

2013

Synthesis Of Biodiesel From Animal Fat And Polymerization Of Glycerin

Zixu Zhang

North Carolina Agricultural and Technical State University

Follow this and additional works at: <https://digital.library.ncat.edu/theses>

Recommended Citation

Zhang, Zixu, "Synthesis Of Biodiesel From Animal Fat And Polymerization Of Glycerin" (2013). *Theses*. 318.

<https://digital.library.ncat.edu/theses/318>

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at Aggie Digital Collections and Scholarship. It has been accepted for inclusion in Theses by an authorized administrator of Aggie Digital Collections and Scholarship. For more information, please contact iyanna@ncat.edu.

Synthesis of Biodiesel from Animal Fat and Polymerization of Glycerin

Zixu Zhang

North Carolina A&T State University

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department: Chemistry

Major: Chemistry

Major Professor: Dr. Mufeed Basti

Greensboro, North Carolina

2013

School of Graduate Studies
North Carolina Agricultural and Technical State University
This is to certify that the Master's Thesis of

Zixu Zhang

has met the thesis requirements of
North Carolina Agricultural and Technical State University

Greensboro, North Carolina
2013

Approved by:

Mufeed Basti, Ph.D
Major Professor

Alex Williamson, Ph.D
Committee Member

Marion Franks, Ph.D
Committee Member

Margaret Kanipes, Ph.D
Department Chair

Sanjiv Sarin, Ph.D
Dean, The Graduate School

© Copyright by

Zixu Zhang

2013

Biographical Sketch

Zixu Zhang was born on March 30th, 1984 in Beijing, China as the only child of Hong Zhang and Yi Guo. His K-12 grade schools years were all spent at Xicheng District in Beijing. He received the Bachelor of Science degree in Chemistry from North Carolina A&T State University in 2009. Zixu Zhang is a candidate for the Master of Science in Chemistry at North Carolina A&T State University.

Acknowledgements

It is with my great appreciation I acknowledge the support and help of my research advisor Dr. Mufeed Basti who sacrificed a lot to make the completion of my M.S. degree in Chemistry happen. He has guided me a path which has led me a more dedicated, mature, and educated person. I am forever grateful.

I would also like to thank the entire NC A&T University Chemistry Department from which I received support and help in my graduate study life. From the bottom of my heart, I would like to give special thanks to Mrs. Carolyn W. Mayo for her hard work and dedication towards the Chemistry Department.

Table of Contents

List of Figures	vii
List of Tables	ix
Abstract	2
CHAPTER I Synthesis of Biodiesel from Animal Fat	3
1.1 Introduction.....	3
1.2 Materials and Methods.....	6
1.2.1 Materials.	6
1.2.2 Methods.....	6
1.2.2 (A) Production of refined fat.....	6
1.2.2 (B) Thermal gravimetric analysis (TGA).	6
1.2.2 (C) Saponification.	7
1.2.2 (D) Acid/base titration to determine free fatty acids (FFA).	7
1.2.2 (E) Production and characterization of biodiesel.....	7
1.3 Results and Discussion	7
1.4 Conclusions.....	14
CHAPTER II Polymerization of Glycerin.....	15
2.1 Introduction.....	15
2.2 Materials and Methods.....	17
2.2.1 Experimental procedures.	17
2.2.2 Methods.....	17
2.2.2 (A) FT-IR.....	17
2.2.2 (B) ^1H NMR and ^{13}C NMR.....	18

2.2.2 (C) Viscometer.....	18
2.3 Results and Discussion	18
2.4 Conclusions.....	29
References.....	30

List of Figures

Figure 1-1. A scheme for esterification reaction between free fatty acids and an alcohol.	4
Figure 1-2. A scheme for transesterification reaction.....	4
Figure 1-3. TGA patterns of refined fat.	8
Figure 1-4. Obtained homogeneous liquid after the transesterification.....	8
Figure 1-5. 45 minutes after adding adding 200 μ L of DI water to 10 ml of homogenous liquid.	10
Figure 1-6. IR spectrum of the upper layer.....	10
Figure 1-7. IR spectrum of the bottom layer.....	11
Figure 1-8. IR spectrum of methanol.....	12
Figure 1-9. IR spectrum of glycerin.....	12
Figure 1-10. IR spectrum of biodiesel that is made from vegetable oil.....	13
Figure 2-1. A scheme for the formation of a dimer.	15
Figure 2-2. IR spectra of trimer, pentamer, heptamer and decamer polyglycerins.	20
Figure 2-3. ^1H NMR spectra of glycerin, trimer, pentamer, heptamer, and decamer.....	21
Figure 2-4. ^{13}C NMR spectra of glycerin, trimer, pentamer, heptamer, and decamer.....	22
Figure 2-5. The viscosity versus the degree of polymerization.	22
Figure 2-6. Viscosity of glycerin vs temperature.....	23
Figure 2-7. Viscosity of polyglyerin vs temperature.	23
Figure 2-8. A plot of mass of water that is reduced every five minutes vs time.	24
Figure 2-9. Total mass of water vs time.	24
Figure 2-10. IR Plot of glycerin (absorbance vs frequency).....	25
Figure 2-11. IR plot of glycerin from 1000 cm^{-1} to 1250 cm^{-1} (absorbance vs frequency).	25

Figure 2-12. A 3D plot of Figure 2-10.....	26
Figure 2-13. Absorbance of OH group vs sample number.	26
Figure 2-14. A 3D plot of IR spectrum from 2600 cm^{-1} to 3800 cm^{-1}	27
Figure 2-15. Multivariate Curve Resolution of 24 samples.....	27
Figure 2-16. IR spectra of 4 different polyglycerin samples.	28

List of Tables

Table 1-1 Titration Data.....	9
Table 1-2 Assignment of major peaks in the IR spectrum of the upper layer	10
Table 1-3 Assignment of major peaks in the IR spectrum of the bottom layer	11
Table 1-4 Assignment of major peaks in the IR spectrum of methanol	12
Table 1-5 Assignment of major peaks in the IR spectrum of glycerin	13
Table 1-6 Assignment of major peaks in the IR spectrum of biodiesel that is made from biodiesel	13
Table 2-1 Mass of glycerin used, theoretical mass of water eliminated and actual mass of water eliminated when polyglycerins were made.....	19
Table 2-2 The assigned peaks with the corresponding functional groups	21

Abstract

Biodiesel was synthesized using raw beef fat using esterification and transesterification reaction. The obtained biodiesel-glycerin mixture was tested using Fourier transform infrared resonance (FT-IR) and compared with the FT-IR of raw beef fat, glycerin, biodiesel made from vegetable oil and commercial biodiesel. The FT-IR spectrum of the synthesized biodiesel was identical to that of biodiesel made from vegetable oil.

Poly-glycerin was synthesized from glycerin by water elimination reaction, where solid NaOH was used as a catalyst under a stream of nitrogen gas. The water-elimination reaction obeys the “N-1” rule. “N-1” is the degree of polymerization and “N” is the number of glycerin molecules. The polymers were produced either by batch synthesis or continuous synthesis. In the former, the trimer, pentamer, heptamer, and the decamer were individually synthesized. In the latter, a higher degree of polymers were produced by continuously heating glycerin where the mass of water that was reduced from the reaction was monitored and samples of the polymer were obtained at regular time. FT-IR samples were acquired and the viscosity of the glycerin and the final product was obtained at different temperatures. FT-IR, viscosity, ^1H and ^{13}C nuclear magnetic resonance (^1H and ^{13}C NMR), and principal component analysis (PCA) based on FT-IR data were used to monitor and study the polymerization process. The results indicate that among the spectroscopy methods that we used, FT-IR yields consistent data on monitoring the polymerization reaction. PCA calculations indicate that the amount of dimer peaks an hour after the initiation of the polymerization reaction then it goes down as higher- degree polymers are made.

CHAPTER I

Synthesis of Biodiesel from Animal Fat

1.1 Introduction

Fuels play a major role in the world's economy. Energy needs have been supplied mainly by the petroleum-based and coal-based fuels (Venu BabuBorugadda, 2012). However, these two types of fuels have created negative influences on the ecosystem including the emission of pollutant gases like CO₂, NO_x and SO_x from burning of these fuels (ShahidEM, 2008). Other negative factors such as increasing prices and uncertainties of irreversible consumption of petroleum and coals are concerns as well. These factors have stimulated researches for alternative sources of fuels which can be produced from renewable feedstock (Daming Huang, 2012; May Ying Koh, 2011). One of these alternatives is bio-fuels such as biodiesel. Biodiesel has been considered as one of the most promising alternative fuels because it is renewable, biodegradable and non-toxic (Fazal, Haseeb, & Masjuki, 2011). Moreover, the use of such fuels in engines can reduce the exhaust emission of greenhouse gases, unburned hydrocarbons, poly-aromatics as well as NO_x and SO_x (Diya'uddeen, Aziz, & Daud, 2012; Santacesaria & Vicente, 2012; Venu BabuBorugadda, 2012).

Biodiesel is a fatty acid alkyl ester which can be derived from the trans-esterification reaction of vegetable oils or animal fats. Oils and fats are basically triglycerides that are not suitable for the use as fuel. However, upon trans-esterification triglycerides can be converted to glycerol and esters. Esters are then collected as biodiesel (Diya'uddeen et al., 2012; Fazal et al., 2011).

Esterification and trans-esterification reactions are currently the most favored reaction pathways to synthesize biodiesel (Janaun & Ellis, 2010). Trans-esterification is one of the most

efficient methods to form biodiesel and the process involves a reaction between triglyceride and alcohol to form an ester and glycerol (Zabeti, Daud, & Aroua, 2009). Figure 1-1 and Figure 1-2 show the esterification reaction between fatty acid and alcohol and the trans-esterification reaction between triglyceride and methanol.

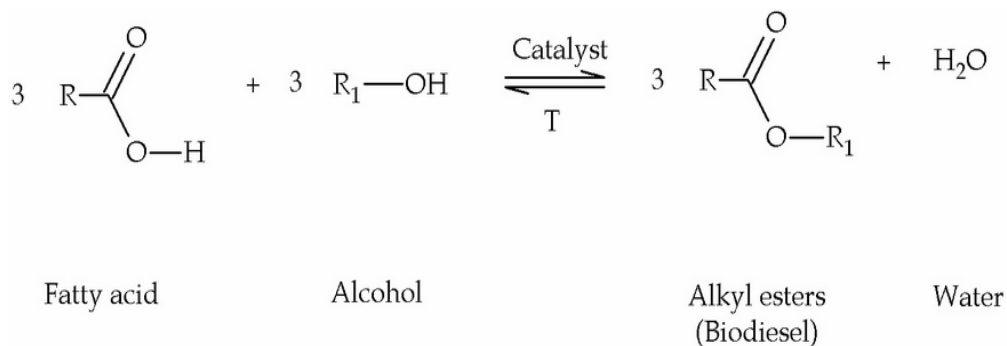


Figure 1-1. A scheme for esterification reaction between free fatty acids and an alcohol.

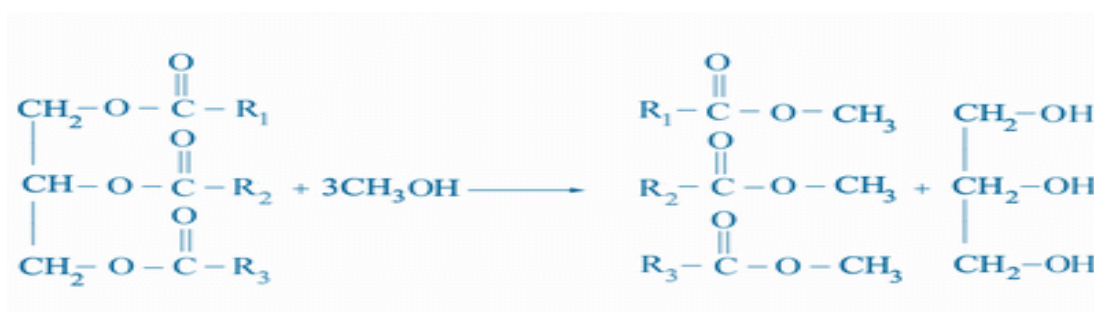


Figure 1-2. A scheme for transesterification reaction.

