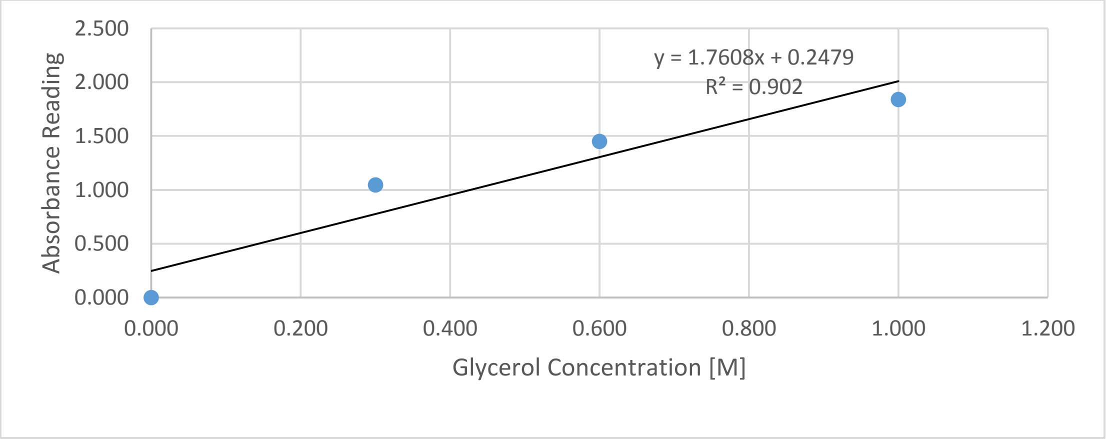
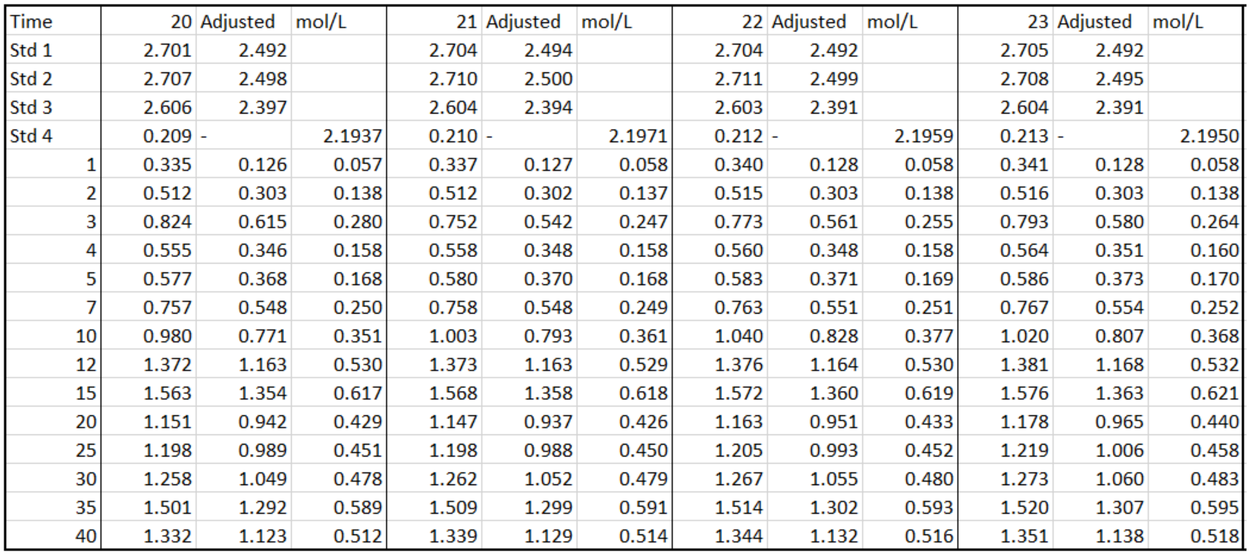


Figure I-11: Calibration Curve at 25 Minute Reading

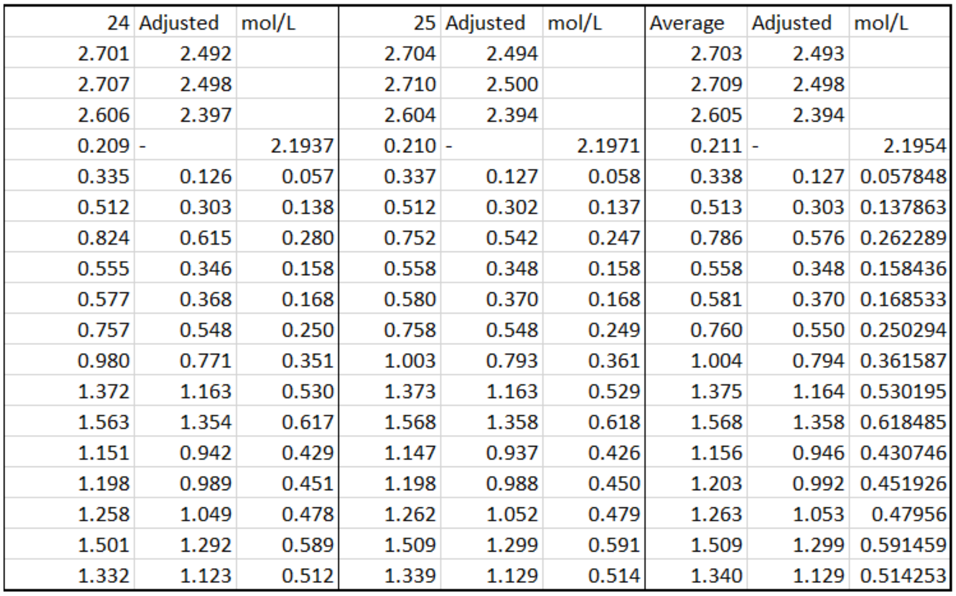
Experiment – 12/14/15

Calculated

Table I-8: Ethanolysis at 35°C Using Calculated Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	2.701	2.492		2.704	2.494		2.704	2.492		2.705	2.492	
Std 2	2.707	2.498		2.710	2.500		2.711	2.499		2.708	2.495	
Std 3	2.606	2.397		2.604	2.394		2.603	2.391		2.604	2.391	
Std 4	0.209	-	2.1937	0.210	-	2.1971	0.212	-	2.1959	0.213	-	2.1950
1	0.335	0.126	0.057	0.337	0.127	0.058	0.340	0.128	0.058	0.341	0.128	0.058
2	0.512	0.303	0.138	0.512	0.302	0.137	0.515	0.303	0.138	0.516	0.303	0.138
3	0.824	0.615	0.280	0.752	0.542	0.247	0.773	0.561	0.255	0.793	0.580	0.264
4	0.555	0.346	0.158	0.558	0.348	0.158	0.560	0.348	0.158	0.564	0.351	0.160
5	0.577	0.368	0.168	0.580	0.370	0.168	0.583	0.371	0.169	0.586	0.373	0.170
7	0.757	0.548	0.250	0.758	0.548	0.249	0.763	0.551	0.251	0.767	0.554	0.252
10	0.980	0.771	0.351	1.003	0.793	0.361	1.040	0.828	0.377	1.020	0.807	0.368
12	1.372	1.163	0.530	1.373	1.163	0.529	1.376	1.164	0.530	1.381	1.168	0.532
15	1.563	1.354	0.617	1.568	1.358	0.618	1.572	1.360	0.619	1.576	1.363	0.621
20	1.151	0.942	0.429	1.147	0.937	0.426	1.163	0.951	0.433	1.178	0.965	0.440
25	1.198	0.989	0.451	1.198	0.988	0.450	1.205	0.993	0.452	1.219	1.006	0.458
30	1.258	1.049	0.478	1.262	1.052	0.479	1.267	1.055	0.480	1.273	1.060	0.483
35	1.501	1.292	0.589	1.509	1.299	0.591	1.514	1.302	0.593	1.520	1.307	0.595
40	1.332	1.123	0.512	1.339	1.129	0.514	1.344	1.132	0.516	1.351	1.138	0.518



24	Adjusted	mol/L	25	Adjusted	mol/L	Average	Adjusted	mol/L
2.701	2.492		2.704	2.494		2.703	2.493	
2.707	2.498		2.710	2.500		2.709	2.498	
2.606	2.397		2.604	2.394		2.605	2.394	
0.209	-	2.1937	0.210	-	2.1971	0.211	-	2.1954
0.335	0.126	0.057	0.337	0.127	0.058	0.338	0.127	0.057848
0.512	0.303	0.138	0.512	0.302	0.137	0.513	0.303	0.137863
0.824	0.615	0.280	0.752	0.542	0.247	0.786	0.576	0.262289
0.555	0.346	0.158	0.558	0.348	0.158	0.558	0.348	0.158436
0.577	0.368	0.168	0.580	0.370	0.168	0.581	0.370	0.168533
0.757	0.548	0.250	0.758	0.548	0.249	0.760	0.550	0.250294
0.980	0.771	0.351	1.003	0.793	0.361	1.004	0.794	0.361587
1.372	1.163	0.530	1.373	1.163	0.529	1.375	1.164	0.530195
1.563	1.354	0.617	1.568	1.358	0.618	1.568	1.358	0.618485
1.151	0.942	0.429	1.147	0.937	0.426	1.156	0.946	0.430746
1.198	0.989	0.451	1.198	0.988	0.450	1.203	0.992	0.451926
1.258	1.049	0.478	1.262	1.052	0.479	1.263	1.053	0.47956
1.501	1.292	0.589	1.509	1.299	0.591	1.509	1.299	0.591459
1.332	1.123	0.512	1.339	1.129	0.514	1.340	1.129	0.514253

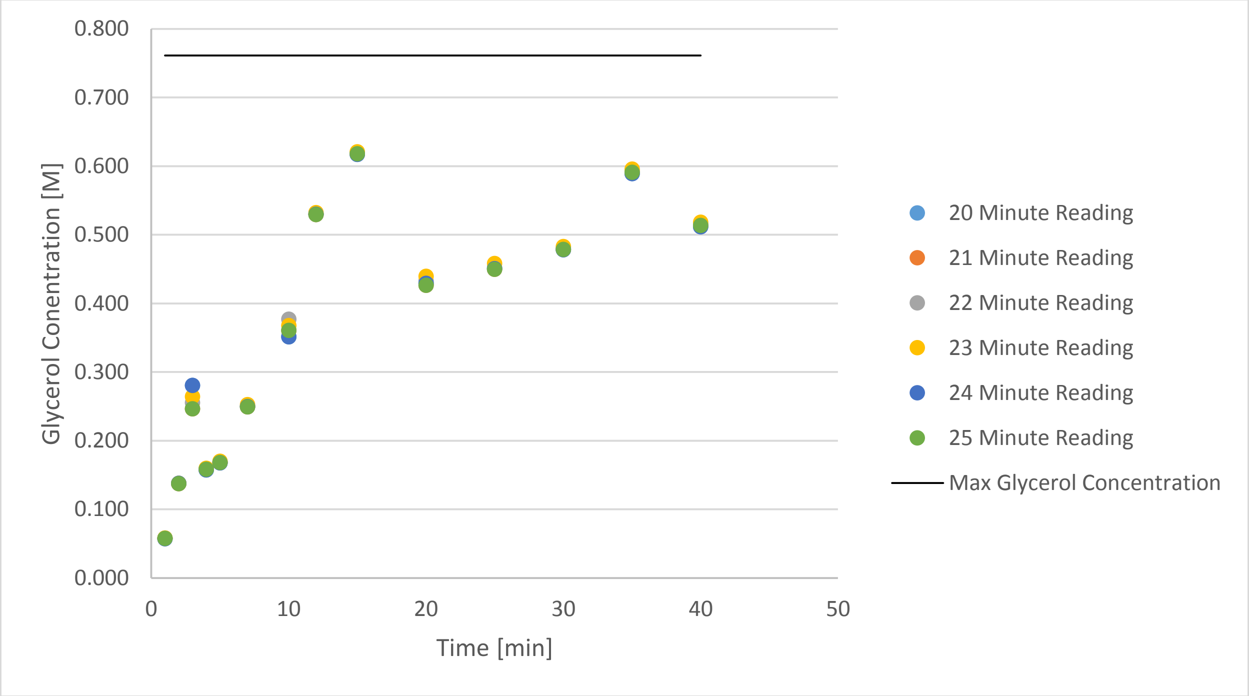


Figure I-12 - Ethanolysis at 35°C using Calculated Calibration Curves

Ideal

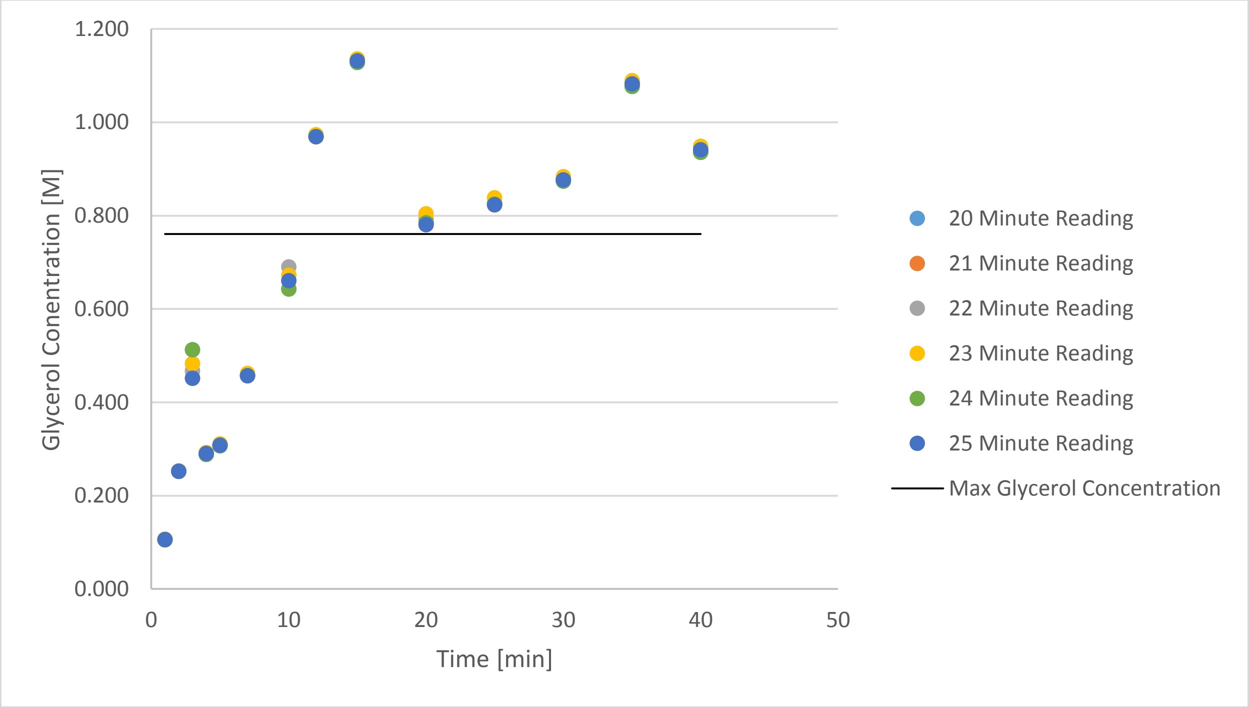


Figure I-13 - Ethanolysis at 35°C using Ideal Calibration Curves

Calibration Curves

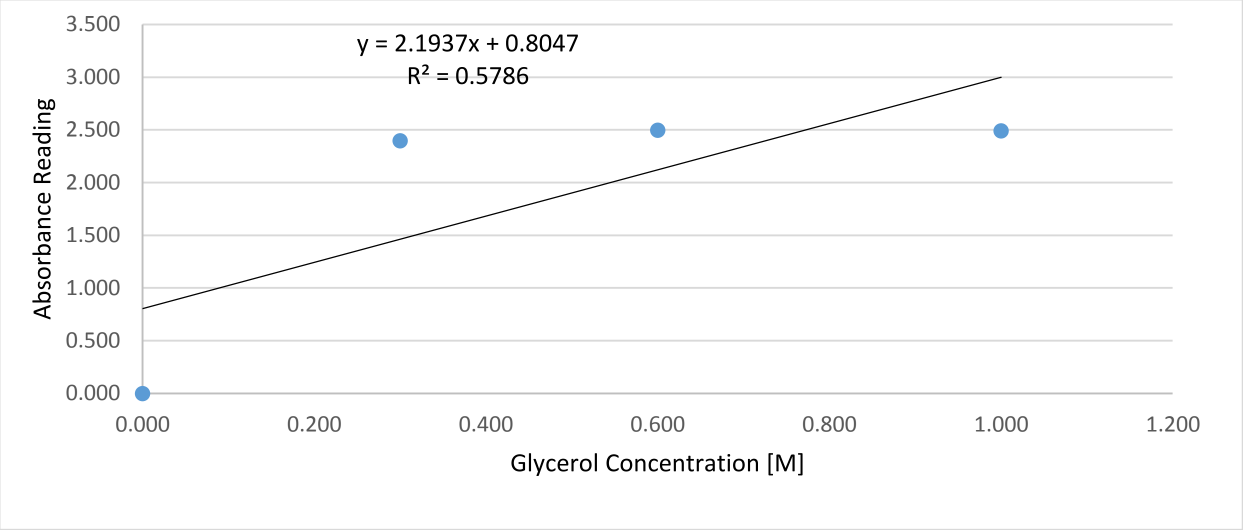


Figure I-14 - Calibration Curve from 20 Minute Reading

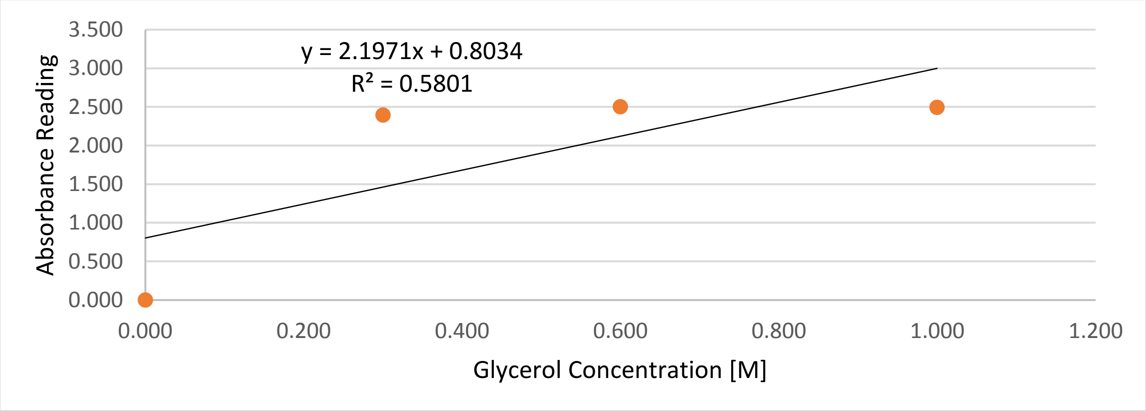


Figure I-15 - Calibration Curve from 21 Minute Reading

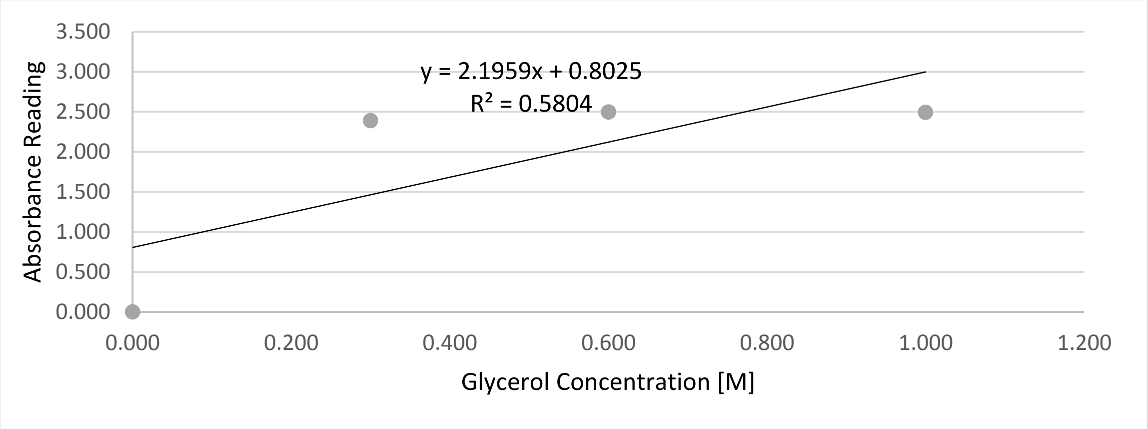


Figure I-16 - Calibration Curve from 22 Minute Reading

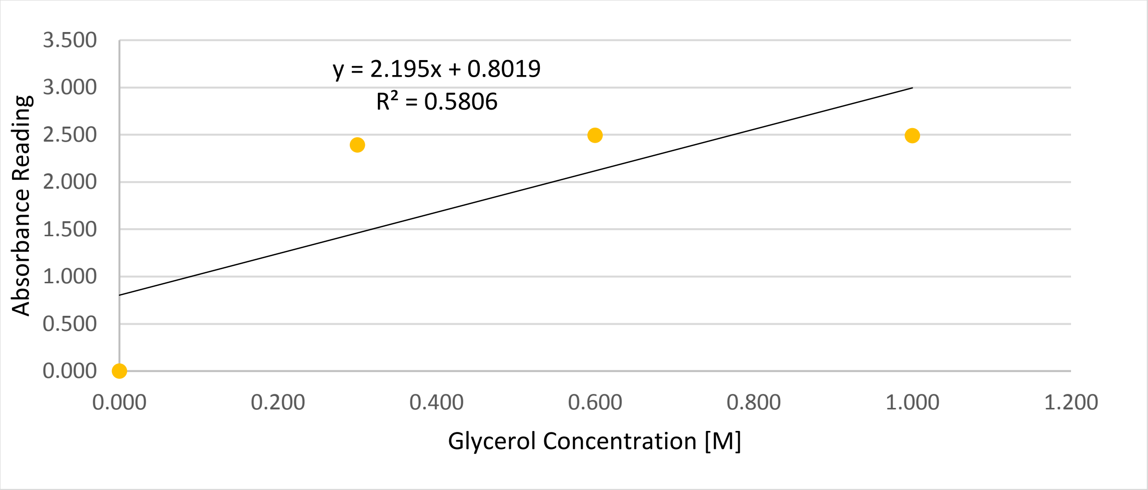


Figure I-17 - Calibration Curve from 23 Minute Reading

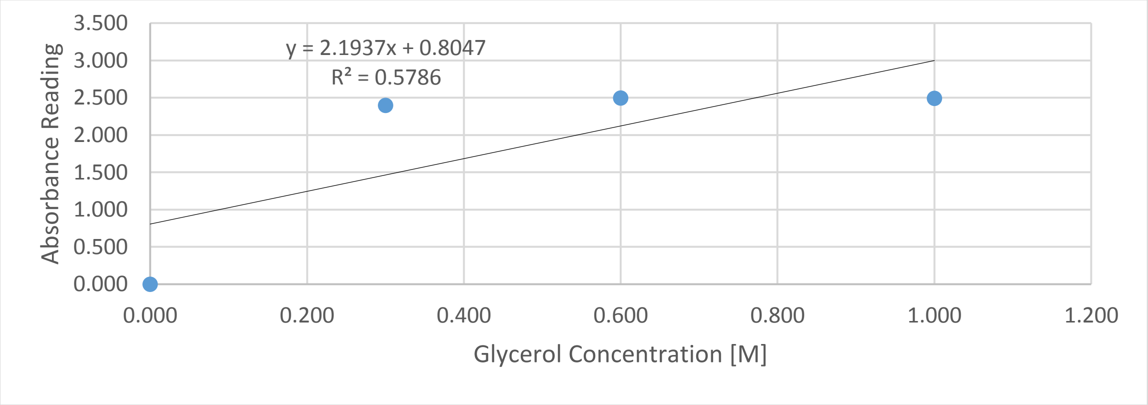


Figure I-18 - Calibration Curve from 24 Minute Reading

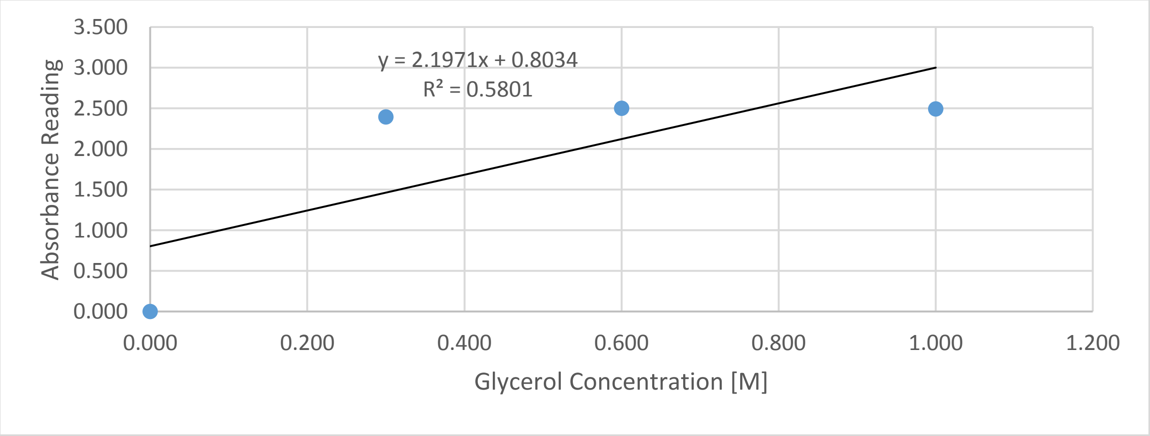
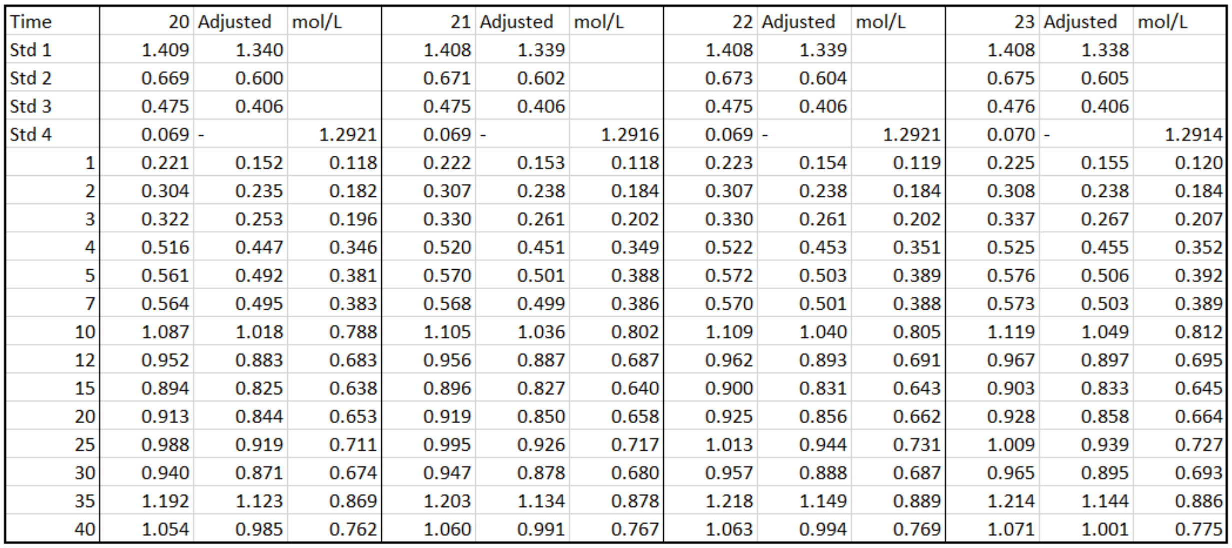


Figure I-19 - Calibration Curve from 25 Minute Reading

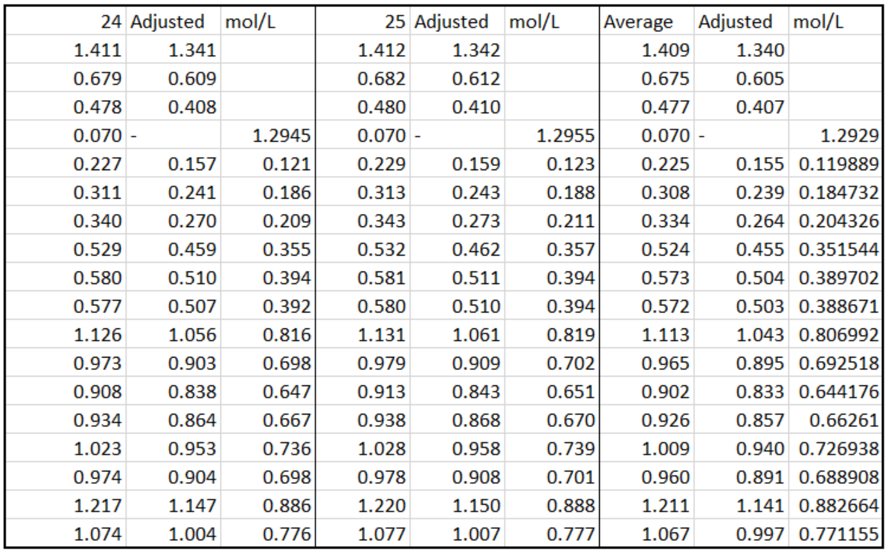
Experiment – 1/20/16

Calculated

Table I-9: Ethanolysis at 45°C Using Calculated Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	1.409	1.340		1.408	1.339		1.408	1.339		1.408	1.338	
Std 2	0.669	0.600		0.671	0.602		0.673	0.604		0.675	0.605	
Std 3	0.475	0.406		0.475	0.406		0.475	0.406		0.476	0.406	
Std 4	0.069	-	1.2921	0.069	-	1.2916	0.069	-	1.2921	0.070	-	1.2914
1	0.221	0.152	0.118	0.222	0.153	0.118	0.223	0.154	0.119	0.225	0.155	0.120
2	0.304	0.235	0.182	0.307	0.238	0.184	0.307	0.238	0.184	0.308	0.238	0.184
3	0.322	0.253	0.196	0.330	0.261	0.202	0.330	0.261	0.202	0.337	0.267	0.207
4	0.516	0.447	0.346	0.520	0.451	0.349	0.522	0.453	0.351	0.525	0.455	0.352
5	0.561	0.492	0.381	0.570	0.501	0.388	0.572	0.503	0.389	0.576	0.506	0.392
7	0.564	0.495	0.383	0.568	0.499	0.386	0.570	0.501	0.388	0.573	0.503	0.389
10	1.087	1.018	0.788	1.105	1.036	0.802	1.109	1.040	0.805	1.119	1.049	0.812
12	0.952	0.883	0.683	0.956	0.887	0.687	0.962	0.893	0.691	0.967	0.897	0.695
15	0.894	0.825	0.638	0.896	0.827	0.640	0.900	0.831	0.643	0.903	0.833	0.645
20	0.913	0.844	0.653	0.919	0.850	0.658	0.925	0.856	0.662	0.928	0.858	0.664
25	0.988	0.919	0.711	0.995	0.926	0.717	1.013	0.944	0.731	1.009	0.939	0.727
30	0.940	0.871	0.674	0.947	0.878	0.680	0.957	0.888	0.687	0.965	0.895	0.693
35	1.192	1.123	0.869	1.203	1.134	0.878	1.218	1.149	0.889	1.214	1.144	0.886
40	1.054	0.985	0.762	1.060	0.991	0.767	1.063	0.994	0.769	1.071	1.001	0.775



24	Adjusted	mol/L	25	Adjusted	mol/L	Average	Adjusted	mol/L
1.411	1.341		1.412	1.342		1.409	1.340	
0.679	0.609		0.682	0.612		0.675	0.605	
0.478	0.408		0.480	0.410		0.477	0.407	
0.070	-	1.2945	0.070	-	1.2955	0.070	-	1.2929
0.227	0.157	0.121	0.229	0.159	0.123	0.225	0.155	0.119889
0.311	0.241	0.186	0.313	0.243	0.188	0.308	0.239	0.184732
0.340	0.270	0.209	0.343	0.273	0.211	0.334	0.264	0.204326
0.529	0.459	0.355	0.532	0.462	0.357	0.524	0.455	0.351544
0.580	0.510	0.394	0.581	0.511	0.394	0.573	0.504	0.389702
0.577	0.507	0.392	0.580	0.510	0.394	0.572	0.503	0.388671
1.126	1.056	0.816	1.131	1.061	0.819	1.113	1.043	0.806992
0.973	0.903	0.698	0.979	0.909	0.702	0.965	0.895	0.692518
0.908	0.838	0.647	0.913	0.843	0.651	0.902	0.833	0.644176
0.934	0.864	0.667	0.938	0.868	0.670	0.926	0.857	0.66261
1.023	0.953	0.736	1.028	0.958	0.739	1.009	0.940	0.726938
0.974	0.904	0.698	0.978	0.908	0.701	0.960	0.891	0.688908
1.217	1.147	0.886	1.220	1.150	0.888	1.211	1.141	0.882664
1.074	1.004	0.776	1.077	1.007	0.777	1.067	0.997	0.771155

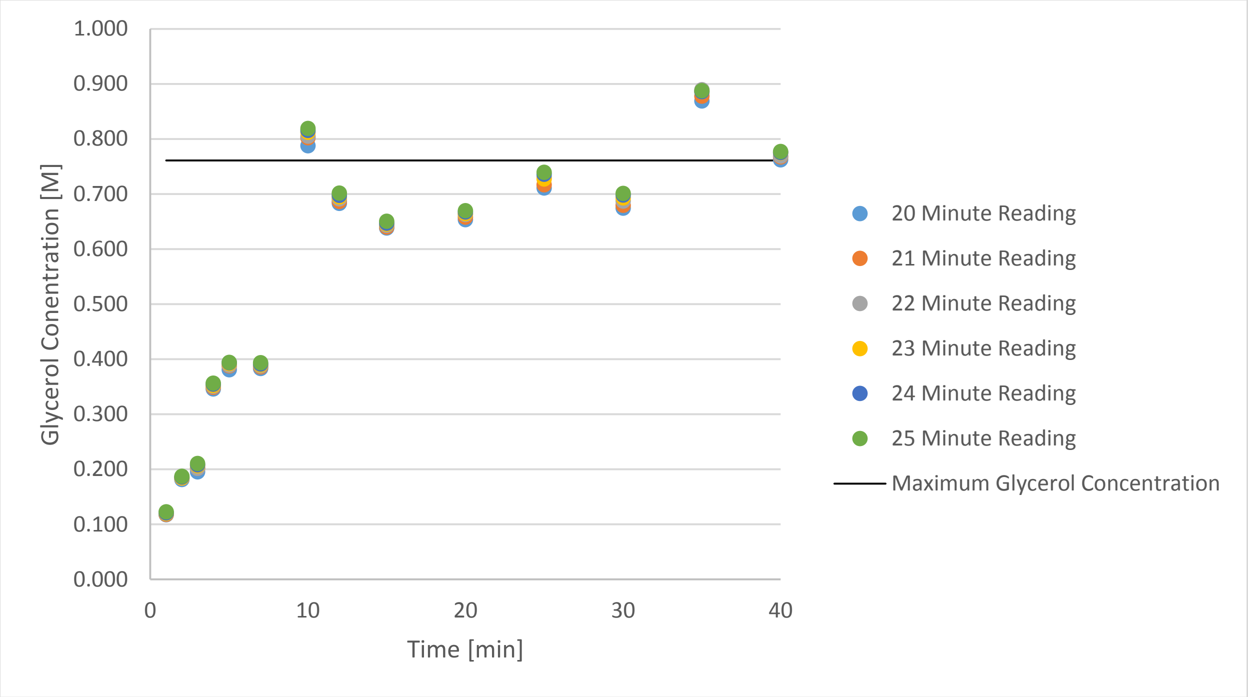


Figure I-20 - Ethanolysis at 45°C Using Calculated Calibration Curves

Ideal

Table I-10: Ethanolysis at 45°C Using Ideal Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	1.409	1.340		1.408	1.339		1.408	1.339	
Std 2	0.669	0.600		0.671	0.602		0.673	0.604	
Std 3	0.475	0.406		0.475	0.406		0.475	0.406	
Std 4	0.069	-	1.200	0.069	-	1.2000	0.069	-	1.2000
1	0.221	0.152	0.127	0.222	0.153	0.128	0.223	0.154	0.128
2	0.304	0.235	0.196	0.307	0.238	0.198	0.307	0.238	0.198
3	0.322	0.253	0.211	0.330	0.261	0.218	0.330	0.261	0.218
4	0.516	0.447	0.373	0.520	0.451	0.376	0.522	0.453	0.378
5	0.561	0.492	0.410	0.570	0.501	0.418	0.572	0.503	0.419
7	0.564	0.495	0.413	0.568	0.499	0.416	0.570	0.501	0.418
10	1.087	1.018	0.848	1.105	1.036	0.863	1.109	1.040	0.867
12	0.952	0.883	0.736	0.956	0.887	0.739	0.962	0.893	0.744
15	0.894	0.825	0.688	0.896	0.827	0.689	0.900	0.831	0.693
20	0.913	0.844	0.703	0.919	0.850	0.708	0.925	0.856	0.713
25	0.988	0.919	0.766	0.995	0.926	0.772	1.013	0.944	0.787
30	0.940	0.871	0.726	0.947	0.878	0.732	0.957	0.888	0.740
35	1.192	1.123	0.936	1.203	1.134	0.945	1.218	1.149	0.958
40	1.054	0.985	0.821	1.060	0.991	0.826	1.063	0.994	0.828

