

Electronic Thesis and Dissertation Repository

1-14-2015 12:00 AM

Thermal Conversion of Triglycerides of Vegetable Oil for Production of Renewable Lamp Fuel

Jamie A. Gregory, *The University of Western Ontario*

Supervisor: Cedric Briens, *The University of Western Ontario*

Joint Supervisor: Franco Berruti, *The University of Western Ontario*

A thesis submitted in partial fulfillment of the requirements for the Master of Engineering Science degree in Chemical and Biochemical Engineering

© Jamie A. Gregory 2015

Follow this and additional works at: <https://ir.lib.uwo.ca/etd>

 Part of the [Chemical Engineering Commons](#)

Recommended Citation

Gregory, Jamie A., "Thermal Conversion of Triglycerides of Vegetable Oil for Production of Renewable Lamp Fuel" (2015). *Electronic Thesis and Dissertation Repository*. 2786.
<https://ir.lib.uwo.ca/etd/2786>

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact wlsadmin@uwo.ca.

THERMAL CONVERSION OF TRIGLYCERIDES OF VEGETABLE OIL FOR
PRODUCTION OF RENEWABLE LAMP FUEL

(Thesis format: Integrated Article)

by

Jamie A. Gregory

Graduate Program in Chemical and Environmental Engineering

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Engineering Science

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

© Jamie Gregory 2014

Abstract

The thermal treatment of crop oils was investigated with the aim to produce a renewable, liquid fuel suitable for use in wick-based lighting systems. Specific objectives include reducing fuel viscosity and improving wickability in traditional flat cotton wicks. Pyrolysis and visbreaking processes were the two methods of thermal treatment that were studied. Visbreaking was a semi-batch process carried out in a stirred tank reactor at temperatures ranging from 300 to 500 °C. Pyrolysis utilized a continuous system with a mechanically fluidized bed reactor at temperatures ranging from 400- 650 °C. Initial testing with soybean oil feedstock demonstrated that pyrolysis was the superior process for the application due to its greater severity. Organic liquid yields of up to 93 wt% were observed, with reduction in viscosity as high as 96%. Wickability of the fuel was greatly improved as demonstrated with dedicated testing. Product yields and properties were heavily reliant on reaction temperature in both processes. Feedstocks representing a wide spectrum of crop oil composition were tested with pyrolysis. The proportion of saturated chemical bonds was found to have a negative impact on the product quality at low temperatures. Highly saturated oils required increased temperatures to produce liquid product. Fuels produced from the thermal treatment of crop oils can provide up to 60 wt% in blends with kerosene to produce a successful lamp fuel.

Keywords

Pyrolysis, Vegetable Oil, Triglycerides, Fuel, Wicking

Co-Authorship Statement

Chapter 2

Article Title:

Visbreaking of Triglycerides of Soybean Oil for the Production of Renewable Lamp Fuel

Authors:

Jamie A. Gregory, Anil Jhavar, Franco Berruti and Cedric Briens

Article Status:

To be submitted

Contributions:

Jamie A. Gregory performed all experimental design, work and data analysis. Support and guidance was given by Anil Jhavar. Review of this work was given by Franco Berruti and Cedric Briens. Various analytical testing was performed by Caitlin Marshall. Manuscript drafting and revision was completed by Jamie A. Gregory, and reviewed by Anil Jhavar and Cedric Briens.

Chapter 3

Article Title:

Pyrolysis of Triglycerides of Soybean Oil for the Production of Renewable Lamp Fuel

Authors:

Jamie A. Gregory, Anil Jhavar, Franco Berruti and Cedric Briens

Article Status:

To be submitted

Contributions:

Jamie A. Gregory performed all experimental design, work and data analysis. Support and guidance was given by Anil Jhavar. Review of this work was given by Franco Berruti and Cedric Briens. Various analytical testing was performed by Caitlin Marshall. Manuscript drafting and revision was completed by Jamie A. Gregory, and reviewed by Anil Jhavar and Cedric Briens.