One of the benefits of biodiesel is that it can be produced from a wide range of feed stocks such as waste oil, edible oil, and animal fat (Janaun & Ellis, 2010). Another benefit is that biodiesel can be used directly in the diesel engine due to similar physicochemical properties, such as phase and viscosity, to the diesel that is produced from crude oil (HarrisonLikNangLau & JunhuiChen, 2012). The flash points of diesel and biodiesel fuels are 62°C and 150°C, respectively. Thus biodiesel is less volatile and safer than diesel (S. Lee, Posarac, & Ellis, 2012).

As far as industrial production, cost is a key point that has to be paid attention to. It has been indicated that feedstock could represent more than 75% of the entire biodiesel production

cost (A.E. Atabani, 2012). Therefore, it is crucial to find an economical raw material to produce biodiesel. Another important factor to take into consideration, which is also a part of the cost of biodiesel production process, is the catalyst. Homogeneous catalysts are in the same liquid phase as the reaction mixture, whereas heterogeneous catalysts are solid. Solid acid catalysts such as ZnO/ZrO₂ (Borges & Díaz, 2012) can support free fatty acid esterification reactions while solid base catalyst such as CaO (Xuejun Liu, 2008) can support triglyceride trans-esterification reactions (Borges & Díaz, 2012). Solid base catalysts generally are more active than solid acid catalysts requiring relatively shorter reaction times and lower reaction temperatures (Borges & Díaz, 2012). Nevertheless, over all, economically heterogeneous catalysts are a better choice than homogeneous catalysts because the heterogeneous catalyst process costs the least total capital investment and manufacturing resulting from their ability to recover catalysts (Janaun & Ellis, 2010).

Free fatty acid content in the feedstock is also important in the synthesis of biodiesel because surplus free fatty acid could result in a significant amount of soap, especially when base catalyst is used (Borges & Díaz, 2012).

As far as alcohol, higher chain alcohols result in higher viscosity and increased production cost, so methanol and ethanol are the most frequently used alcohols, particularly methanol due to its low price and availability (Zabeti et al., 2009). In transesterification, the stoichiometric ratio of alcohol to oil is three to one. Therefore excess alcohol in the reaction favors the formation of methyl esters (Zabeti et al., 2009).

Thermogravimetric analysis (TGA) is a tool to analyze thermal stability of materials (H.-J. Lee, 2002) and to determine the composition from the weight loss at different temperature (H.-J. Lee, 2002). FT-IR is one of the most widely used methods to identify the chemical

constituents and elucidate the compounds structures. It could also be used to test raw materials, product quality, etc (S.T.H. Sherazi, 2011). It gains more interests probably because it is easy to operate, and the sample preparation is not time-consuming. Generally, a single spectrum can identify all the function groups in the sample (S.T.H. Sherazi, 2011).

Since there is lacking of information on the synthesis of biodiesel using raw beef fat, we aim to investigate the production of biodiesel from raw beef fat. In our research, raw beef fat was pre-treated first without any chemicals and was saponificated using Na_2SO_4 . TGA was used to detect the trace of free fatty acids. 0.025M of NaOH solution and phenolphthalein were used to titrate pre-treated fat. Biodiesel was synthesized using pre-treated fat, methanol and solid NaOH through esterification reaction. FT-IR was used to monitor the products.

1.2 Materials and Methods

1.2.1 Materials.

The beef fat was obtained from Harris Teeter. NaOH pellets, methanol, sodium sulfate, isopropanol were purchased from Fisher and used without further purification.

1.2.2 Methods.

1.2.2 (A) Production of refined fat.

83 grams of raw beef fat were placed in a 400 ml beaker and heated to 40°C. 45 grams of refined fat were separated by decanting it from the beaker. Thus 45 grams of fat, referred to hereafter as refined fat, were obtained. This is fat that we used to produce biodiesel.

1.2.2 (B) Thermal gravimetric analysis (TGA).

The Q50 TGA instrument was used to obtain TGA. 27.027 mg of refined fat before were placed on a small pan. The temperature rate was set to 5 °C and 1 °C per minute, respectively.

The temperature range was set from 0 °C to 600 °C. The analysis is obtained in N₂(g) atmosphere so it is considered as non-oxidative TGA.

1.2.2 (C) Saponification.

16.5956 grams of refined fat were placed in a beaker and heated to 40 °C. 0.5000 g of Na₂SO₄ was added and the saponification reaction was carried out for 1 hour at 40 °C. The formed soap was left in the beaker after decanting the fat on the top layer.

1.2.2 (D) Acid/base titration to determine free fatty acids (FFA).

15.5 mg and 15.2 mg of refined fat before saponification and 18.5 mg and 18.0 mg of fat after saponification were mixed with 15 ml of isopropanol and were placed in an Erlenmeyer flask. The titration was carried out using 0.025M of NaOH in the presence of phenolphthalein.

1.2.2 (E) Production and characterization of biodiesel.

10.0364 grams of the fat after saponification was mixed with 90 ml of methanol (mass ratio of methanol/fat is 7/1) and 0.2207 g of NaOH. The mixture's temperature was raised to 55 °C and the transesterification reaction was run for 90 minutes. A homogeneous liquid was obtained. To separate the glycerin, 200 µl of DI water was added to 10 ml of the homogeneous liquid at room temperature. The mixture was left at room temperature for about 45 minutes before observing two separate layers. A sample was taken from each layer to obtain using SHIMADZU IR PRESTIGE-21 Fourier Transform Infrared Spectrophotometer at scan number of 40 and resolution of 1.0.

1.3 Results and Discussion

Figure 1-3 (A) and (B) show the TGA patterns of the refined fat before the saponification. Figure 1-3 (A) shows the TGA pattern when the temperature rate was 5 °C per minute. Figure 1-3 (B) shows the TGA pattern when the temperature rate was 1 °C per minute.

In both patterns, only the peak at around 380 °C that corresponds to triglycerides, appears in the TGA profile. Usually FFA peak appears between 210-220 °C. Table 1 shows the titration data, with 0.025 M NaOH, of refined fat when dissolved in isopropanol. Assuming 1/1 stoichiometric ratio for the reaction between FFA and NaOH, the number of moles of FFA was calculated. The number of moles of FFA has dropped approximately 27% by the saponification.

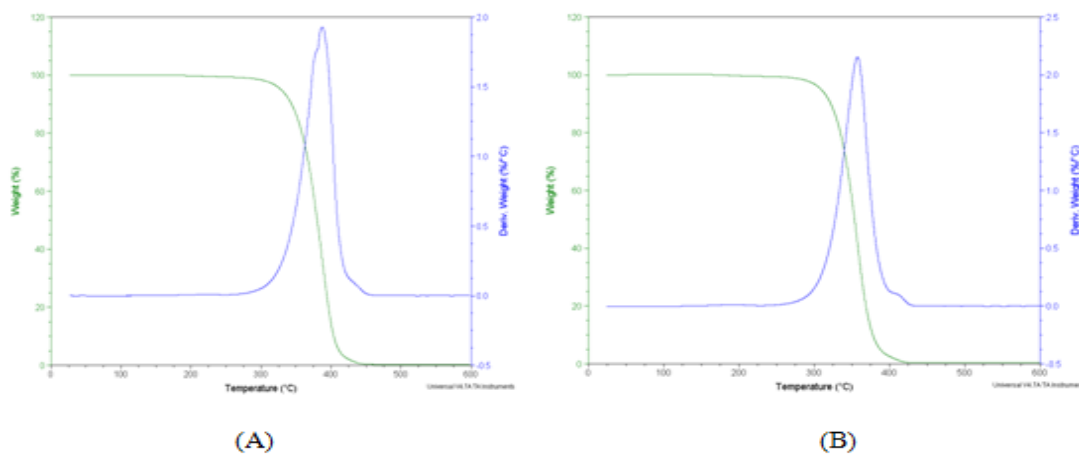


Figure 1-3. TGA patterns of refined fat.

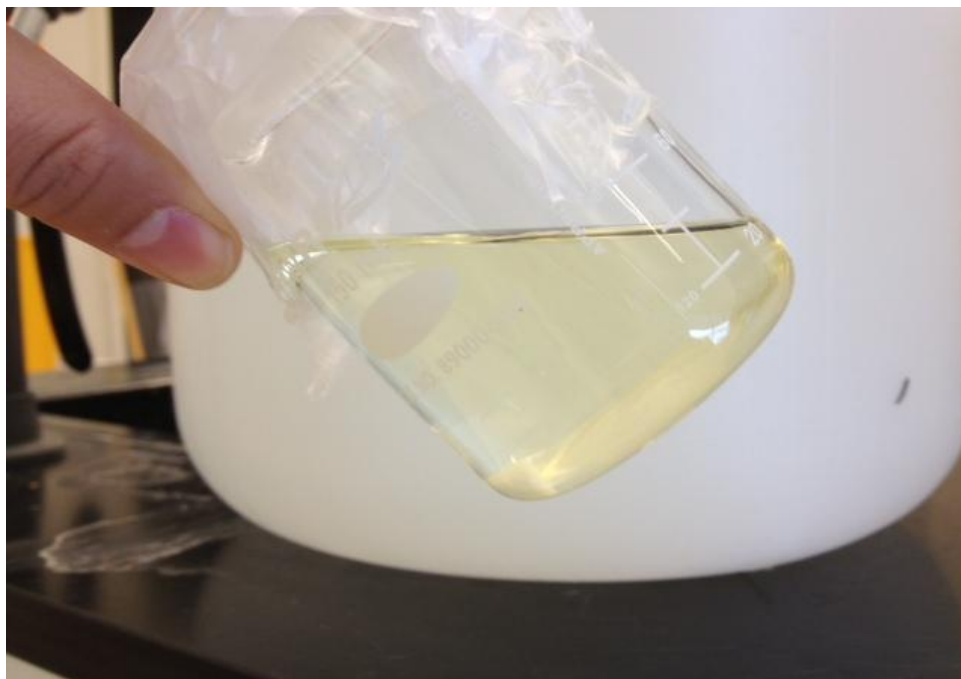


Figure 1-4. Obtained homogeneous liquid after the transesterification.

Table 1-1

Titration Data

	Mass of fat (mg)	Conc. Of NaOH (M)	NaOH titrated (mL)	Moles of free fatty acid
Before saponification	15.5	0.025	1.10	0.2750×10^{-4}
	15.2	0.025	1.05	0.2625×10^{-4}
After saponification	18.5	0.025	0.80	0.2000×10^{-4}
	18.0	0.025	0.65	0.1625×10^{-4}

In Figure 1-3 (A) and (B) , we expected to see a peak near indicating the presence of free fatty acid, but there was no such peak in the TGA pattern. We then repeat the experiment at a lower heating rate, 1°C/minute, but the peak indicating free fatty acid is still missing, which could be attributed to that the free fatty acid in the fat was converted to triglyceride when the sample was heated.