Time	23	Adjusted	mol/L	24	Adjusted	mol/L	25	Adjusted	mol/L
Std 1	1.408	1.338		1.411	1.341		1.412	1.342	
Std 2	0.675	0.605		0.679	0.609		0.682	0.612	
Std 3	0.476	0.406		0.478	0.408		0.480	0.410	
Std 4	0.070	-	1.2000	0.070	-	1.2000	0.070	-	1.2000
1	0.225	0.155	0.129	0.227	0.157	0.131	0.229	0.159	0.133
2	0.308	0.238	0.198	0.311	0.241	0.201	0.313	0.243	0.203
3	0.337	0.267	0.223	0.340	0.270	0.225	0.343	0.273	0.228
4	0.525	0.455	0.379	0.529	0.459	0.383	0.532	0.462	0.385
5	0.576	0.506	0.422	0.580	0.510	0.425	0.581	0.511	0.426
7	0.573	0.503	0.419	0.577	0.507	0.423	0.580	0.510	0.425
10	1.119	1.049	0.874	1.126	1.056	0.880	1.131	1.061	0.884
12	0.967	0.897	0.748	0.973	0.903	0.753	0.979	0.909	0.758
15	0.903	0.833	0.694	0.908	0.838	0.698	0.913	0.843	0.703
20	0.928	0.858	0.715	0.934	0.864	0.720	0.938	0.868	0.723
25	1.009	0.939	0.783	1.023	0.953	0.794	1.028	0.958	0.798
30	0.965	0.895	0.746	0.974	0.904	0.753	0.978	0.908	0.757
35	1.214	1.144	0.953	1.217	1.147	0.956	1.220	1.150	0.958
40	1.071	1.001	0.834	1.074	1.004	0.837	1.077	1.007	0.839

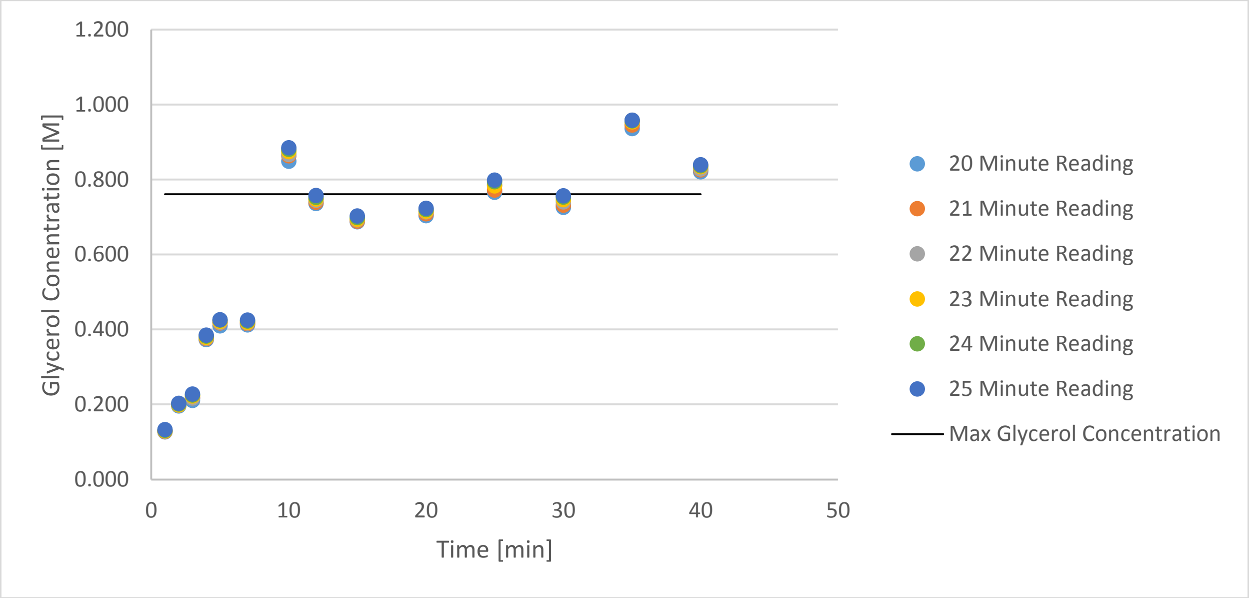


Figure I-21 – Ethanolysis at 45°C using Ideal Calibration Curve

Calibration Curves

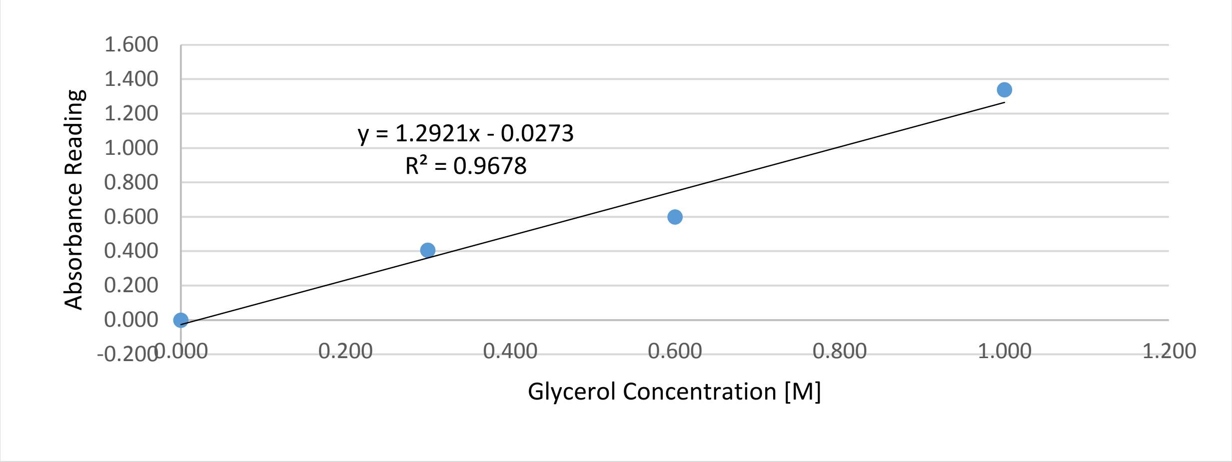


Figure I-22 - Calculated Calibration Curve from 20 Minute Reading

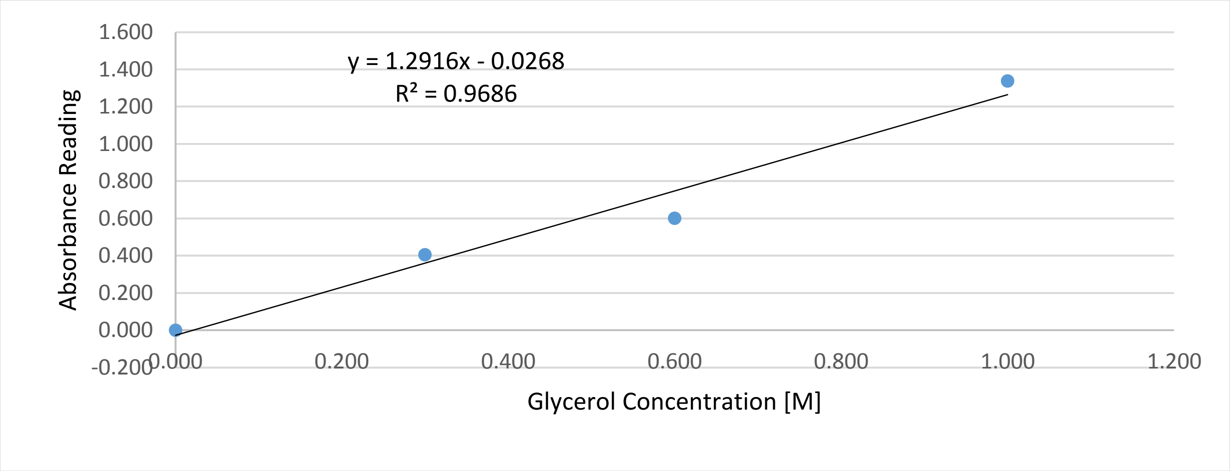


Figure I-23 - Calculated Calibration Curve from 21 Minute Reading

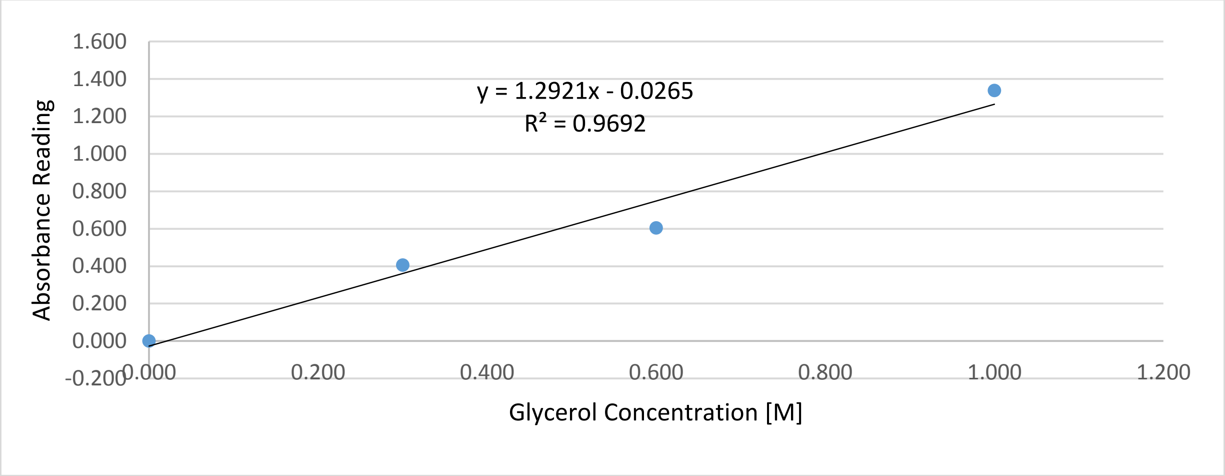


Figure I-24 - Calculated Calibration Curve from 22 Minute Reading

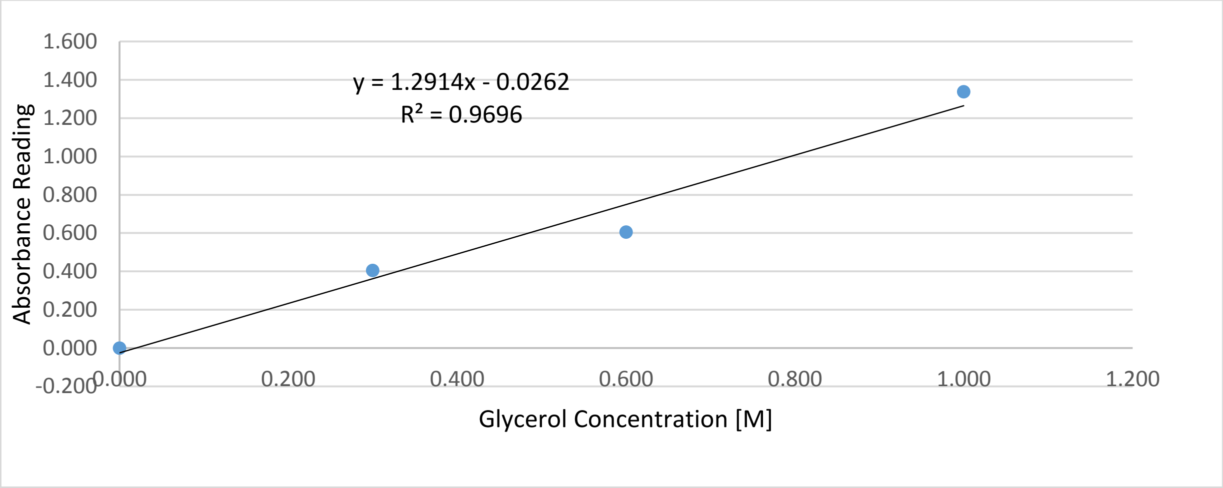


Figure I-25 - Calculated Calibration Curve from 23 Minute Reading

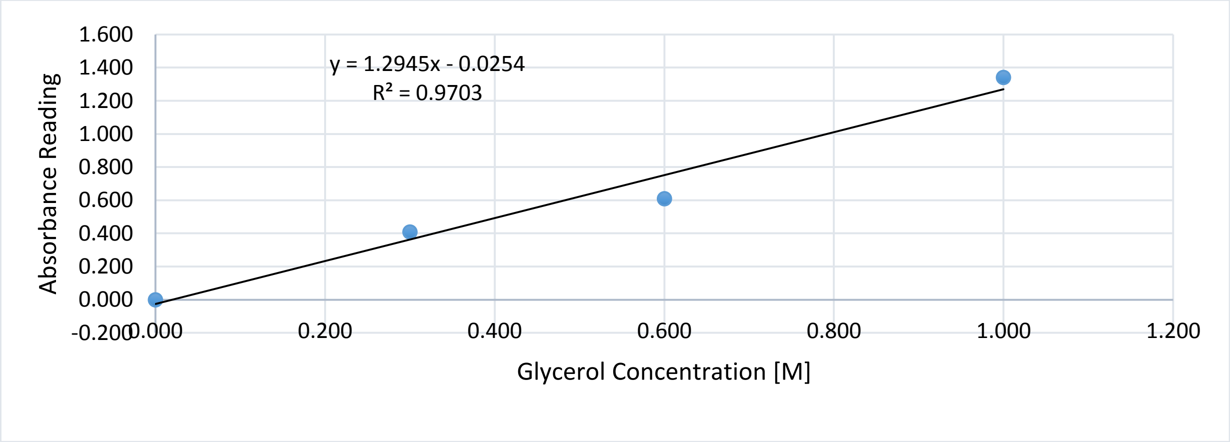


Figure I-26 - Calculated Calibration Curve from 24 Minute Reading

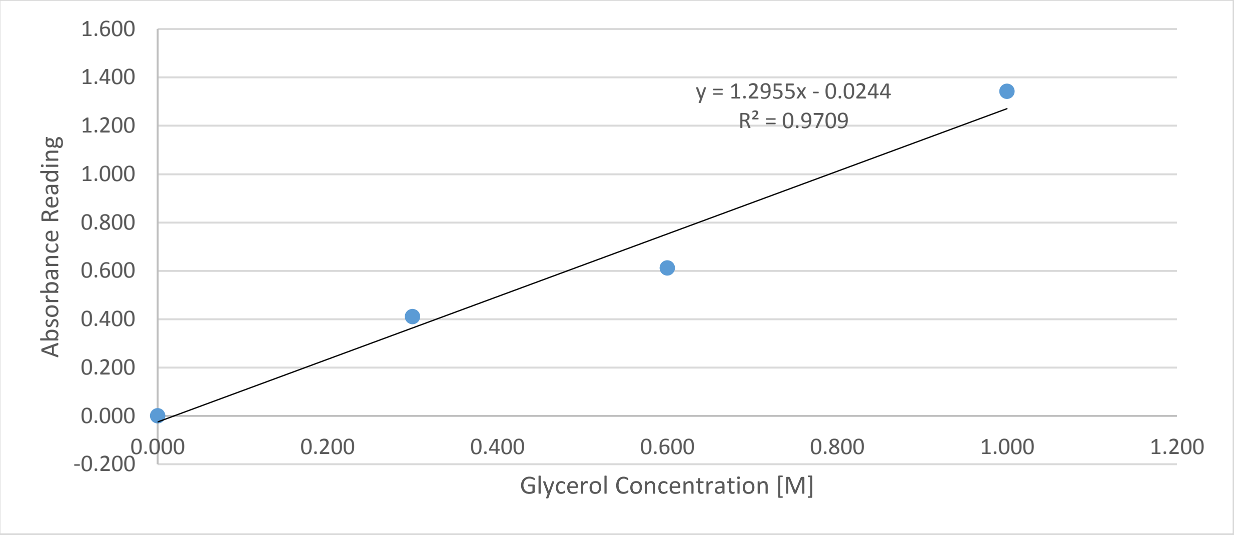


Figure I-27 - Calculated Calibration Curve from 25 Minute Reading

Experiment – 1/27/16

Calculated

Table I-11: Ethanolysis at 25°C Using Calculated Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	1.387	1.323		1.425	1.361		1.430	1.365		1.441	1.376	
Std 2	1.026	0.962		1.018	0.954		1.020	0.955		1.022	0.957	
Std 3	0.614	0.550		0.615	0.551		0.616	0.551		0.619	0.554	
Std 4	0.064	-	1.3125	0.064	-	1.3468	0.065	-	1.3508	0.065	-	1.3609
1	0.141	0.077	0.059	0.140	0.076	0.056	0.143	0.078	0.058	0.145	0.080	0.059
2	0.223	0.159	0.121	0.224	0.160	0.119	0.223	0.158	0.117	0.222	0.157	0.115
3	0.350	0.286	0.218	0.325	0.261	0.194	0.332	0.267	0.198	0.330	0.265	0.195
4	0.284	0.220	0.168	0.286	0.222	0.165	0.289	0.224	0.166	0.293	0.228	0.168
5	0.246	0.182	0.139	0.247	0.183	0.136	0.250	0.185	0.137	0.255	0.190	0.140
7	0.324	0.260	0.198	0.333	0.269	0.200	0.339	0.274	0.203	0.347	0.282	0.207
10	0.468	0.404	0.308	0.468	0.404	0.300	0.473	0.408	0.302	0.473	0.408	0.300
12	0.471	0.407	0.310	0.480	0.416	0.309	0.488	0.423	0.313	0.486	0.421	0.309
15	0.596	0.532	0.405	0.622	0.558	0.414	0.638	0.573	0.424	0.646	0.581	0.427
20	0.555	0.491	0.374	0.573	0.509	0.378	0.589	0.524	0.388	0.592	0.527	0.387
25	0.606	0.542	0.413	0.626	0.562	0.417	0.638	0.573	0.424	0.643	0.578	0.425
30	0.664	0.600	0.457	0.670	0.606	0.450	0.697	0.632	0.468	0.705	0.640	0.470
35	0.742	0.678	0.517	0.756	0.692	0.514	0.786	0.721	0.534	0.809	0.744	0.547
40	0.796	0.732	0.558	0.798	0.734	0.545	0.802	0.737	0.546	0.805	0.740	0.544

Time	24	Adjusted	mol/L	25	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	1.441	1.376		1.443	1.378		1.428	1.363	
Std 2	1.024	0.959		1.026	0.961		1.023	0.958	
Std 3	0.621	0.556		0.623	0.558		0.618	0.553	
Std 4	0.065	-	1.3607	0.065	-	1.3624	0.065	-	1.3490
1	0.143	0.078	0.057	0.144	0.079	0.058	0.143	0.078	0.058
2	0.223	0.158	0.116	0.224	0.159	0.117	0.223	0.159	0.117
3	0.336	0.271	0.199	0.345	0.280	0.206	0.336	0.272	0.201
4	0.295	0.230	0.169	0.296	0.231	0.170	0.291	0.226	0.167
5	0.257	0.192	0.141	0.257	0.192	0.141	0.252	0.187	0.139
7	0.349	0.284	0.209	0.350	0.285	0.209	0.340	0.276	0.204
10	0.475	0.410	0.301	0.479	0.414	0.304	0.473	0.408	0.302
12	0.490	0.425	0.312	0.492	0.427	0.313	0.485	0.420	0.311
15	0.650	0.585	0.430	0.655	0.590	0.433	0.635	0.570	0.422
20	0.596	0.531	0.390	0.599	0.534	0.392	0.584	0.519	0.385
25	0.645	0.580	0.426	0.646	0.581	0.426	0.634	0.569	0.422
30	0.710	0.645	0.474	0.714	0.649	0.476	0.693	0.629	0.466
35	0.807	0.742	0.545	0.809	0.744	0.546	0.785	0.720	0.534
40	0.807	0.742	0.545	0.811	0.746	0.548	0.803	0.739	0.547

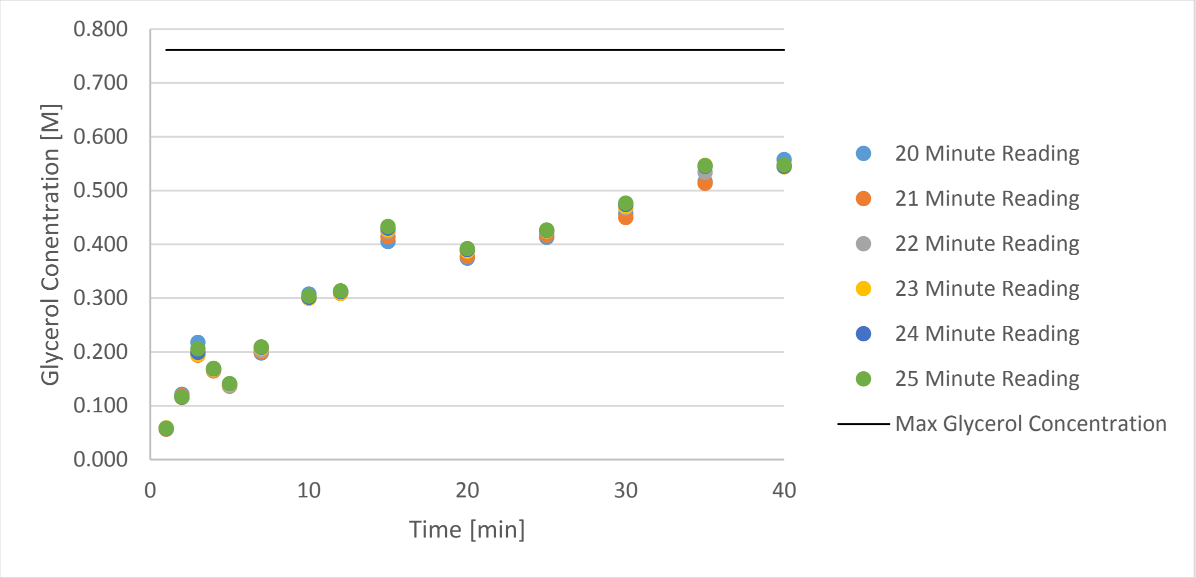
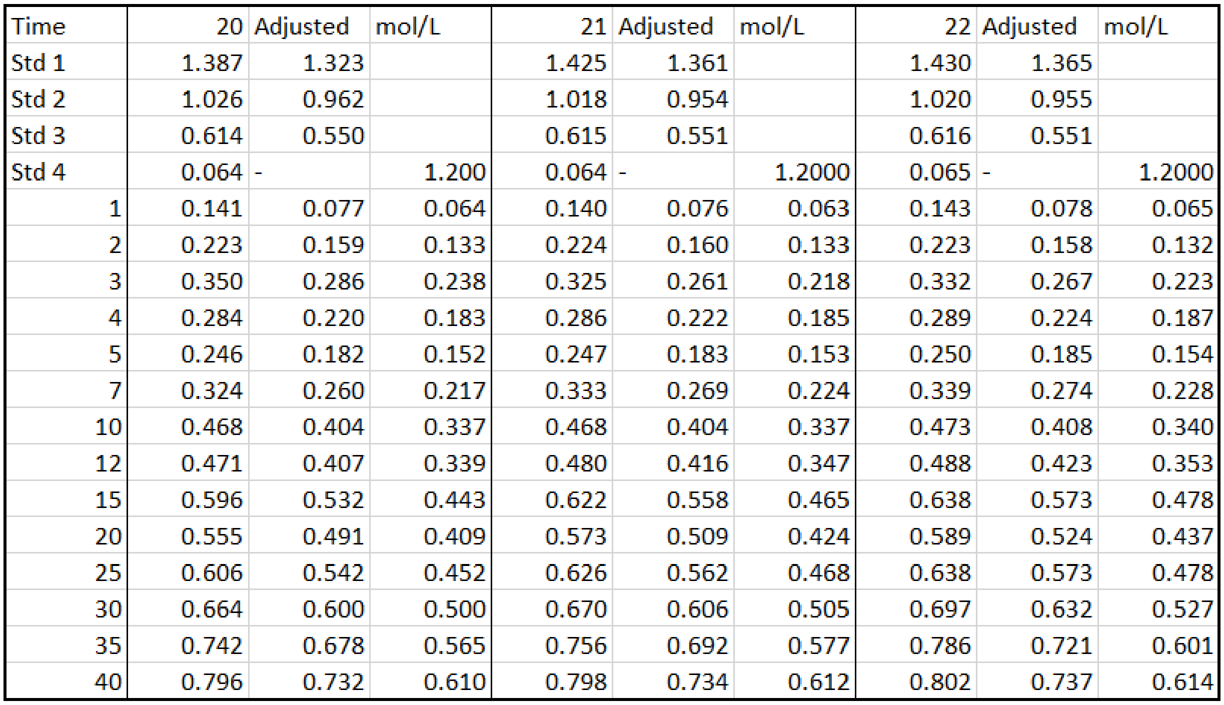


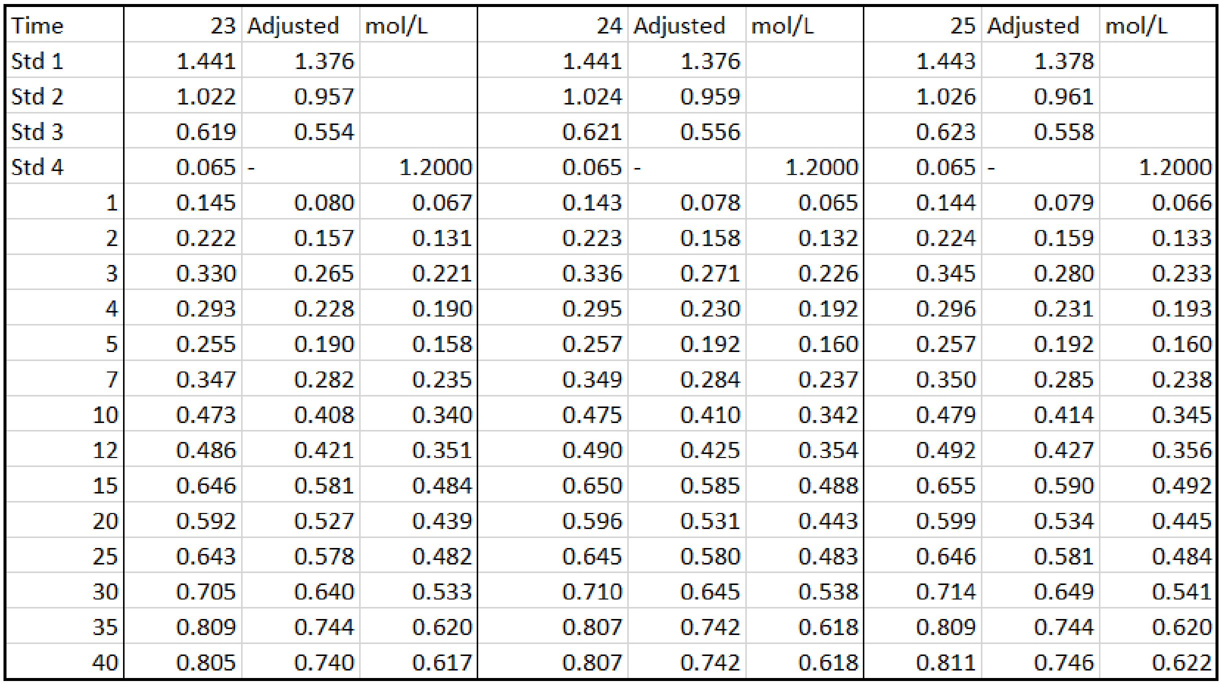
Figure I-28 - Ethanolysis at 25°C Using Calculated Calibration Curves

Ideal

Table I-12: Ethanolysis at 25°C Using Ideal Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	1.387	1.323		1.425	1.361		1.430	1.365	
Std 2	1.026	0.962		1.018	0.954		1.020	0.955	
Std 3	0.614	0.550		0.615	0.551		0.616	0.551	
Std 4	0.064	-	1.200	0.064	-	1.2000	0.065	-	1.2000
1	0.141	0.077	0.064	0.140	0.076	0.063	0.143	0.078	0.065
2	0.223	0.159	0.133	0.224	0.160	0.133	0.223	0.158	0.132
3	0.350	0.286	0.238	0.325	0.261	0.218	0.332	0.267	0.223
4	0.284	0.220	0.183	0.286	0.222	0.185	0.289	0.224	0.187
5	0.246	0.182	0.152	0.247	0.183	0.153	0.250	0.185	0.154
7	0.324	0.260	0.217	0.333	0.269	0.224	0.339	0.274	0.228
10	0.468	0.404	0.337	0.468	0.404	0.337	0.473	0.408	0.340
12	0.471	0.407	0.339	0.480	0.416	0.347	0.488	0.423	0.353
15	0.596	0.532	0.443	0.622	0.558	0.465	0.638	0.573	0.478
20	0.555	0.491	0.409	0.573	0.509	0.424	0.589	0.524	0.437
25	0.606	0.542	0.452	0.626	0.562	0.468	0.638	0.573	0.478
30	0.664	0.600	0.500	0.670	0.606	0.505	0.697	0.632	0.527
35	0.742	0.678	0.565	0.756	0.692	0.577	0.786	0.721	0.601
40	0.796	0.732	0.610	0.798	0.734	0.612	0.802	0.737	0.614



Time	23	Adjusted	mol/L	24	Adjusted	mol/L	25	Adjusted	mol/L
Std 1	1.441	1.376		1.441	1.376		1.443	1.378	
Std 2	1.022	0.957		1.024	0.959		1.026	0.961	
Std 3	0.619	0.554		0.621	0.556		0.623	0.558	
Std 4	0.065	-	1.2000	0.065	-	1.2000	0.065	-	1.2000
1	0.145	0.080	0.067	0.143	0.078	0.065	0.144	0.079	0.066
2	0.222	0.157	0.131	0.223	0.158	0.132	0.224	0.159	0.133
3	0.330	0.265	0.221	0.336	0.271	0.226	0.345	0.280	0.233
4	0.293	0.228	0.190	0.295	0.230	0.192	0.296	0.231	0.193
5	0.255	0.190	0.158	0.257	0.192	0.160	0.257	0.192	0.160
7	0.347	0.282	0.235	0.349	0.284	0.237	0.350	0.285	0.238
10	0.473	0.408	0.340	0.475	0.410	0.342	0.479	0.414	0.345
12	0.486	0.421	0.351	0.490	0.425	0.354	0.492	0.427	0.356
15	0.646	0.581	0.484	0.650	0.585	0.488	0.655	0.590	0.492
20	0.592	0.527	0.439	0.596	0.531	0.443	0.599	0.534	0.445
25	0.643	0.578	0.482	0.645	0.580	0.483	0.646	0.581	0.484
30	0.705	0.640	0.533	0.710	0.645	0.538	0.714	0.649	0.541
35	0.809	0.744	0.620	0.807	0.742	0.618	0.809	0.744	0.620
40	0.805	0.740	0.617	0.807	0.742	0.618	0.811	0.746	0.622