Chapter 4

Article Title:

Pyrolysis of Various Crop Oils for the Production of Renewable Lamp Fuel

Authors:

Jamie A. Gregory, Anil Jhavar, Franco Berruti and Cedric Briens

Article Status:

To be submitted

Contributions:

Jamie A. Gregory performed all experimental design, work and data analysis. Support and guidance was given by Anil Jhavar. Review of this work was given by Franco Berruti and Cedric Briens. Various analytical testing was performed by Caitlin Marshall. Manuscript drafting and revision was completed by Jamie A. Gregory, and reviewed by Anil Jhavar and Cedric Briens.

In addition, review of the remaining dissertation was performed by Cedric Briens.

Acknowledgments

I wish to acknowledge the guidance and support provided by Professors Franco Berruti and Cedric Briens as my supervisors during my time at ICFAR. I would also like to express a special thanks to Dr. Anil Jhawar for his dedication, assistance, and support throughout the experimental stage. A very deep appreciation is sent out to Rob Taylor, Tom Johnston, and Quinn Rush for their mechanical support throughout the process. Without their help, this study would not have been possible. In addition, I would like to thank Caitlin Marshall for her support with the analytical lab testing. I would also like to thank my colleagues and friends at ICFAR. Their mentoring and willingness to help was invaluable throughout my study.

I express gratitude to NSERC and BioFuelNet for their generous funding.

Finally, I would like to thank my family and close friends for their continuous encouragement and support: Tracey Gregory, Steve Gregory, Shirley Morrison, Anna Nuhn, and my brothers David, Ryan, and Jake Gregory.

Table of Contents

Abstract	ii
Co-Authorship Statement.....	iii
Acknowledgments.....	iv
Table of Contents	v
List of Tables	ix
List of Figures	xi
List of Appendices	xv
Chapter 1	1
1. INTRODUCTION	1
1.1 Background and Motivation	1
1.2 Crop Oils.....	2
1.3 Wick-based lamps.....	4
1.4 Wicking in Porous Media	9
1.5 Conversion Technologies.....	13
1.5.1 Fractional crystallization.....	13
1.5.2 Transesterification.....	15
1.5.3 Visbreaking.....	17
1.5.4 Pyrolysis.....	18
1.6 Present thesis work	19
1.7 References.....	20
Chapter 2	24
2. VISBREAKING OF TRIGLYCERIDES OF SOYBEAN OIL FOR THE PRODUCTION OF RENEWABLE LAMP FUEL	24
2.1 Introduction.....	24
2.2 Materials	29

2.2.1	Feedstock Selection	29
2.2.2	Commercial Fuels	30
2.3	Methods.....	30
2.3.1	Equipment.....	30
2.3.2	Experimental Procedure.....	32
2.3.3	Experimental design.....	33
2.3.4	Product Analysis	35
2.4	Results and Discussion	42
2.4.1	Design of Experiments Evaluation	42
2.4.2	Phase Yields.....	46
2.4.3	Liquid Properties.....	51
2.4.4	Wickability.....	54
2.4.5	Lamp Performance.....	58
2.4.6	Product Blending	59
2.5	Conclusions and Recommendations	62
2.6	References.....	63
Chapter 3	65
3.	PYROLYSIS OF TRIGLYCERIDES OF SOYBEAN OIL FOR PRODUCTION OF RENEWABLE LAMP FUEL	65
3.1	Introduction.....	65
3.2	Materials	68
3.2.1	Feedstock Selection	68
3.2.2	Commercial Fuels	68
3.2.3	Bed Material.....	68
3.3	Methods.....	68
3.3.1	Equipment.....	68

3.3.2	Experimental Procedure	71
3.3.3	Product Analysis	71
3.4	Results and Discussion	72
3.4.1	Effect of Reaction Parameters	72
3.4.2	Phase Yields.....	73
3.4.3	Liquid Properties.....	77
3.4.4	Wickability.....	80
3.4.5	Lamp Performance.....	83
3.4.6	Product Blending	85
3.4.7	Pyrolysis vs. Visbreaking.....	88
3.5	Conclusions and Recommendations	92
3.6	References.....	94
Chapter 4	96
4.	PYROLYSIS OF VARIOUS CROP OILS FOR PRODUCTION OF RENEWABLE LAMP FUEL	96
4.1	Introduction.....	96
4.2	Materials	98
4.2.1	Feedstock	98
4.2.2	Commercial Fuels	100
4.2.3	Bed Material.....	100
4.3	Methods.....	101
4.3.1	Equipment.....	101
4.3.2	Experimental Procedure.....	101
4.3.3	Product Analysis	102
4.4	Results and Discussion	102
4.4.1	Phase Yields.....	102