As shown in Table 1-1, the mass of fat after saponification is more than that mass of fat before saponification. The NaOH was consumed by the fat after saponification more than before saponification. The number of mole of free fatty acid in the fat before saponification and after saponification was calculated (1.75×10^{-6} mol/mg and 0.99×10^{-6} mol/mg). Thus, it can be concluded that Na_2SO_4 significantly reduced the amount of free fatty acid in the refined fat. However, a better reaction condition will be invested so that there is no more excess Na_2SO_4 and all of the free fatty acid can be reacted in the saponification reaction. After the transesterification reaction, a homogenous liquid was obtained (Figure 1-4). However, we expected to see a separation of two layers, a layer of glycerin and a layer of biodiesel. Two hundred microliter of distilled water was added to the homogeneous liquid. After 45 minutes, a separation of two layers was displayed (Figure 1-5). IR spectrum of each layer was then acquired.

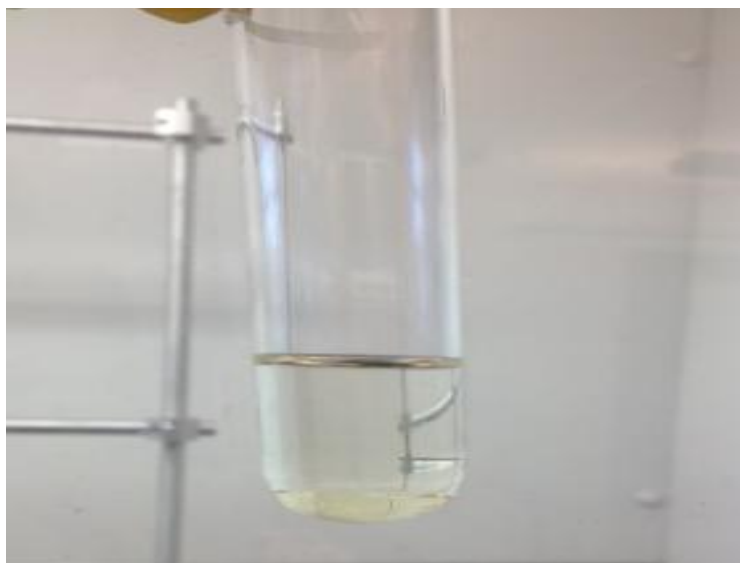


Figure 1-5. 45 minutes after adding adding 200 μL of DI water to 10 ml of homogenous liquid.

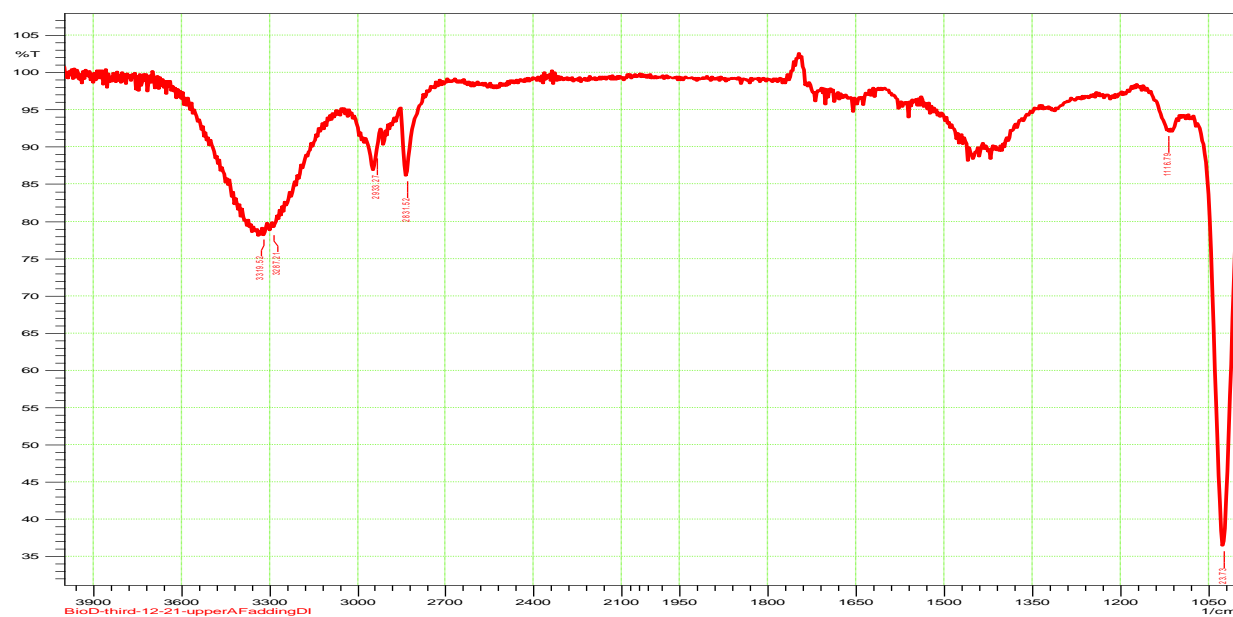


Figure 1-6. IR spectrum of the upper layer.

Table 1-2

Assignment of major peaks in the IR spectrum of the upper layer

peak 1	peak 2	peak 3	peak 4	peak 5
3320cm^{-1}	2950cm^{-1}	2830cm^{-1}	1120cm^{-1}	1030cm^{-1}
OH in alcohol	C-H in CH_2 or CH_3	C-H in CH_2 or CH_3	C-O in alcohol	C-O in $\text{CH}_2\text{-OH}$

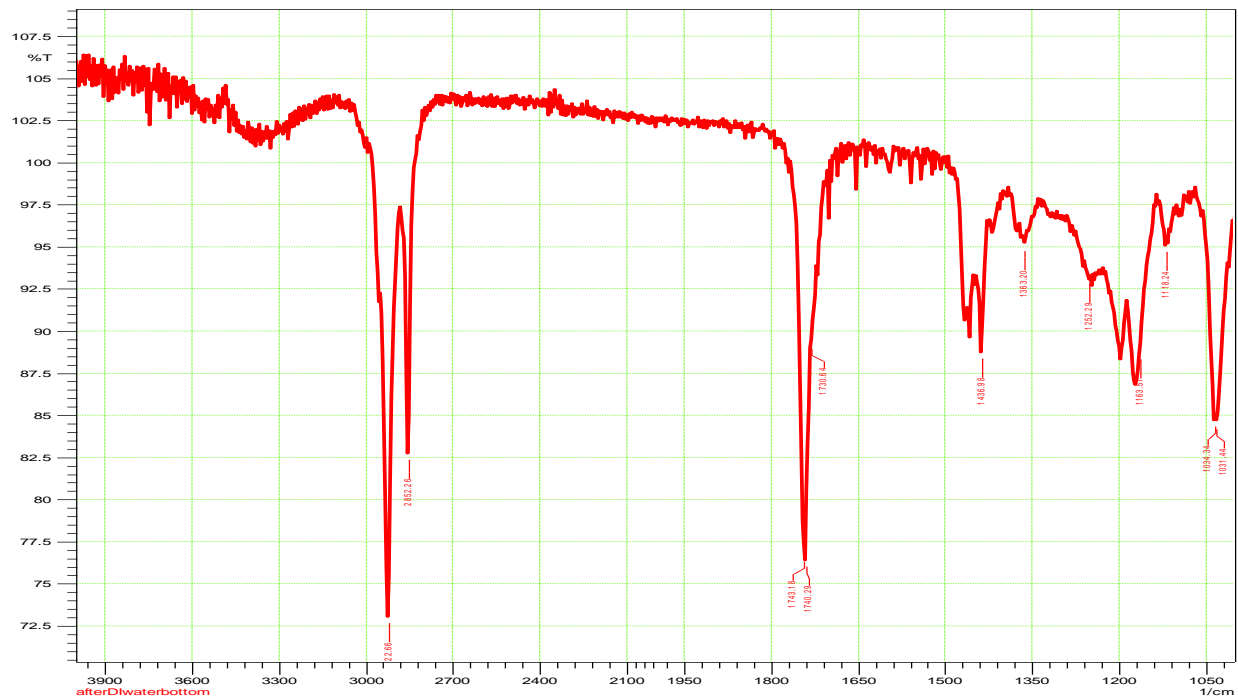


Figure 1-7. IR spectrum of the bottom layer.

Table 1-3

Assignment of major peaks in the IR spectrum of the bottom layer

peak 1	peak 2	peak 3	peak 4	peak 5	peak 6	peak 7
2922cm ⁻¹	2852cm ⁻¹	1740cm ⁻¹	1436cm ⁻¹	1163cm ⁻¹	1143cm ⁻¹	1030cm ⁻¹
C-H in CH ₂ or CH ₃	C-H in CH ₂ or CH ₃	C=O in ester	CH ₃ antisym	C-O in alcohol	C-O in alcohol	C-O in CH ₂ -OH

As shown in Table 1-2, Table 1-4, and Table 1-5, the peaks in the IR spectrum of the upper layer (Figure 1-7), the methanol (Figure 1-8), and the glycerin (Figure 1-9) were assigned. The IR spectrum of the upper layer was compared to the IR spectra of methanol and glycerin. The IR spectrum of upper layer is almost identical to IR spectra of the methanol and the glycerin. It then can be concluded that the upper layer is probably the mixture of methanol and glycerin.



Figure 1-8. IR spectrum of methanol.

Table 1-4

Assignment of major peaks in the IR spectrum of methanol

peak 1	peak 2	peak 3	peak 4
3310cm^{-1}	2950cm^{-1}	2830cm^{-1}	1030cm^{-1}
OH in alcohol	C-H in CH_2 or CH_3	C-H in CH_2 or CH_3	C-O in $\text{CH}_2\text{-OH}$



Figure 1-9. IR spectrum of glycerin.

Table 1-5

Assignment of major peaks in the IR spectrum of glycerin

peak 1	peak 2	peak 3	peak 4	peak 5
3334cm ⁻¹	2950cm ⁻¹	2890cm ⁻¹	1100cm ⁻¹	1030cm ⁻¹
OH in alcohol	C-H in CH ₂ or CH ₃	C-H in CH ₂ or CH ₃	C-O in alcohol	C-O in CH ₂ -OH

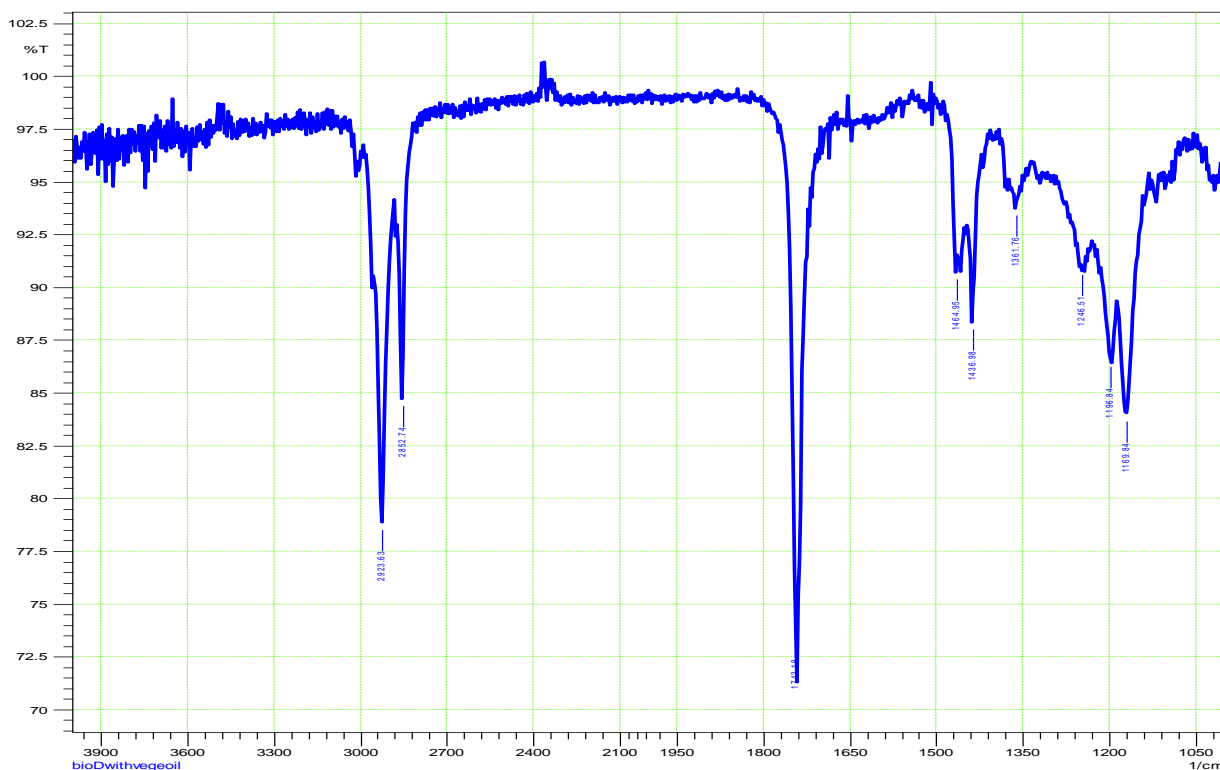


Figure 1-10. IR spectrum of biodiesel that is made from vegetable oil.