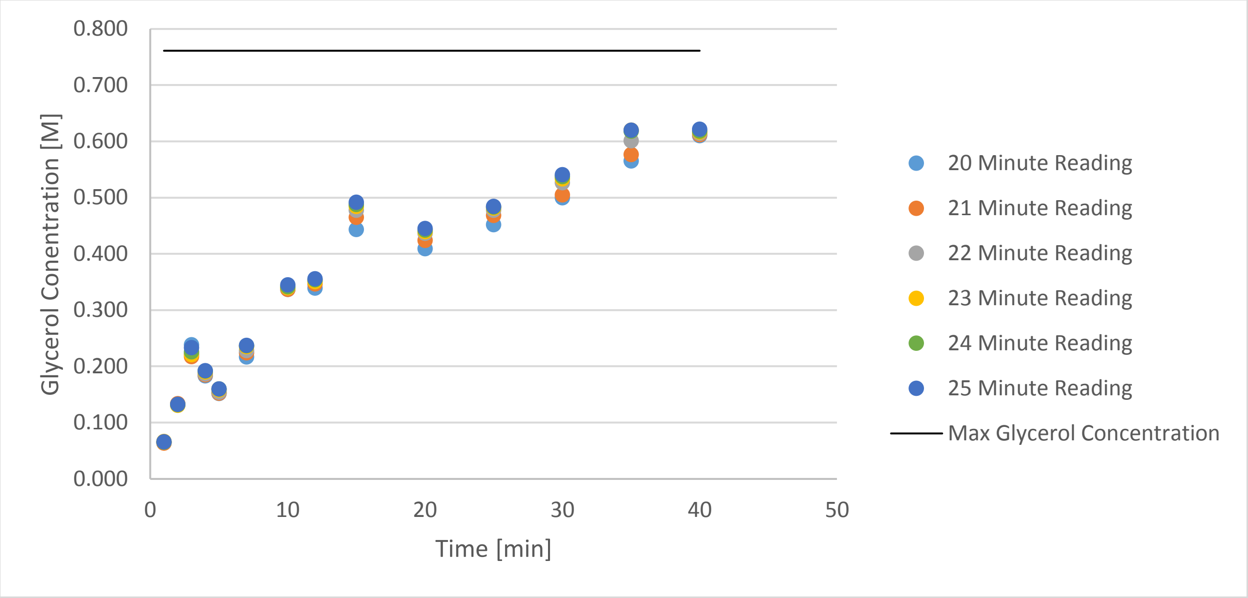


Figure I-29 - Ethanolysis at 25°C Using Ideal Calibration Curves

Calibration Curves

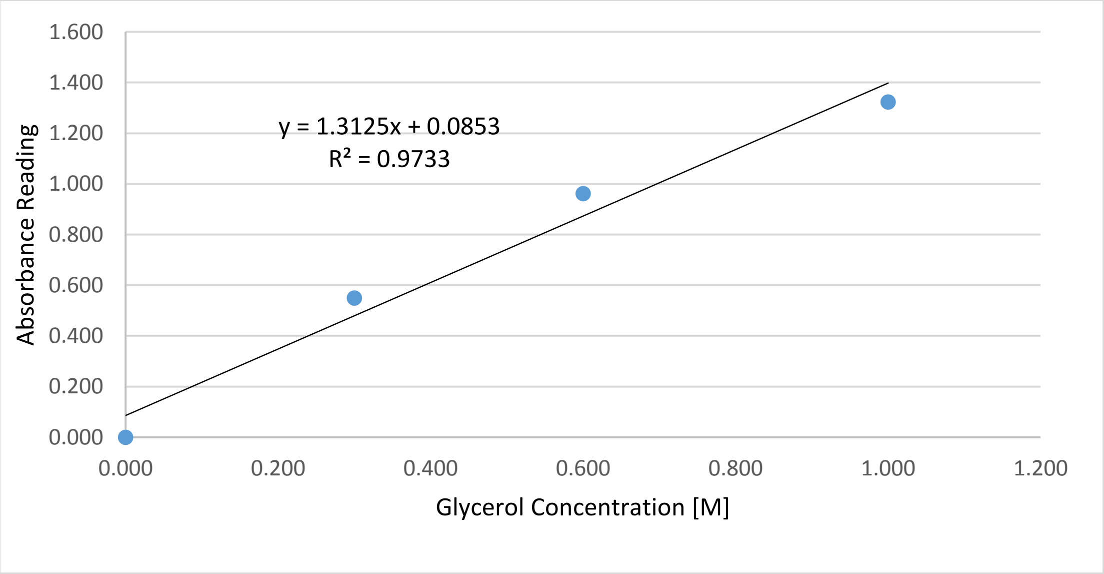


Figure I-30 - Calibration Curve at 20 Minute Reading

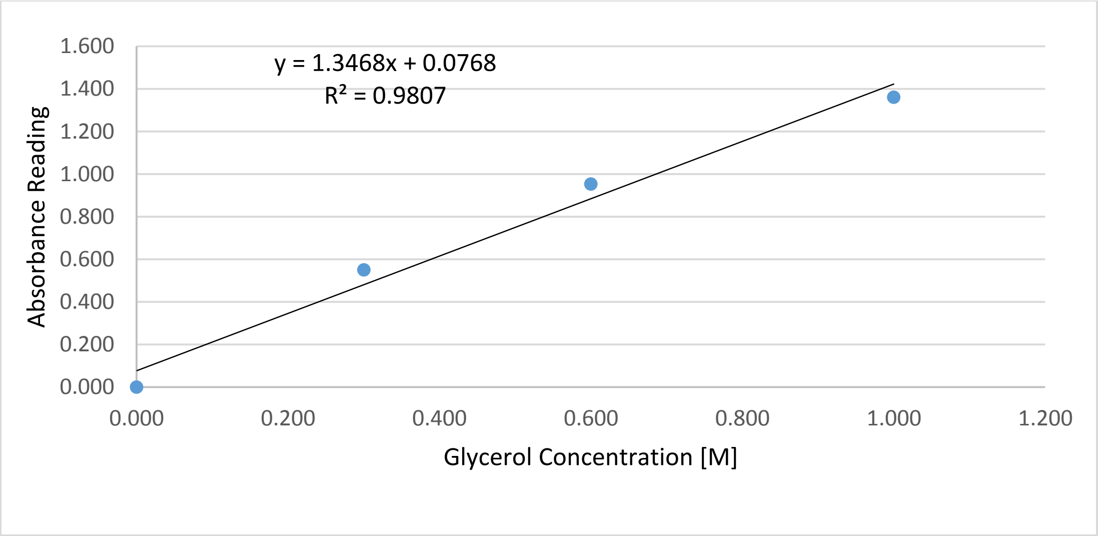


Figure I-31 - Calibration Curve at 21 Minute Reading

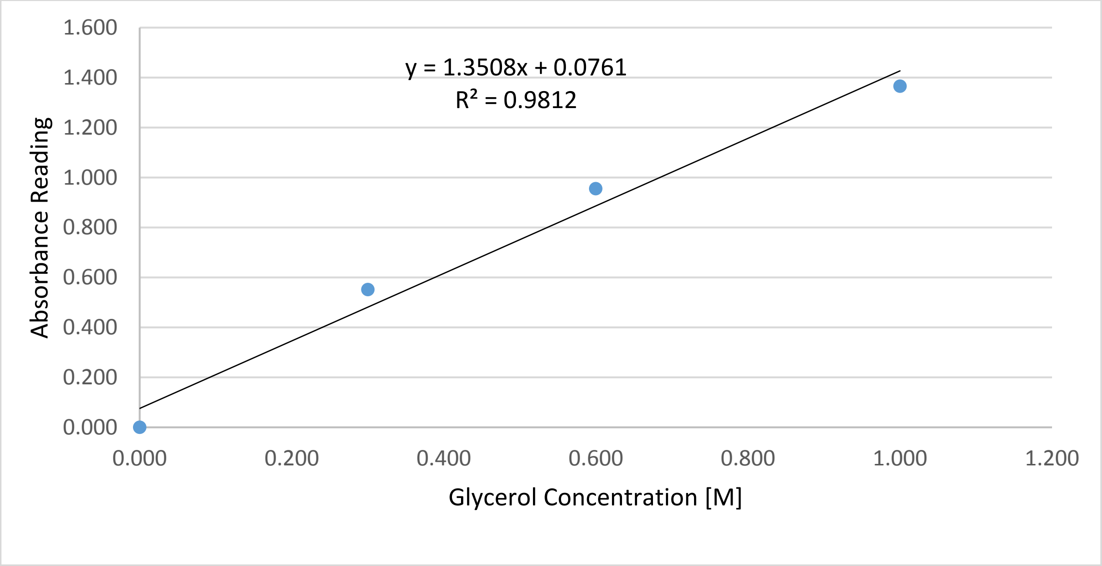


Figure I-32 - Calibration Curve at 22 Minute Reading

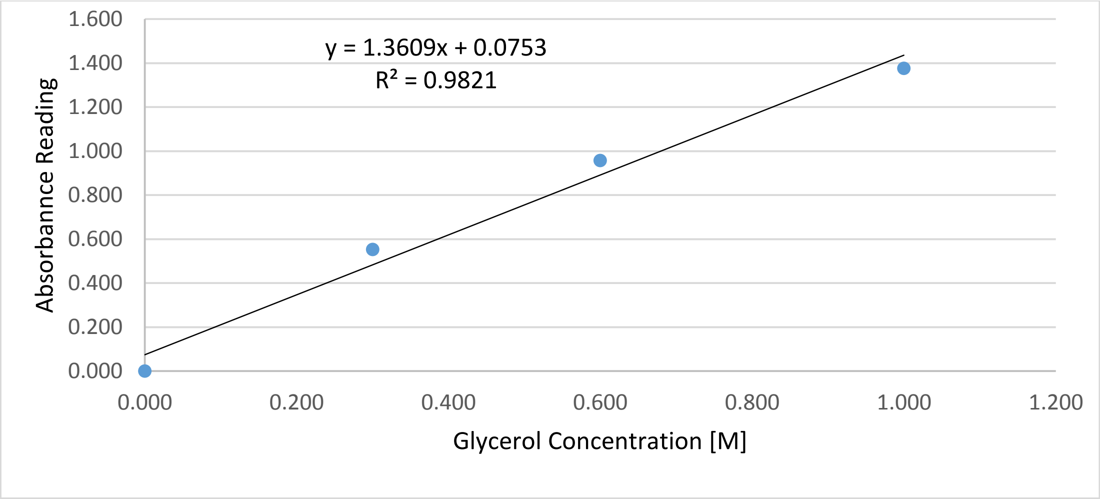


Figure I-33 - Calibration Curve at 23 Minute Reading

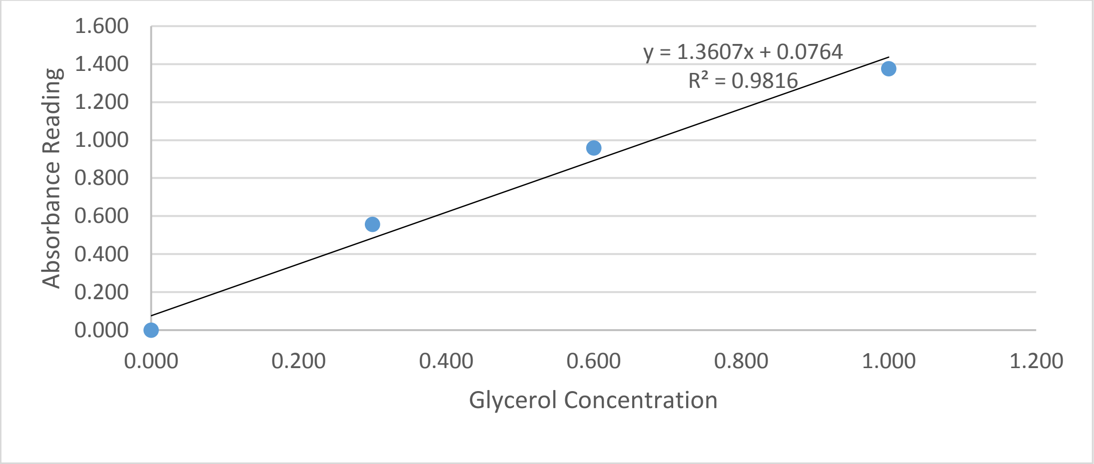


Figure I-34 - Calibration Curve at 24 Minute Reading

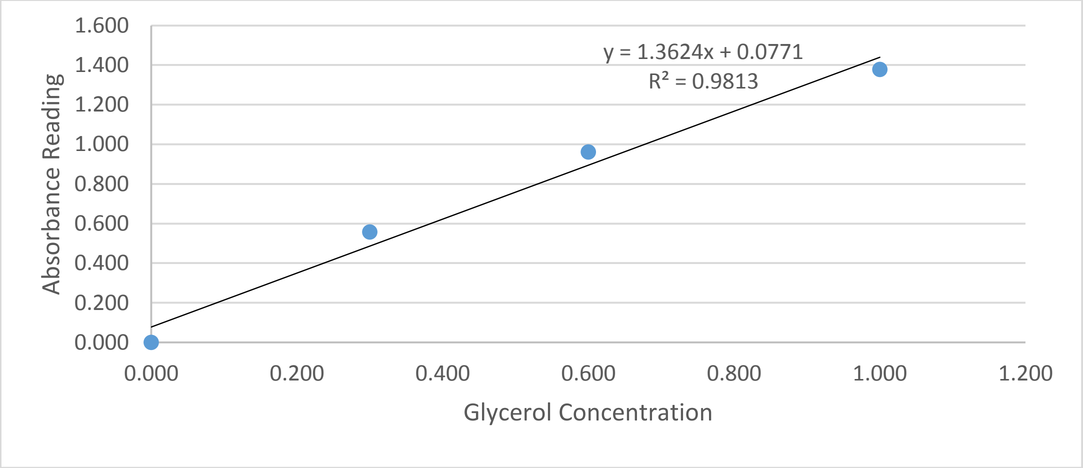
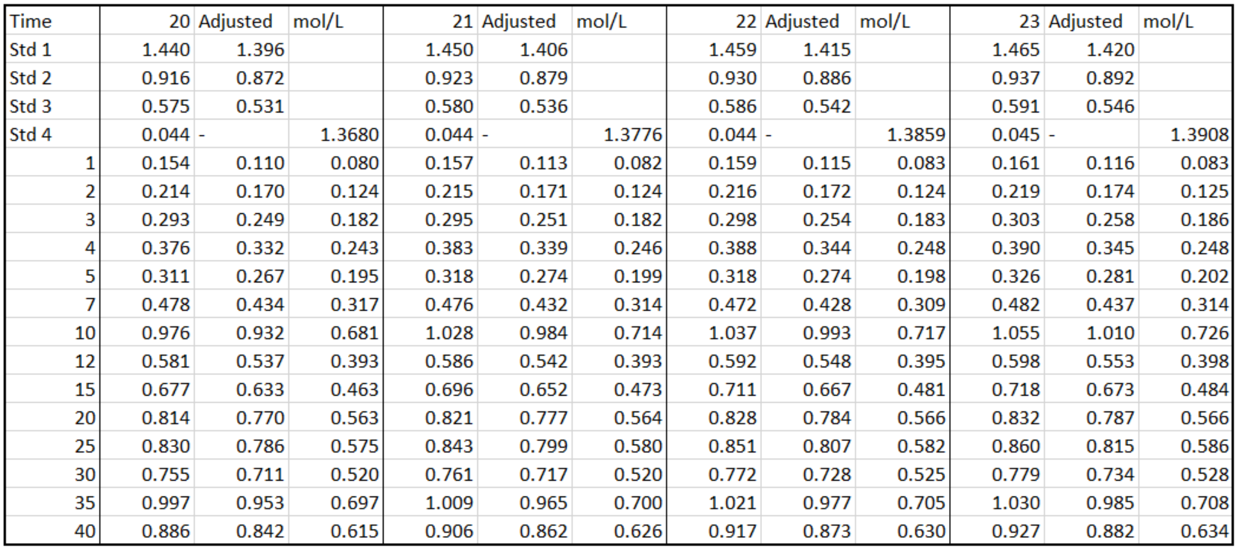


Figure I-35 - Calibration Curve at 25 Minute Reading

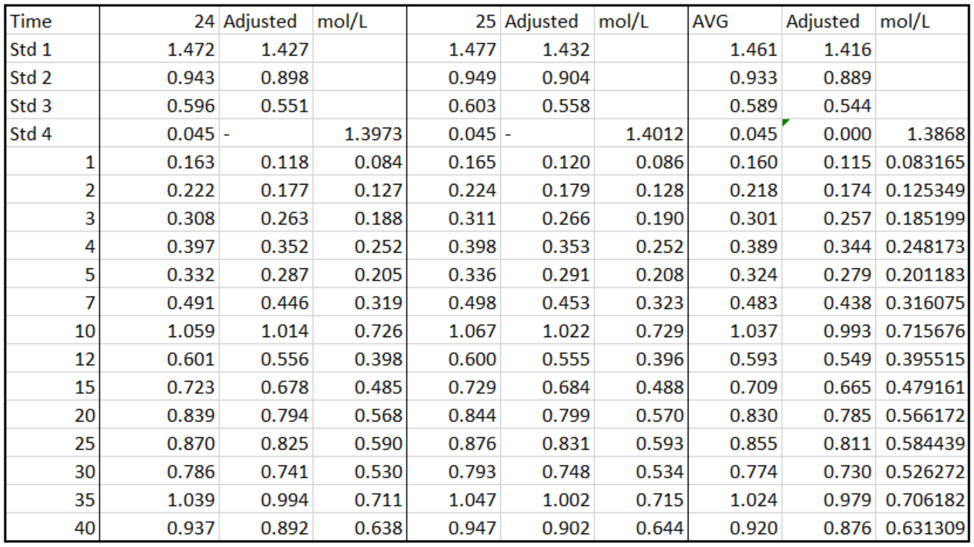
Experiment – 2/1/16

Calculated

Table I-13: Ethanolysis at 35°C Using Calculated Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	1.440	1.396		1.450	1.406		1.459	1.415		1.465	1.420	
Std 2	0.916	0.872		0.923	0.879		0.930	0.886		0.937	0.892	
Std 3	0.575	0.531		0.580	0.536		0.586	0.542		0.591	0.546	
Std 4	0.044	-	1.3680	0.044	-	1.3776	0.044	-	1.3859	0.045	-	1.3908
1	0.154	0.110	0.080	0.157	0.113	0.082	0.159	0.115	0.083	0.161	0.116	0.083
2	0.214	0.170	0.124	0.215	0.171	0.124	0.216	0.172	0.124	0.219	0.174	0.125
3	0.293	0.249	0.182	0.295	0.251	0.182	0.298	0.254	0.183	0.303	0.258	0.186
4	0.376	0.332	0.243	0.383	0.339	0.246	0.388	0.344	0.248	0.390	0.345	0.248
5	0.311	0.267	0.195	0.318	0.274	0.199	0.318	0.274	0.198	0.326	0.281	0.202
7	0.478	0.434	0.317	0.476	0.432	0.314	0.472	0.428	0.309	0.482	0.437	0.314
10	0.976	0.932	0.681	1.028	0.984	0.714	1.037	0.993	0.717	1.055	1.010	0.726
12	0.581	0.537	0.393	0.586	0.542	0.393	0.592	0.548	0.395	0.598	0.553	0.398
15	0.677	0.633	0.463	0.696	0.652	0.473	0.711	0.667	0.481	0.718	0.673	0.484
20	0.814	0.770	0.563	0.821	0.777	0.564	0.828	0.784	0.566	0.832	0.787	0.566
25	0.830	0.786	0.575	0.843	0.799	0.580	0.851	0.807	0.582	0.860	0.815	0.586
30	0.755	0.711	0.520	0.761	0.717	0.520	0.772	0.728	0.525	0.779	0.734	0.528
35	0.997	0.953	0.697	1.009	0.965	0.700	1.021	0.977	0.705	1.030	0.985	0.708
40	0.886	0.842	0.615	0.906	0.862	0.626	0.917	0.873	0.630	0.927	0.882	0.634



Time	24	Adjusted	mol/L	25	Adjusted	mol/L	AVG	Adjusted	mol/L
Std 1	1.472	1.427		1.477	1.432		1.461	1.416	
Std 2	0.943	0.898		0.949	0.904		0.933	0.889	
Std 3	0.596	0.551		0.603	0.558		0.589	0.544	
Std 4	0.045	-	1.3973	0.045	-	1.4012	0.045	0.000	1.3868
1	0.163	0.118	0.084	0.165	0.120	0.086	0.160	0.115	0.083165
2	0.222	0.177	0.127	0.224	0.179	0.128	0.218	0.174	0.125349
3	0.308	0.263	0.188	0.311	0.266	0.190	0.301	0.257	0.185199
4	0.397	0.352	0.252	0.398	0.353	0.252	0.389	0.344	0.248173
5	0.332	0.287	0.205	0.336	0.291	0.208	0.324	0.279	0.201183
7	0.491	0.446	0.319	0.498	0.453	0.323	0.483	0.438	0.316075
10	1.059	1.014	0.726	1.067	1.022	0.729	1.037	0.993	0.715676
12	0.601	0.556	0.398	0.600	0.555	0.396	0.593	0.549	0.395515
15	0.723	0.678	0.485	0.729	0.684	0.488	0.709	0.665	0.479161
20	0.839	0.794	0.568	0.844	0.799	0.570	0.830	0.785	0.566172
25	0.870	0.825	0.590	0.876	0.831	0.593	0.855	0.811	0.584439
30	0.786	0.741	0.530	0.793	0.748	0.534	0.774	0.730	0.526272
35	1.039	0.994	0.711	1.047	1.002	0.715	1.024	0.979	0.706182
40	0.937	0.892	0.638	0.947	0.902	0.644	0.920	0.876	0.631309

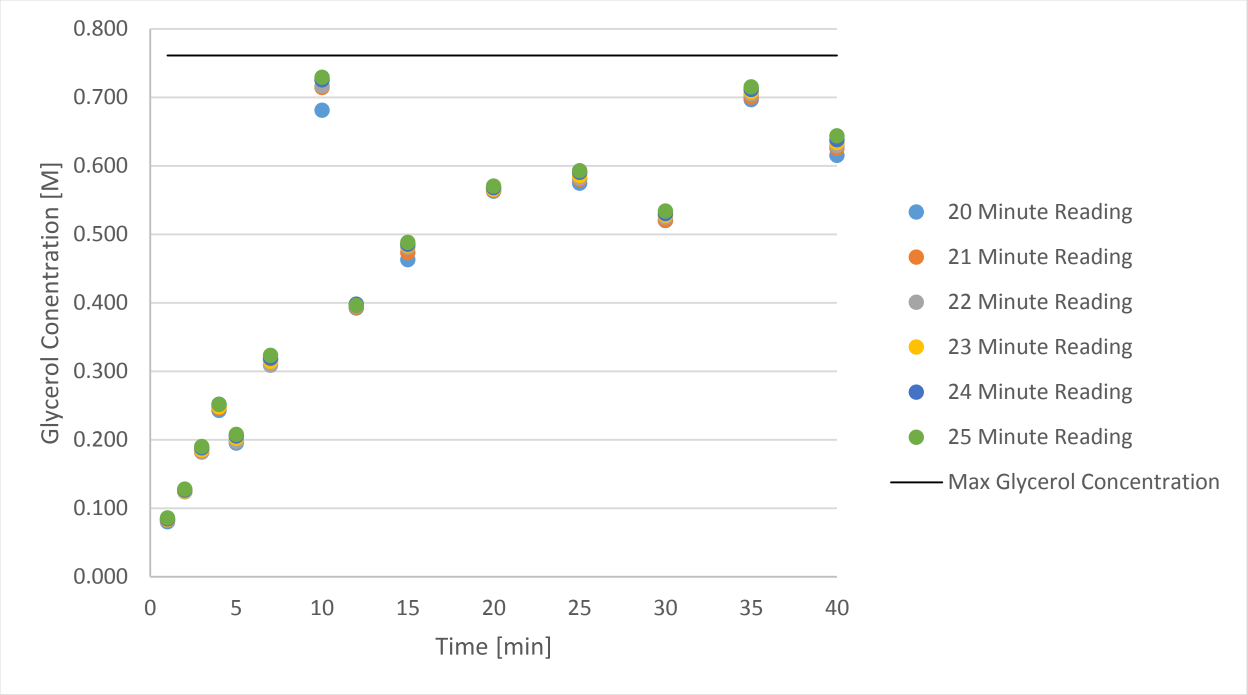


Figure I-36 - Ethanolysis at 35°C Using Calculated Calibration Curves

Ideal

Table I-14: Ethanolysis at 35°C Using Ideal Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	2.701	2.492		2.704	2.494		2.704	2.492	
Std 2	2.707	2.498		2.710	2.500		2.711	2.499	
Std 3	2.606	2.397		2.604	2.394		2.603	2.391	
Std 4	0.209	-	1.200	0.210	-	1.2000	0.212	-	1.2000
1	0.335	0.126	0.105	0.337	0.127	0.106	0.340	0.128	0.107
2	0.512	0.303	0.253	0.512	0.302	0.252	0.515	0.303	0.253
3	0.824	0.615	0.513	0.752	0.542	0.452	0.773	0.561	0.468
4	0.555	0.346	0.288	0.558	0.348	0.290	0.560	0.348	0.290
5	0.577	0.368	0.307	0.580	0.370	0.308	0.583	0.371	0.309
7	0.757	0.548	0.457	0.758	0.548	0.457	0.763	0.551	0.459
10	0.980	0.771	0.643	1.003	0.793	0.661	1.040	0.828	0.690
12	1.372	1.163	0.969	1.373	1.163	0.969	1.376	1.164	0.970
15	1.563	1.354	1.128	1.568	1.358	1.132	1.572	1.360	1.133
20	1.151	0.942	0.785	1.147	0.937	0.781	1.163	0.951	0.793
25	1.198	0.989	0.824	1.198	0.988	0.823	1.205	0.993	0.828
30	1.258	1.049	0.874	1.262	1.052	0.877	1.267	1.055	0.879
35	1.501	1.292	1.077	1.509	1.299	1.083	1.514	1.302	1.085
40	1.332	1.123	0.936	1.339	1.129	0.941	1.344	1.132	0.943

Time	23	Adjusted	mol/L	24	Adjusted	mol/L	25	Adjusted	mol/L
Std 1	2.705	2.492		2.701	2.492		2.704	2.494	
Std 2	2.708	2.495		2.707	2.498		2.710	2.500	
Std 3	2.604	2.391		2.606	2.397		2.604	2.394	
Std 4	0.213	-	1.2000	0.209	-	1.2000	0.210	-	1.2000
1	0.341	0.128	0.107	0.335	0.126	0.105	0.337	0.127	0.106
2	0.516	0.303	0.253	0.512	0.303	0.253	0.512	0.302	0.252
3	0.793	0.580	0.483	0.824	0.615	0.513	0.752	0.542	0.452
4	0.564	0.351	0.293	0.555	0.346	0.288	0.558	0.348	0.290
5	0.586	0.373	0.311	0.577	0.368	0.307	0.580	0.370	0.308
7	0.767	0.554	0.462	0.757	0.548	0.457	0.758	0.548	0.457
10	1.020	0.807	0.673	0.980	0.771	0.643	1.003	0.793	0.661
12	1.381	1.168	0.973	1.372	1.163	0.969	1.373	1.163	0.969
15	1.576	1.363	1.136	1.563	1.354	1.128	1.568	1.358	1.132
20	1.178	0.965	0.804	1.151	0.942	0.785	1.147	0.937	0.781
25	1.219	1.006	0.838	1.198	0.989	0.824	1.198	0.988	0.823
30	1.273	1.060	0.883	1.258	1.049	0.874	1.262	1.052	0.877
35	1.520	1.307	1.089	1.501	1.292	1.077	1.509	1.299	1.083
40	1.351	1.138	0.948	1.332	1.123	0.936	1.339	1.129	0.941

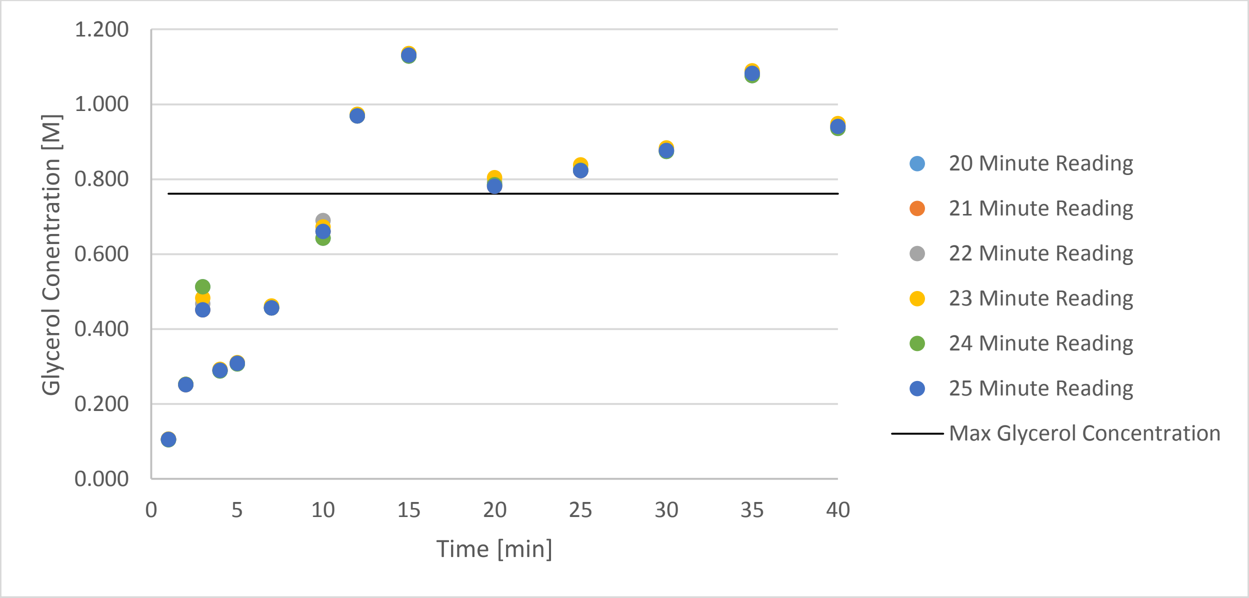


Figure I-37 - Ethanolysis at 35°C Using Ideal Calibration Curves

Calibration Curves

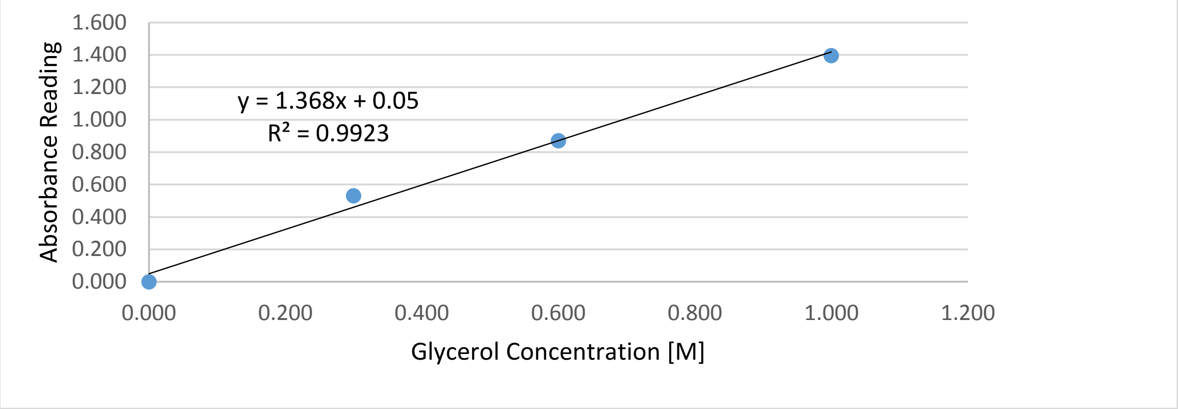


Figure I-38: Calculated Calibration Curve from 20 Minute Reading

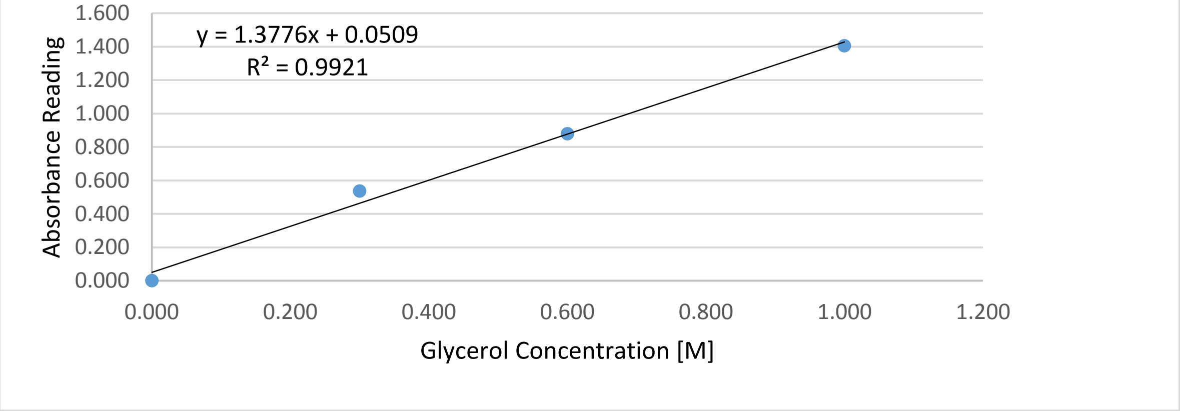


Figure I-39: Calculated Calibration Curve from 21 Minute Reading

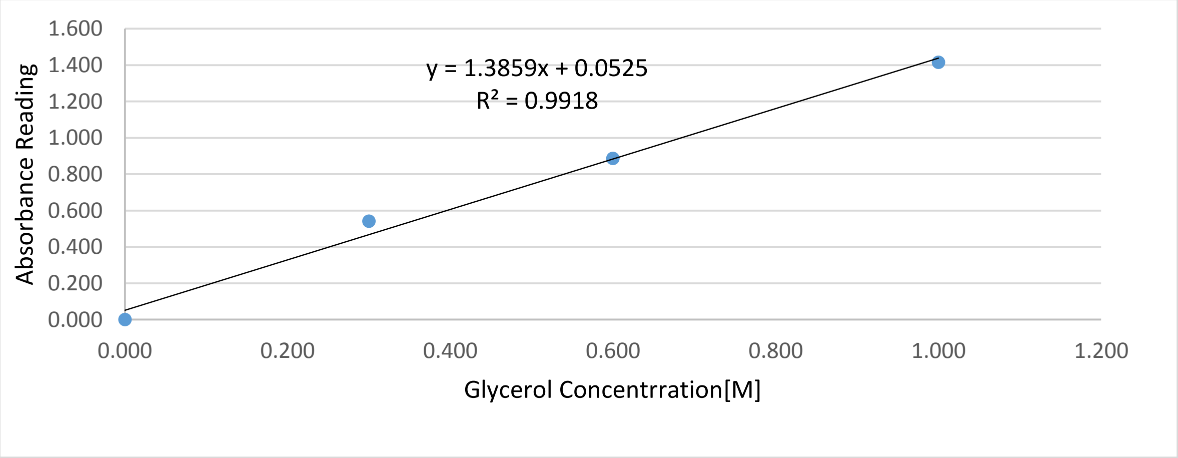


Figure I-40: Calculated Calibration Curve from 22 Minute Reading

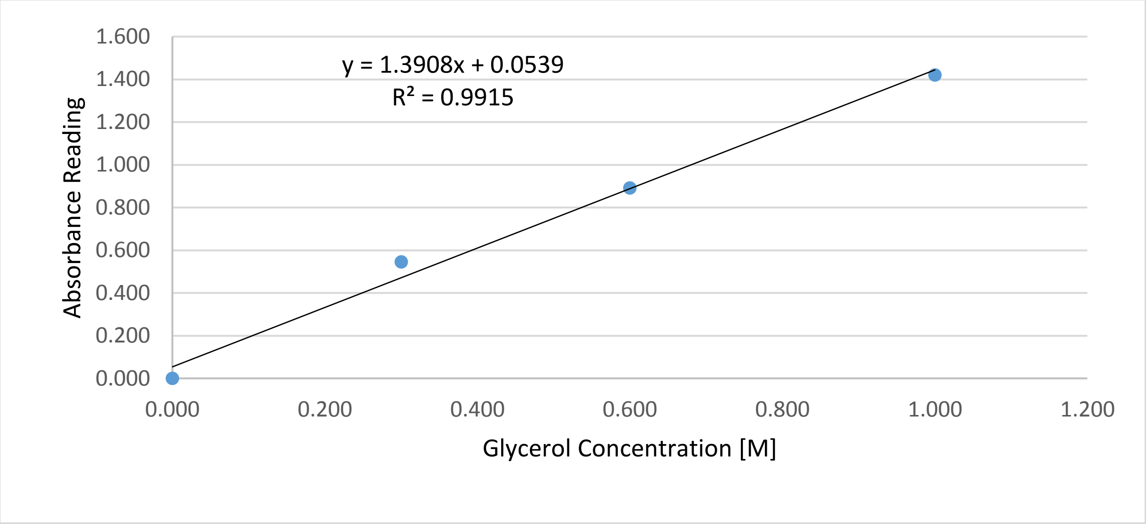


Figure I-41: Calculated Calibration Curve from 23 Minute Reading

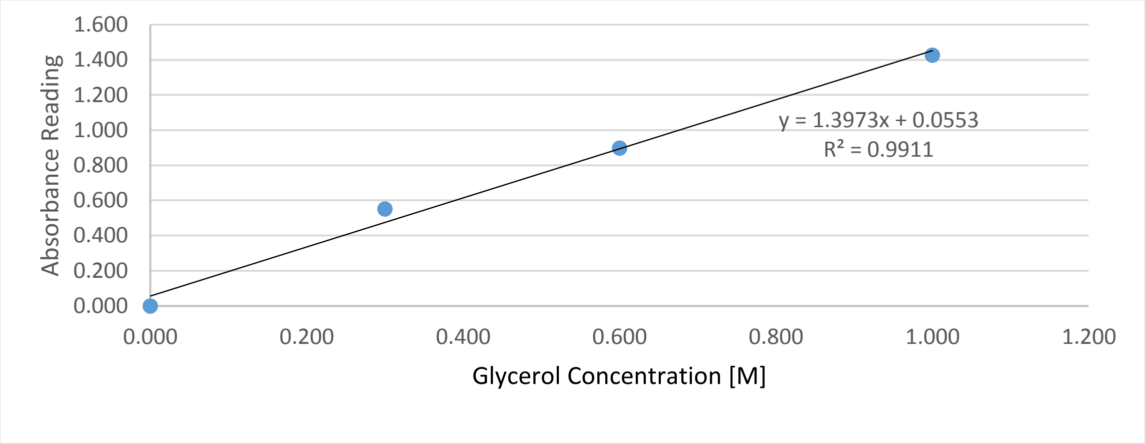


Figure I-42: Calculated Calibration Curve from 24 Minute Reading

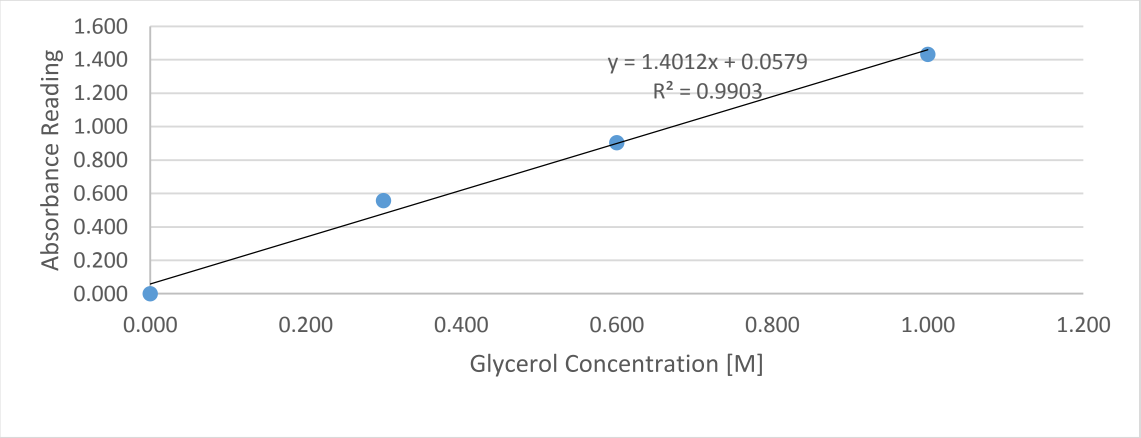
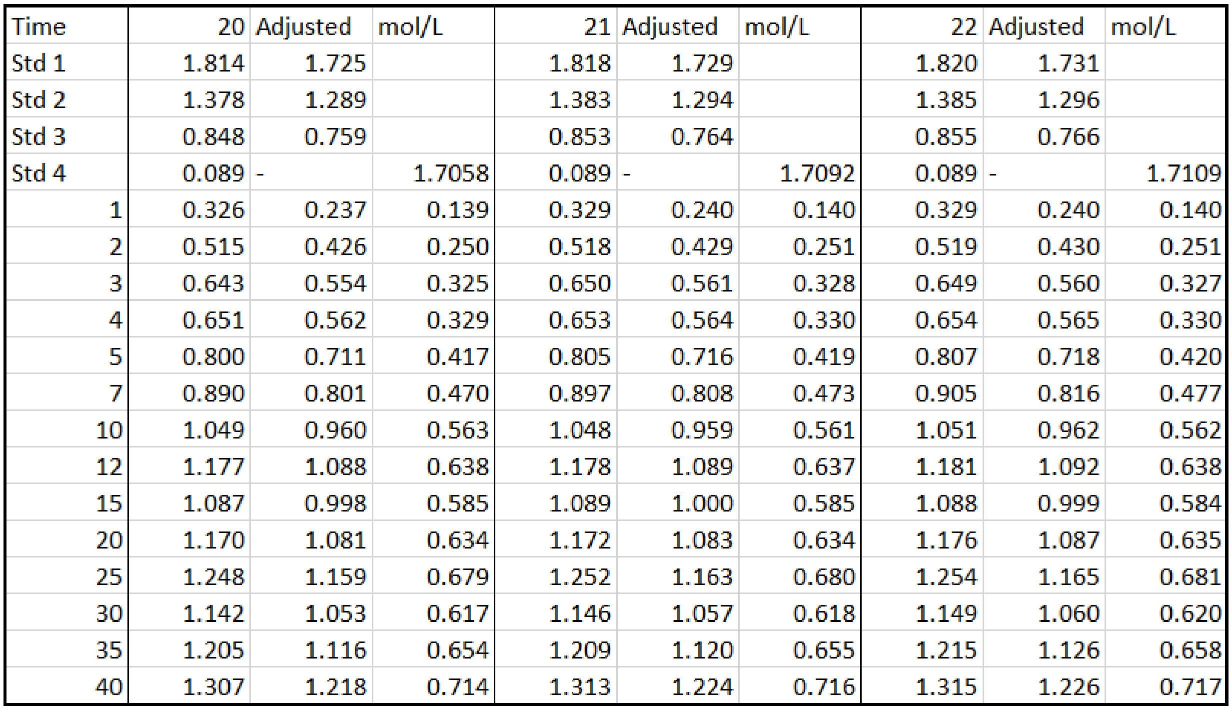