4.4.2	Liquid Properties.....	107
4.4.3	Wickability.....	110
4.4.4	Lamp Performance.....	113
4.4.5	Product Blending	113
4.5	Conclusions and Recommendations	116
4.6	References.....	117
5.	Conclusions and Future Outlook.....	118
6.	Appendix A	120
	Curriculum Vitae	123

List of Tables

Table 1.1: Fatty Acid Composition (wt%)	3
Table 1.2: Liquid Fuel Property Comparison of Kerosene and Soybean Oil	6
Table 1.3: Liquid Fuel Properties of AGOWA Lamp Oil	7
Table 1.4: Pure Triglyceride Viscosities (Valeri & Meirelles, 1997).....	15
Table 2.1 Properties of Pyrolyzed Fuel Obtained from Soybean Oil ¹	27
Table 2.2: Fatty Acid Composition of Soybean Oil	29
Table 2.3: Experimental Design: Multi-level Three-Factor	34
Table 2.4: Viscometer Specifications	35
Table 2.5: Surface Tensions of Known Liquids used in Method Calibration	37
Table 2.6: ANOVA Values for Response 1- Organic Liquid Yield	44
Table 2.7: Summary of p- values for Responses and Model	46
Table 2.8: Surface Tension Comparison.....	54
Table 2.9: Wicking Coefficients of Untreated Oil, Visbreaking Liquid Products, and Kerosene	56
Table 2.10: Liquid Properties of Successful Fuels	61
Table 3.1: Wicking Coefficients of Untreated Oil, Pyrolysis Products, and Kerosene	82
Table 3.2: Optimal Visbreaking and Pyrolysis Conditions	91
Table 4.1: Fatty Acid Composition of Various Crop Oils(wt%)	99
Table 4.2: Saturation of Various Crop Oils	99
Table 4.3: Feedstock Viscosities (cP).....	100

Table 4.4: Feedstock Saturation Levels	106
Table 4.5: Wicking Coefficient Comparison of Various Liquids.....	111

List of Figures

Figure 1.1: Triglyceride molecule.....	2
Figure 1.2: a.) kerosene lamp, b.) cotton wicks	5
Figure 1.3: Flame comparison of a- kerosene and b- soybean oil fuel in traditional wick-based lamp	9
Figure 1.4: Liquid rise in capillary tube (Pillai & Hooman, 2012).....	10
Figure 1.5: Transesterification of triglyceride molecule (“Biodiesel production and the transesterification process,” n.d.).....	16
Figure 2.1: Process schematic of pool visbreaking unit	31
Figure 2.2: Liquid droplet in equilibrium with surface tension	36
Figure 2.3: Wickability test. a- schematic, b- photo	39
Figure 2.4: Vertical penetration of wicking paper vs. cotton wick. Organic liquid shown obtained from pyrolysis at T= 450 C.	40
Figure 2.5: Half-Normal Plot for Organic Liquid Yield.....	43
Figure 2.6: Predicted vs. Actual Values of Organic Liquid Yield.....	45
Figure 2.7: Factor effects on visbreaking liquid yield. a) one factor (Temperature). b) two factor interaction	48
Figure 2.8: Effect of temperature on visbreaking phase yields	50
Figure 2.9: Factor effects on dynamic viscosity of visbreaking liquid products. a) one factor (Temperature). b) two factor interaction.....	52
Figure 2.10: Factor effects on surface tension of visbreaking liquid products. a) one factor (Temperature). b) two factor interaction.....	53