Table 1-6

Assignment of major peaks in the IR spectrum of biodiesel that is made from biodiesel

peak 1	peak 2	peak 3	peak 4	peak 5
2922cm ⁻¹	2852cm ⁻¹	1743cm ⁻¹	1436cm ⁻¹	1169cm ⁻¹
C-H in CH ₂ or CH ₃	C-H in CH ₂ or CH ₃	C=O in ester	CH ₃ antisym	C-O in alcohol

The peaks in the IR spectrum of bottom layer (Figure 1-7) and in the biodiesel that is made from vegetable oil (Figure 1-10) were assigned and were shown in Table 1-3 and Table 1-6. The peaks in the IR spectrum is almost identical to the IR spectrum of biodiesel that is made from vegetable oil except the peak at 1030 cm^{-1} (C-O peak) which is only appeared in the IR spectrum of the bottom layer. It can be caused by a trace of methanol or glycerin or both in the bottom layer when DI water was added to the homogeneous liquid as shown in Figure 1-4.

1.4 Conclusions

Raw beef fat can be used after the refinement to synthesize biodiesel, but the fat has to be refined first. Saponification using solid Na_2SO_4 can be used to reduce the amount of free fatty acid in the refined fat. Acid/base titration can be used to test the amount of free fatty acid in the refined beef fat. TGA did not help to determine the amount of free fatty acid in the beef fat at a rate of either $5\text{ }^\circ\text{C}/\text{min}$ or $1\text{ }^\circ\text{C}/\text{min}$ under nitrogen environment. Methanol, NaOH pellet and refined beef fat can be used to initiate trans-esterification to synthesize biodiesel at $55\text{ }^\circ\text{C}$. When the transesterification reaction was stopped, glycerin, excess methanol and obtained biodiesel are more than likely mixed together to form a homogeneous liquid. When DI water is introduced to such liquid, it can separate synthesized biodiesel and glycerin from that liquid and form a two-layer mixture. The glycerin is on top and the synthesized biodiesel is at the bottom.

CHAPTER II

Polymerization of Glycerin

2.1 Introduction

Biodiesel production has significantly increased in the past few years (M. L. Pisarello, 2010). Biodiesel is now produced from different feed stocks such as used cooking oil and animal fats, where glycerin is always a byproduct (Anna Maria A. P. Fernandes, 2012). The huge amount of biodiesel being made in USA has created a surplus of glycerin, and researchers are studying how to make useful products from it. One of these products is polyglycerin.

Polyglycerin has been studied in several areas. For example, the chemical activity of polyglycerin fatty esters as surfactants was studied in relation to the degree of glycerin polymerization (S. Cassel, 2001). Some research for the use of polyglycerin in the food industry has been established (R. WILSON, 1998). Polyglycerin can be used to replace superplasticizers in the production of concrete. Super plasticizers such as polynaphthalene sulfonate and polyacrylate esters (X. Zhang, 2006) are compounds that are used in the concrete mix to reduce the amount of needed water. Such reduction will reduce the micro gaps in the concrete structure as it dries up. This then will reduce the chances of these gaps compromising the concrete strength. Our experiments have shown that up to a certain limit the replacement of some of the superplasticizer in the concrete by polyglycerin reduces the amount of water needed in the mix without affecting the quality of the concrete.

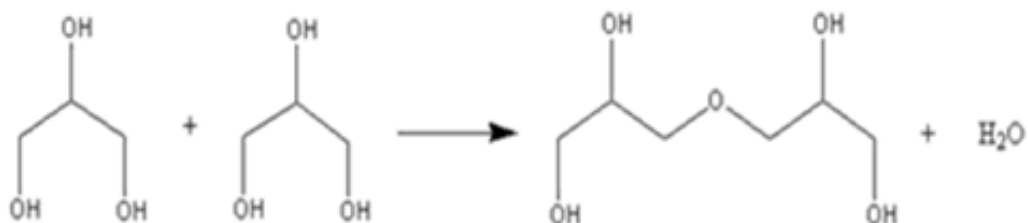


Figure 2-1. A scheme for the formation of a dimer.

Polymerization of glycerin occurs through water elimination reactions. Theoretically the amount of eliminated water is proportional to the degree of polymerization. Figure 2-1 shows a schematic representation for the production of one mole of dimer and one mole of water from two moles of glycerin. Thus, the mass of water can be used to estimate the degree of polymerization.

A number of analytical methods such as Fourier Transform Infrared (FT-IR) spectroscopy, and NMR can be used to monitor chemical synthesis. NMR is also an invaluable analytical method in the characterization of chemical compounds (Tammo Diercks) including the determination of their three dimensional structures. FT-IR spectroscopy is considered as one of the most widely used methods to identify the chemical constituents and elucidate the compounds structures (Hong-xia Liu). It could also be used to test raw materials and quality of products of chemical reactions (M. Blanco, 2004). FT-IR has a number of advantages among which: 1) it is easy to operate; 2) sample preparation is not time-consuming; and 3) it is informative since a single spectrum can provide all the functional groups in the sample (S.T.H. Sherazi, 2011).

Viscosity is a temperature-dependent measurement of fluid resistance to flow or friction resulting from shear stress (Yilmaz, 2011). It is widely used in several ways such as quality control of biodiesel (Naoko Ellis, 2008), and for investigating the correlation between lubricant performance and engine components wear (M.Mofijura, 2012).

Principle component analysis (PCA) is a reliable method to analyze a multivariate data set. Usually, such multivariate data is represented as a matrix and then plotted to show any trend. The advantage of PCA is that it could be plotted in up to 3-dimension and as well as reveal what could possibly happened behind the phenomena. Esbensen, K.H (2001). *Multivariate Data Analysis*, Esbjerg: CAMO

In this research, we aim in to show the applicability of FT-IR, NMR and viscosity measurements in monitoring the degree of glycerin polymerization, and to investigate whether these methods correlate well with the mass of eliminated water during the polymerization reaction. Thus the goal of this research is to introduce more reliable methods in determining the degree of glycerin polymerization than the mass of eliminated water.

2.2 Materials and Methods

2.2.1 Experimental procedures.

Grade C glycerin was obtained through our collaboration with Tenstech. Sodium hydroxide was purchased from Fisher and used without any purification. Polymerization reaction was performed in two different ways. In the first way, a polymer was synthesized by heating a certain amount of glycerin to 220 °C and the reaction was stopped when the amount of the water generated corresponding to the polymer. The polymerization reaction was catalyzed by the solid NaOH (0.75 g solid NaOH/100 g glycerin) and was run under a stream of nitrogen. The sample was tested using IR, ¹³C NMR, and viscosity. In the second way, 204 g of glycerin, 1.5 g of NaOH were placed in a flask and the polymerization reaction was run under a stream of nitrogen. The water that was eliminated from the reaction was collected and the mass of it was weighed at five minute intervals for 120 minutes. A sample was obtained from the flask every five minute interval for 120 minutes and was tested using FT-IR. Viscosity of glycerin and the polyglycerin after the reaction were measured.

2.2.2 Methods.

2.2.2 (A) FT-IR.

Shimadzu IR Prestige FT-IR was used at room temperature. The range of wave number was from 1000 to 4000. The resolution and mirror speed were set to 1.0 and 5.0, respectively.

Number of scans was 48 (samples of polymerization method 1) and 120 scans (samples of polymerization method 2).

2.2.2 (B) ^1H NMR and ^{13}C NMR.

All NMR spectra were acquired on 300 MHz Varian NMR with relaxation delay at 1 second, pulse at 4.5 micro second, and 4000 scans. Two-hundred and fifty micro liters of each polymer sample was transferred to an NMR tube. To prepare the NMR samples, two hundred and fifty micro liters of deuterium oxide were added to each NMR tube and was mixed with the polymer using vortex genie.

2.2.2 (C) *Viscometer.*

Viscosity Monitoring and Control Electronics of CAMBRIDGE applied systems was used to monitor the viscosity of glycerin and sample obtained from the polymerization reaction that was run in the first way. An amount of 0.1065 g of Glycerin, 0.1072 g of trimer, 0.1063 g of pentamer, 0.1065 g of heptamer, and 0.1066 g of decamer were put in five different vials. One milliliter of distilled water was then added to each vial. The viscosity of the resulted solutions was measured at the following temperatures 30.0 °C, 38.8 °C, 50.0 °C and 60.0 °C.

BROOKFIELD DV-III ULTRA Programmable Rheometer was used to test the viscosity of 10.4 g of both the glycerin and the final product obtained from the polymerization reaction in the second way. The viscosity of glycerin was measured from 30 °C to 60 °C at a 5 °C interval. The viscosity of the final product was collected from 60 °C to 200 °C at 20 °C intervals. Matlab was used to analyze the data using multivariate curve resolution.

2.3 Results and Discussion

The polyglycerins were synthesized based on the mass of water to be eliminated. Table 2-1 shows how the polymerization reaction was monitored and stopped. The reaction was

stopped when the mass of eliminated water was equal to the theoretical mass. Determining the degree of polymerization based on the amount of water has some degree of error since a certain amount of water is trapped during the synthesis in different parts of the synthesis setup.

Figure 2-2 shows that the transmittance of those eight major peaks increases when the degree of polymerization increases, indicating that the decrease of transmittance is proportional to the increase of the degree of polymerization. Likewise, Figure 2-2 shows that at wave number of 3327 cm^{-1} , 2927.94 cm^{-1} , 2875.86 cm^{-1} , 1109.06 cm^{-1} and 1035.77 cm^{-1} , the transmittance decreases when the degree of polymerization increases.

Table 2-1

Mass of glycerin used, theoretical mass of water eliminated and actual mass of water eliminated when polyglycerins were made.

Polymers	mass of glycerin in g	theoretical mass of water eliminated in g	actual mass of water eliminated in g
Trimer	39.7028	5.176	5.19
Pentamer	40.1608	6.274	6.29
Heptamer	39.5917	6.633	6.56
Decamer	41.2862	7.263	7.32

In ^1H NMR spectra (Figure 2-3), it indicates that at approximately 4.66 ppm, the intensity of the peak is proportional to the degree of polymerization as we expected. However, at approximately 3.1 ppm to 3.5 ppm, there is no consistency between glycerin and polyglycerins.

In Figure 2-4, there are some new peaks appeared at 70.4 ppm which can be predicted as peaks of ether group. The intensity of the peaks increases when the degree of polymerization

increases. However, the peak splits in the ^{13}C NMR spectrum of decamer. It can be caused by the even number of carbon atom in the structure of decamer. Figure 2-4 shows that there are common chemical shifts at approximately 62.5 ppm and 72 ppm which correspond to the carbon atom connected to alcohol group and carbon connected to a hydrogen atom. It also shows that the intensity of peaks is proportional to the degree of polymerization, except the chemical shift of decamer at 62.5 ppm. Therefore, proton and ^{13}C NMR cannot be used to monitor the degree of polymerization since the synthesis results in the formation of more than one polymer, so the changes in the proton and ^{13}C NMR spectra were not consistent with the degree of polymerization.