Figure I-43: Calculated Calibration Curve from 25 Minute Reading

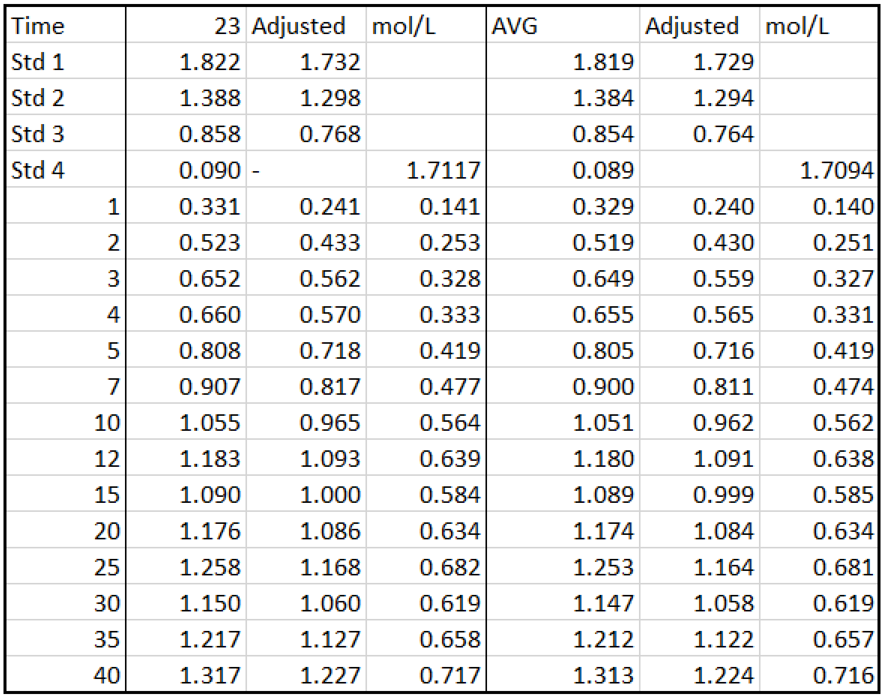
Experiment – 2/8/16

Calculated

Table I-15: Ethanolysis at 45°C Using Calculated Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	1.814	1.725		1.818	1.729		1.820	1.731	
Std 2	1.378	1.289		1.383	1.294		1.385	1.296	
Std 3	0.848	0.759		0.853	0.764		0.855	0.766	
Std 4	0.089	-	1.7058	0.089	-	1.7092	0.089	-	1.7109
1	0.326	0.237	0.139	0.329	0.240	0.140	0.329	0.240	0.140
2	0.515	0.426	0.250	0.518	0.429	0.251	0.519	0.430	0.251
3	0.643	0.554	0.325	0.650	0.561	0.328	0.649	0.560	0.327
4	0.651	0.562	0.329	0.653	0.564	0.330	0.654	0.565	0.330
5	0.800	0.711	0.417	0.805	0.716	0.419	0.807	0.718	0.420
7	0.890	0.801	0.470	0.897	0.808	0.473	0.905	0.816	0.477
10	1.049	0.960	0.563	1.048	0.959	0.561	1.051	0.962	0.562
12	1.177	1.088	0.638	1.178	1.089	0.637	1.181	1.092	0.638
15	1.087	0.998	0.585	1.089	1.000	0.585	1.088	0.999	0.584
20	1.170	1.081	0.634	1.172	1.083	0.634	1.176	1.087	0.635
25	1.248	1.159	0.679	1.252	1.163	0.680	1.254	1.165	0.681
30	1.142	1.053	0.617	1.146	1.057	0.618	1.149	1.060	0.620
35	1.205	1.116	0.654	1.209	1.120	0.655	1.215	1.126	0.658
40	1.307	1.218	0.714	1.313	1.224	0.716	1.315	1.226	0.717



Time	23	Adjusted	mol/L	AVG	Adjusted	mol/L
Std 1	1.822	1.732		1.819	1.729	
Std 2	1.388	1.298		1.384	1.294	
Std 3	0.858	0.768		0.854	0.764	
Std 4	0.090	-	1.7117	0.089		1.7094
1	0.331	0.241	0.141	0.329	0.240	0.140
2	0.523	0.433	0.253	0.519	0.430	0.251
3	0.652	0.562	0.328	0.649	0.559	0.327
4	0.660	0.570	0.333	0.655	0.565	0.331
5	0.808	0.718	0.419	0.805	0.716	0.419
7	0.907	0.817	0.477	0.900	0.811	0.474
10	1.055	0.965	0.564	1.051	0.962	0.562
12	1.183	1.093	0.639	1.180	1.091	0.638
15	1.090	1.000	0.584	1.089	0.999	0.585
20	1.176	1.086	0.634	1.174	1.084	0.634
25	1.258	1.168	0.682	1.253	1.164	0.681
30	1.150	1.060	0.619	1.147	1.058	0.619
35	1.217	1.127	0.658	1.212	1.122	0.657
40	1.317	1.227	0.717	1.313	1.224	0.716

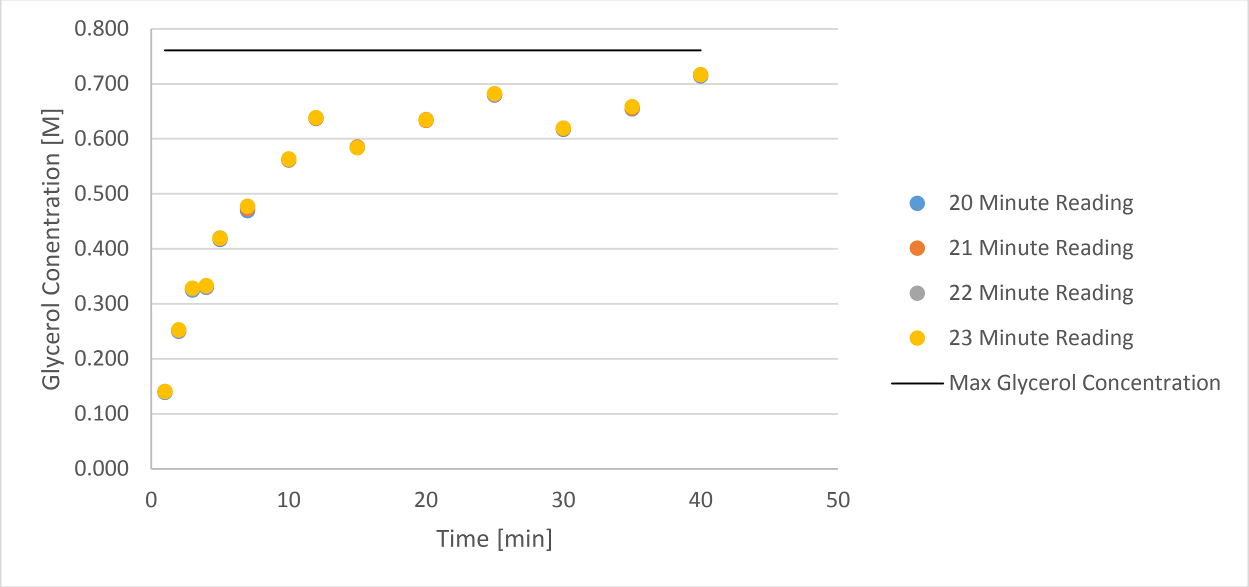


Figure I-44: Ethanolysis at 45°C Using Calculated Calibration Curves

Ideal

Table I-16: Ethanolysis at 45°C Using Ideal Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	1.814	1.725		1.818	1.729		1.820	1.731	
Std 2	1.378	1.289		1.383	1.294		1.385	1.296	
Std 3	0.848	0.759		0.853	0.764		0.855	0.766	
Std 4	0.089	-	1.200	0.089	-	1.2000	0.089	-	1.2000
1	0.326	0.237	0.198	0.329	0.240	0.200	0.329	0.240	0.200
2	0.515	0.426	0.355	0.518	0.429	0.358	0.519	0.430	0.358
3	0.643	0.554	0.462	0.650	0.561	0.468	0.649	0.560	0.467
4	0.651	0.562	0.468	0.653	0.564	0.470	0.654	0.565	0.471
5	0.800	0.711	0.593	0.805	0.716	0.597	0.807	0.718	0.598
7	0.890	0.801	0.668	0.897	0.808	0.673	0.905	0.816	0.680
10	1.049	0.960	0.800	1.048	0.959	0.799	1.051	0.962	0.802
12	1.177	1.088	0.907	1.178	1.089	0.908	1.181	1.092	0.910
15	1.087	0.998	0.832	1.089	1.000	0.833	1.088	0.999	0.833
20	1.170	1.081	0.901	1.172	1.083	0.903	1.176	1.087	0.906
25	1.248	1.159	0.966	1.252	1.163	0.969	1.254	1.165	0.971
30	1.142	1.053	0.878	1.146	1.057	0.881	1.149	1.060	0.883
35	1.205	1.116	0.930	1.209	1.120	0.933	1.215	1.126	0.938
40	1.307	1.218	1.015	1.313	1.224	1.020	1.315	1.226	1.022

Time	23	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	1.822	1.732		1.819	1.729	
Std 2	1.388	1.298		1.384	1.294	
Std 3	0.858	0.768		0.854	0.764	
Std 4	0.090	-	1.2000	0.089	0.000	1.2000
1	0.331	0.241	0.201	0.329	0.240	0.200
2	0.523	0.433	0.361	0.519	0.430	0.358
3	0.652	0.562	0.468	0.649	0.559	0.466
4	0.660	0.570	0.475	0.655	0.565	0.471
5	0.808	0.718	0.598	0.805	0.716	0.596
7	0.907	0.817	0.681	0.900	0.811	0.675
10	1.055	0.965	0.804	1.051	0.962	0.801
12	1.183	1.093	0.911	1.180	1.091	0.909
15	1.090	1.000	0.833	1.089	0.999	0.833
20	1.176	1.086	0.905	1.174	1.084	0.904
25	1.258	1.168	0.973	1.253	1.164	0.970
30	1.150	1.060	0.883	1.147	1.058	0.881
35	1.217	1.127	0.939	1.212	1.122	0.935
40	1.317	1.227	1.023	1.313	1.224	1.020

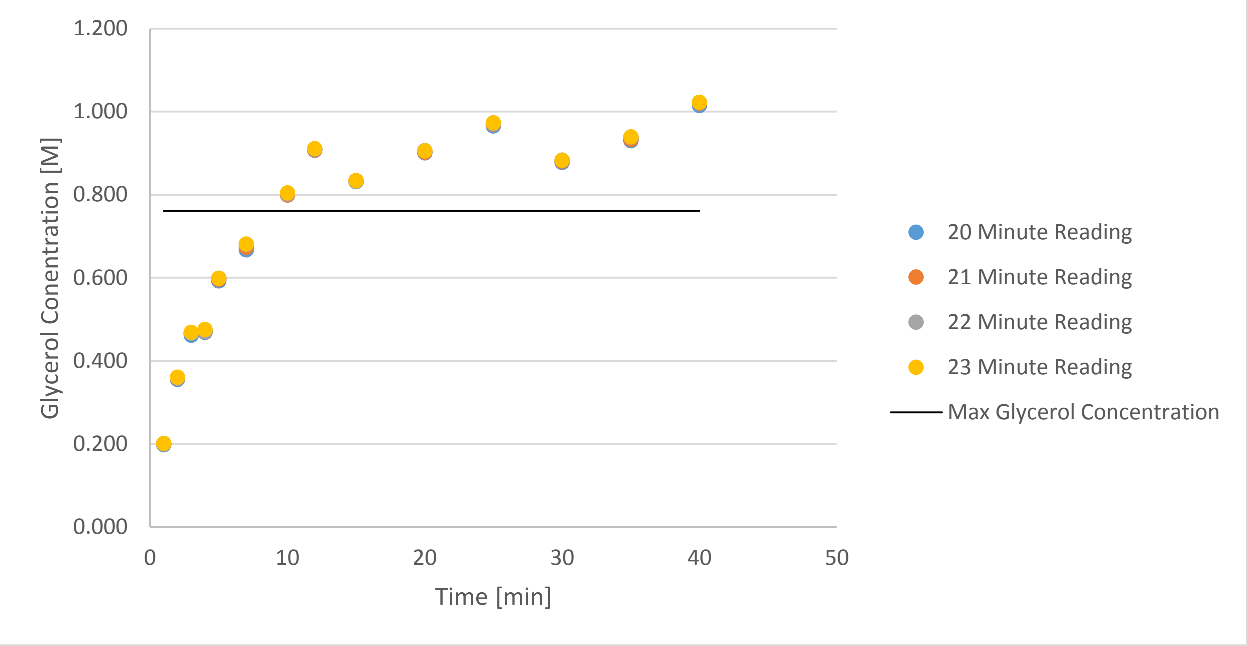


Figure I-45: Ethanolysis at 45°C Using Ideal Calibration Curves

Calibration Curves

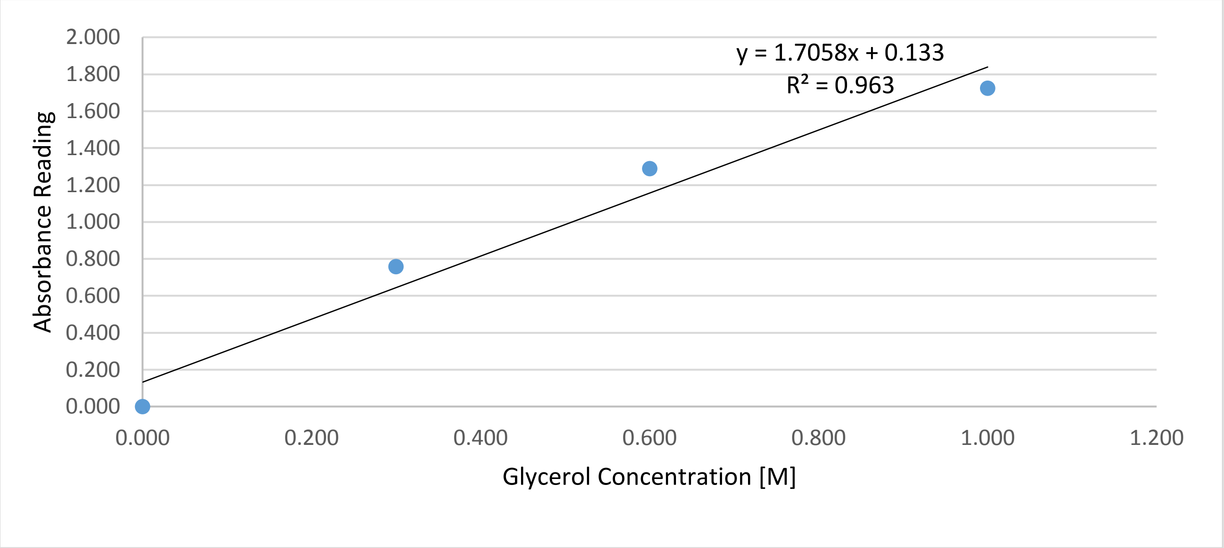


Figure I-46: Calculated Calibration Curve from 20 Minute Reading

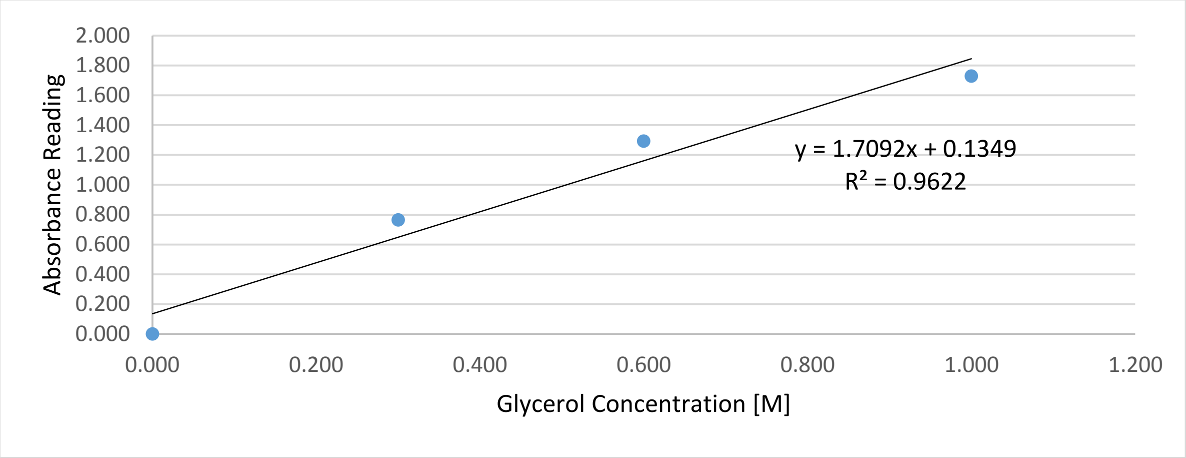


Figure I-47: Calculated Calibration Curve from 21 Minute Reading

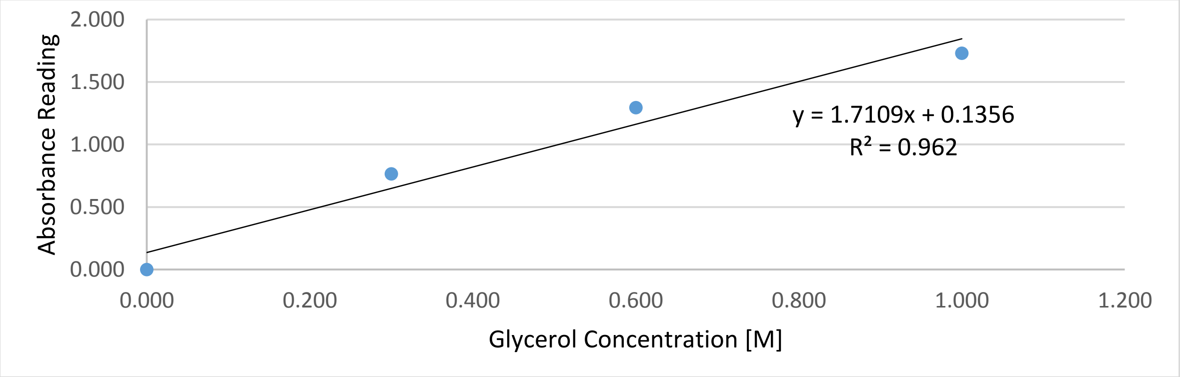


Figure I-48: Calculated Calibration Curve from 21 Minute Reading

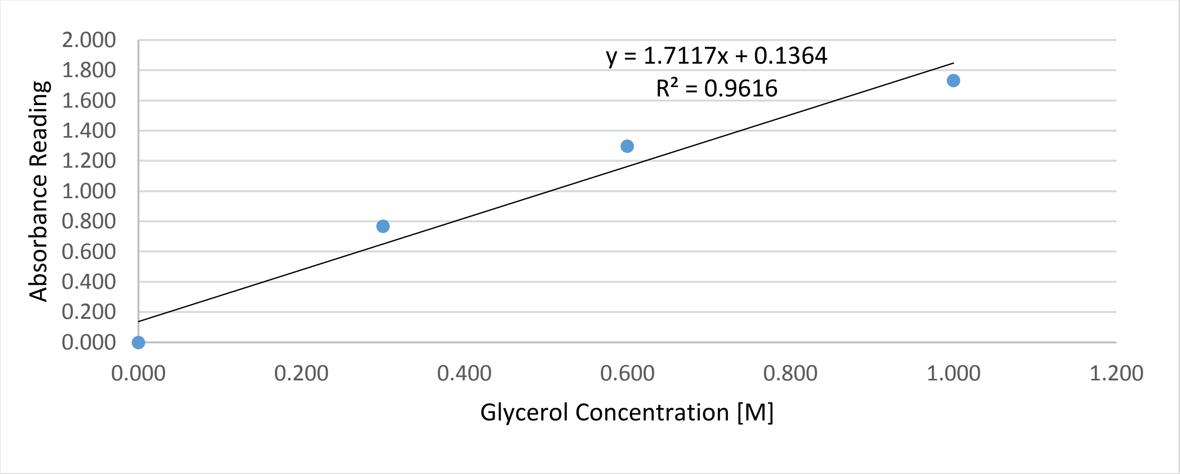
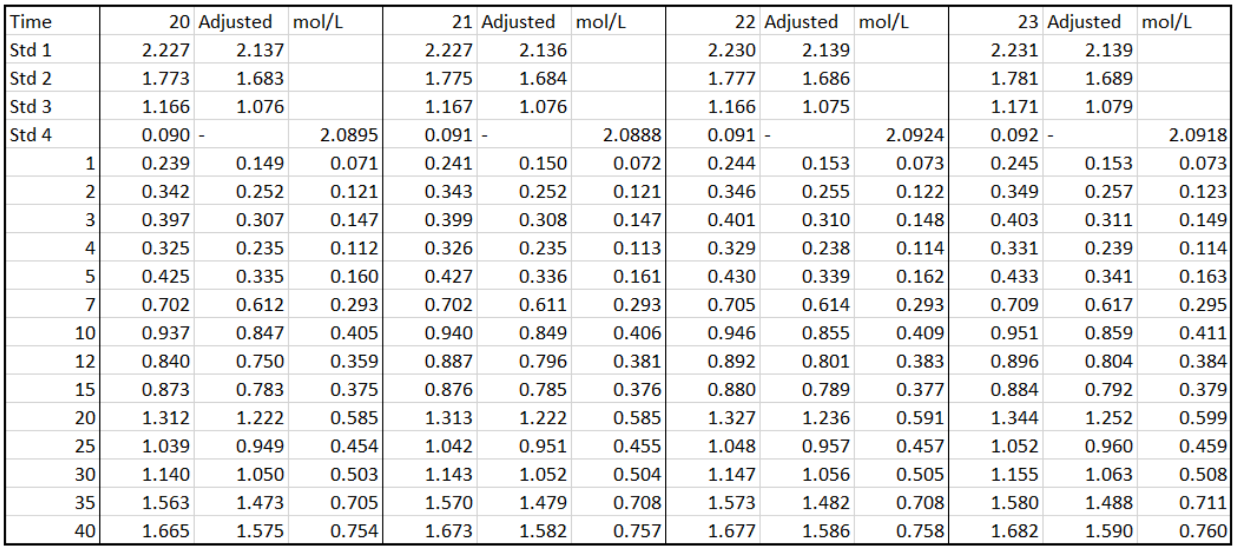


Figure I-49: Calculated Calibration Curve from 23 Minute Reading

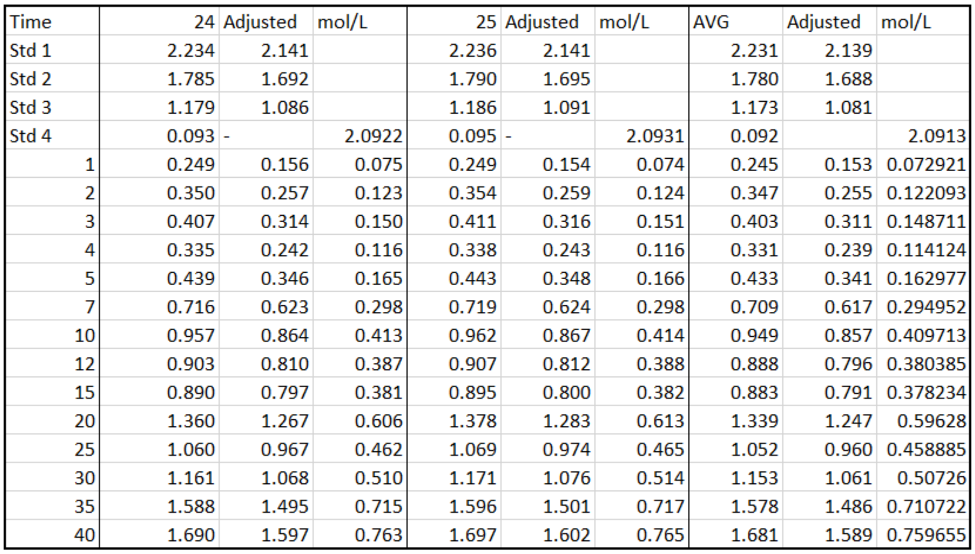
Experiment – 2/10/16

Calculated

Table I-17: Ethanolysis at 25°C Using Calculated Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	2.227	2.137		2.227	2.136		2.230	2.139		2.231	2.139	
Std 2	1.773	1.683		1.775	1.684		1.777	1.686		1.781	1.689	
Std 3	1.166	1.076		1.167	1.076		1.166	1.075		1.171	1.079	
Std 4	0.090	-	2.0895	0.091	-	2.0888	0.091	-	2.0924	0.092	-	2.0918
1	0.239	0.149	0.071	0.241	0.150	0.072	0.244	0.153	0.073	0.245	0.153	0.073
2	0.342	0.252	0.121	0.343	0.252	0.121	0.346	0.255	0.122	0.349	0.257	0.123
3	0.397	0.307	0.147	0.399	0.308	0.147	0.401	0.310	0.148	0.403	0.311	0.149
4	0.325	0.235	0.112	0.326	0.235	0.113	0.329	0.238	0.114	0.331	0.239	0.114
5	0.425	0.335	0.160	0.427	0.336	0.161	0.430	0.339	0.162	0.433	0.341	0.163
7	0.702	0.612	0.293	0.702	0.611	0.293	0.705	0.614	0.293	0.709	0.617	0.295
10	0.937	0.847	0.405	0.940	0.849	0.406	0.946	0.855	0.409	0.951	0.859	0.411
12	0.840	0.750	0.359	0.887	0.796	0.381	0.892	0.801	0.383	0.896	0.804	0.384
15	0.873	0.783	0.375	0.876	0.785	0.376	0.880	0.789	0.377	0.884	0.792	0.379
20	1.312	1.222	0.585	1.313	1.222	0.585	1.327	1.236	0.591	1.344	1.252	0.599
25	1.039	0.949	0.454	1.042	0.951	0.455	1.048	0.957	0.457	1.052	0.960	0.459
30	1.140	1.050	0.503	1.143	1.052	0.504	1.147	1.056	0.505	1.155	1.063	0.508
35	1.563	1.473	0.705	1.570	1.479	0.708	1.573	1.482	0.708	1.580	1.488	0.711
40	1.665	1.575	0.754	1.673	1.582	0.757	1.677	1.586	0.758	1.682	1.590	0.760



Time	24	Adjusted	mol/L	25	Adjusted	mol/L	AVG	Adjusted	mol/L
Std 1	2.234	2.141		2.236	2.141		2.231	2.139	
Std 2	1.785	1.692		1.790	1.695		1.780	1.688	
Std 3	1.179	1.086		1.186	1.091		1.173	1.081	
Std 4	0.093	-	2.0922	0.095	-	2.0931	0.092		2.0913
1	0.249	0.156	0.075	0.249	0.154	0.074	0.245	0.153	0.072921
2	0.350	0.257	0.123	0.354	0.259	0.124	0.347	0.255	0.122093
3	0.407	0.314	0.150	0.411	0.316	0.151	0.403	0.311	0.148711
4	0.335	0.242	0.116	0.338	0.243	0.116	0.331	0.239	0.114124
5	0.439	0.346	0.165	0.443	0.348	0.166	0.433	0.341	0.162977
7	0.716	0.623	0.298	0.719	0.624	0.298	0.709	0.617	0.294952
10	0.957	0.864	0.413	0.962	0.867	0.414	0.949	0.857	0.409713
12	0.903	0.810	0.387	0.907	0.812	0.388	0.888	0.796	0.380385
15	0.890	0.797	0.381	0.895	0.800	0.382	0.883	0.791	0.378234
20	1.360	1.267	0.606	1.378	1.283	0.613	1.339	1.247	0.59628
25	1.060	0.967	0.462	1.069	0.974	0.465	1.052	0.960	0.458885
30	1.161	1.068	0.510	1.171	1.076	0.514	1.153	1.061	0.50726
35	1.588	1.495	0.715	1.596	1.501	0.717	1.578	1.486	0.710722
40	1.690	1.597	0.763	1.697	1.602	0.765	1.681	1.589	0.759655

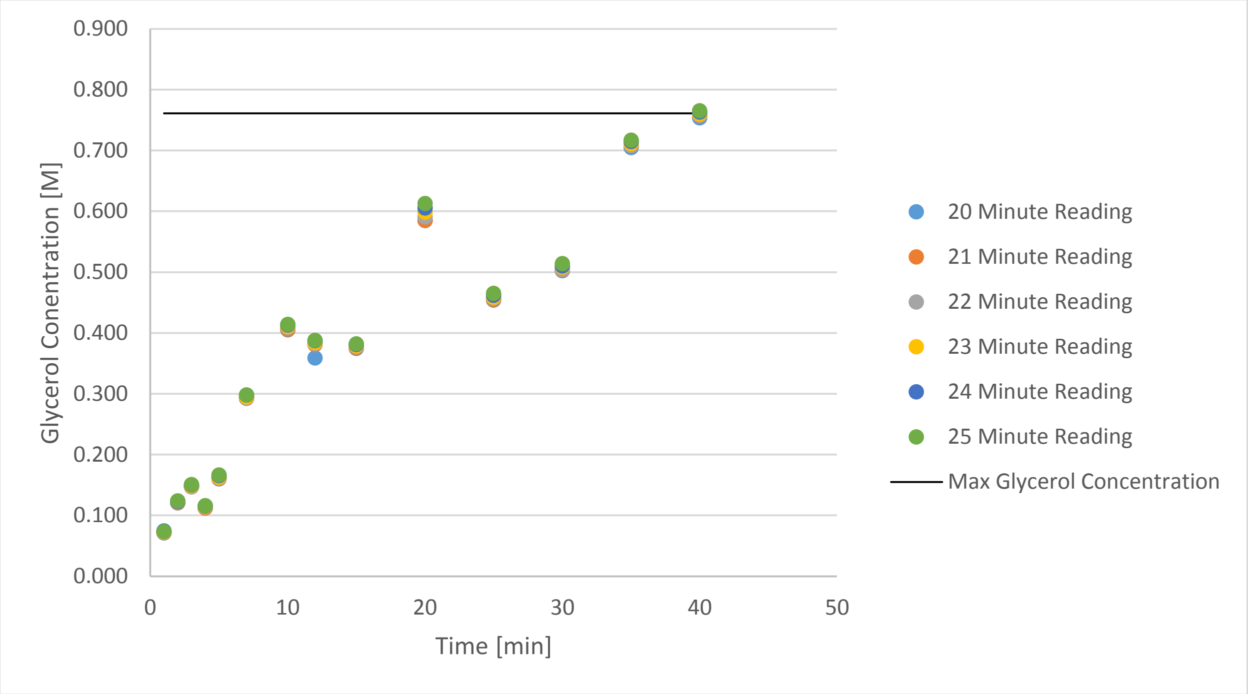
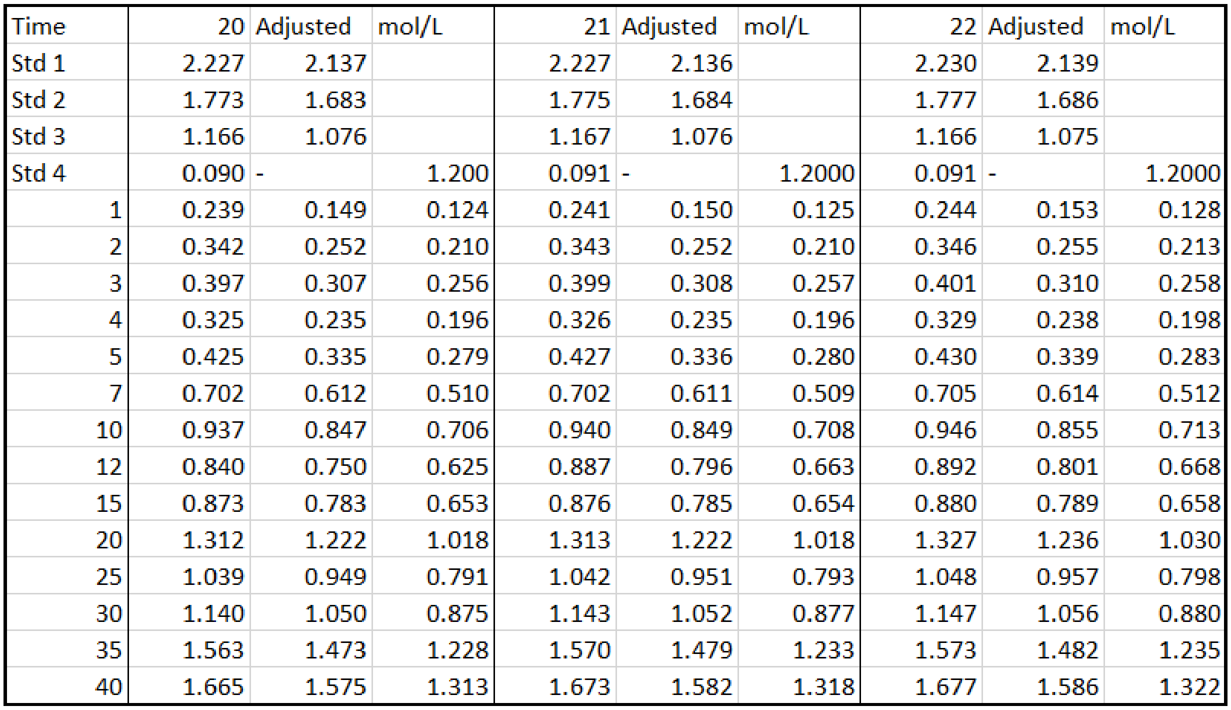


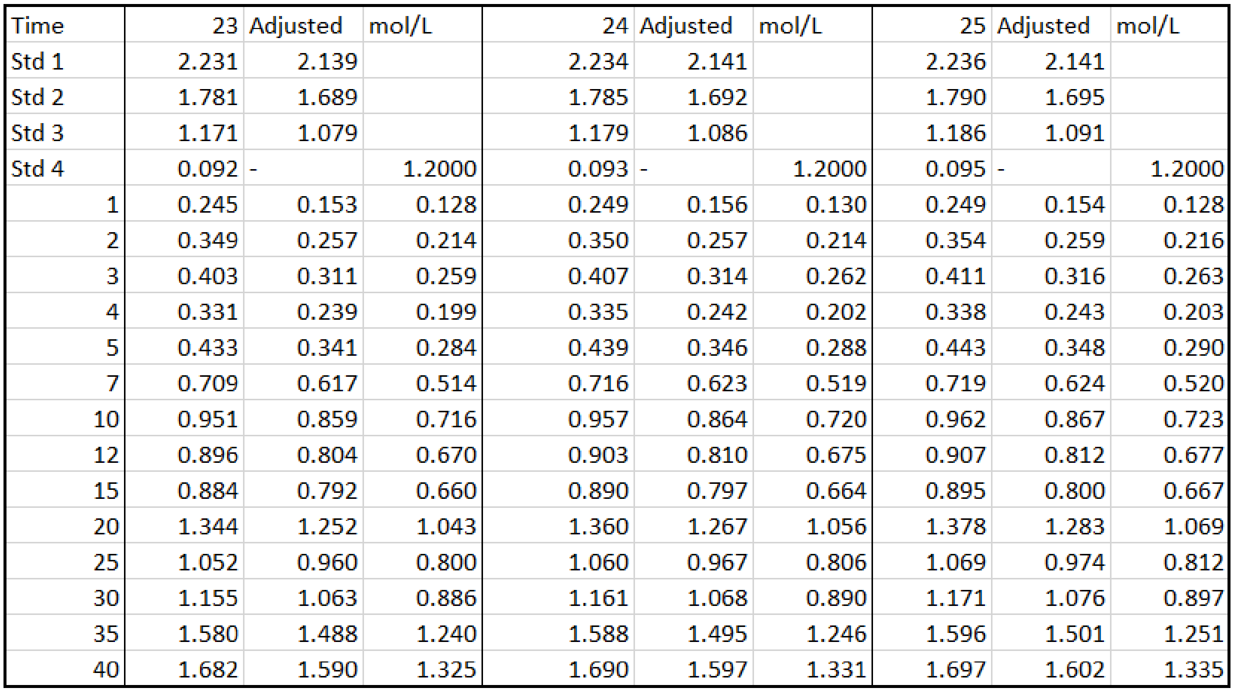
Figure I-50: Ethanolysis at 25°C Using Calculated Calibration Curves

Ideal

Table I-18: Ethanolysis at 25°C Using Ideal Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	2.227	2.137		2.227	2.136		2.230	2.139	
Std 2	1.773	1.683		1.775	1.684		1.777	1.686	
Std 3	1.166	1.076		1.167	1.076		1.166	1.075	
Std 4	0.090	-	1.200	0.091	-	1.2000	0.091	-	1.2000
1	0.239	0.149	0.124	0.241	0.150	0.125	0.244	0.153	0.128
2	0.342	0.252	0.210	0.343	0.252	0.210	0.346	0.255	0.213
3	0.397	0.307	0.256	0.399	0.308	0.257	0.401	0.310	0.258
4	0.325	0.235	0.196	0.326	0.235	0.196	0.329	0.238	0.198
5	0.425	0.335	0.279	0.427	0.336	0.280	0.430	0.339	0.283
7	0.702	0.612	0.510	0.702	0.611	0.509	0.705	0.614	0.512
10	0.937	0.847	0.706	0.940	0.849	0.708	0.946	0.855	0.713
12	0.840	0.750	0.625	0.887	0.796	0.663	0.892	0.801	0.668
15	0.873	0.783	0.653	0.876	0.785	0.654	0.880	0.789	0.658
20	1.312	1.222	1.018	1.313	1.222	1.018	1.327	1.236	1.030
25	1.039	0.949	0.791	1.042	0.951	0.793	1.048	0.957	0.798
30	1.140	1.050	0.875	1.143	1.052	0.877	1.147	1.056	0.880
35	1.563	1.473	1.228	1.570	1.479	1.233	1.573	1.482	1.235
40	1.665	1.575	1.313	1.673	1.582	1.318	1.677	1.586	1.322



Time	23	Adjusted	mol/L	24	Adjusted	mol/L	25	Adjusted	mol/L
Std 1	2.231	2.139		2.234	2.141		2.236	2.141	
Std 2	1.781	1.689		1.785	1.692		1.790	1.695	
Std 3	1.171	1.079		1.179	1.086		1.186	1.091	
Std 4	0.092	-	1.2000	0.093	-	1.2000	0.095	-	1.2000
1	0.245	0.153	0.128	0.249	0.156	0.130	0.249	0.154	0.128
2	0.349	0.257	0.214	0.350	0.257	0.214	0.354	0.259	0.216
3	0.403	0.311	0.259	0.407	0.314	0.262	0.411	0.316	0.263
4	0.331	0.239	0.199	0.335	0.242	0.202	0.338	0.243	0.203
5	0.433	0.341	0.284	0.439	0.346	0.288	0.443	0.348	0.290
7	0.709	0.617	0.514	0.716	0.623	0.519	0.719	0.624	0.520
10	0.951	0.859	0.716	0.957	0.864	0.720	0.962	0.867	0.723
12	0.896	0.804	0.670	0.903	0.810	0.675	0.907	0.812	0.677
15	0.884	0.792	0.660	0.890	0.797	0.664	0.895	0.800	0.667
20	1.344	1.252	1.043	1.360	1.267	1.056	1.378	1.283	1.069
25	1.052	0.960	0.800	1.060	0.967	0.806	1.069	0.974	0.812
30	1.155	1.063	0.886	1.161	1.068	0.890	1.171	1.076	0.897
35	1.580	1.488	1.240	1.588	1.495	1.246	1.596	1.501	1.251
40	1.682	1.590	1.325	1.690	1.597	1.331	1.697	1.602	1.335