Figure 2.11: Wickability test of visbreaking samples.....	55
Figure 2.12: Effect of visbreaker temperature on wickability of visbreaking liquid products	55
Figure 2.13: Linearized plot of penetration test. ($T= 450\text{ C}$, $W_c = 0.254\text{ cm/s}^{1/2}$).....	57
Figure 2.14: Effect of temperature on wicking coefficient (W_c) of visbreaking liquid products	57
Figure 2.15: Wick consumption with inadequate fuel. . Visbreaking sample obtained at 450 C, $t= 120\text{ min}$	58
Figure 2.16: Insufficient fuel supply in a traditional wick lamp. (left) initial ignition, (right) flame diminishing. Visbreaking sample obtained at 450 C, $t= 120\text{ min}$	59
Figure 2.17: Effect of reaction temperature on kerosene loading required for successful lamp operation	60
Figure 2.18: Kerosene loading vs. wicking coefficient of visbreaking fuel	61
Figure 3.1: Fast pyrolysis schematic.....	70
Figure 3.2: Effect of mixing speed on pyrolysis liquid product yield	73
Figure 3.3: Effect of temperature on pyrolysis liquid product yield.....	74
Figure 3.4: Effect of temperature on pyrolysis gas product yield.....	75
Figure 3.5: Effect of temperature on pyrolysis residue yield.....	75
Figure 3.6: Effect of temperature on pyrolysis product phase yields	76
Figure 3.7: Effect of reaction temperature on dynamic viscosity of pyrolysis liquid products	78
Figure 3.8: Effect of reaction temperature on surface tension of pyrolysis liquid products...	78
Figure 3.9: Surface Tension vs. Viscosity map of various pyrolysis liquids, untreated oil, and commercial fuels.....	79

Figure 3.10: Wickability test of paraffin, pyrolysis liquid products, and untreated oil.	81
Figure 3.11: Effect of pyrolysis temperature on wicking of pyrolysis liquid products	81
Figure 3.12: Effect of temperature on wicking coefficient (W_c) of pyrolysis liquid products	82
Figure 3.13: Wick consumption with inadequate fuel. Pyrolysis sample obtained at 450 C .	84
Figure 3.14: Insufficient fuel supply in a traditional wick lamp. (left) initial ignition, (right) flame diminishing. Pyrolysis sample obtained at 450 C.....	84
Figure 3.15: Effect of reaction temperature on required kerosene fraction of kerosene-pyrolysis oil fuel mixture for successful lamp operation.....	86
Figure 3.16: Effect of pyrolysis product viscosity on required kerosene fraction of kerosene-pyrolysis oil fuel mixture for successful lamp operation.....	86
Figure 3.17: Surface tension vs. viscosity map of successful fuel blends, pyrolysis liquid products, and untreated oil.....	87
Figure 3.18: Effect of temperature on phase yields of visbreaking and pyrolysis processes .	89
Figure 3.19: Wicking coefficient vs. surface tension for visbreaking and pyrolysis products	89
Figure 3.20: Wicking coefficient vs. viscosity for visbreaking and pyrolysis products.....	90
Figure 3.21: Performance comparison between visbreaking and pyrolysis- Wicking Coefficient vs. Liquid Product Yield.....	91
Figure 4.1: Effect of temperature on pyrolysis phase yields (Canola Oil)	104
Figure 4.2: Effect of temperature on pyrolysis phase yields (Safflower Oil).....	104
Figure 4.3: Effect of temperature on pyrolysis phase yields (Palm Kernel Oil).....	105
Figure 4.4: Effect of temperature on pyrolysis phase yields (Palm Oil)	105
Figure 4.5: Effect of saturation on pyrolysis liquid product yield of varying unsaturated contents (Soybean, Safflower, Canola).....	107

Figure 4.6: Viscosities of organic liquids from pyrolysis of various crop oils.....	109
Figure 4.7: Surface tension of organic liquids from pyrolysis of various crop oils.....	110
Figure 4.8: Surface Tension vs. Viscosity map of commercial fuels, pyrolysis liquid products, and untreated crop oils	110
Figure 4.9: Wicking coefficient of liquid product from various feedstocks.....	112
Figure 4.10: Effect of reaction temperature on kerosene blending (multiple feedstocks)....	115
Figure 4.11: Surface tension vs. viscosity map of successful fuel blends (multiple feedstocks)	115
Figure 6.1: Surface tension drop mass calibration curve	120
Figure 6.2: Factor effects on Gas Yield. a) one factor (Temperature). b) two factor interaction	121
Figure 6.3: Factor effects on Residue + Wax Yield. a) one factor (Temperature). b) two factor interaction	122