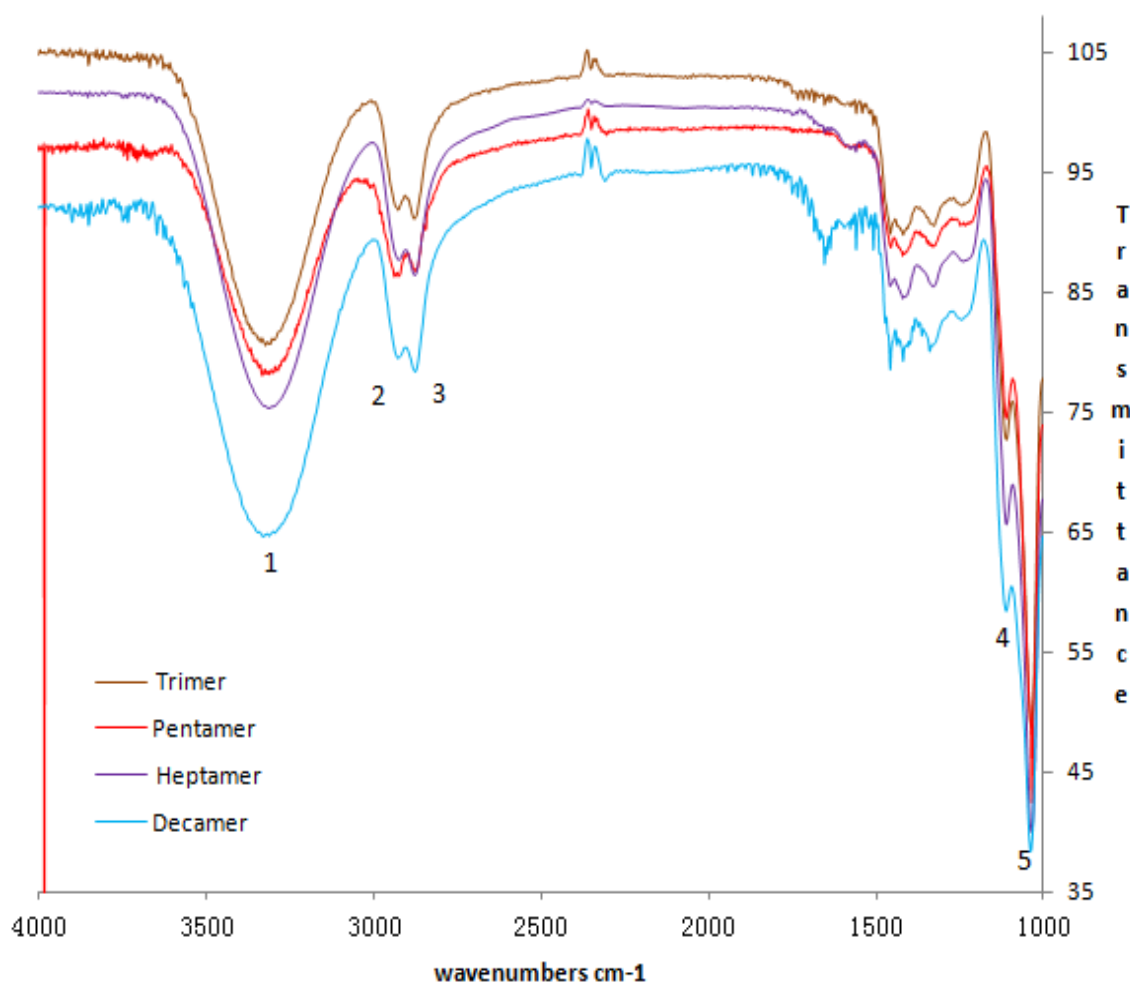


Figure 2-2. IR spectra of trimer, pentamer, heptamer and decamer polyglycerins.

Table 2-2

The assigned peaks with the corresponding functional groups

Wavenumber in cm^{-1}	Functional groups
3327 (peak 1)	O-H in alcohol
2927 (peak 2)	C-H in CH_2 or CH_3
2875 (peak 3)	C-H in CH_2 or CH_3
1109 (peak 4)	C-O in ether
1035 (peak 5)	C-O in alcohol

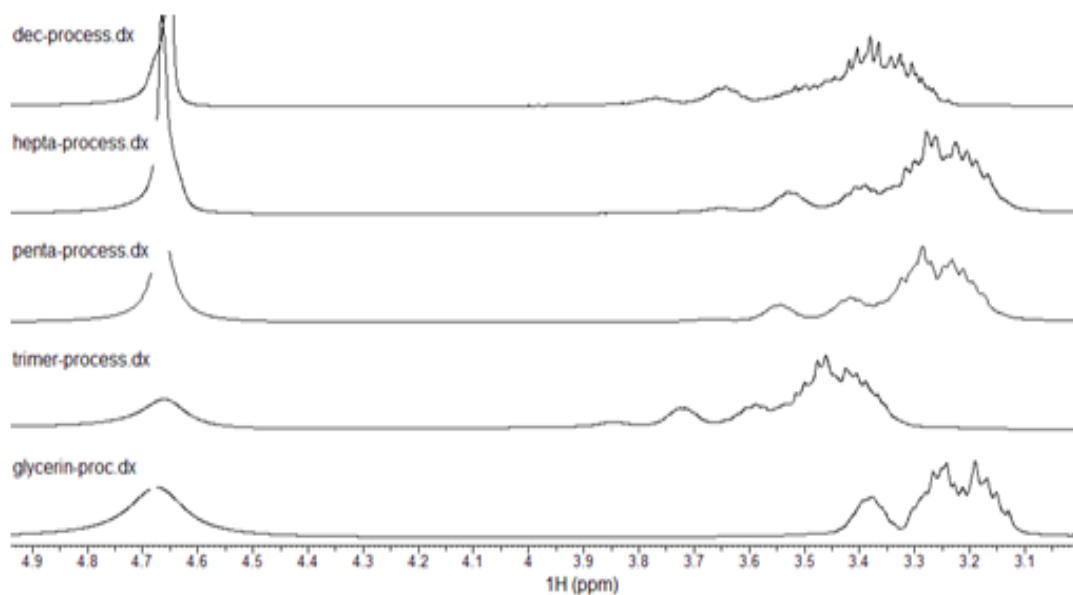


Figure 2-3. ^1H NMR spectra of glycerin, trimer, pentamer, heptamer, and decamer.

The viscosity reading was out of scale for the instrumentation used when glycerin and polyglycerin that were synthesized using method 1 were directly measured. It also occurred when glycerin and polyglycerin were mixed with distilled water solutions 50% (v/v). As shown in Figure 2-4, the experiments were eventually based on 9% (m/m) solutions and the change in the viscosity of the glycerin and the other polymer solutions was not consistent with the degree of polymerization.

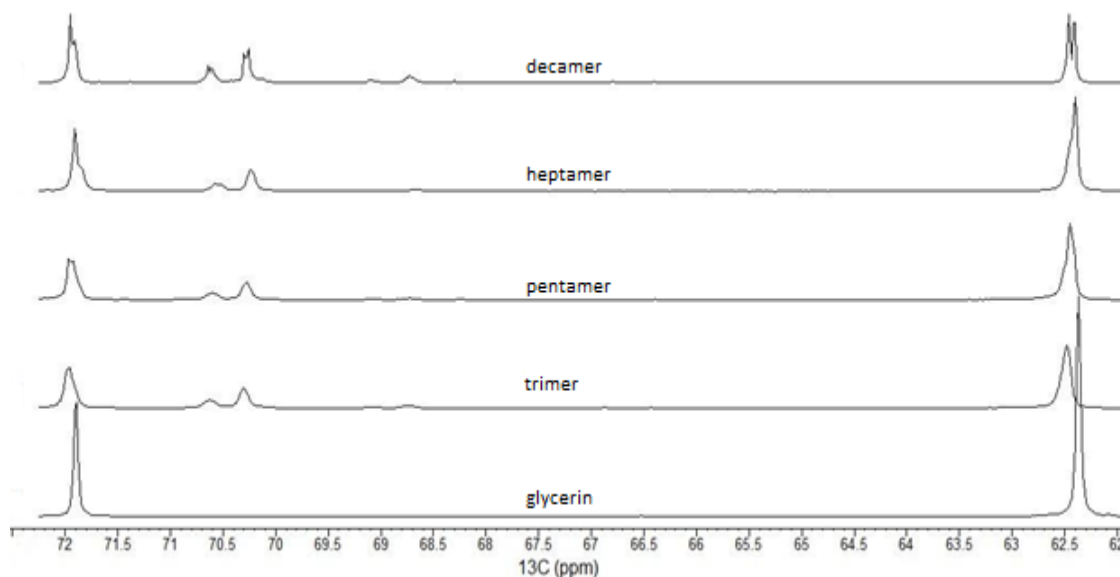


Figure 2-4. ^{13}C NMR spectra of glycerin, trimer, pentamer, heptamer, and decamer.

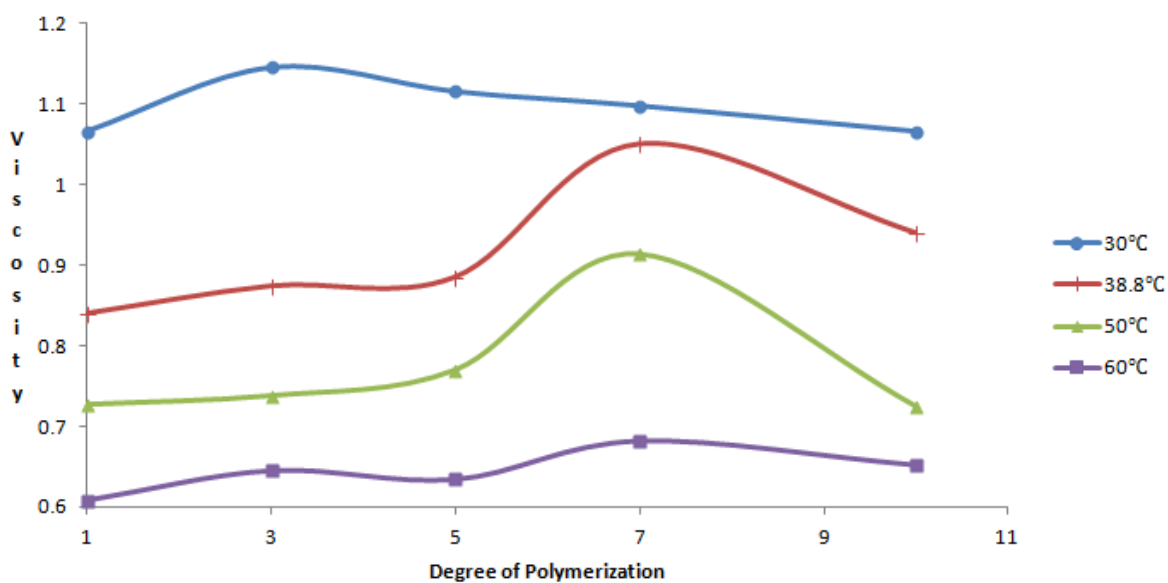


Figure 2-5. The viscosity versus the degree of polymerization.

We expected that the viscosity of polyglycerin decreases while the temperature increases. However, Figure 2-4 does not provide any evidence showing that there is any consistence between the viscosity and the degree of polymerization at 30.0 °C, 38.8 °C, 50.0 °C and 60.0 °C, which can be attributed to the change of intermolecular forces when the DI water was introduced to the polyglycerins.