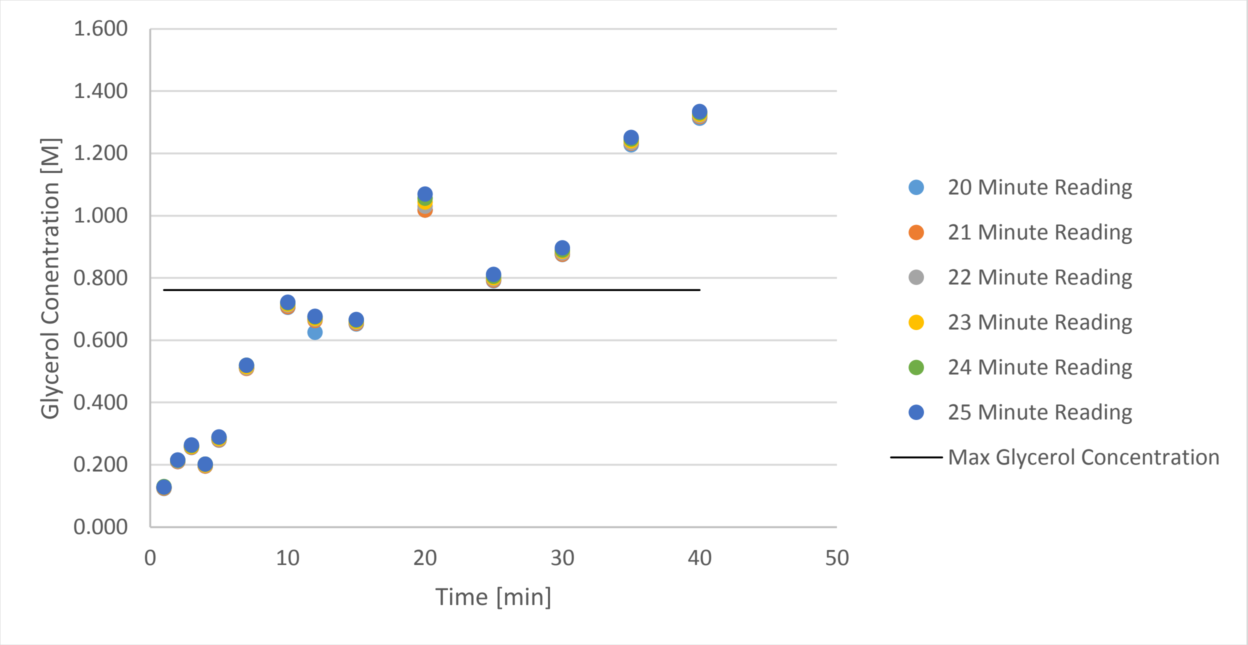


Figure I-51: Ethanolysis at 25°C Using Ideal Calibration Curves

Calibration Curves

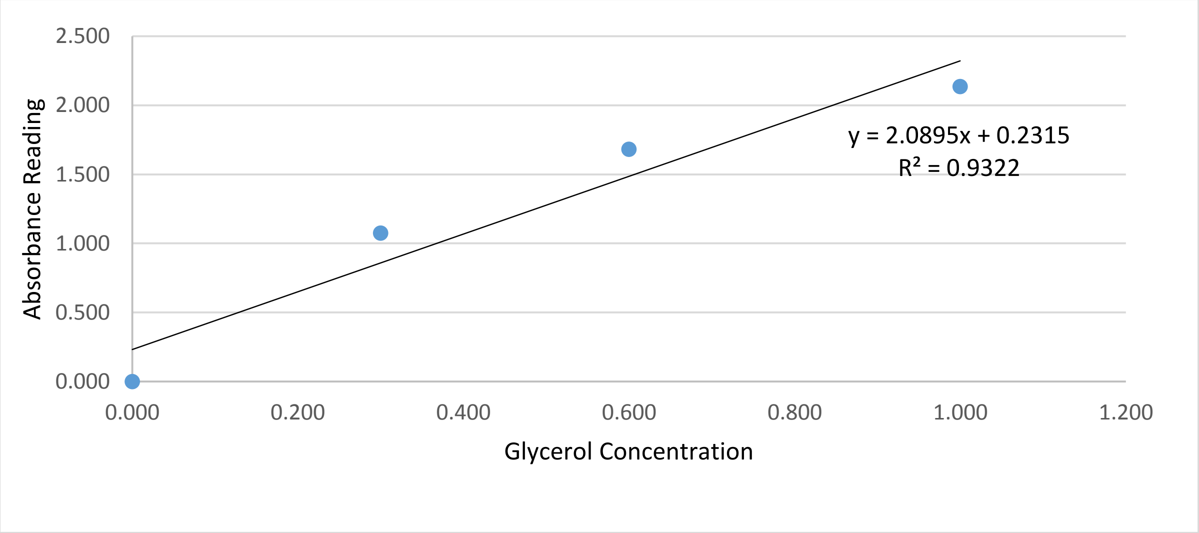


Figure I-52: Calculated Calibration Curve from 20 Minute Reading

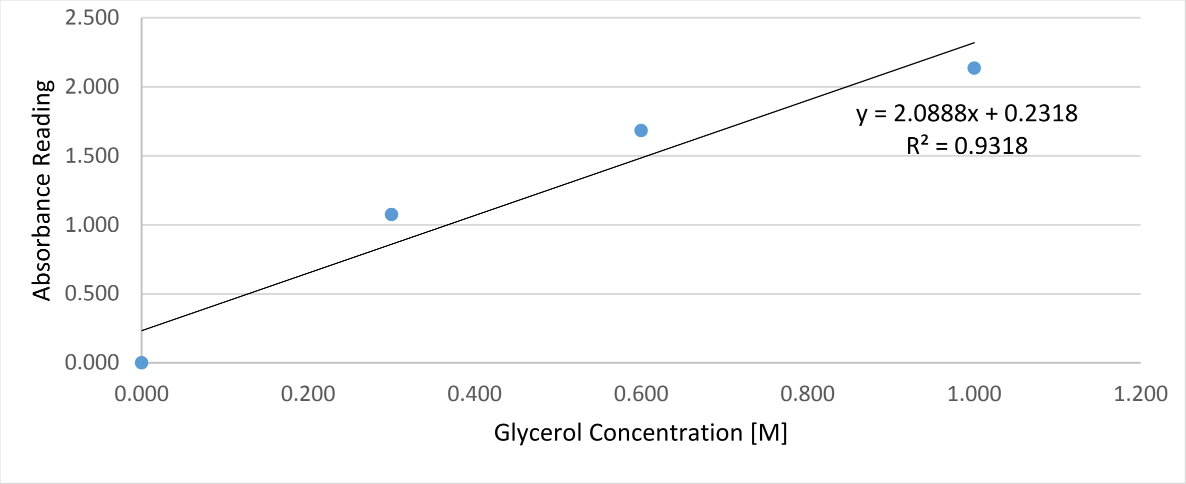


Figure I-53: Calculated Calibration Curve from 21 Minute Reading

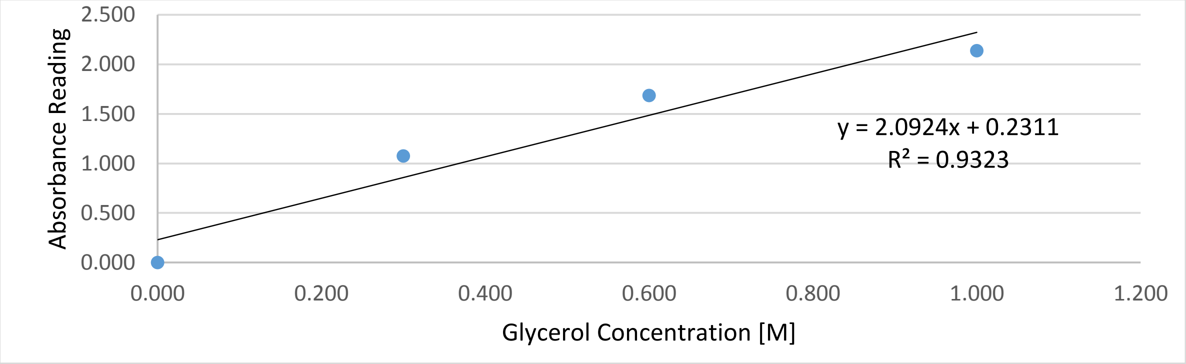


Figure I-54: Calculated Calibration Curve from 22 Minute Reading

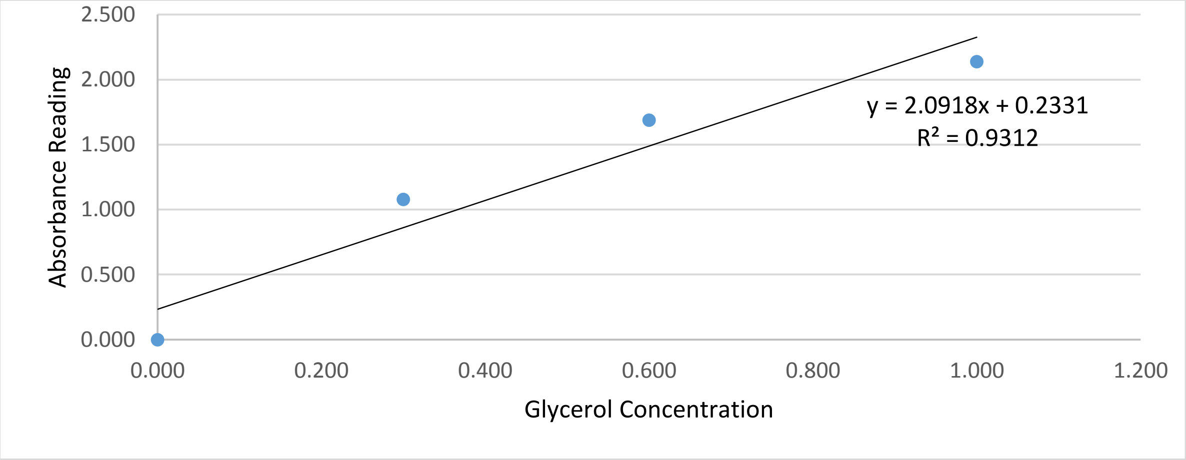


Figure I-55: Calculated Calibration Curve from 23 Minute Reading

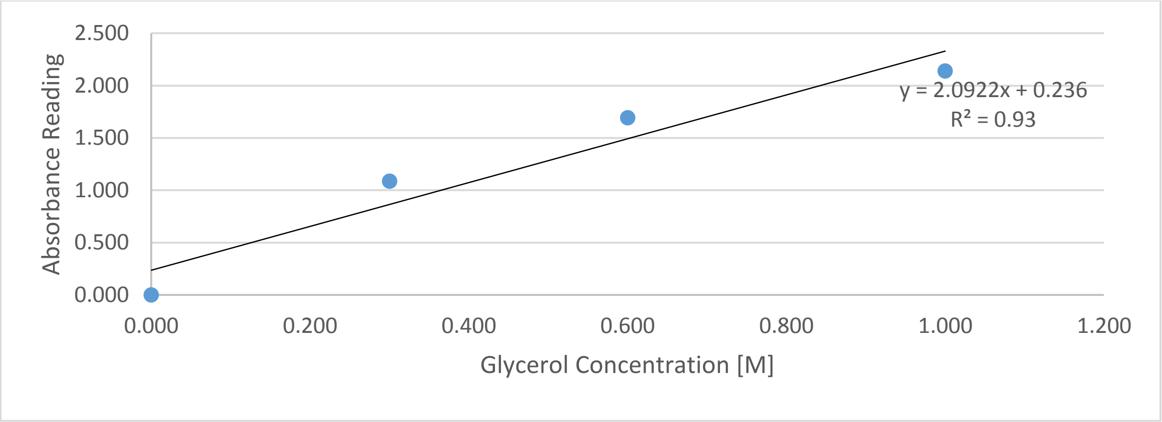


Figure I-56: Calculated Calibration Curve from 24 Minute Reading

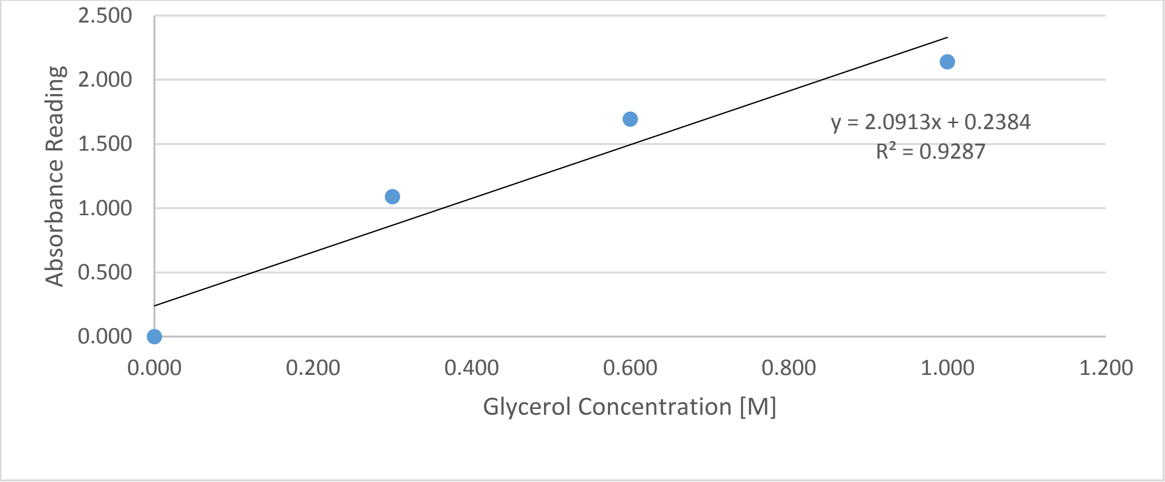
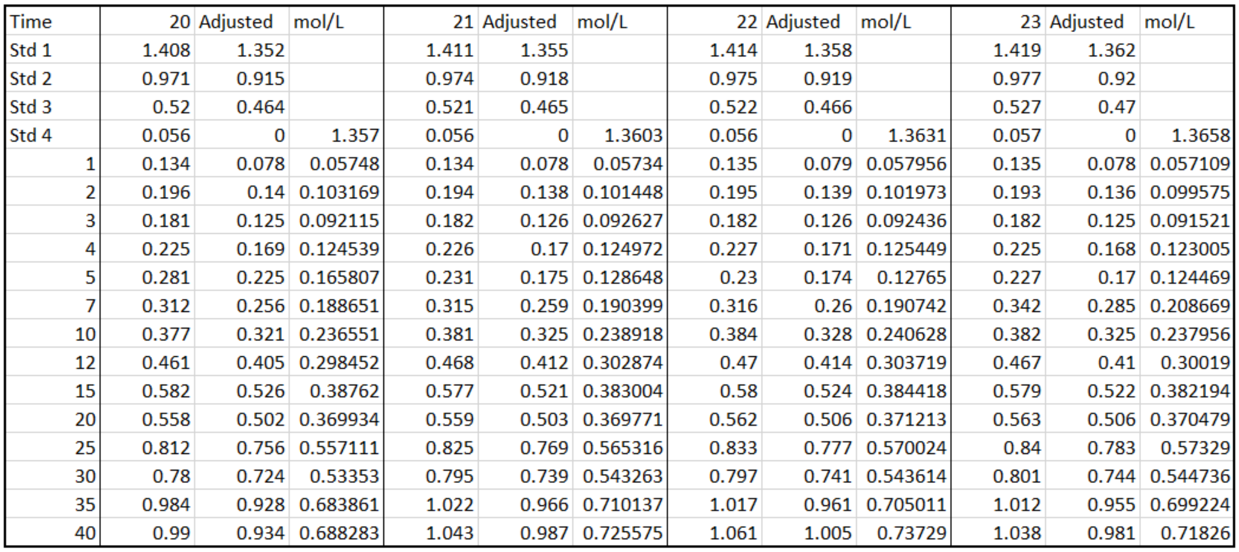


Figure I-57: Calculated Calibration Curve from 25 Minute Reading

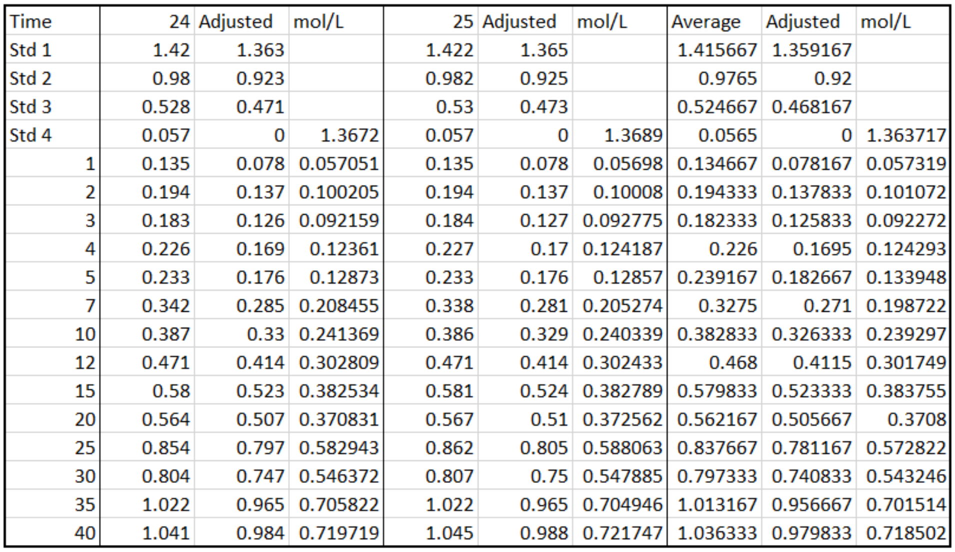
Experiment – 2/15/16

Calculated

Table I-19: Ethanolysis at 25°C Using Calculated Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	1.408	1.352		1.411	1.355		1.414	1.358		1.419	1.362	
Std 2	0.971	0.915		0.974	0.918		0.975	0.919		0.977	0.92	
Std 3	0.52	0.464		0.521	0.465		0.522	0.466		0.527	0.47	
Std 4	0.056	0	1.357	0.056	0	1.3603	0.056	0	1.3631	0.057	0	1.3658
1	0.134	0.078	0.05748	0.134	0.078	0.05734	0.135	0.079	0.057956	0.135	0.078	0.057109
2	0.196	0.14	0.103169	0.194	0.138	0.101448	0.195	0.139	0.101973	0.193	0.136	0.099575
3	0.181	0.125	0.092115	0.182	0.126	0.092627	0.182	0.126	0.092436	0.182	0.125	0.091521
4	0.225	0.169	0.124539	0.226	0.17	0.124972	0.227	0.171	0.125449	0.225	0.168	0.123005
5	0.281	0.225	0.165807	0.231	0.175	0.128648	0.23	0.174	0.12765	0.227	0.17	0.124469
7	0.312	0.256	0.188651	0.315	0.259	0.190399	0.316	0.26	0.190742	0.342	0.285	0.208669
10	0.377	0.321	0.236551	0.381	0.325	0.238918	0.384	0.328	0.240628	0.382	0.325	0.237956
12	0.461	0.405	0.298452	0.468	0.412	0.302874	0.47	0.414	0.303719	0.467	0.41	0.30019
15	0.582	0.526	0.38762	0.577	0.521	0.383004	0.58	0.524	0.384418	0.579	0.522	0.382194
20	0.558	0.502	0.369934	0.559	0.503	0.369771	0.562	0.506	0.371213	0.563	0.506	0.370479
25	0.812	0.756	0.557111	0.825	0.769	0.565316	0.833	0.777	0.570024	0.84	0.783	0.57329
30	0.78	0.724	0.53353	0.795	0.739	0.543263	0.797	0.741	0.543614	0.801	0.744	0.544736
35	0.984	0.928	0.683861	1.022	0.966	0.710137	1.017	0.961	0.705011	1.012	0.955	0.699224
40	0.99	0.934	0.688283	1.043	0.987	0.725575	1.061	1.005	0.73729	1.038	0.981	0.71826



Time	24	Adjusted	mol/L	25	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	1.42	1.363		1.422	1.365		1.415667	1.359167	
Std 2	0.98	0.923		0.982	0.925		0.9765	0.92	
Std 3	0.528	0.471		0.53	0.473		0.524667	0.468167	
Std 4	0.057	0	1.3672	0.057	0	1.3689	0.0565	0	1.363717
1	0.135	0.078	0.057051	0.135	0.078	0.05698	0.134667	0.078167	0.057319
2	0.194	0.137	0.100205	0.194	0.137	0.10008	0.194333	0.137833	0.101072
3	0.183	0.126	0.092159	0.184	0.127	0.092775	0.182333	0.125833	0.092272
4	0.226	0.169	0.12361	0.227	0.17	0.124187	0.226	0.1695	0.124293
5	0.233	0.176	0.12873	0.233	0.176	0.12857	0.239167	0.182667	0.133948
7	0.342	0.285	0.208455	0.338	0.281	0.205274	0.3275	0.271	0.198722
10	0.387	0.33	0.241369	0.386	0.329	0.240339	0.382833	0.326333	0.239297
12	0.471	0.414	0.302809	0.471	0.414	0.302433	0.468	0.4115	0.301749
15	0.58	0.523	0.382534	0.581	0.524	0.382789	0.579833	0.523333	0.383755
20	0.564	0.507	0.370831	0.567	0.51	0.372562	0.562167	0.505667	0.3708
25	0.854	0.797	0.582943	0.862	0.805	0.588063	0.837667	0.781167	0.572822
30	0.804	0.747	0.546372	0.807	0.75	0.547885	0.797333	0.740833	0.543246
35	1.022	0.965	0.705822	1.022	0.965	0.704946	1.013167	0.956667	0.701514
40	1.041	0.984	0.719719	1.045	0.988	0.721747	1.036333	0.979833	0.718502

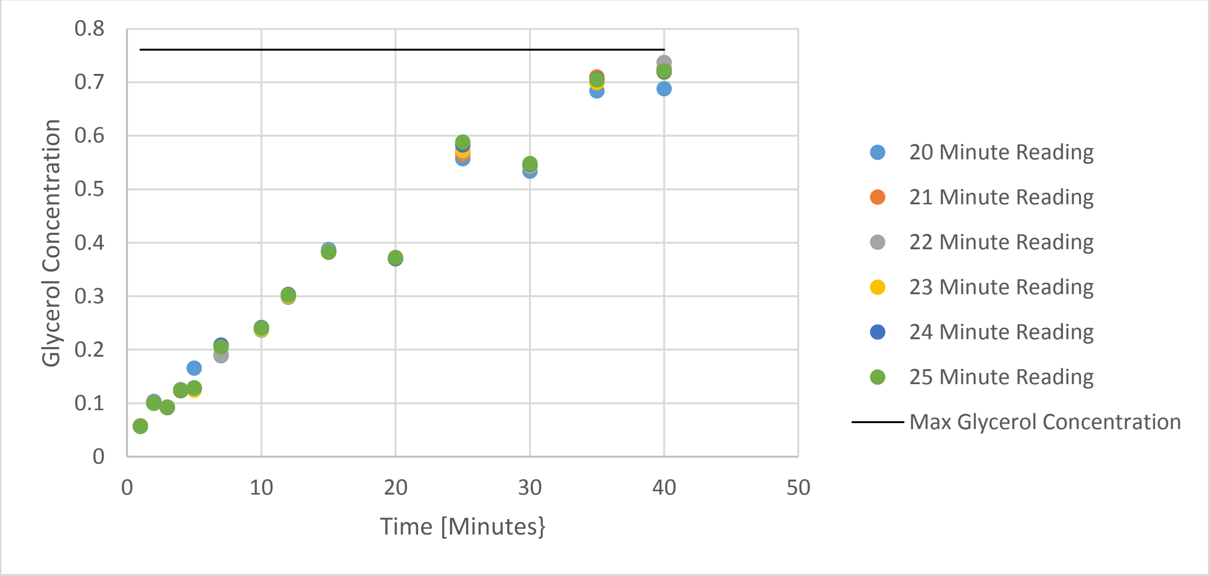


Figure I-58: Ethanolysis at 25°C Using Calculated Calibration Curves

Ideal

Table I-20: Ethanolysis at 25°C Using Ideal Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	1.408	1.352		1.411	1.355		1.414	1.358		1.419	1.362	
Std 2	0.971	0.915		0.974	0.918		0.975	0.919		0.977	0.92	
Std 3	0.52	0.464		0.521	0.465		0.522	0.466		0.527	0.47	
Std 4	0.056	0	1.2	0.056	0	1.2	0.056	0	1.2	0.057	0	1.2
1	0.134	0.078	0.065	0.134	0.078	0.065	0.135	0.079	0.065833	0.135	0.078	0.065
2	0.196	0.14	0.116667	0.194	0.138	0.115	0.195	0.139	0.115833	0.193	0.136	0.113333
3	0.181	0.125	0.104167	0.182	0.126	0.105	0.182	0.126	0.105	0.182	0.125	0.104167
4	0.225	0.169	0.140833	0.226	0.17	0.141667	0.227	0.171	0.1425	0.225	0.168	0.14
5	0.281	0.225	0.1875	0.231	0.175	0.145833	0.23	0.174	0.145	0.227	0.17	0.141667
7	0.312	0.256	0.213333	0.315	0.259	0.215833	0.316	0.26	0.216667	0.342	0.285	0.2375
10	0.377	0.321	0.2675	0.381	0.325	0.270833	0.384	0.328	0.273333	0.382	0.325	0.270833
12	0.461	0.405	0.3375	0.468	0.412	0.343333	0.47	0.414	0.345	0.467	0.41	0.341667
15	0.582	0.526	0.438333	0.577	0.521	0.434167	0.58	0.524	0.436667	0.579	0.522	0.435
20	0.558	0.502	0.418333	0.559	0.503	0.419167	0.562	0.506	0.421667	0.563	0.506	0.421667
25	0.812	0.756	0.63	0.825	0.769	0.640833	0.833	0.777	0.6475	0.84	0.783	0.6525
30	0.78	0.724	0.603333	0.795	0.739	0.615833	0.797	0.741	0.6175	0.801	0.744	0.62
35	0.984	0.928	0.773333	1.022	0.966	0.805	1.017	0.961	0.800833	1.012	0.955	0.795833
40	0.99	0.934	0.778333	1.043	0.987	0.8225	1.061	1.005	0.8375	1.038	0.981	0.8175

Time	24	Adjusted	mol/L	25	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	1.42	1.363		1.422	1.365		1.415667	1.359167	
Std 2	0.98	0.923		0.982	0.925		0.9765	0.92	
Std 3	0.528	0.471		0.53	0.473		0.524667	0.468167	
Std 4	0.057	0	1.2	0.057	0	1.2	0.0565	0	1.2
1	0.135	0.078	0.065	0.135	0.078	0.065	0.134667	0.078167	0.065139
2	0.194	0.137	0.114167	0.194	0.137	0.114167	0.194333	0.137833	0.114861
3	0.183	0.126	0.105	0.184	0.127	0.105833	0.182333	0.125833	0.104861
4	0.226	0.169	0.140833	0.227	0.17	0.141667	0.226	0.1695	0.14125
5	0.233	0.176	0.146667	0.233	0.176	0.146667	0.239167	0.182667	0.152222
7	0.342	0.285	0.2375	0.338	0.281	0.234167	0.3275	0.271	0.225833
10	0.387	0.33	0.275	0.386	0.329	0.274167	0.382833	0.326333	0.271944
12	0.471	0.414	0.345	0.471	0.414	0.345	0.468	0.4115	0.342917
15	0.58	0.523	0.435833	0.581	0.524	0.436667	0.579833	0.523333	0.436111
20	0.564	0.507	0.4225	0.567	0.51	0.425	0.562167	0.505667	0.421389
25	0.854	0.797	0.664167	0.862	0.805	0.670833	0.837667	0.781167	0.650972
30	0.804	0.747	0.6225	0.807	0.75	0.625	0.797333	0.740833	0.617361
35	1.022	0.965	0.804167	1.022	0.965	0.804167	1.013167	0.956667	0.797222
40	1.041	0.984	0.82	1.045	0.988	0.823333	1.036333	0.979833	0.816528