List of Appendices

6. **Appendix A** 120

Chapter 1

1. INTRODUCTION

1.1 Background and Motivation

Global energy consumption is rising. Driven by increasing energy demand in developing countries, global consumption is projected to increase by 56% over the next 30 years (Fletcher, 2013). An interesting, and often overlooked sector of the energy market is fuel-based lighting. Worldwide this accounts for \$38 billion in fuel requirements and 260 MT of carbon dioxide emissions annually (Mills & Ph, 2003). With population growth far exceeding the spreading availability of electricity, this market is steadily increasing. There are close to 1.8 billion people, almost 20% of the global population, without access to electricity (Mills & Ph, 2003). Developing countries such as India and many African countries make up the majority of that population. In addition, communities such as the Amish and Mennonite populations traditionally turn to fuels over electricity for their energy needs. While petroleum-derived fuels provide the majority of this demand, renewable sources have increased 300% over the past 60 years and will be of crucial importance as the finite source of fossil fuels continues to dwindle. The anticipated scarcity of fossil fuels, their climbing costs, and the increasing emissions of combustion products are propelling world interest in the research and production of biofuels (Demirbas, 2009).

Biofuels are a category of alternative fuels that in principle represent any fuel of biological origin (Kubičková & Kubička, 2010). Biofuels are being produced worldwide and include fuels such as biodiesel, green diesel, bioalcohols, and bioethers to name a few. Feedstocks range from switchgrass to woody biomass to sewage sludge to crop oils. Much of the interest is focused on biofuels for use as transportation fuels, but the potential for biofuels in fuel-based lighting is strong.

1.2 Crop Oils

The abundance of triglycerides (TGs) and their high content of carbon and hydrogen suggest the possibility of a renewable, alternative feedstock to crude-derived products. Crop oils, such as canola oil and soybean oil, are made up almost exclusively of TGs. Crop, or vegetable, oils are extracted from oil-rich crops such as soybeans, rapeseed, sunflowers, peanuts, and olives. There are over 350 oil-bearing crops currently identified (Dupain, Costa, & Schaverien, 2007). These oils are comprised of various combinations of TGs, dependent on the crop origin.

Although different crop oils can exhibit a variety of physical properties, the chemical structure is similar. TG molecules consist of three moles of fatty acid chains linked to one mole of glycerin, as seen in Figure 1. Small amounts of di- and monoglycerides are also present in the oils (< 5 wt%).

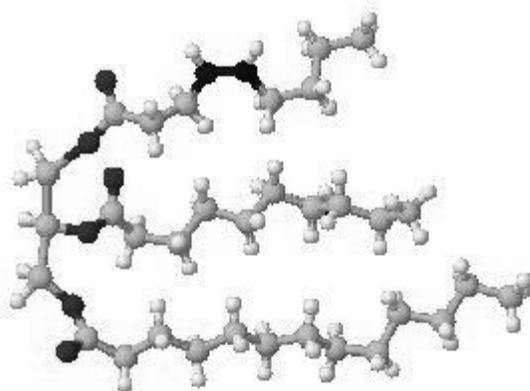


Figure 1.1: Triglyceride molecule

Fatty acids are carboxylic acids with a long aliphatic tail. This tail, or chain, can be either saturated or unsaturated. The fatty acid tails are typically 8-18 carbon molecules in length, containing up to three C=C double bonds. Fatty acid composition of some common crop oils can be found in Table 1.

Table 1.1: Fatty Acid Composition (wt%)

Vegetable Oil	Caprylic C8	Capric C10	Lauric C12	Myristic C14	Palmitic C16	Stearic C18	Oleic C18:1	Linoleic C18:2	Linolenic C18:3
Canola					4	2	56	26	10
Safflower					7	3	14	75	
Soybean					11	4	24	54	7
Palm				1	44	4	40	10	
Palm Kernel	3	3	48	16	8	3	15	2	

The use of vegetable oils as fuels dates back almost as far as the diesel engine itself. Rudolf Diesel, the creator of the first diesel engine, reportedly used peanut oil as a fuel for demonstration purposes in 1900 (Nitske & Wilson, 1965). In the 1920s, soybean oil was used to fuel the early diesel engines (Kubičková & Kubička, 2010). The inexpensive, petroleum-derived, hydrocarbon-based fuels then dominated the market for decades. Research interest in vegetable oil-derived fuels decreased drastically, transitioning to petroleum derivatives. The use of vegetable oils as an alternative renewable fuel to compete with petroleum was re-introduced in the beginning of the 1980s (Bartholomew, 1981).