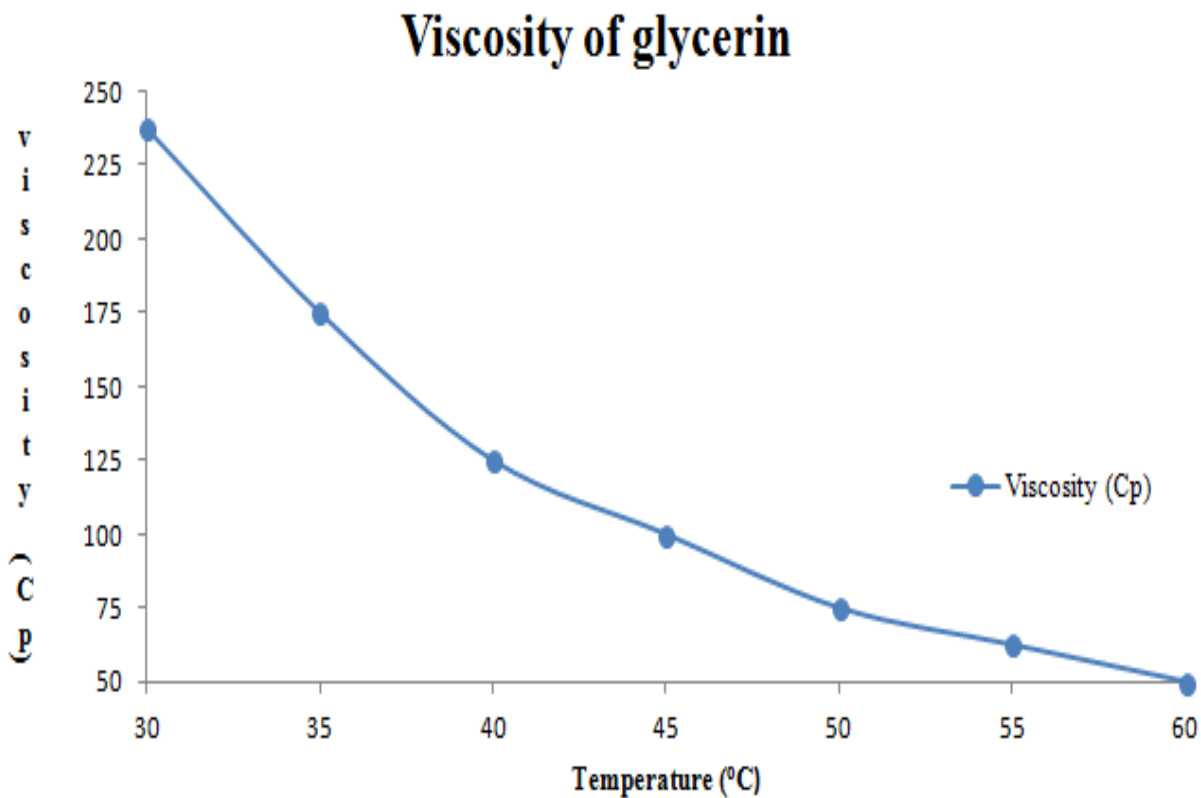


Figure 2-6. Viscosity of glycerin vs temperature.

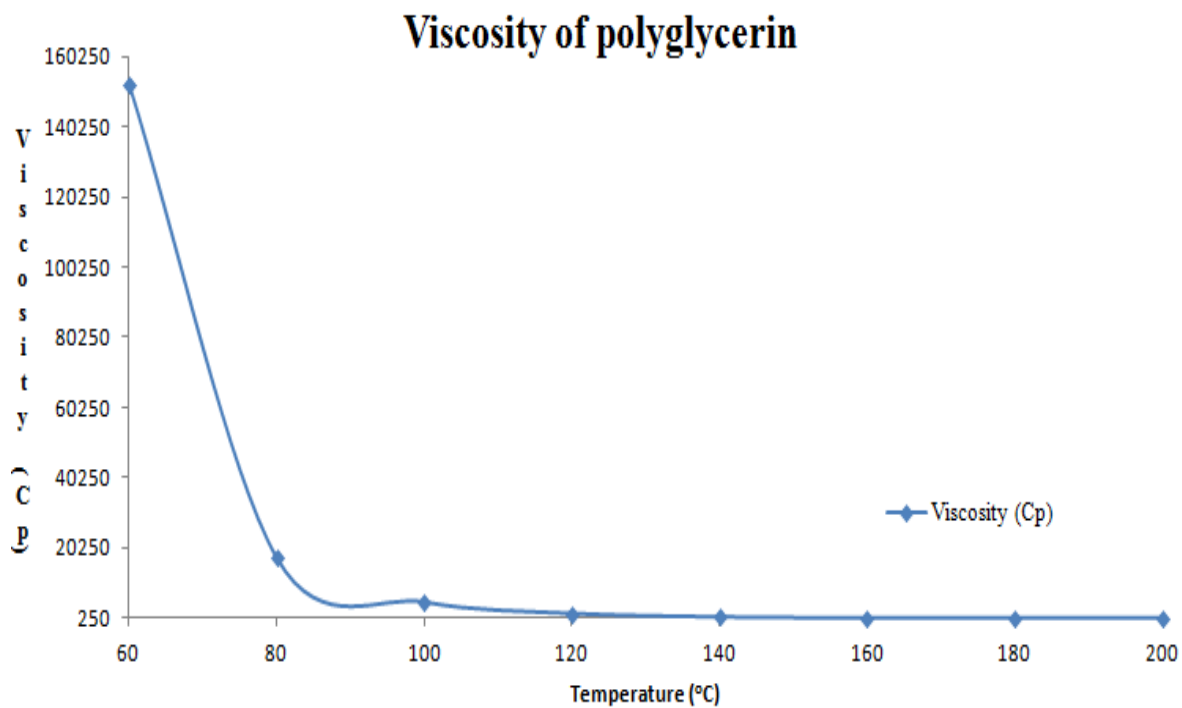


Figure 2-7. Viscosity of polyglycerin vs temperature.

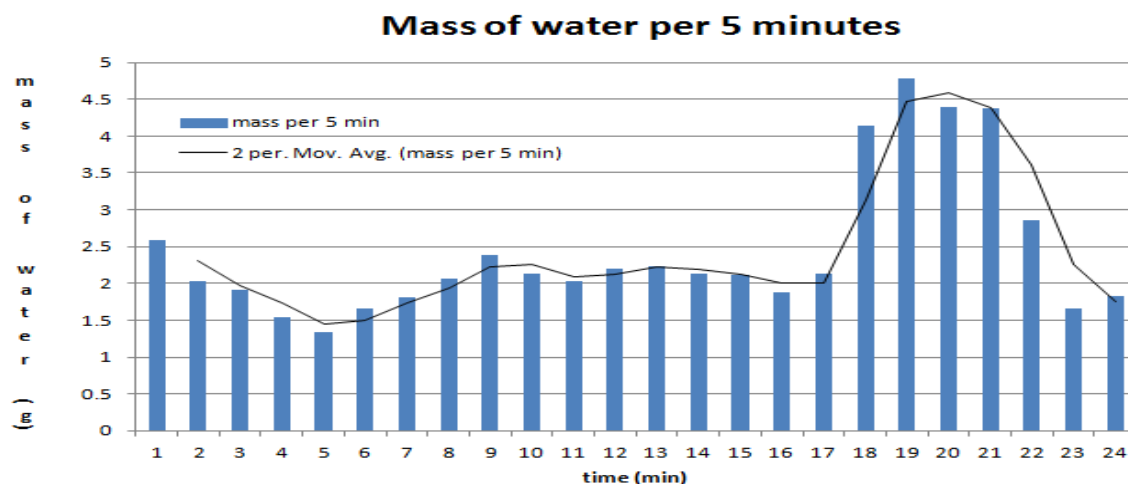


Figure 2-8. A plot of mass of water that is reduced every five minutes vs time.

Figure 2-5 and Figure 2-6 show that the viscosity of glycerin and polyglycerin that were synthesized using method 2 decreases when the temperature increases. As shown in Figure 2.9, the viscosity of polyglycerin decreases dramatically from 60 °C to 80 °C and remained unchanged when the temperature reaches 180 °C. Figure 2-7 shows the mass of water every five minutes during the reaction. We expected to observe a trend from the first five minute to the last one, but the figure does not prove such a trend. It could be caused by the unstable rate of stream of nitrogen gas or the connection with environment when polyglycerins were withdrew from the reaction.

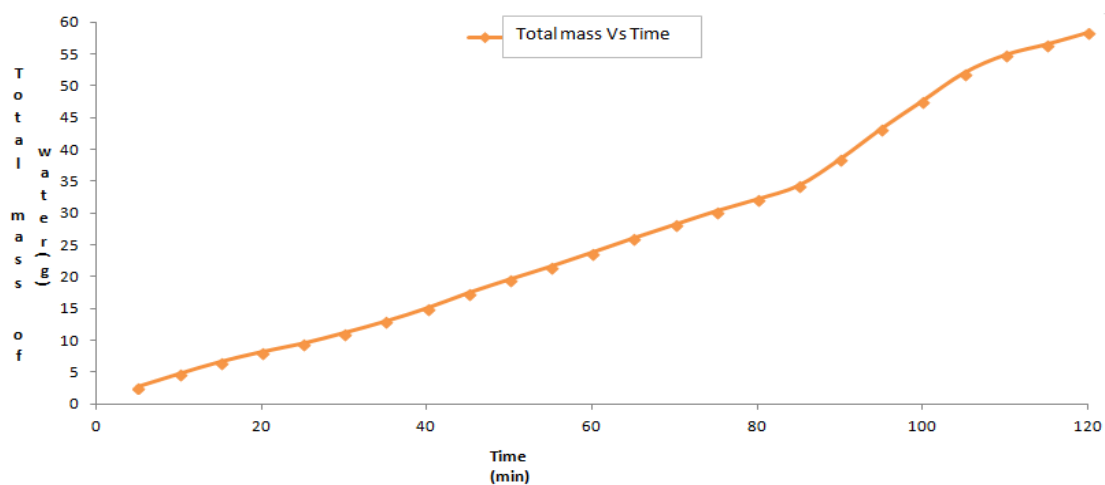


Figure 2-9. Total mass of water vs time.

As shown in Figure 2-8, there are three slope changes that appeared at the 35th minute, the 85th minute, and the 100th minute. It is possibly due to the change of the reaction rate that was caused by a different flow rate of stream of nitrogen and the connection with the environment when polyglycerins were withdrew from the reaction.

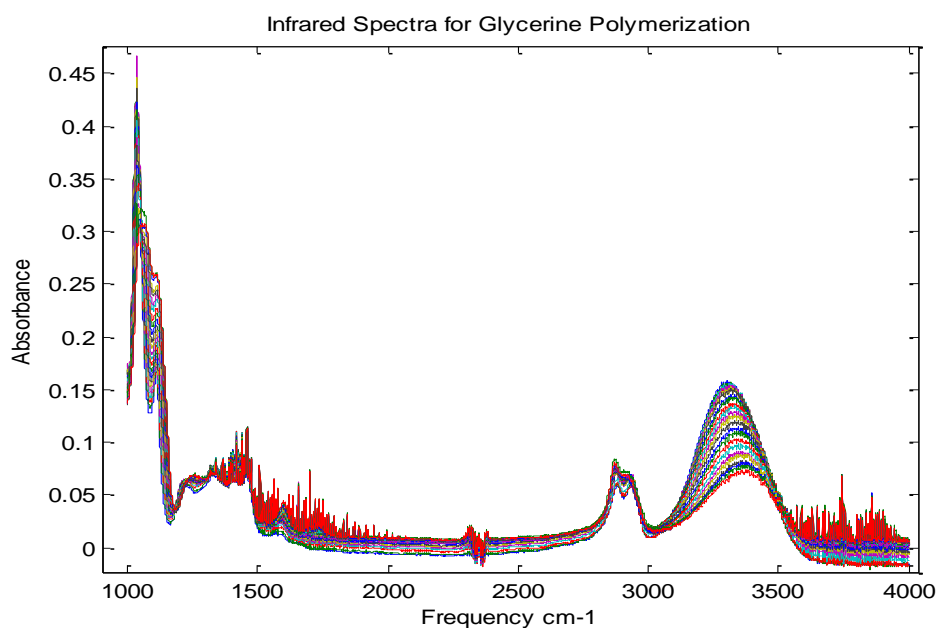


Figure 2-10. IR Plot of glycerin (absorbance vs frequency).