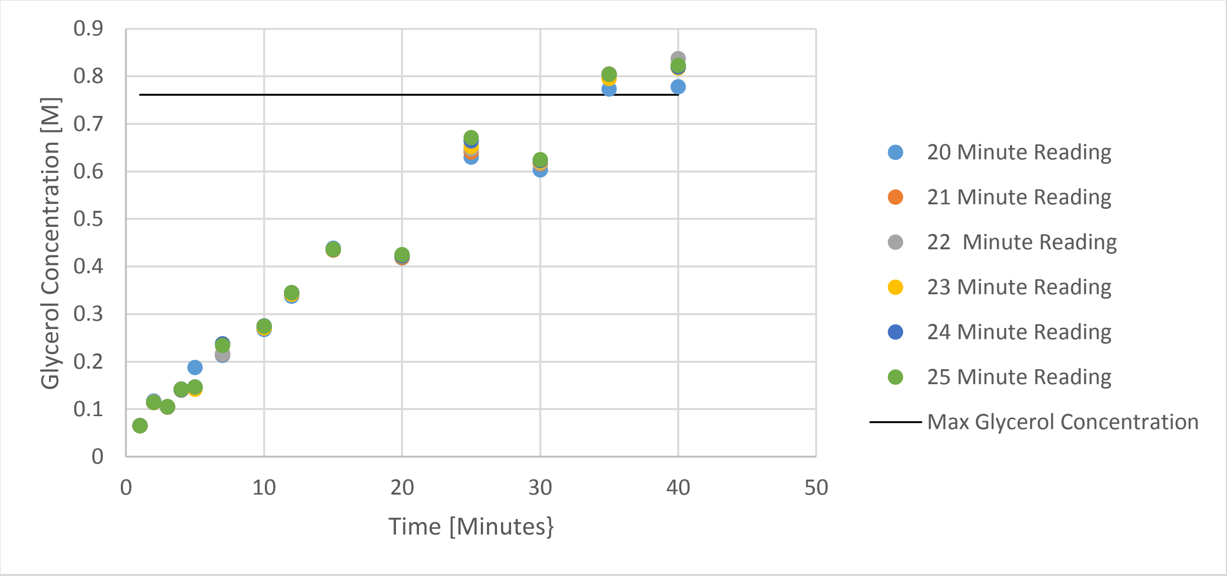


Figure I-59: Ethanolysis at 25°C Using Ideal Calibration Curves

Calibration Curves

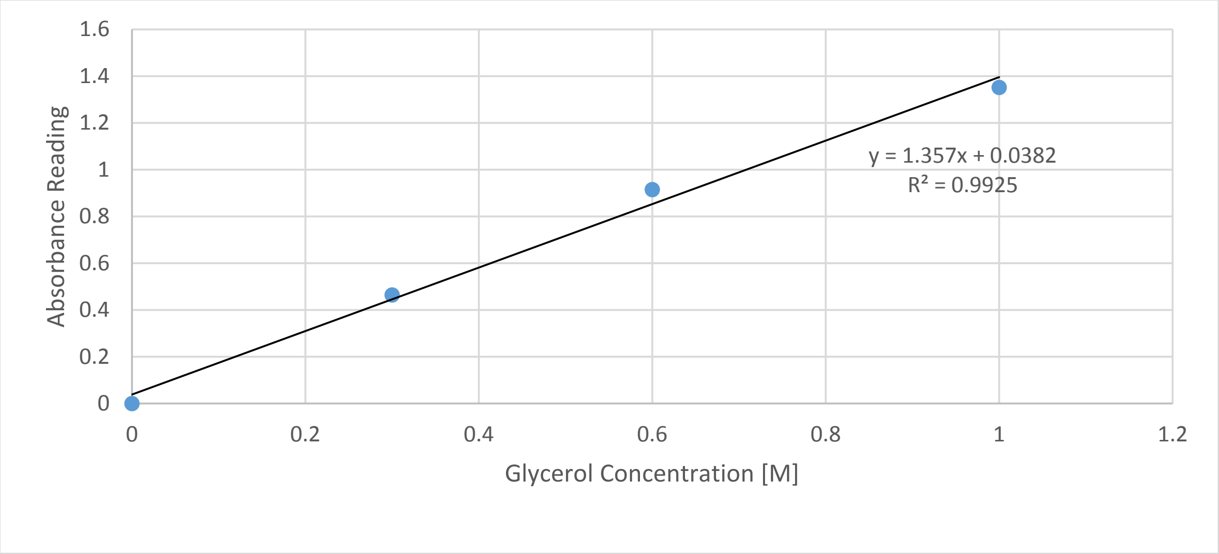


Figure I-60: Calculated Calibration Curve from 20 Minute Reading

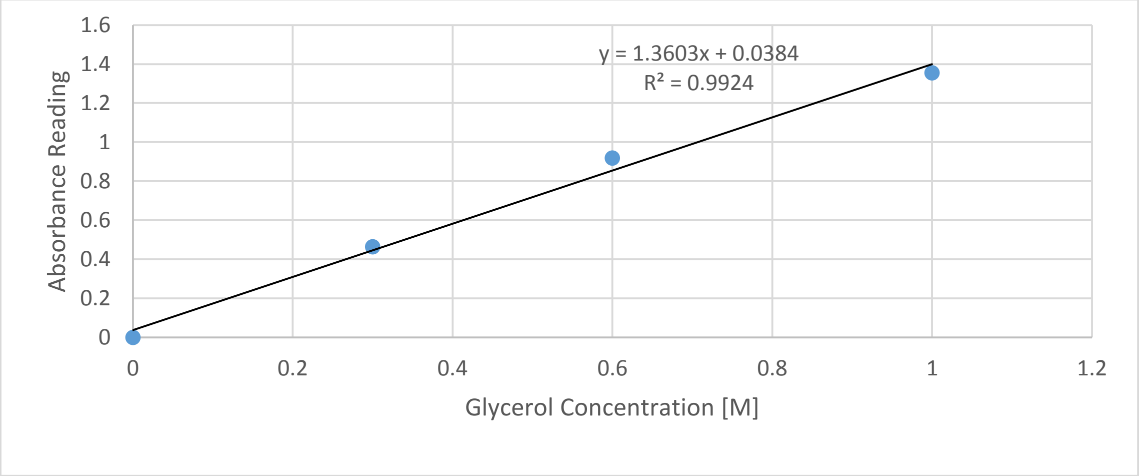


Figure I-61: Calculated Calibration Curve from 21 Minute Reading

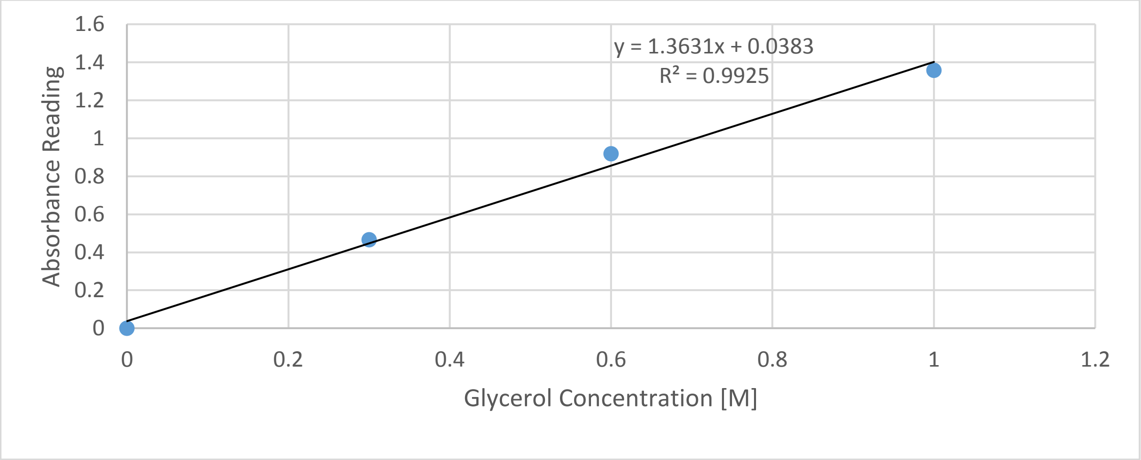


Figure I-62: Calculated Calibration Curve from 22 Minute Reading

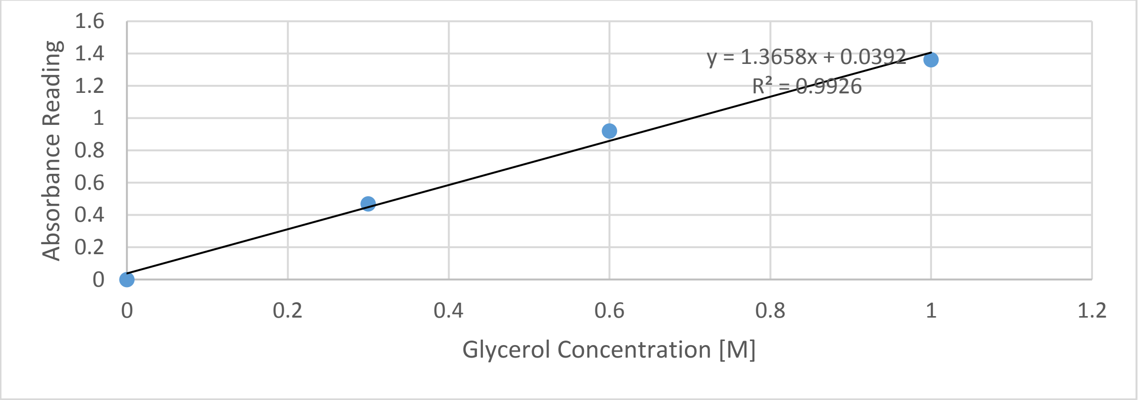


Figure I-63: Calculated Calibration Curve from 23 Minute Reading

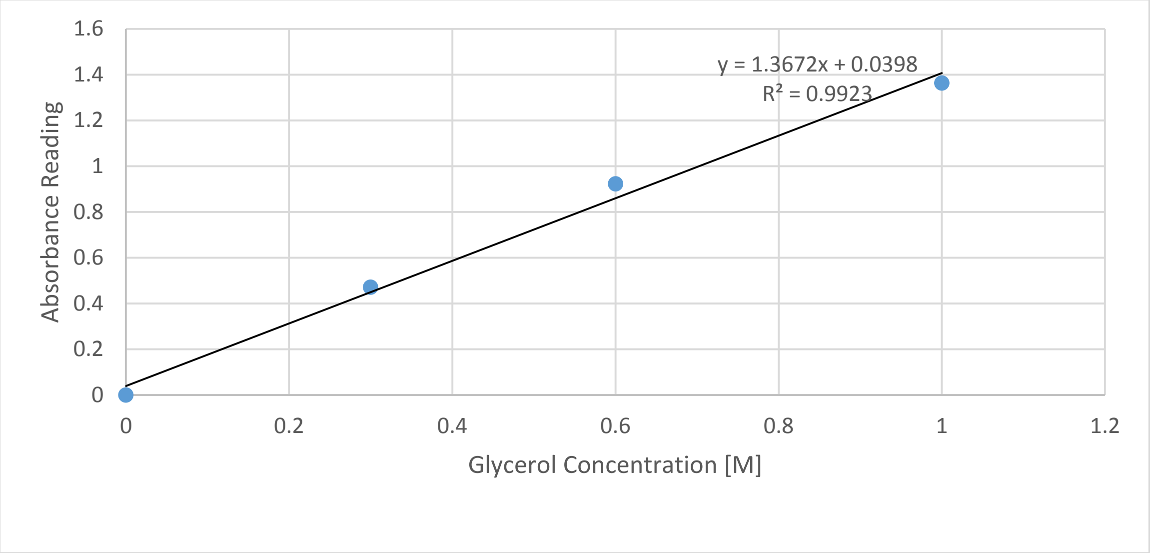


Figure I-64: Calculated Calibration Curve from 24 Minute Reading

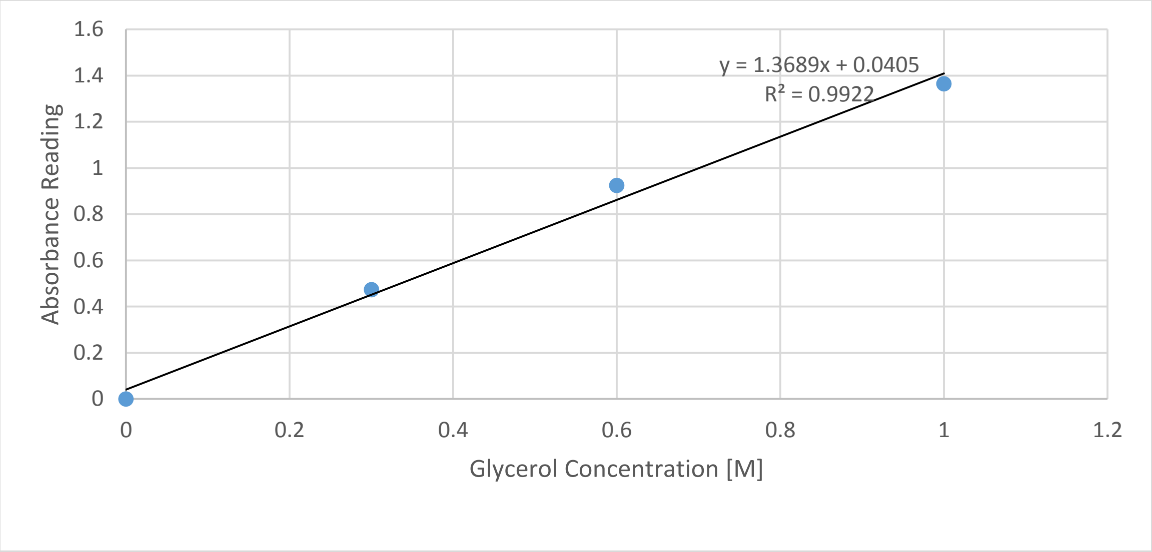


Figure I-65: Calculated Calibration Curve from 25 Minute Reading

Experiment – 2/17/16

Calculated

Table I-21: Ethanolysis at 35°C Using Calculated Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	1.681	1.625		1.680	1.624		1.682	1.626	
Std 2	1.022	0.966		1.021	0.965		1.025	0.969	
Std 3	0.548	0.492		0.551	0.495		0.554	0.498	
Std 4	0.056	-	1.6215	0.056	-	1.6194	0.056	-	1.6212
1	0.143	0.087	0.054	0.145	0.089	0.055	0.145	0.089	0.055
2	0.235	0.179	0.110	0.234	0.178	0.110	0.236	0.180	0.111
3	0.269	0.213	0.131	0.268	0.212	0.131	0.270	0.214	0.132
4	0.376	0.320	0.197	0.382	0.326	0.201	0.382	0.326	0.201
5	0.481	0.425	0.262	0.478	0.422	0.261	0.479	0.423	0.261
7	0.487	0.431	0.266	0.497	0.441	0.272	0.503	0.447	0.276
10	0.592	0.536	0.331	0.614	0.558	0.345	0.613	0.557	0.344
12	0.842	0.786	0.485	0.862	0.806	0.498	0.871	0.815	0.503
15	0.708	0.652	0.402	0.710	0.654	0.404	0.720	0.664	0.410
20	0.944	0.888	0.548	0.949	0.893	0.551	0.957	0.901	0.556
25	0.932	0.876	0.540	0.937	0.881	0.544	0.939	0.883	0.545
30	1.003	0.947	0.584	1.005	0.949	0.586	1.012	0.956	0.590
35	1.268	1.212	0.747	1.266	1.210	0.747	1.287	1.231	0.759
40	0.962	0.906	0.559	1.005	0.949	0.586	1.008	0.952	0.587

Time	23	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	1.682	1.626		1.681	1.625	
Std 2	1.026	0.970		1.024	0.968	
Std 3	0.556	0.500		0.552	0.496	
Std 4	0.056	-	1.6208	0.056	0.000	1.6207
1	0.145	0.089	0.055	0.145	0.089	0.055
2	0.235	0.179	0.110	0.235	0.179	0.110
3	0.271	0.215	0.133	0.270	0.214	0.132
4	0.383	0.327	0.202	0.381	0.325	0.200
5	0.480	0.424	0.262	0.480	0.424	0.261
7	0.505	0.449	0.277	0.498	0.442	0.273
10	0.616	0.560	0.346	0.609	0.553	0.341
12	0.875	0.819	0.505	0.863	0.807	0.498
15	0.722	0.666	0.411	0.715	0.659	0.407
20	0.960	0.904	0.558	0.953	0.897	0.553
25	0.940	0.884	0.545	0.937	0.881	0.544
30	1.015	0.959	0.592	1.009	0.953	0.588
35	1.295	1.239	0.764	1.279	1.223	0.755
40	1.002	0.946	0.584	0.994	0.938	0.579

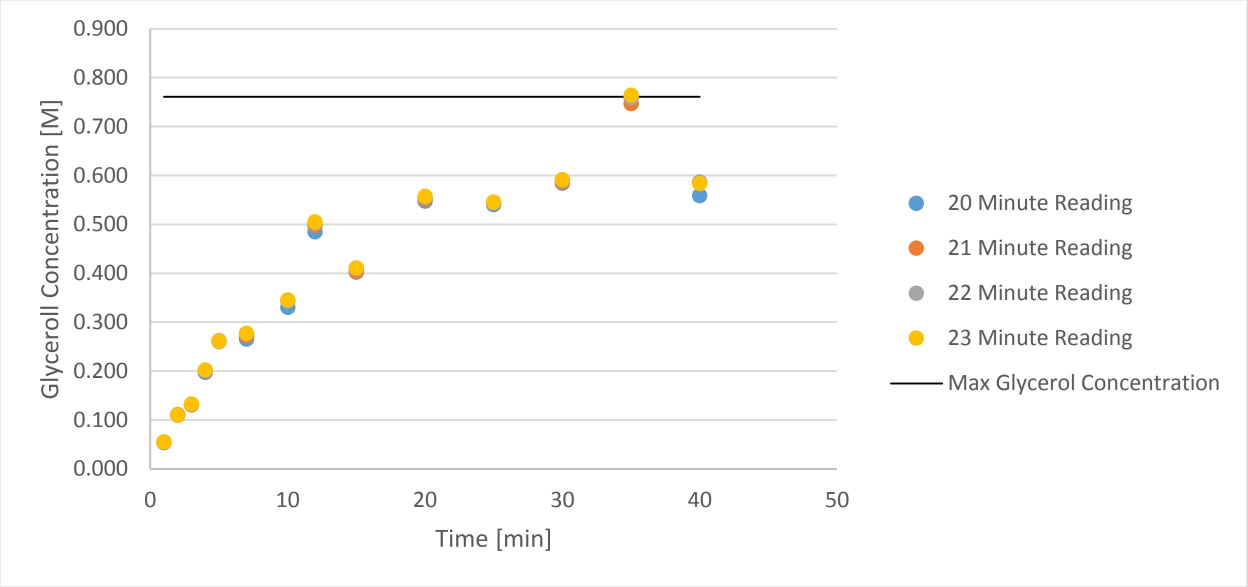


Figure I-66: Ethanolysis at 35°C Using Calculated Calibration Curves

Ideal

Table I-22: Ethanolysis at 35°C Using Ideal Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	1.681	1.625		1.680	1.624		1.682	1.626		1.682	1.626	
Std 2	1.022	0.966		1.021	0.965		1.025	0.969		1.026	0.970	
Std 3	0.548	0.492		0.551	0.495		0.554	0.498		0.556	0.500	
Std 4	0.056	-	1.200	0.056	-	1.2000	0.056	-	1.2000	0.056	-	1.2000
1	0.143	0.087	0.073	0.145	0.089	0.074	0.145	0.089	0.074	0.145	0.089	0.074
2	0.235	0.179	0.149	0.234	0.178	0.148	0.236	0.180	0.150	0.235	0.179	0.149
3	0.269	0.213	0.178	0.268	0.212	0.177	0.270	0.214	0.178	0.271	0.215	0.179
4	0.376	0.320	0.267	0.382	0.326	0.272	0.382	0.326	0.272	0.383	0.327	0.273
5	0.481	0.425	0.354	0.478	0.422	0.352	0.479	0.423	0.353	0.480	0.424	0.353
7	0.487	0.431	0.359	0.497	0.441	0.368	0.503	0.447	0.373	0.505	0.449	0.374
10	0.592	0.536	0.447	0.614	0.558	0.465	0.613	0.557	0.464	0.616	0.560	0.467
12	0.842	0.786	0.655	0.862	0.806	0.672	0.871	0.815	0.679	0.875	0.819	0.683
15	0.708	0.652	0.543	0.710	0.654	0.545	0.720	0.664	0.553	0.722	0.666	0.555
20	0.944	0.888	0.740	0.949	0.893	0.744	0.957	0.901	0.751	0.960	0.904	0.753
25	0.932	0.876	0.730	0.937	0.881	0.734	0.939	0.883	0.736	0.940	0.884	0.737
30	1.003	0.947	0.789	1.005	0.949	0.791	1.012	0.956	0.797	1.015	0.959	0.799
35	1.268	1.212	1.010	1.266	1.210	1.008	1.287	1.231	1.026	1.295	1.239	1.033
40	0.962	0.906	0.755	1.005	0.949	0.791	1.008	0.952	0.793	1.002	0.946	0.788

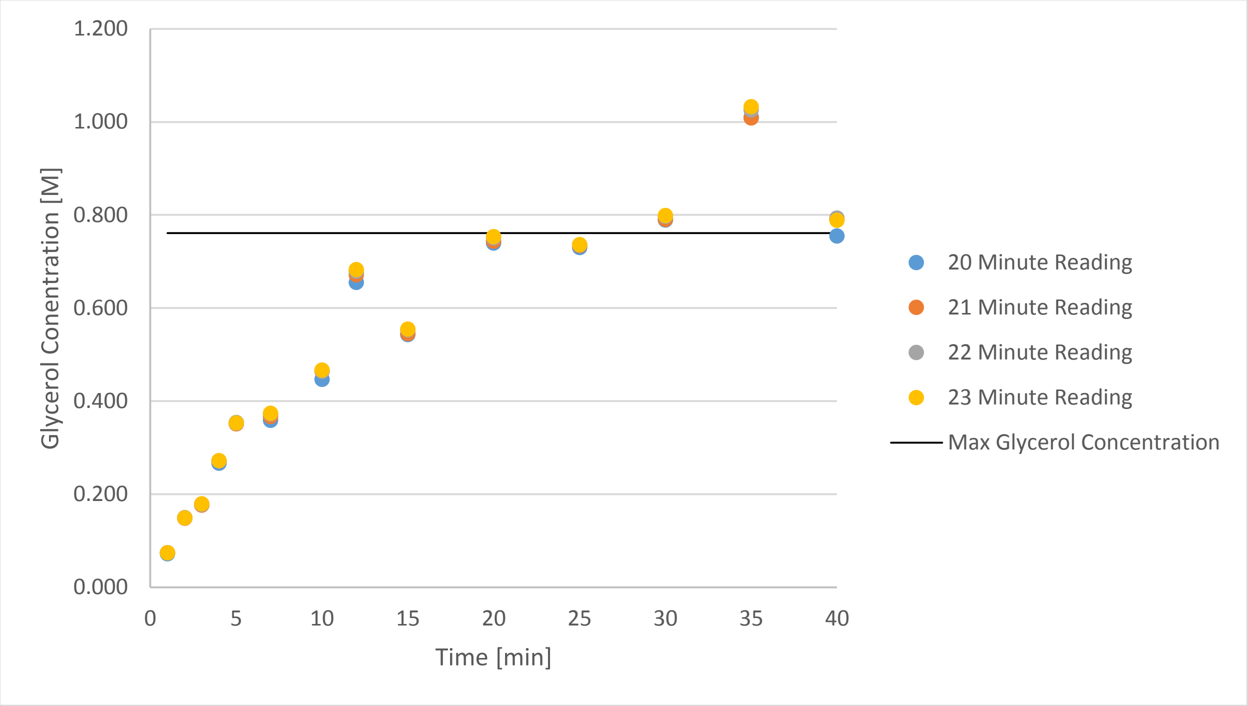


Figure I-67: Ethanolysis at 35°C Using Ideal Calibration Curves

Calibration Curves

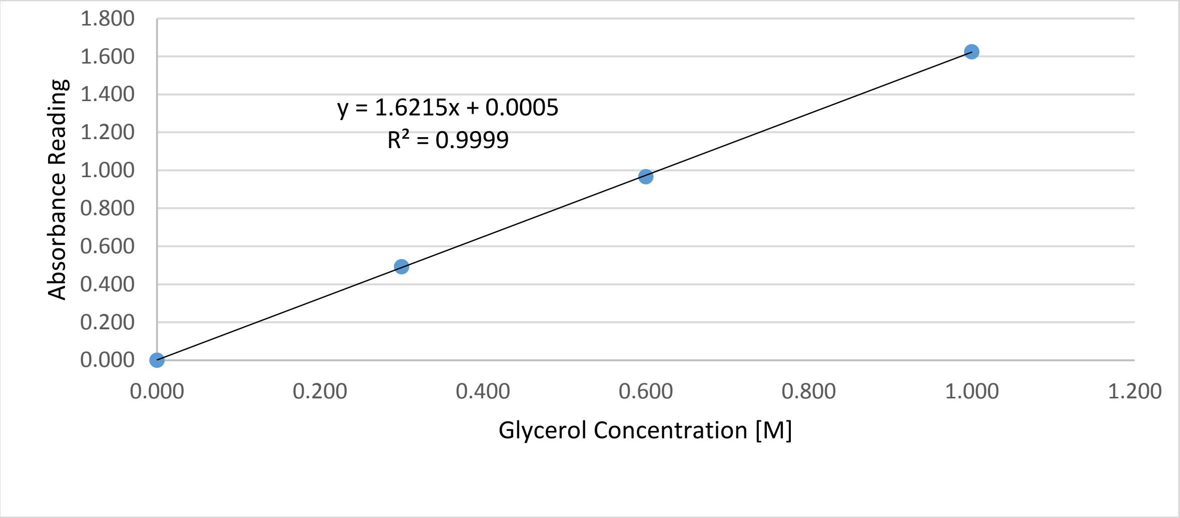


Figure I-68: Calculated Calibration Curve from 20 Minute Reading

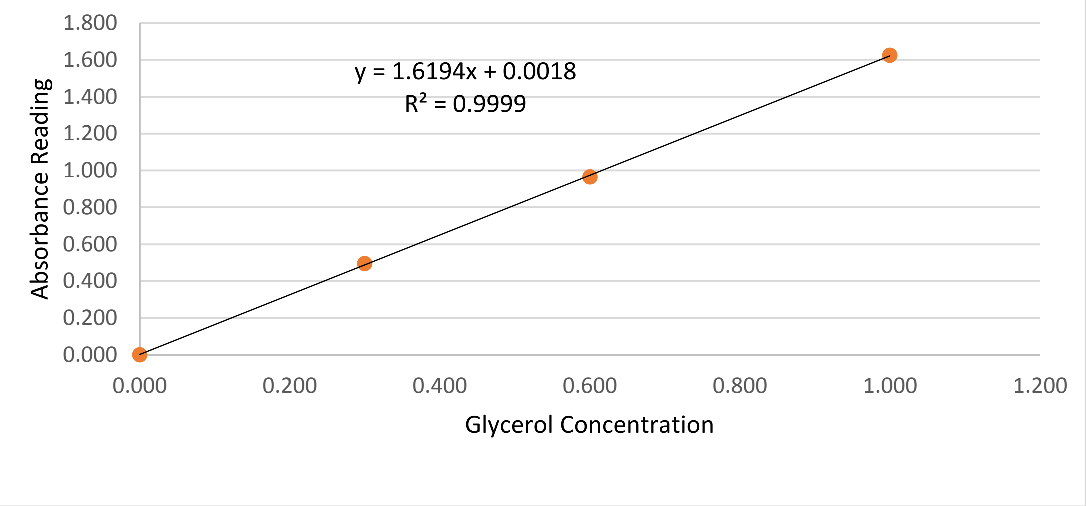


Figure I-69: Calculated Calibration Curve from 21 Minute Reading

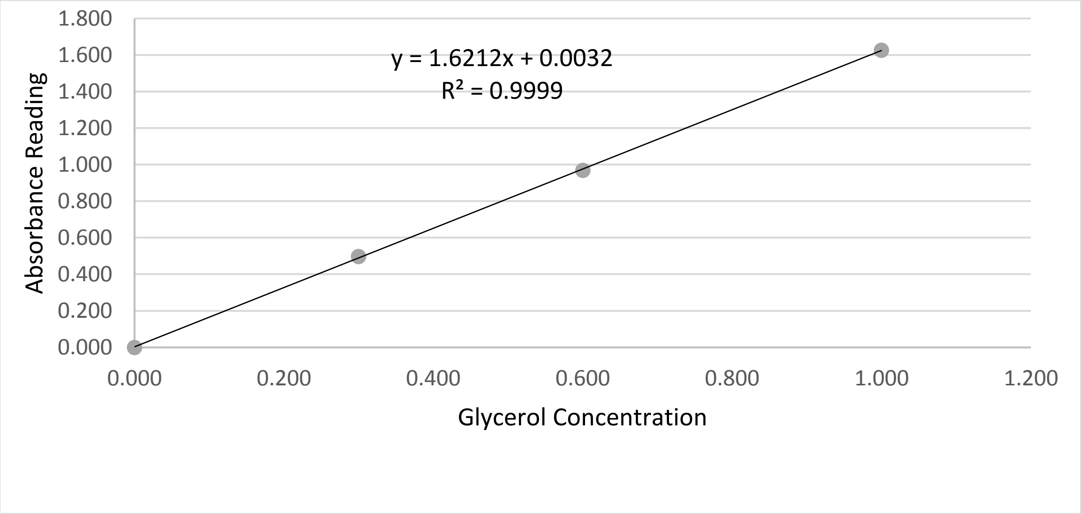


Figure I-70: Calculated Calibration Curve from 22 Minute Reading

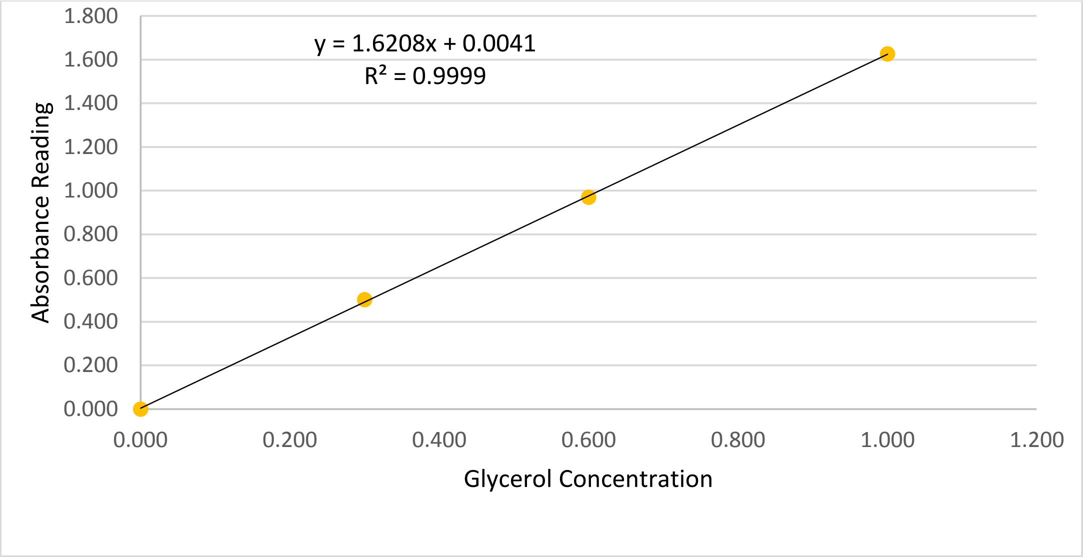
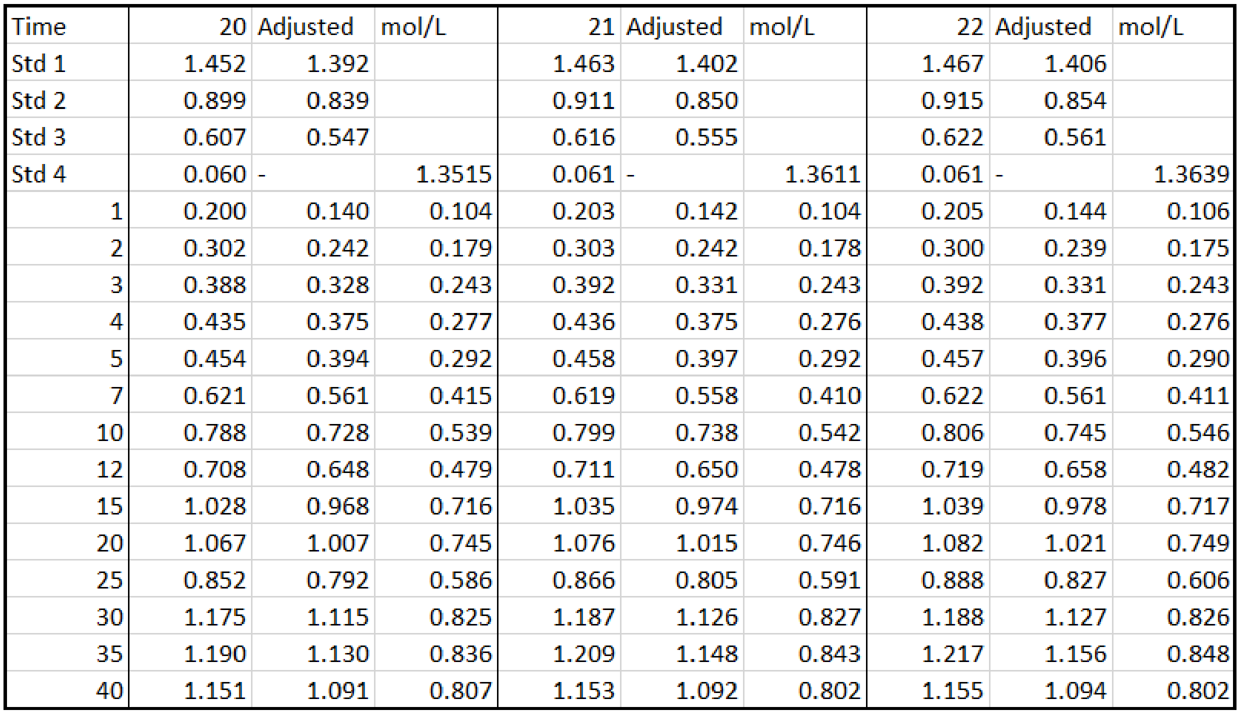


Figure I-71: Calculated Calibration Curve from 23 Minute Reading

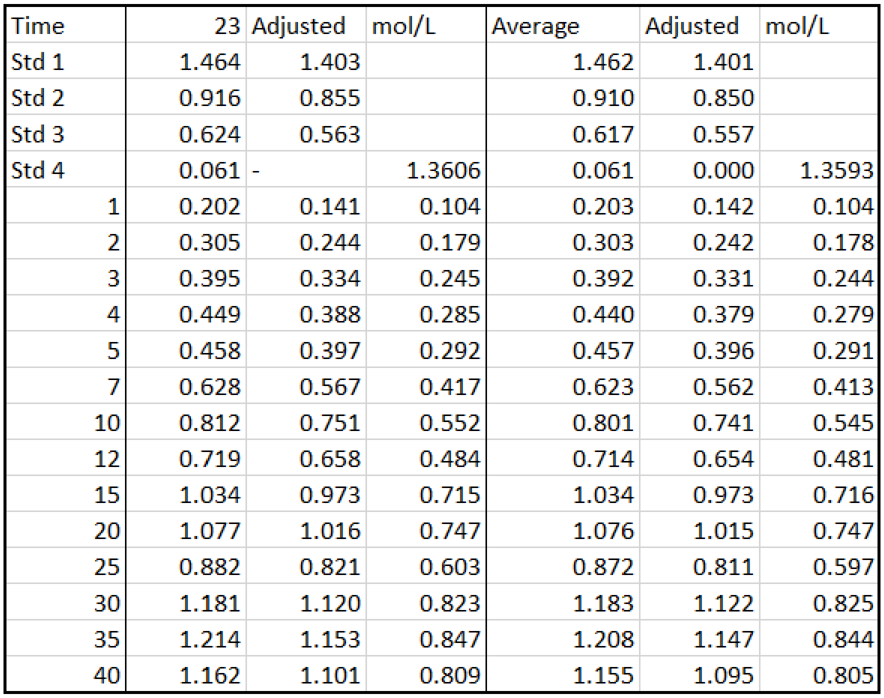
Experiment – 2/22/16

Calculated

Table I-23: Ethanolysis at 35°C Using Calculated Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	1.452	1.392		1.463	1.402		1.467	1.406	
Std 2	0.899	0.839		0.911	0.850		0.915	0.854	
Std 3	0.607	0.547		0.616	0.555		0.622	0.561	
Std 4	0.060	-	1.3515	0.061	-	1.3611	0.061	-	1.3639
1	0.200	0.140	0.104	0.203	0.142	0.104	0.205	0.144	0.106
2	0.302	0.242	0.179	0.303	0.242	0.178	0.300	0.239	0.175
3	0.388	0.328	0.243	0.392	0.331	0.243	0.392	0.331	0.243
4	0.435	0.375	0.277	0.436	0.375	0.276	0.438	0.377	0.276
5	0.454	0.394	0.292	0.458	0.397	0.292	0.457	0.396	0.290
7	0.621	0.561	0.415	0.619	0.558	0.410	0.622	0.561	0.411
10	0.788	0.728	0.539	0.799	0.738	0.542	0.806	0.745	0.546
12	0.708	0.648	0.479	0.711	0.650	0.478	0.719	0.658	0.482
15	1.028	0.968	0.716	1.035	0.974	0.716	1.039	0.978	0.717
20	1.067	1.007	0.745	1.076	1.015	0.746	1.082	1.021	0.749
25	0.852	0.792	0.586	0.866	0.805	0.591	0.888	0.827	0.606
30	1.175	1.115	0.825	1.187	1.126	0.827	1.188	1.127	0.826
35	1.190	1.130	0.836	1.209	1.148	0.843	1.217	1.156	0.848
40	1.151	1.091	0.807	1.153	1.092	0.802	1.155	1.094	0.802



Time	23	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	1.464	1.403		1.462	1.401	
Std 2	0.916	0.855		0.910	0.850	
Std 3	0.624	0.563		0.617	0.557	
Std 4	0.061	-	1.3606	0.061	0.000	1.3593
1	0.202	0.141	0.104	0.203	0.142	0.104
2	0.305	0.244	0.179	0.303	0.242	0.178
3	0.395	0.334	0.245	0.392	0.331	0.244
4	0.449	0.388	0.285	0.440	0.379	0.279
5	0.458	0.397	0.292	0.457	0.396	0.291
7	0.628	0.567	0.417	0.623	0.562	0.413
10	0.812	0.751	0.552	0.801	0.741	0.545
12	0.719	0.658	0.484	0.714	0.654	0.481
15	1.034	0.973	0.715	1.034	0.973	0.716
20	1.077	1.016	0.747	1.076	1.015	0.747
25	0.882	0.821	0.603	0.872	0.811	0.597
30	1.181	1.120	0.823	1.183	1.122	0.825
35	1.214	1.153	0.847	1.208	1.147	0.844
40	1.162	1.101	0.809	1.155	1.095	0.805

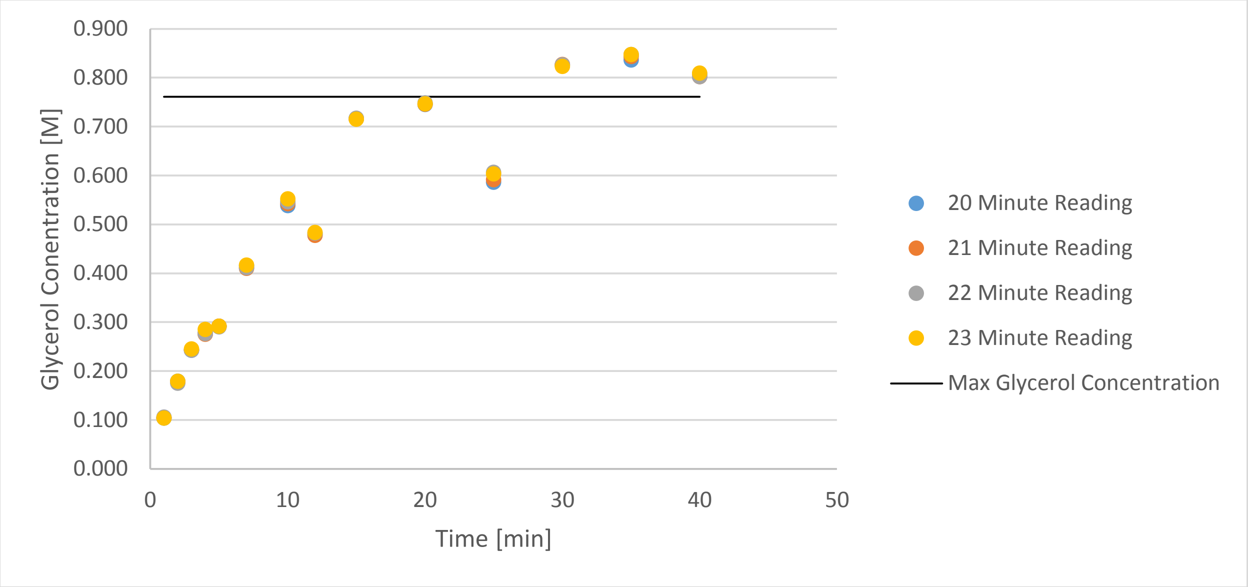


Figure I-72: Ethanolysis at 35°C Using Calculated Calibration Curves

Ideal

Table I-24: Ethanolysis at 35°C Using Ideal Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	23	Adjusted	mol/L
Std 1	1.452	1.392		1.463	1.402		1.467	1.406		1.464	1.403	
Std 2	0.899	0.839		0.911	0.850		0.915	0.854		0.916	0.855	
Std 3	0.607	0.547		0.616	0.555		0.622	0.561		0.624	0.563	
Std 4	0.060	-	1.200	0.061	-	1.2000	0.061	-	1.2000	0.061	-	1.2000
1	0.200	0.140	0.117	0.203	0.142	0.118	0.205	0.144	0.120	0.202	0.141	0.118
2	0.302	0.242	0.202	0.303	0.242	0.202	0.300	0.239	0.199	0.305	0.244	0.203
3	0.388	0.328	0.273	0.392	0.331	0.276	0.392	0.331	0.276	0.395	0.334	0.278
4	0.435	0.375	0.313	0.436	0.375	0.313	0.438	0.377	0.314	0.449	0.388	0.323
5	0.454	0.394	0.328	0.458	0.397	0.331	0.457	0.396	0.330	0.458	0.397	0.331
7	0.621	0.561	0.468	0.619	0.558	0.465	0.622	0.561	0.468	0.628	0.567	0.473
10	0.788	0.728	0.607	0.799	0.738	0.615	0.806	0.745	0.621	0.812	0.751	0.626
12	0.708	0.648	0.540	0.711	0.650	0.542	0.719	0.658	0.548	0.719	0.658	0.548
15	1.028	0.968	0.807	1.035	0.974	0.812	1.039	0.978	0.815	1.034	0.973	0.811
20	1.067	1.007	0.839	1.076	1.015	0.846	1.082	1.021	0.851	1.077	1.016	0.847
25	0.852	0.792	0.660	0.866	0.805	0.671	0.888	0.827	0.689	0.882	0.821	0.684
30	1.175	1.115	0.929	1.187	1.126	0.938	1.188	1.127	0.939	1.181	1.120	0.933
35	1.190	1.130	0.942	1.209	1.148	0.957	1.217	1.156	0.963	1.214	1.153	0.961
40	1.151	1.091	0.909	1.153	1.092	0.910	1.155	1.094	0.912	1.162	1.101	0.918