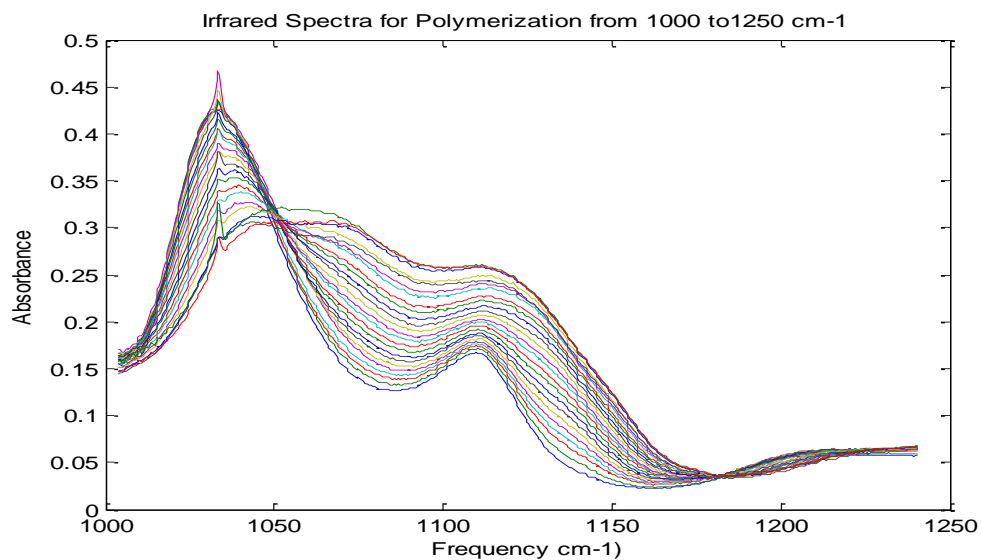


Figure 2-11. IR plot of glycerin from 1000 cm⁻¹ to 1250 cm⁻¹ (absorbance vs frequency).

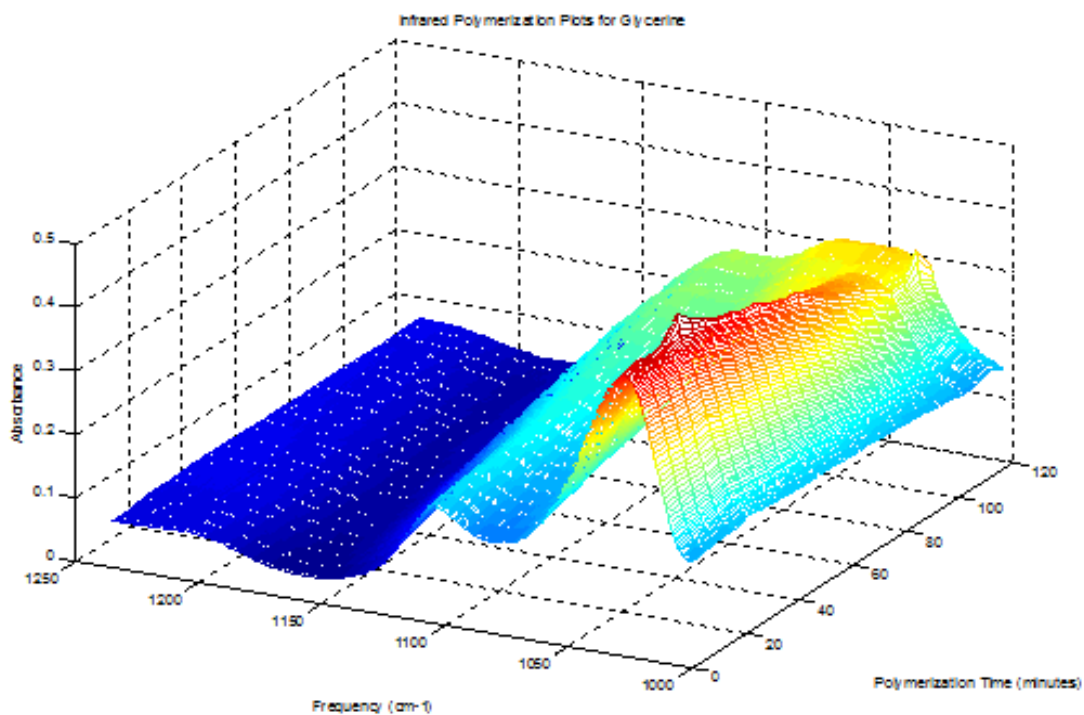


Figure 2-12. A 3D plot of Figure 2-10.

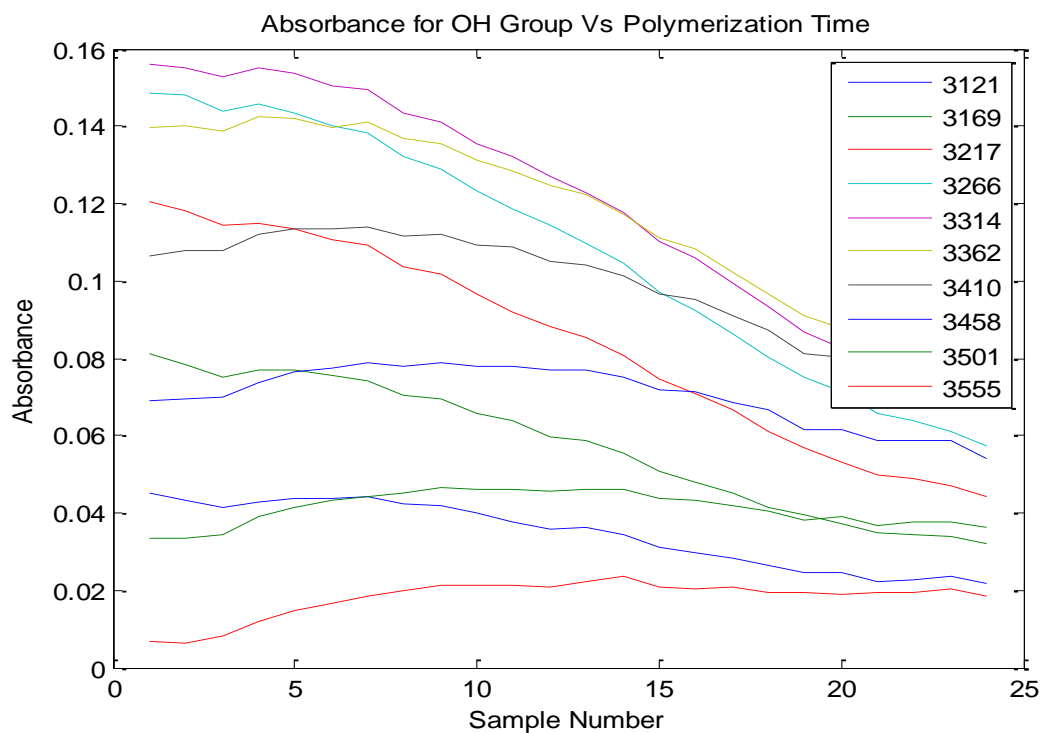


Figure 2-13. Absorbance of OH group vs sample number.

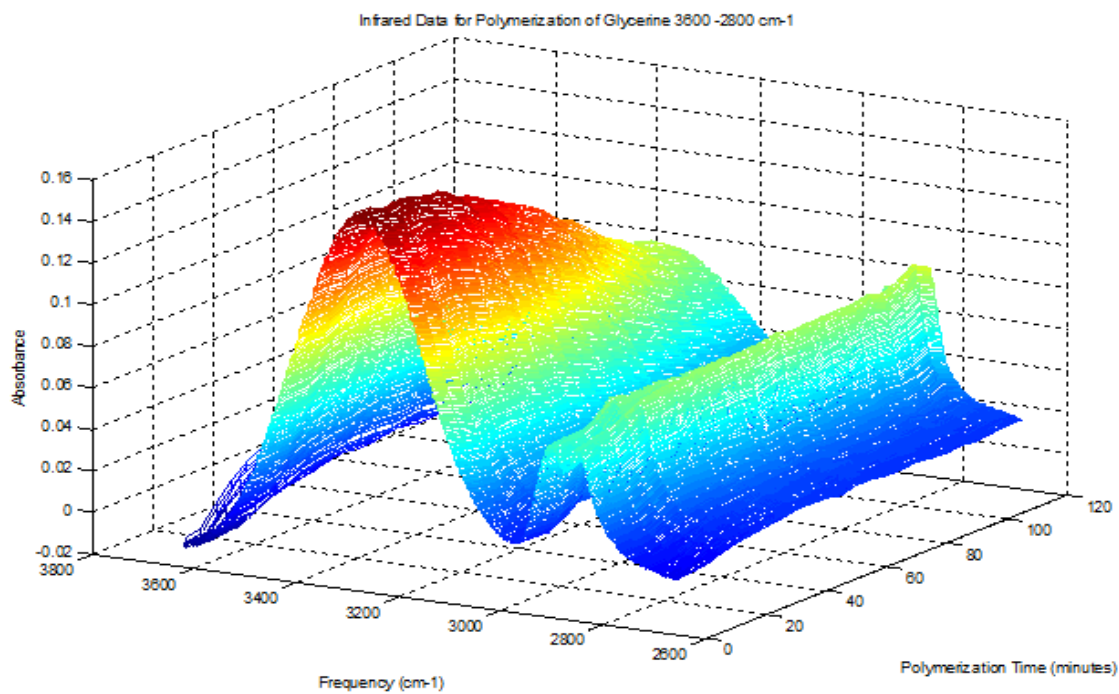


Figure 2-14. A 3D plot of IR spectrum from 2600 cm^{-1} to 3800 cm^{-1} .