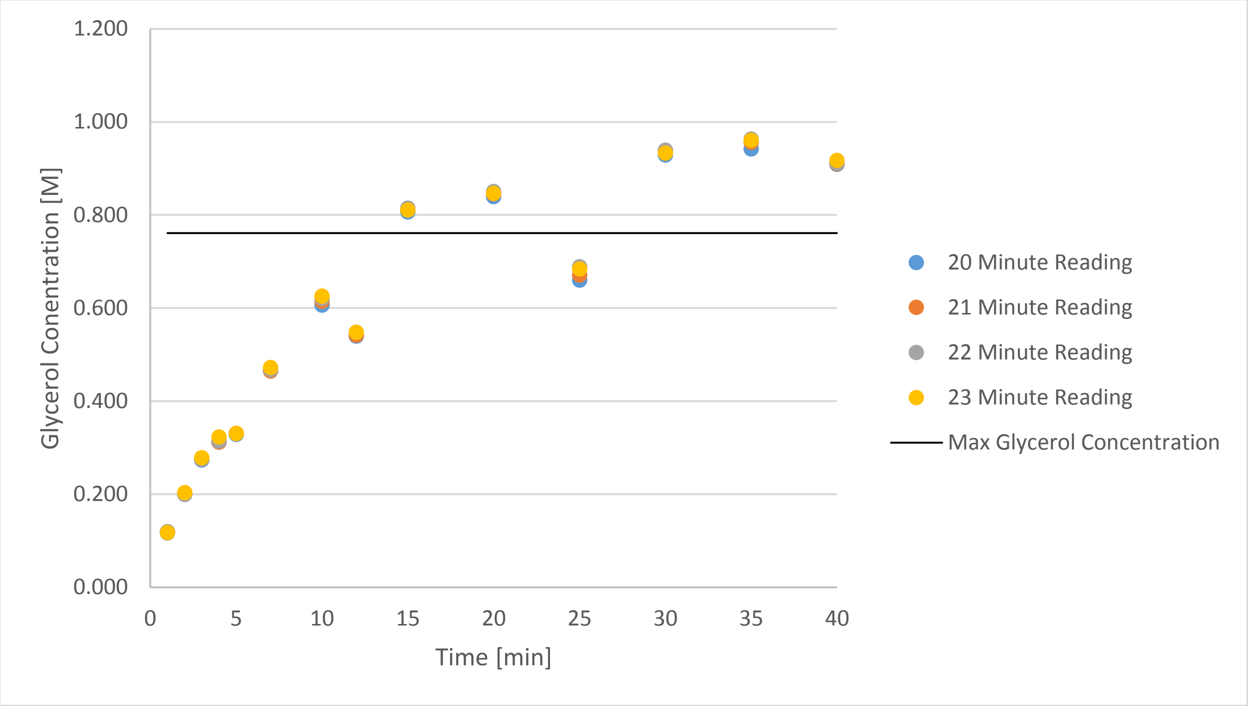


Figure I-73: Ethanolysis at 35°C Using Ideal Calibration Curves

Calibration Curves

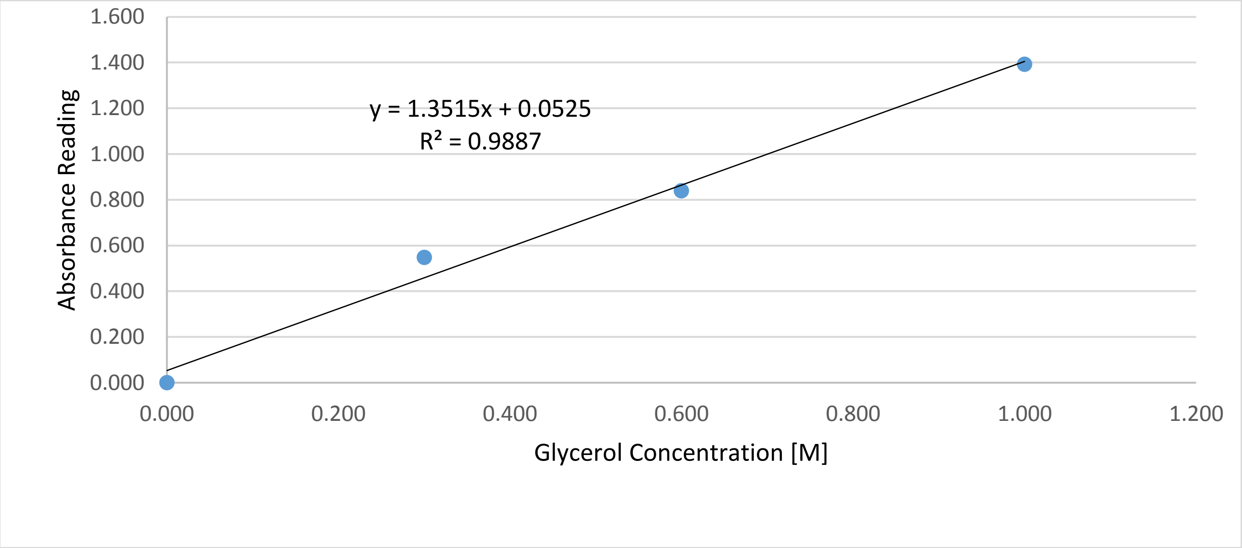


Figure I-74: Calculated Calibration Curve from 20 Minute Reading

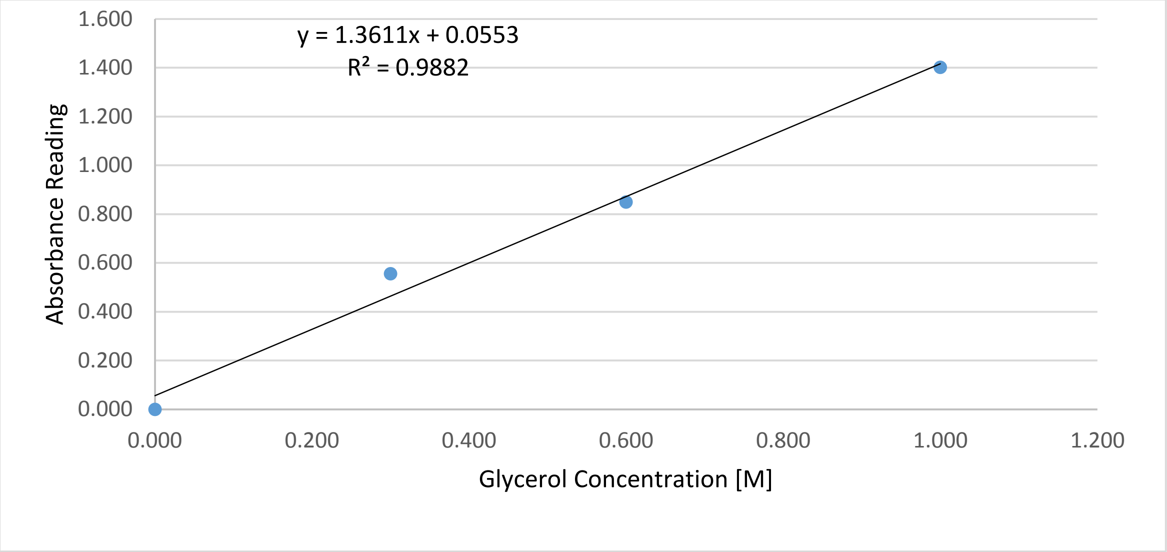


Figure I-75: Calculated Calibration Curve from 21 Minute Reading

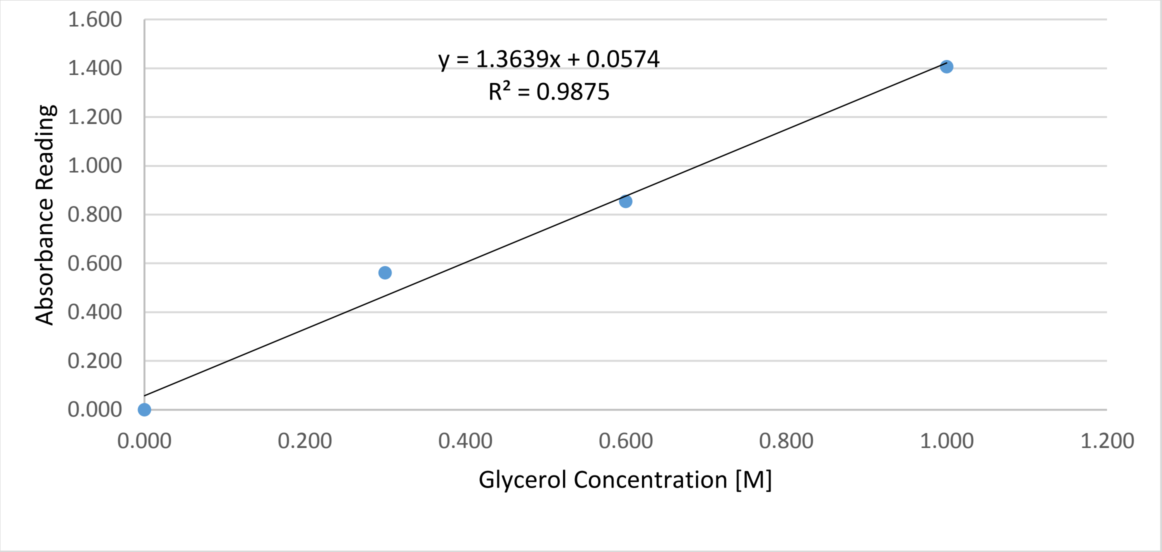


Figure I-76: Calculated Calibration Curve from 22 Minute Reading

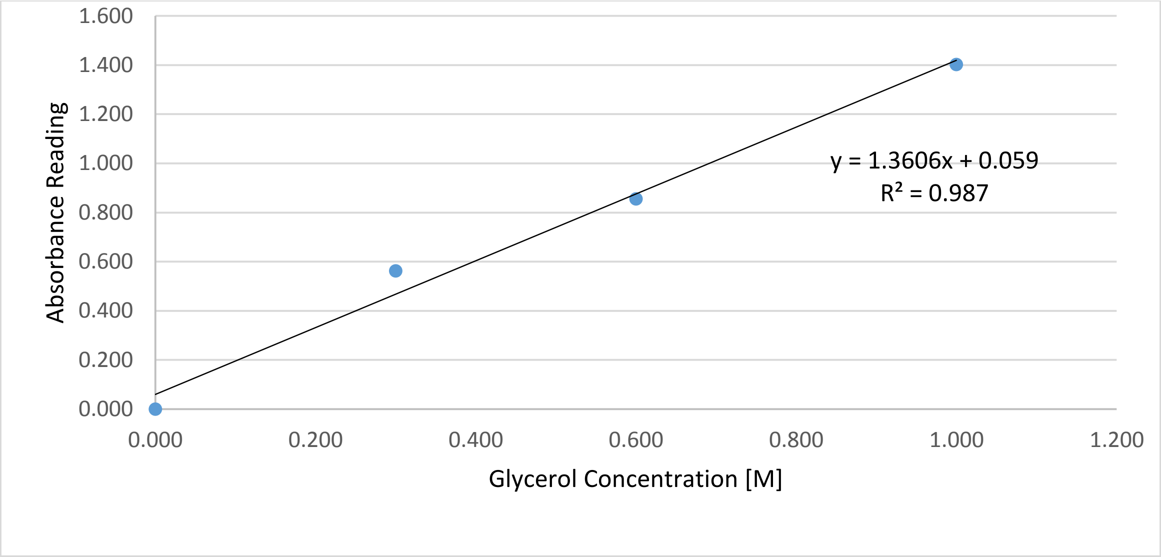
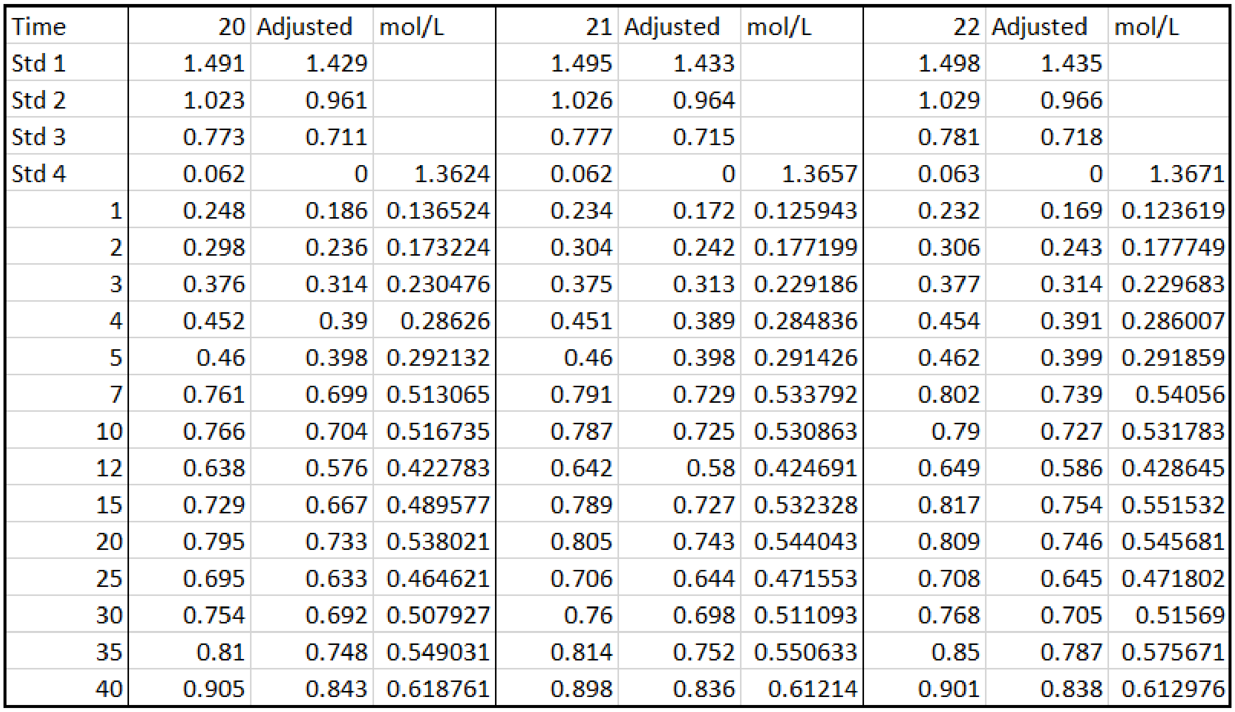


Figure I-77: Calculated Calibration Curve from 23 Minute Reading

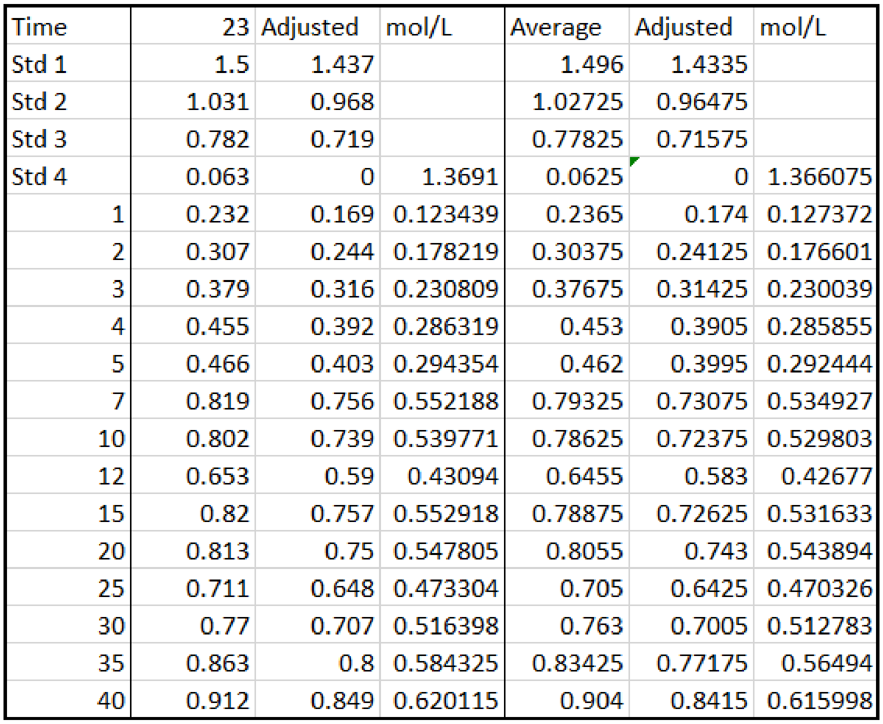
Experiment – 2/27/16

Calculated

Table I-25: Ethanolysis at 45°C Using Calculated Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	1.491	1.429		1.495	1.433		1.498	1.435	
Std 2	1.023	0.961		1.026	0.964		1.029	0.966	
Std 3	0.773	0.711		0.777	0.715		0.781	0.718	
Std 4	0.062	0	1.3624	0.062	0	1.3657	0.063	0	1.3671
1	0.248	0.186	0.136524	0.234	0.172	0.125943	0.232	0.169	0.123619
2	0.298	0.236	0.173224	0.304	0.242	0.177199	0.306	0.243	0.177749
3	0.376	0.314	0.230476	0.375	0.313	0.229186	0.377	0.314	0.229683
4	0.452	0.39	0.28626	0.451	0.389	0.284836	0.454	0.391	0.286007
5	0.46	0.398	0.292132	0.46	0.398	0.291426	0.462	0.399	0.291859
7	0.761	0.699	0.513065	0.791	0.729	0.533792	0.802	0.739	0.54056
10	0.766	0.704	0.516735	0.787	0.725	0.530863	0.79	0.727	0.531783
12	0.638	0.576	0.422783	0.642	0.58	0.424691	0.649	0.586	0.428645
15	0.729	0.667	0.489577	0.789	0.727	0.532328	0.817	0.754	0.551532
20	0.795	0.733	0.538021	0.805	0.743	0.544043	0.809	0.746	0.545681
25	0.695	0.633	0.464621	0.706	0.644	0.471553	0.708	0.645	0.471802
30	0.754	0.692	0.507927	0.76	0.698	0.511093	0.768	0.705	0.51569
35	0.81	0.748	0.549031	0.814	0.752	0.550633	0.85	0.787	0.575671
40	0.905	0.843	0.618761	0.898	0.836	0.61214	0.901	0.838	0.612976



Time	23	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	1.5	1.437		1.496	1.4335	
Std 2	1.031	0.968		1.02725	0.96475	
Std 3	0.782	0.719		0.77825	0.71575	
Std 4	0.063	0	1.3691	0.0625	0	1.366075
1	0.232	0.169	0.123439	0.2365	0.174	0.127372
2	0.307	0.244	0.178219	0.30375	0.24125	0.176601
3	0.379	0.316	0.230809	0.37675	0.31425	0.230039
4	0.455	0.392	0.286319	0.453	0.3905	0.285855
5	0.466	0.403	0.294354	0.462	0.3995	0.292444
7	0.819	0.756	0.552188	0.79325	0.73075	0.534927
10	0.802	0.739	0.539771	0.78625	0.72375	0.529803
12	0.653	0.59	0.43094	0.6455	0.583	0.42677
15	0.82	0.757	0.552918	0.78875	0.72625	0.531633
20	0.813	0.75	0.547805	0.8055	0.743	0.543894
25	0.711	0.648	0.473304	0.705	0.6425	0.470326
30	0.77	0.707	0.516398	0.763	0.7005	0.512783
35	0.863	0.8	0.584325	0.83425	0.77175	0.56494
40	0.912	0.849	0.620115	0.904	0.8415	0.615998

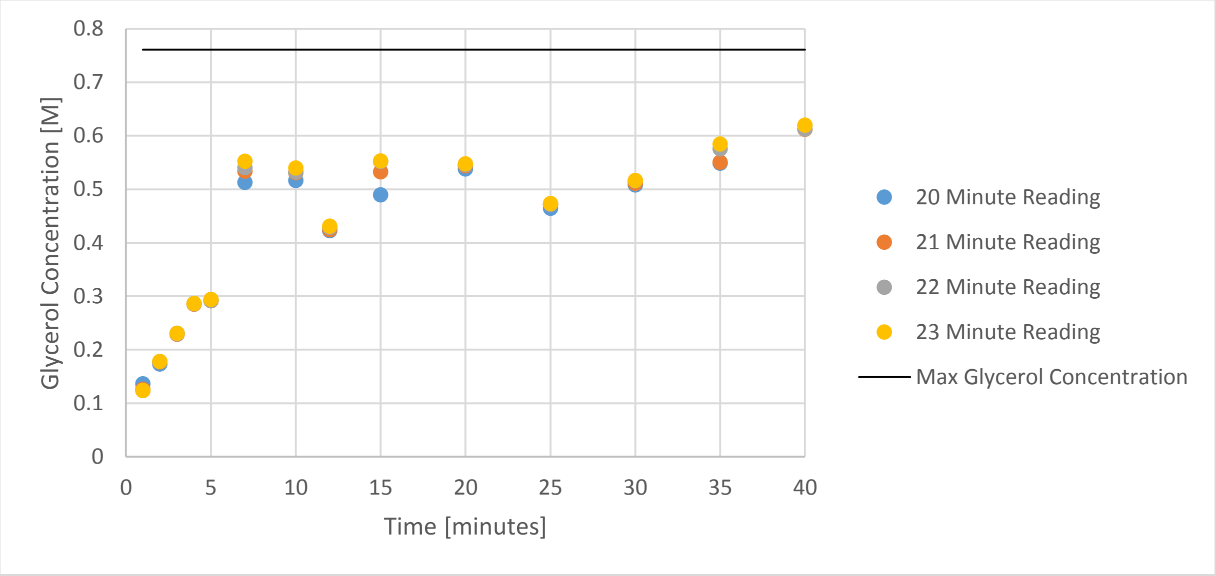
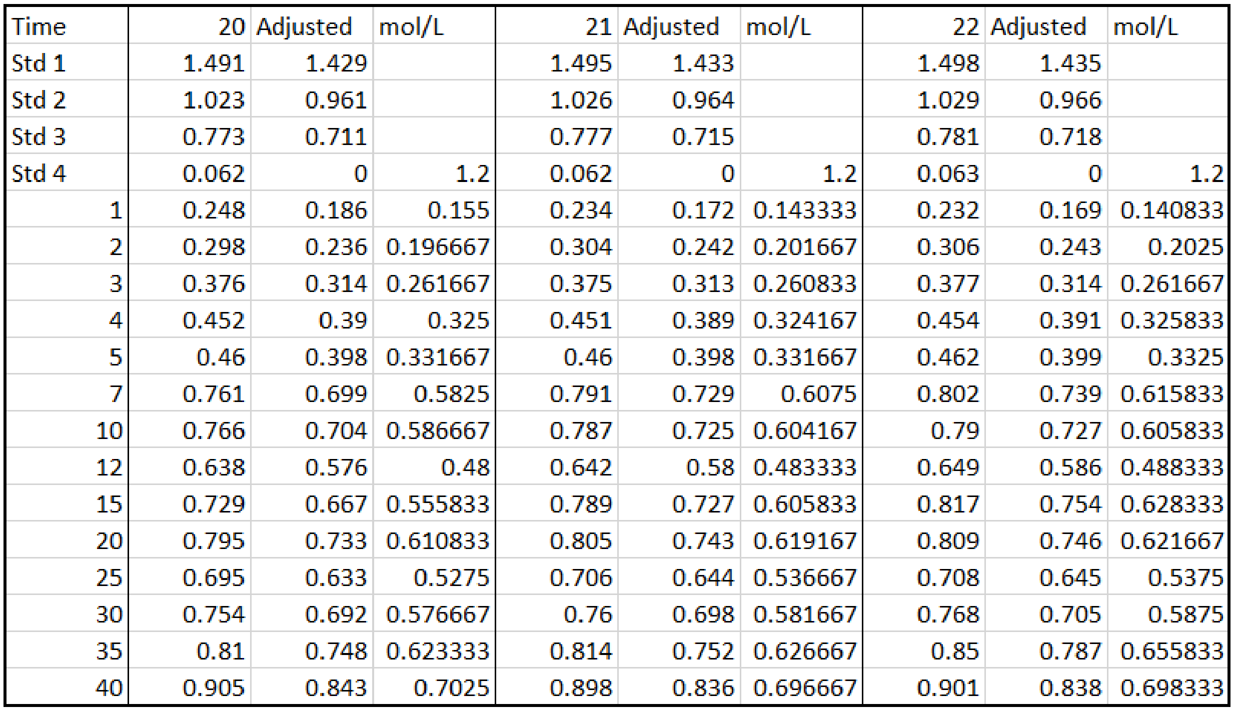


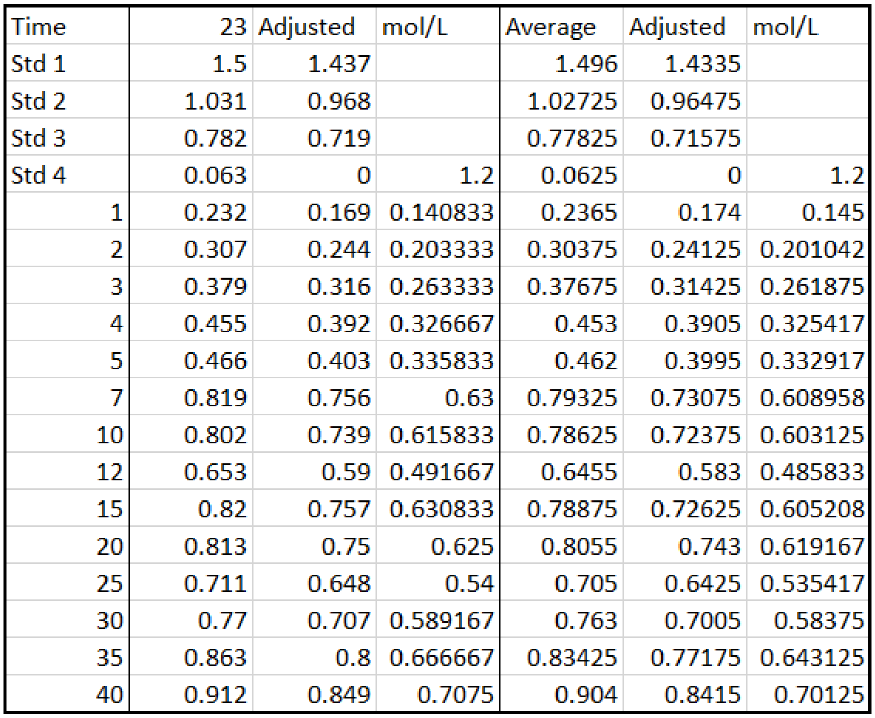
Figure I-78: Ethanolysis at 45°C Using Calculated Calibration Curves

Ideal

Table I-26: Ethanolysis at 45°C Using Ideal Calibration Curves



Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	1.491	1.429		1.495	1.433		1.498	1.435	
Std 2	1.023	0.961		1.026	0.964		1.029	0.966	
Std 3	0.773	0.711		0.777	0.715		0.781	0.718	
Std 4	0.062	0	1.2	0.062	0	1.2	0.063	0	1.2
1	0.248	0.186	0.155	0.234	0.172	0.143333	0.232	0.169	0.140833
2	0.298	0.236	0.196667	0.304	0.242	0.201667	0.306	0.243	0.2025
3	0.376	0.314	0.261667	0.375	0.313	0.260833	0.377	0.314	0.261667
4	0.452	0.39	0.325	0.451	0.389	0.324167	0.454	0.391	0.325833
5	0.46	0.398	0.331667	0.46	0.398	0.331667	0.462	0.399	0.3325
7	0.761	0.699	0.5825	0.791	0.729	0.6075	0.802	0.739	0.615833
10	0.766	0.704	0.586667	0.787	0.725	0.604167	0.79	0.727	0.605833
12	0.638	0.576	0.48	0.642	0.58	0.483333	0.649	0.586	0.488333
15	0.729	0.667	0.555833	0.789	0.727	0.605833	0.817	0.754	0.628333
20	0.795	0.733	0.610833	0.805	0.743	0.619167	0.809	0.746	0.621667
25	0.695	0.633	0.5275	0.706	0.644	0.536667	0.708	0.645	0.5375
30	0.754	0.692	0.576667	0.76	0.698	0.581667	0.768	0.705	0.5875
35	0.81	0.748	0.623333	0.814	0.752	0.626667	0.85	0.787	0.655833
40	0.905	0.843	0.7025	0.898	0.836	0.696667	0.901	0.838	0.698333



Time	23	Adjusted	mol/L	Average	Adjusted	mol/L
Std 1	1.5	1.437		1.496	1.4335	
Std 2	1.031	0.968		1.02725	0.96475	
Std 3	0.782	0.719		0.77825	0.71575	
Std 4	0.063	0	1.2	0.0625	0	1.2
1	0.232	0.169	0.140833	0.2365	0.174	0.145
2	0.307	0.244	0.203333	0.30375	0.24125	0.201042
3	0.379	0.316	0.263333	0.37675	0.31425	0.261875
4	0.455	0.392	0.326667	0.453	0.3905	0.325417
5	0.466	0.403	0.335833	0.462	0.3995	0.332917
7	0.819	0.756	0.63	0.79325	0.73075	0.608958
10	0.802	0.739	0.615833	0.78625	0.72375	0.603125
12	0.653	0.59	0.491667	0.6455	0.583	0.485833
15	0.82	0.757	0.630833	0.78875	0.72625	0.605208
20	0.813	0.75	0.625	0.8055	0.743	0.619167
25	0.711	0.648	0.54	0.705	0.6425	0.535417
30	0.77	0.707	0.589167	0.763	0.7005	0.58375
35	0.863	0.8	0.666667	0.83425	0.77175	0.643125
40	0.912	0.849	0.7075	0.904	0.8415	0.70125

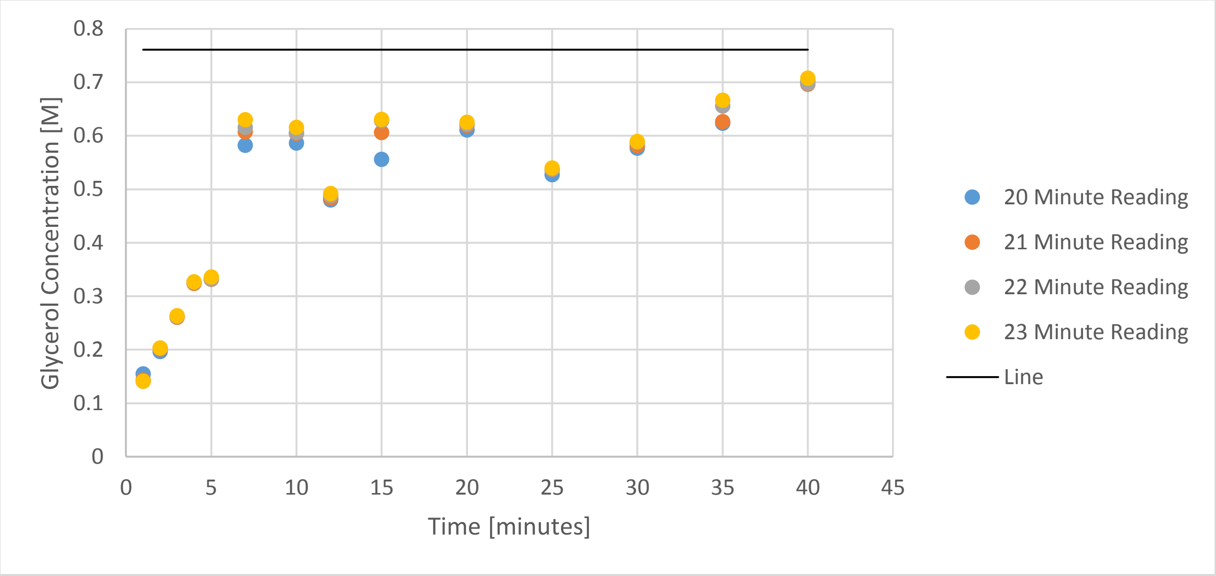


Figure I-79: Ethanolysis at 45°C Using Ideal Calibration Curves

Calibration Curves

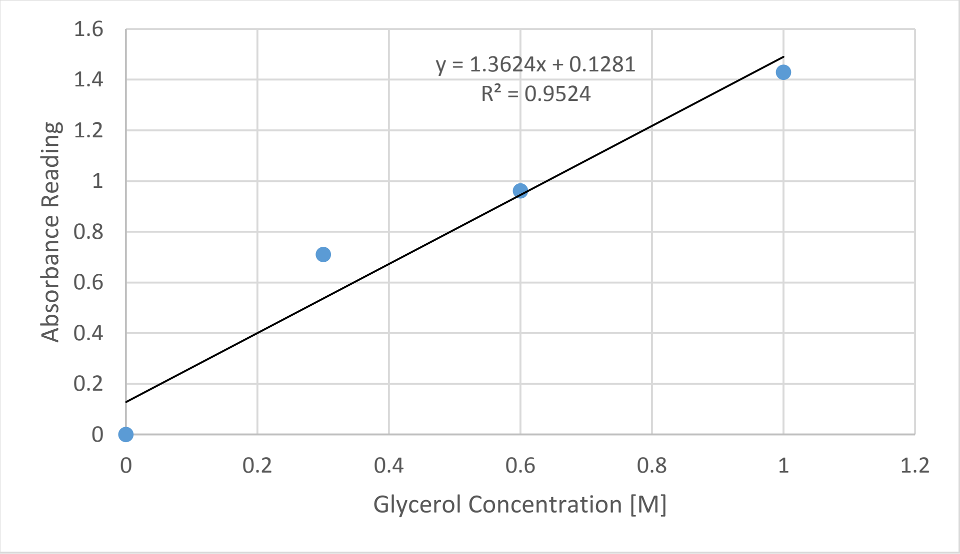


Figure I-80: Calculated Calibration Curve from 20 Minute Reading

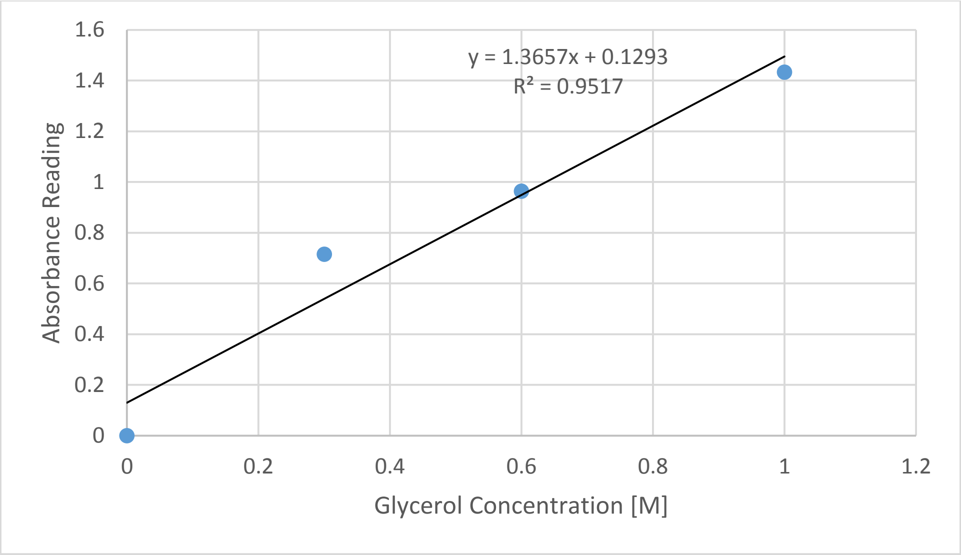


Figure I-81: Calculated Calibration Curve from 21 Minute Reading

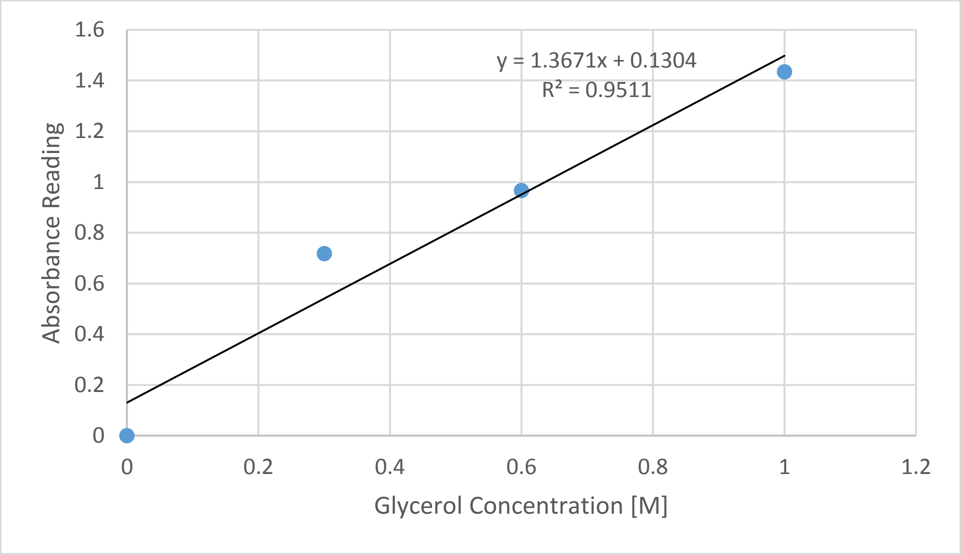


Figure I-82: Calculated Calibration Curve from 22 Minute Reading

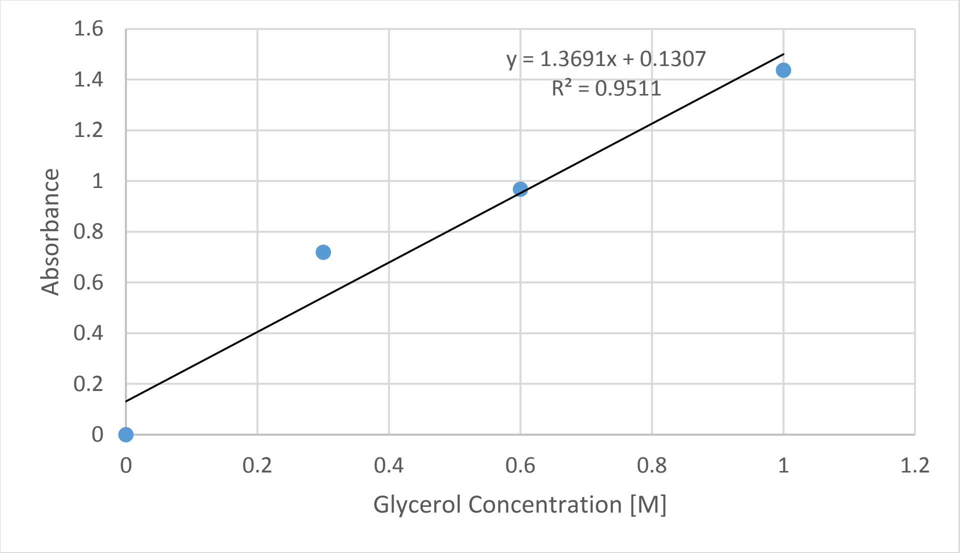


Figure I-83: Calculated Calibration Curve from 23 Minute Reading

Experiment – 3/2/16

Calculated

Table I-27: Ethanolysis at 45°C Using Calculated Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L	AVERAGE	Adjusted	mol/L
Std 1	1.444	1.392		1.450	1.398		1.448	1.396		1.447	1.395	
Std 2	0.968	0.916		0.977	0.925		0.978	0.926		0.974	0.922	
Std 3	0.549	0.497		0.559	0.507		0.559	0.507		0.556	0.504	
Std 4	0.052	-	1.3851	0.052	-	1.3897	0.052	-	1.3880	0.052	0.000	1.3876
1	0.315	0.263	0.190	0.311	0.259	0.186	0.321	0.269	0.194	0.316	0.264	0.190
2	0.381	0.329	0.238	0.386	0.334	0.240	0.390	0.338	0.244	0.386	0.334	0.240
3	0.642	0.590	0.426	0.670	0.618	0.445	0.683	0.631	0.455	0.665	0.613	0.442
4	0.618	0.566	0.409	0.624	0.572	0.412	0.623	0.571	0.411	0.622	0.570	0.411
5	0.481	0.429	0.310	0.492	0.440	0.317	0.502	0.450	0.324	0.492	0.440	0.317
7.66	0.951	0.899	0.649	1.022	0.970	0.698	1.020	0.968	0.697	0.998	0.946	0.682
10	0.948	0.896	0.647	0.957	0.905	0.651	0.984	0.932	0.671	0.963	0.911	0.657
12	1.245	1.193	0.861	1.284	1.232	0.887	1.321	1.269	0.914	1.283	1.231	0.887
15	0.973	0.921	0.665	0.969	0.917	0.660	0.979	0.927	0.668	0.974	0.922	0.664
20	1.085	1.033	0.746	1.096	1.044	0.751	1.099	1.047	0.754	1.093	1.041	0.750
25	1.166	1.114	0.804	1.201	1.149	0.827	1.218	1.166	0.840	1.195	1.143	0.824
30	1.076	1.024	0.739	1.095	1.043	0.751	1.125	1.073	0.773	1.099	1.047	0.754
35	1.116	1.064	0.768	1.205	1.153	0.830	1.280	1.228	0.885	1.200	1.148	0.828
40	0.874	0.822	0.593	0.887	0.835	0.601	0.903	0.851	0.613	0.888	0.836	0.602