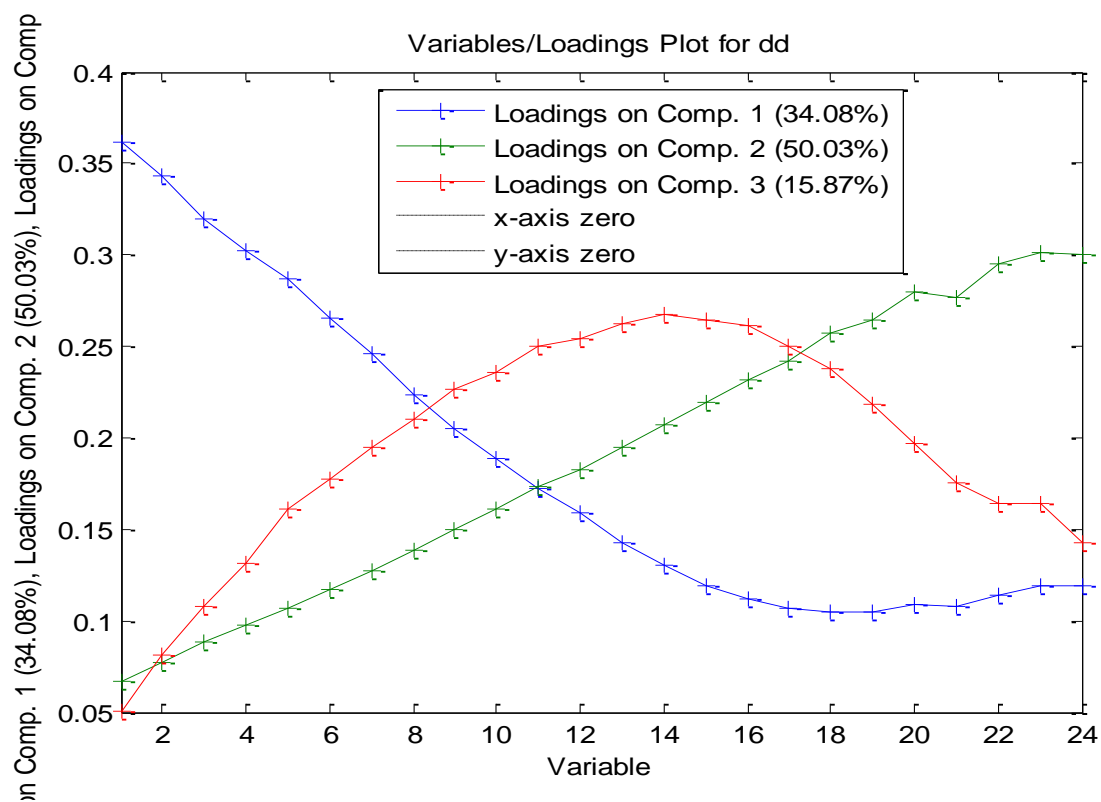


Figure 2-15. Multivariate Curve Resolution of 24 samples.

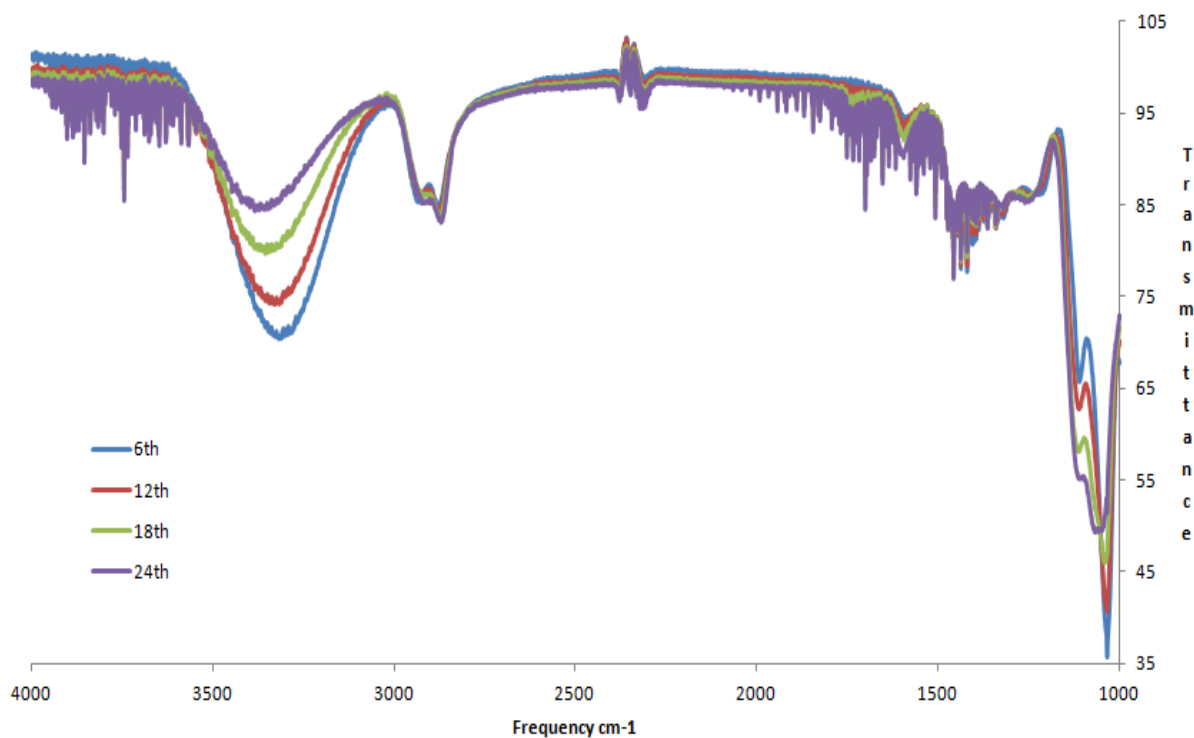


Figure 2-16. IR spectra of 4 different polyglycerin samples.

We expected to see trends at major peaks in Figure 2-9. However, only the OH peak (3400cm^{-1}) shows that the absorbance increases as the time of the polymerization reaction increases. Figure 2-10 shows that at 1050 cm^{-1} , the absorbance of IR spectra is inversely proportional to the time of the reaction. Oppositely, the absorbance of the peaks after 1050 cm^{-1} spectra is proportional to the time of the reaction. It is clearly shown that in the 3-D plot (Figure 2-11) the absorbance of the polyglycerin at 1050 cm^{-1} decreases as the time of the polymerization increases. After 1050 cm^{-1} , the absorbance of polyglycerin increases as the time of the polymerization increases. As shown in Figure 2-12, between 3100 cm^{-1} and 3555 cm^{-1} the IR absorbance of most samples at ten different reciprocal centimeters decreases at the OH peak region when the time increases which is attributed to the increase of the degree of polymerization. In the 3-D plot of IR spectrum of 24 samples (Figure 2-13), it can be seen that absorbance of the O-H peak decreases when the time consumed increases during the reaction

which can be due to the consumption of glycerin when the water molecules were produced from the polymerization reaction. Figure 2-14 shows that there are three components. The blue line may indicate the amount of glycerin during the reaction. The decay of blue line could be caused by the consumption of glycerin. The red line can be predicted as the amount of dimer during the polymerization reaction. It was formed at the beginning and was consumed. The green line can be predicted as the chain of the polymers which continuously increased during the reaction. In Figure 2-15, major peaks at 3400cm^{-1} and 1000cm^{-1} the IR spectra of every six samples from a total of 24 polyglycerins samples. The transmittance of O-H peak at 3400 cm^{-1} is proportional to the sample number or the time consumed which is attributed to the consumption of O-H group in glycerin. The transmittance of the peak corresponding to the C-O group in ether is reversely proportional to the sample number or the time consumed which can be attributed to the formation of ether group from the process of polymerization.

2.4 Conclusions

From the calculation, we can estimate that the polymers were produced as expected. However, in the patch synthesis there was no consistency in ^{13}C NMR and Viscometer but only in IR. It is probably because when polyglycerins mix with DI water or Deuterium oxide the new intermolecular forces is introduced to the mixture. When the polymers are made continuously, it turned out that there are some more consistency than making it individually such as the the viscosity decreases when the temperature increases. The absorbance of major peaks in the IR spectra of all polymer samples increases when time of the reaction increases. However, the method to monitor the degree of polymerization should be improved so that it would be more accurate to determine the degree of polymerization based on the calculation.

References

- A.E. Atabani, A. S. S. (2012). A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *16*, 2070-2093.
- Anna Maria A. P. Fernandes, D. U. T., Jose L. P. Jara. (2012). Free and Total Glycerin in Biodiesel: Accurate Quantitation by Easy Ambient Sonic-Spray Ionization Mass Spectrometry. 3042-3047.
- Borges, M. E., & Díaz, L. (2012). Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. *16*, 2839–2849.
- Daming Huang, H. Z., Lin Lin. (2012). Biodiesel: an Alternative to Conventional Fuel. 1874-1885.
- Diya'uddeen, B. H., Aziz, A. R. A., & Daud, W. M. A. W. (2012). Performance evaluation of biodiesel from used domestic waste oils: A review. *90*, 164-179.
- Fazal, M. A., Haseeb, A. S. M. A., & Masjuki, H. H. (2011). Biodiesel feasibility study: An evaluation of material compatibility; performance; emission and engine durability. *15*, 1314-1324.
- HarrisonLikNangLau, & JunghuiChen. (2012). A review on conventional technologies and emerging process intensification (PI) methods for biodiesel production. *16*, 5131–5145.
- Hong-xia Liu, S.-q. S., Guang-hua Lv. Study on Angelica and its different extracts by Fourier transform infrared spectroscopy and two-dimensional correlation IR spectroscopy. *64*, 321-326.
- Janaun, J., & Ellis, N. (2010). Perspectives on biodiesel as a sustainable fuel. *14*, 1312–1320.
- Lee, H.-J. (2002). Application of TGA techniques to analyze the compositional and structural

degradation of PEMFC MEAs.

Lee, S., Posarac, D., & Ellis, N. (2012). An experimental investigation of biodiesel synthesis from waste canola oil using supercritical methanol. *Fuel*, *91*(1), 229-237. doi: 10.1016/j.fuel.2011.08.029

M. Blanco, D. V., M.S. Bayod, F. Fernández-Mari, I. Llorente, *Anal. Chim. Acta* (2004). *502*, 221–227.

M. L. Pisarello, B. O. D. C., N. S. Veizaga, C. A. Querini. (2010). Volumetric Method for Free and Total Glycerin Determination in Biodiesel. *49*, 8935–8941.

M.Mofijura, H. H. M., M.A. Kalam, M. Shahabuddin, M.A. Hazrat, A.M.Liaquat. (2012). Palm Oil Methyl Ester and Its Emulsions Effect on Lubricant Performance and Engine Components Wear. *14*, 1748 – 1753.

May Ying Koh, T. I. M. (2011). A review of biodiesel production from *Jatropha curcas* L. oil. *15*, 2240-2251.

Naoko Ellis, F. G., Tim Chen, Conrad Poon. (2008). Monitoring biodiesel production (transesterification) using in situ viscometer. *138*, 200-206.

R. WILSON, B. J. V. S., D. HOWES. (1998). Overview of the Preparation, Use and Biological Studies on Polyglycerol Polyricinoleate (PGPR). *36*, 711-718.

S. Cassel, P. C., C. Debaig, T. Benvegnu, S. Claude. (2001). Liquid chromatography of polyglycerol fatty esters and fatty ethers on porous graphitic carbon and octadecyl silica by using evaporative light scattering detection and mass spectrometry *919*, 95-106.

S.T.H. Sherazi, M. A., S.A. Mahesar. (2011). Application of Fourier-transform infrared (FT-IR) transmission spectroscopy for the estimation of roxithromycin in pharmaceutical formulations. *55*, 115-118.

- Santacesaria, E., & Vicente, G. M. (2012). Main technologies in biodiesel production: State of the art and future challenges.
- ShahidEM, J. (2008). A review of biodiesel as vehicular fuel. *Renewable and Sustainable Energy*, *12*, 2484-2494.
- Tammo Diercks, M. C., Horst Kessler. Applications of NMR in drug discovery.
- Venu BabuBorugadda, V. G. (2012). Biodiesel production from renewable feedstocks: Status and opportunities. 4763–4784.
- X. Zhang, M. P., Y. Denomme, and C. Jolicoeur. (2006). *235*, 217-240.
- Xuejun Liu, H. H., Yujun Wang, Shenlin Zhu, Xianglan Piao. (2008). Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *87*, 216-221.
- Yilmaz, N. (2011). Temperature-dependent viscosity correlations of vegetable oils and biofuel diesel mixtures. *35*, 2936-2938.
- Zabeti, M., Daud, W. M. A. W., & Aroua, M. K. (2009). Activity of solid catalysts for biodiesel production: A review. *90*, 770–777.