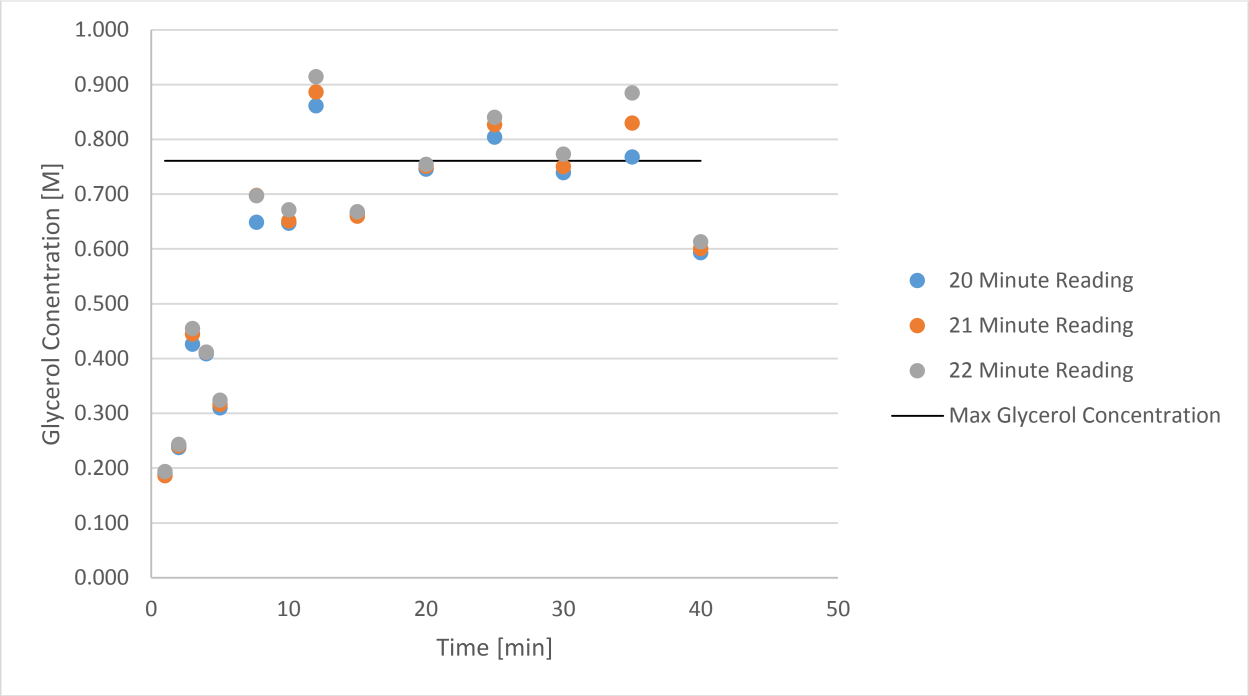


Figure I-84: Ethanolysis at 45°C Using Calculated Calibration Curves

Ideal

Table I-28: Ethanolysis at 45°C Using Ideal Calibration Curves

Time	20	Adjusted	mol/L	21	Adjusted	mol/L	22	Adjusted	mol/L
Std 1	1.444	1.392		1.450	1.398		1.448	1.396	
Std 2	0.968	0.916		0.977	0.925		0.978	0.926	
Std 3	0.549	0.497		0.559	0.507		0.559	0.507	
Std 4	0.052	-	1.200	0.052	-	1.2000	0.052	-	1.2000
1	0.315	0.263	0.219	0.311	0.259	0.216	0.321	0.269	0.224
2	0.381	0.329	0.274	0.386	0.334	0.278	0.390	0.338	0.282
3	0.642	0.590	0.492	0.670	0.618	0.515	0.683	0.631	0.526
4	0.618	0.566	0.472	0.624	0.572	0.477	0.623	0.571	0.476
5	0.481	0.429	0.358	0.492	0.440	0.367	0.502	0.450	0.375
7.66	0.951	0.899	0.749	1.022	0.970	0.808	1.020	0.968	0.807
10	0.948	0.896	0.747	0.957	0.905	0.754	0.984	0.932	0.777
12	1.245	1.193	0.994	1.284	1.232	1.027	1.321	1.269	1.058
15	0.973	0.921	0.768	0.969	0.917	0.764	0.979	0.927	0.773
20	1.085	1.033	0.861	1.096	1.044	0.870	1.099	1.047	0.873
25	1.166	1.114	0.928	1.201	1.149	0.958	1.218	1.166	0.972
30	1.076	1.024	0.853	1.095	1.043	0.869	1.125	1.073	0.894
35	1.116	1.064	0.887	1.205	1.153	0.961	1.280	1.228	1.023
40	0.874	0.822	0.685	0.887	0.835	0.696	0.903	0.851	0.709

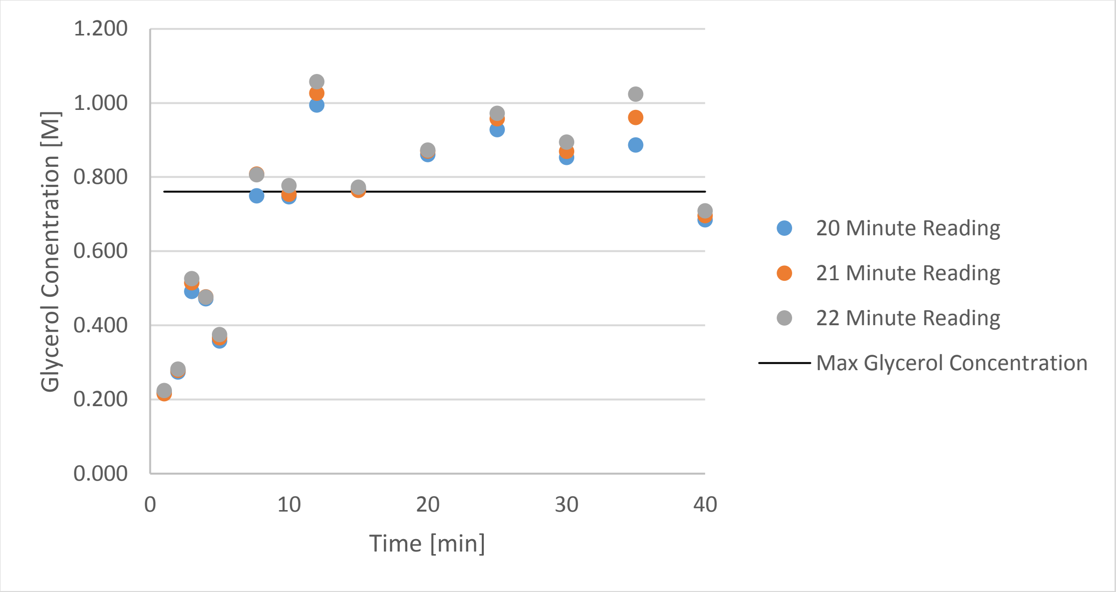


Figure I-85: Ethanolysis at 45°C Using Ideal Calibration Curves

Calibration Curves

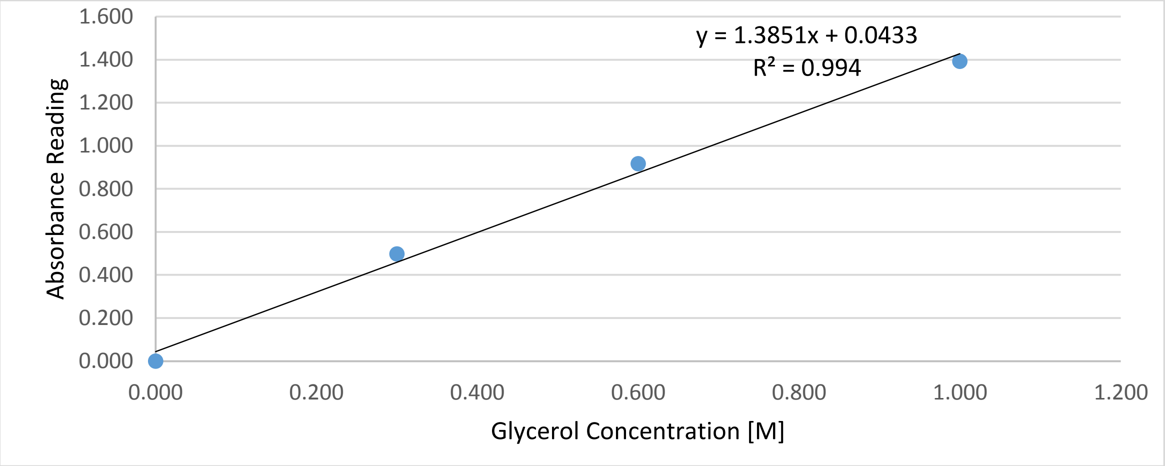


Figure I-86: Calculated Calibration Curve from 20 Minute Reading

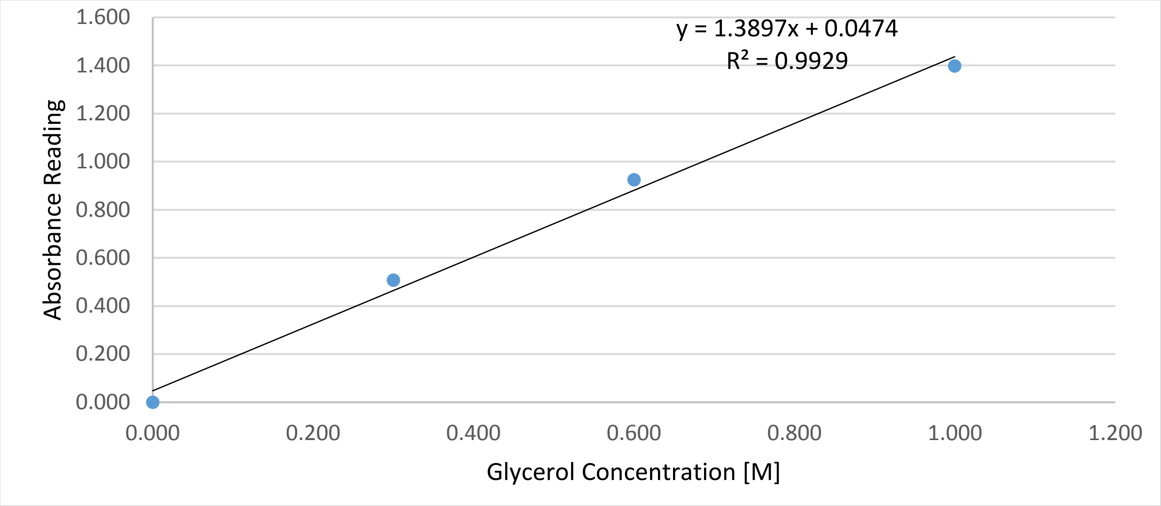


Figure I-87: Calculated Calibration Curve from 21 Minute Reading

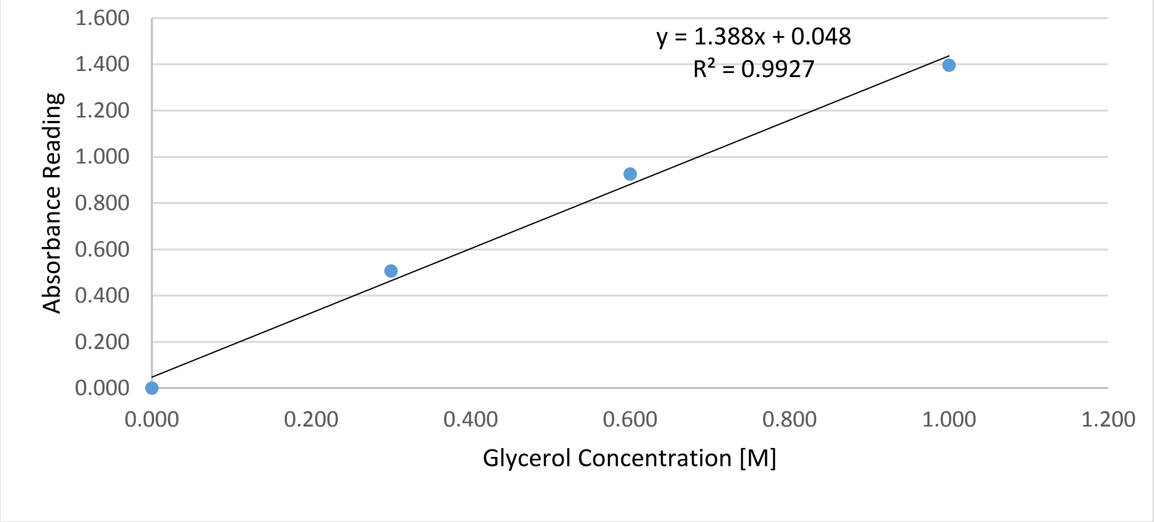
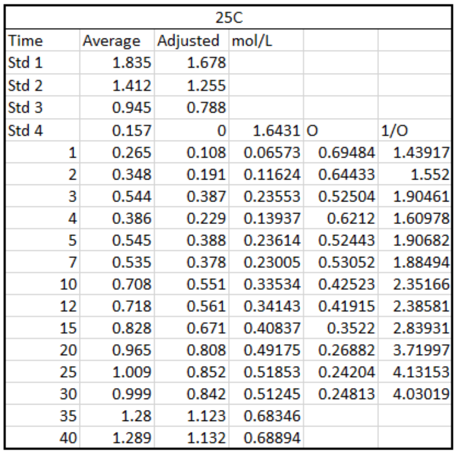


Figure I-88: Calculated Calibration Curve from 22 Minute Reading

J. Calculations for Determining Ethanolysis Rate Constants



25C					
Time	Average	Adjusted	mol/L		
Std 1	1.835	1.678			
Std 2	1.412	1.255			
Std 3	0.945	0.788			
Std 4	0.157	0	1.6431	O	1/O
1	0.265	0.108	0.06573	0.69484	1.43917
2	0.348	0.191	0.11624	0.64433	1.552
3	0.544	0.387	0.23553	0.52504	1.90461
4	0.386	0.229	0.13937	0.6212	1.60978
5	0.545	0.388	0.23614	0.52443	1.90682
7	0.535	0.378	0.23005	0.53052	1.88494
10	0.708	0.551	0.33534	0.42523	2.35166
12	0.718	0.561	0.34143	0.41915	2.38581
15	0.828	0.671	0.40837	0.3522	2.83931
20	0.965	0.808	0.49175	0.26882	3.71997
25	1.009	0.852	0.51853	0.24204	4.13153
30	0.999	0.842	0.51245	0.24813	4.03019
35	1.28	1.123	0.68346		
40	1.289	1.132	0.68894		

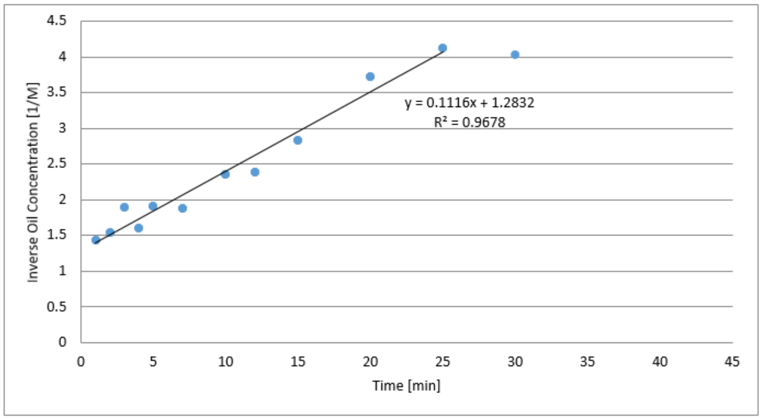
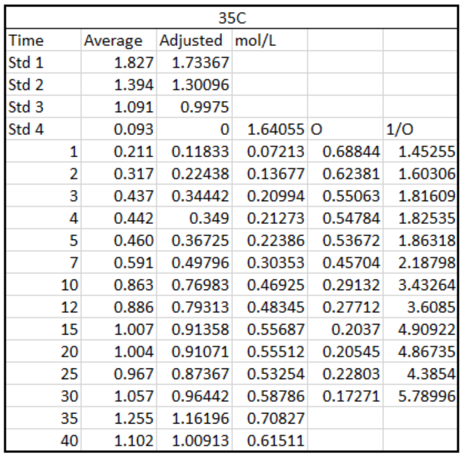


Figure J-1: Calculations for Ethanolysis at 25°C



35C					
Time	Average	Adjusted	mol/L		
Std 1	1.827	1.73367			
Std 2	1.394	1.30096			
Std 3	1.091	0.9975			
Std 4	0.093	0	1.64055	O	1/O
1	0.211	0.11833	0.07213	0.68844	1.45255
2	0.317	0.22438	0.13677	0.62381	1.60306
3	0.437	0.34442	0.20994	0.55063	1.81609
4	0.442	0.349	0.21273	0.54784	1.82535
5	0.460	0.36725	0.22386	0.53672	1.86318
7	0.591	0.49796	0.30353	0.45704	2.18798
10	0.863	0.76983	0.46925	0.29132	3.43264
12	0.886	0.79313	0.48345	0.27712	3.6085
15	1.007	0.91358	0.55687	0.2037	4.90922
20	1.004	0.91071	0.55512	0.20545	4.86735
25	0.967	0.87367	0.53254	0.22803	4.3854
30	1.057	0.96442	0.58786	0.17271	5.78996
35	1.255	1.16196	0.70827		
40	1.102	1.00913	0.61511		

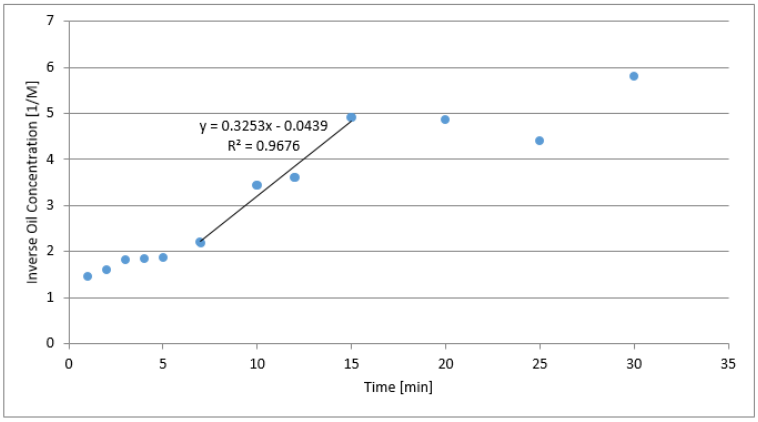
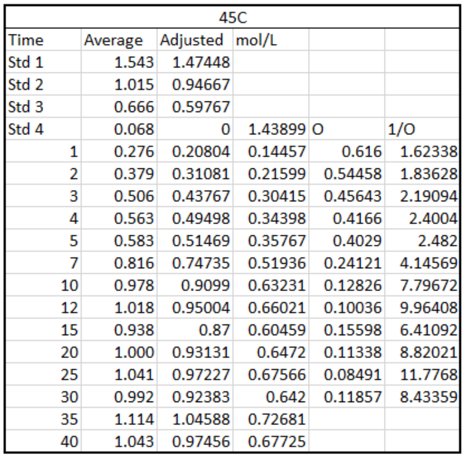


Figure J-2: Calculations for Ethanolysis at 35°C



45C					
Time	Average	Adjusted	mol/L		
Std 1	1.543	1.47448			
Std 2	1.015	0.94667			
Std 3	0.666	0.59767			
Std 4	0.068	0	1.43899	O	1/O
1	0.276	0.20804	0.14457	0.616	1.62338
2	0.379	0.31081	0.21599	0.54458	1.83628
3	0.506	0.43767	0.30415	0.45643	2.19094
4	0.563	0.49498	0.34398	0.4166	2.4004
5	0.583	0.51469	0.35767	0.4029	2.482
7	0.816	0.74735	0.51936	0.24121	4.14569
10	0.978	0.9099	0.63231	0.12826	7.79672
12	1.018	0.95004	0.66021	0.10036	9.96408
15	0.938	0.87	0.60459	0.15598	6.41092
20	1.000	0.93131	0.6472	0.11338	8.82021
25	1.041	0.97227	0.67566	0.08491	11.7768
30	0.992	0.92383	0.642	0.11857	8.43359
35	1.114	1.04588	0.72681		
40	1.043	0.97456	0.67725		

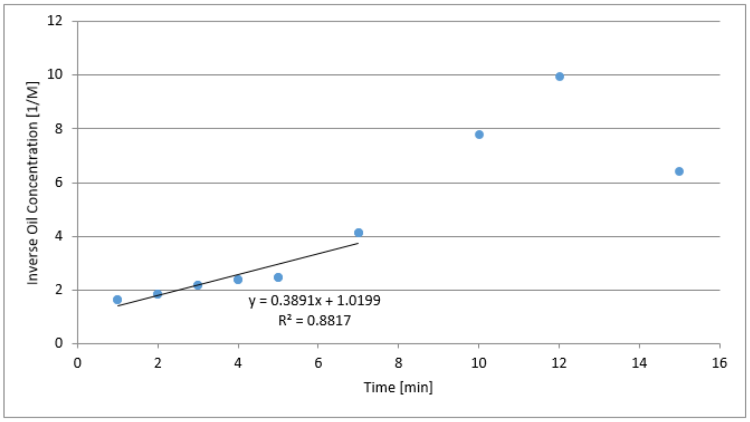
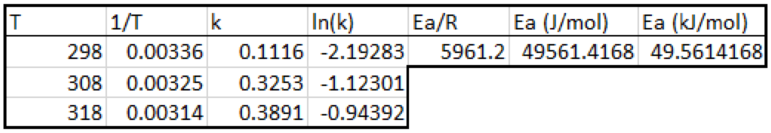


Figure J-3: Calculations for Ethanolysis at 45°C

K. Calculations for Determining Ethanolysis Activation Energy

Table K-1: Summary of Ethanolysis Activation Energy Calculations



T	1/T	k	ln(k)	Ea/R	Ea (J/mol)	Ea (kJ/mol)
298	0.00336	0.1116	-2.19283	5961.2	49561.4168	49.5614168
308	0.00325	0.3253	-1.12301			
318	0.00314	0.3891	-0.94392			

$$\ln(k) = \ln(A) - \frac{E_A}{R}\left(\frac{1}{T}\right)$$

$$R = 8.314\ J/mol \cdot K$$

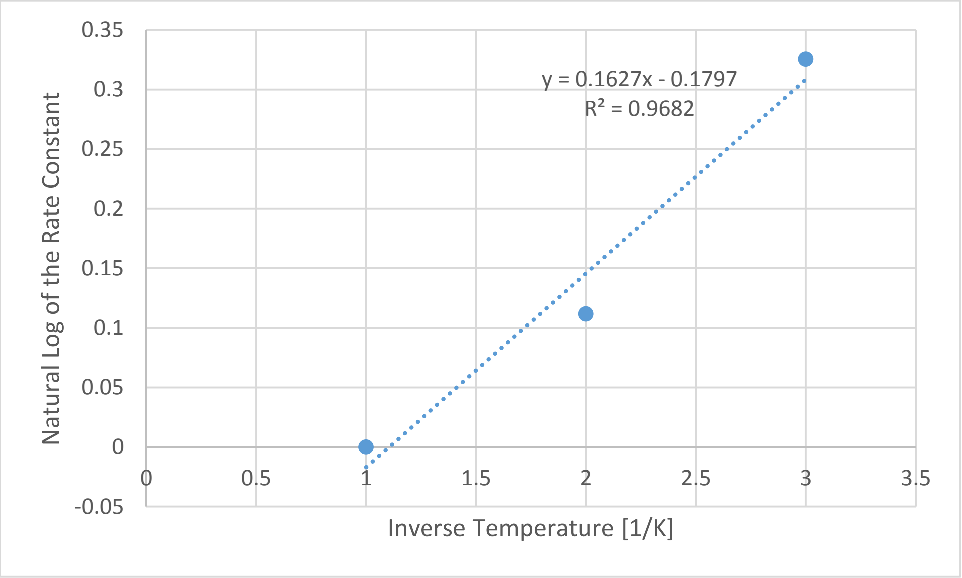


Figure K-1: Ethanolysis Arrhenius Plot

L. Updated Pre-laboratory Exercise

Biodiesel Reaction Safety and Kinetics

Renewable fuels such as ethanol and biodiesel are becoming increasingly popular alternatives to petroleum based fuels. In this laboratory exercise, you will study temperature and mass transfer effects on the base-catalyzed transesterification reaction used to produce biodiesel from vegetable oil. In addition to studying the fundamental chemical engineering principles required to optimize the reaction, you will study the safety requirements for this process and gain experience with following a standard operating procedure and maintaining an electronic batch record.

The overall reaction for production of biodiesel from vegetable oil is shown in Figure 1.

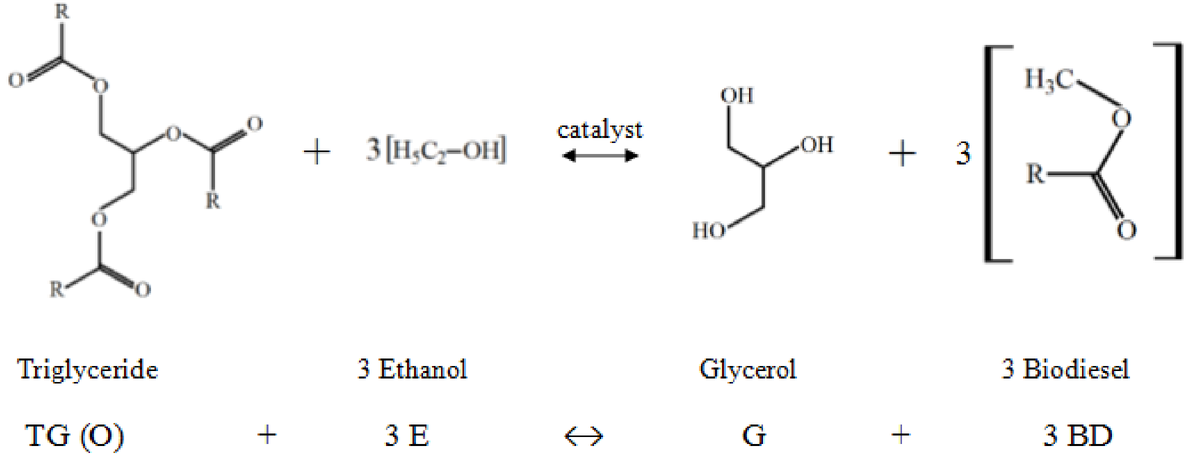


Figure 1. Overall biodiesel production reaction [1][1].

Vegetable oil is primarily composed of triglycerides with long chain aliphatic R groups of the form $CH_3(CH_2)_7CH{=}CH(CH_2)_7$, but different types of oils have different amounts of saturated and unsaturated fats of various types in the R groups [2]. The ethyl esters, also called fatty acid ethyl esters (FAEEs), are the biodiesel product we seek. The reaction can be either base-catalyzed or acid catalyzed. Vegetable oil can be burned directly but is not a good engine fuel due to its high viscosity. Transesterification converts the high viscosity oil into three biodiesel molecules with viscosity and other properties similar to those of petroleum diesel fuel [3].

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[1] Modified for ethanol

The apparent simplicity of the process along with the readily available supply of waste vegetable oil from deep fry food preparation has given rise to a large number of small scale and “home brew” processors who usually use potassium hydroxide as a catalyst. As you will learn in this laboratory experiment, this base-catalyzed biodiesel process is neither particularly simple nor particularly safe. Ethanol is both poisonous and highly flammable. KOH is caustic and when mixed with ethanol forms an extremely dangerous potassium ethoxide solution. Your first objective for the pre-lab exercise will be to obtain and read the MSDS information for KOH, ethanol, and potassium ethoxide. You will need to write a brief discussion of the safety precautions required for handling and processing these materials and the safeguards we have included in the lab. Your second objective for the pre-lab will be to locate (on the web or elsewhere) a report of an accident involving a fire with this process. You will need to write a brief summary of the accident and a discussion of what could have been done to prevent it.

We have converted a 5 ft wide fume hood into a mini biodiesel pilot plant. Our computer controlled reactor system consists of a 250 mL jacketed glass catalyst preparation reactor and a 500 ml jacketed glass process reactor connected to feed and product vessels and each other via peristaltic pumps [4]. Sparkless and brushless overhead electronic stirrers are used to control and monitor the stirrer rpms and torque in each reactor. A constant temperature is maintained with a separate temperature bath circulating water through the jacket of each reactor. Using a computer control panel outside of the hood to operate the process gives it the feel of a larger scale industrial process and minimizes some of the dangers from the hazardous and flammable materials involved.

For a typical experiment, ethanol and vegetable oil are introduced into the catalyst prep reactor and process reactor, respectively, by computer controlled gravimetric dosing from feed vessels on electronic balances working together with the peristaltic pumps. Once both reactors reach the target temperature, solid KOH catalyst is manually added and dissolved in the catalyst prep reactor. The process reaction is initiated by pumping the contents of the catalyst prep reactor into the process reactor. Samples are withdrawn from the process reactor at regular intervals and analyzed for glycerol content via an enzymatic assay to follow the reaction progress [5]. At the end of the experiment all samples can be analyzed at once using a 96 well plate reader at a wavelength of 570 nm. The reactor system is washed with ethanol and allowed to air dry between experimental runs. The ReactorMaster software [4] that controls the process also collects data on each piece of equipment, allows for pauses to insert comments, and effectively keeps and electronic batch record of everything that happens in each experimental run. You will be required to input comments into the batch record indicating that you have either performed or witnessed various aspects of the standard operating procedure as is often required in the bioprocess industry.

As noted above, the biodiesel production process is more complex than it may seem from looking at Figure 1. It has been observed that the production process depends on the type of alcohol used, type of oil used, the water and free fatty acid content of the oil, the type and amount of catalyst, the alcohol to oil ratio, and operating conditions such as temperature, pressure, and mixing rate [6,7]. The reaction is believed to involve multiple steps as indicated in Figure 2 where it can be seen that triglyceride (TG) is first attacked by ethoxide ion C2H5O- (present in the basic KOH/ethanol solution) to produce one biodiesel (BD) and a diglyceride (DG). The DG is next converted to a second BD and a monoglyceride (MG). Finally, in a third reaction step, the MG is converted to a third BD and glycerol (G). Each of these reactions can be considered reversible, giving rise to a forward and a reverse rate constant for each of the three reactions. Side reactions that produce soap (via saponification) instead of biodiesel often occur, especially if water is present in the mixture, but we will neglect side reactions in our analysis. Researchers have shown that in cases with sufficient stirring, experimental data can be modeled using only the reversible reactions shown in Figure 2.

$$\mathrm{TG} + \mathrm{M} \leftrightarrow \mathrm{BD} + \mathrm{DG} \tag{1}$$
$$\mathrm{DG} + \mathrm{M} \leftrightarrow \mathrm{BD} + \mathrm{MG} \tag{2}$$
$$\mathrm{MG} + \mathrm{M} \leftrightarrow \mathrm{BD} + \mathrm{G} \tag{3}$$

Figure 2. Multiple step biodiesel reaction mechanism

For example, Vicente et al [8] studied the base-catalyzed transesterification of sunflower oil with 6:1 mole ratio of methanol to oil and stirring rates that they believed were sufficient to avoid mass transfer limitations. They varied the KOH catalyst concentration and the process temperature and measured the concentration of TG, DG, MG, BD, M, and G with time during the reaction. Assuming that the forward rate constants for reaction 1, 2, and 3 are given by k1, k3, and k5, while the reverse rate constants for the three reactions are given by k2, k4, and k6, they found the values of the rate constants that fit their data according to the mathematical model shown in Figure 3.

$$\begin{gathered}
TG'(t) = -k1\cdot TG(t)\cdot M(t) + k2\cdot BD(t)\cdot DG(t) \\
DG'(t) = k1\cdot TG(t)\cdot M(t) - k2\cdot BD(t)\cdot DG(t) - k3\cdot DG(t)\cdot M(t) + k4\cdot BD(t)\cdot MG(t) \\
MG'(t) = k3\cdot DG(t)\cdot M(t) - k4\cdot BD(t)\cdot MG(t) - k5\cdot MG(t)\cdot M(t)) + k_6\cdot BD(t)\cdot G(t) \\
M'(t) = -k1\cdot TG(t)\cdot M(t) + k2BD(t)\cdot DG(t) - k3\cdot DG(t)\cdot M(t) + k4\cdot BD(t)\cdot MG(t) - k5\cdot MG(t)\cdot M(t)+k6\cdot BD(t)\cdot G(t) \\
BD'(t)= k1\cdot TG(t)\cdot M(t) - k2\cdot BD(t)\cdot DG(t) + k3\cdot DG(t)\cdot M(t) - k4\cdot BD(t)\cdot MG(t) + k5\cdot MG(t)\cdot M(t) - k6\cdot BD(t)\cdot G(t) \\
G'(t) = k5\cdot MG(t)\cdot M(t) - k6\cdot BD(t)\cdot G(t)
\end{gathered}$$

Figure 3. Mathematical model equations for multistep biodiesel reaction shown in Figure 2.

Note that in the mathematical model, the symbol TG'(t) represents the time derivative of the triglyceride concentration, dTG/dt. At 35°C and 0.5 weight percent KOH (on a percent weight of oil basis) they found the following rate constants with units of L/(mol min): k1=0.20, k2=0.98, k3=1.67, k4= 2.18, k5=0.27, and k6=0.01 (sufficiently small that it has been omitted in the model). A Mathcad file that solves this model is available on the course website for your use.

In your experiments you will use canola oil rather than sunflower oil, ethanol rather than methanol, and will only be able to follow overall reaction conversion by following the glycerol concentration with time. It will, therefore, be difficult, if not impossible, to fit all six rate constants to your data. Some researchers have suggested that it is advantageous to consider the methanolysis reaction in three stages: a brief initial mixing/mass transfer limited stage, an irreversible chemical reaction controlled stage, and a reversible equilibrium reaction controlled stage near the end [9]. These authors have further suggested that the pseudo 2nd order reaction:

$$O'(t) = dO(t)/dt = -k\, O(t)^2$$

provides an approximate model for the overall reaction shown in Figure 1, at least in the middle stage. Others have suggested that the initial mass transfer controlled reaction is not observed in the production of ethyl esters [10].

You will want to test this hypothesis using the Mathcad model of the reaction at 35°C. That is, use the multistep model results for concentration with time to test if a 2nd order model could fit those results and determine the pseudo 2nd order rate constant, k. You should consult a chemical reaction engineering text for information on how to fit reaction data to a 2nd order model. Note that in the 2nd order model for oil (O) of Equation 4 there is no accounting for DG or MG, and the total oil concentration, O, is used instead of TG. To compare the results of this simple model to those of the multistep Mathcad model that solves the equations in Figure 3, you will need to follow total oil, O=TG+DG+MG, as indicated in the multistep Mathcad model.

For your lab exercise and final report, you will want to assume a pseudo 2nd order overall reaction and study the temperature dependence and evaluate an activation energy for canola oil conversion to BD with 0.5 weight % KOH and 6:1 ethanol to oil ratio. You will also want to discuss any mass transfer limitations of the reaction. For the pre-lab you should explain how you will study the temperature dependence, evaluate the activation energy, and study the mass transfer limitations. Densities and molecular weights for reactants and products are given in Table 1.

Table 1. Densities and molecular weights of canola biodiesel reactants and products [11][2].

Component	Density (g/ml)	Molecular Weight (g/mol)
canola oil	0.92	887.3
ethanol	0.789	46.1
glycerol	1.26	92.1
biodiesel	0.88	297.1

Summary of deliverables for your pre-lab report:

1. Locate, copy, and read the MSDS for ethanol, KOH, and potassium ethoxide.

2. Write a brief discussion of the safety precautions needed in handling and processing these materials and include a brief discussion of the safeguards we have included to conduct this reaction safely.

3. Locate (on the web or elsewhere) a report of an accident involving a fire in biodiesel production. Write a brief summary of the accident and a discussion of what could have been done to prevent it.

4. Use the data generated in the Mathcad file that solves the multistep biodiesel reaction mathematical model to test the validity of using a pseudo 2nd order rate equation for sunflower oil at 35°C, 0.5 weight % KOH, and 6:1 methanol to oil ratio. Report the pseudo 2nd order rate constant.

5. Explain how you will study the temperature dependence and evaluate the activation energy for a pseudo 2nd order rate equation using canola oil in the lab.

6. Explain how you will investigate any mass transfer limitations of the transesterification reaction in the lab.

---

[2] Modified for ethanol

References

1. http://upload.wikimedia.org/wikipedia/commons/7/72/Generic_Biodiesel_Reaction1.gif

2. http://www.scientificpsychic.com/fitness/fattyacids1.html

3. Van Gerpen, J., Biodiesel processing and production, Fuel Processing Technology, 86, 1097-1107, (2005).

4. http://syrris.com/batch-products/globe-chemical-reactor

5. http://www.bioassaysys.com/file_dir/EGLY.pdf

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