Crop oils contain negligible sulphur, nitrogen, and heavy metal content resulting in low environmental impact. Due to their chemical composition and physiochemical properties, TGs prove to be a viable fuel source. Their liquid state makes for an easily transportable feedstock. Vegetable oils also possess a high energy density, up to 90% of traditional diesel (Maher & Bressler, 2007). As much of the target population for this technology are farming communities already producing oil seed crops, the opportunity arises for a cost-effective, environmentally-friendly fuel source, utilizing local feedstock.

1.3 Wick-based lamps

Since the discovery of fire, man began seeking solutions to obtain portable, controllable forms of light. The first solution dates back as far as 70 000 B.C. in the form of an oil lamp (“History of Kerosene Lamps,” n.d.). This primitive technology consisted of shells or hollow rocks filled with moss and soaked in animal fats. As time went on man-made containers were developed of materials such as terracotta, bronze, or clay. A glass tube chimney was added to direct the draft and intensify the flame. Fuels ranged from animal fats to olive oil to fish oil to beeswax. The same basic design has not changed. Lamps consist of a non-flammable container to hold a flammable substance which is soaked up by a wicking material to carry the fuel to the flame.

Oil lamps were quickly made obsolete by the discovery of kerosene. Oil lamps were inefficient, dirty, and produced little light in comparison (“History of Kerosene Lamps,” n.d.). The use of oil lamps is currently limited to religious events and ambient, decorative lighting. In the case of developing countries, as well as Mennonite or Amish communities, the main source of lighting is kerosene lamps. Kerosene lamps, also known as hurricane lamps or barn lamps, are wick-based lighting systems that utilize mainly cotton wicks. An example of a typical kerosene lamp can be seen in Figure 1a. These lamps consist of a glass reservoir where the kerosene is stored, a special metal housing component, a glass chimney (or globe), and of course a wick. The metal component serves three functions. Firstly it holds the wick in place and contains an adjustment dial to move the wick vertically up and down. Secondly, it contains a metal wick sleeve surrounding the wick which heats up as the lamp burns, aiding the heat transfer of the flame to the wick, in turn causing evaporation of the fuel into flammable vapours. The wick sleeve also prevents the flame from travelling down the wick to the reservoir. Lastly, the metal housing contains small holes allowing air to flow upwards feeding oxygen to the flame and intensifying the light.

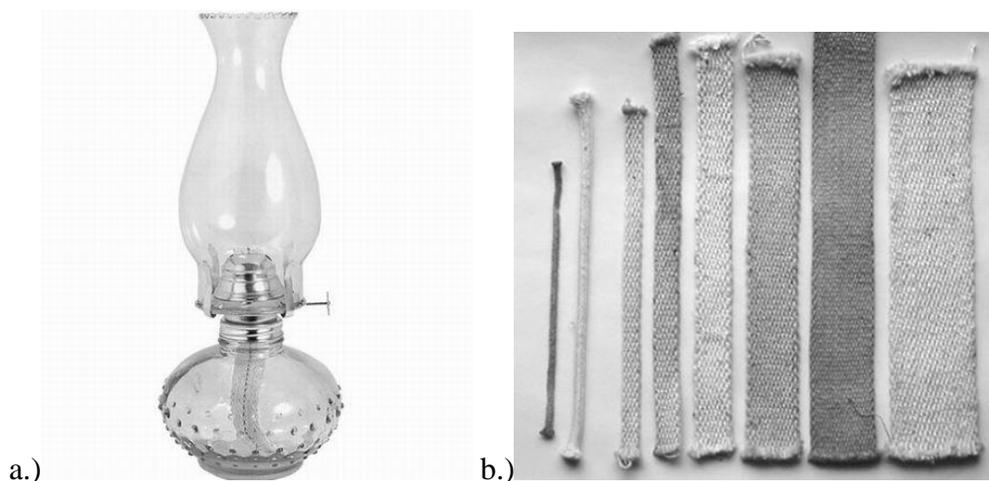


Figure 1.2: a.) kerosene lamp, b.) cotton wicks

Wicks come in all shapes and sizes, in many materials. The purpose of the wick is to draw fuel from the reservoir to supply the flame. The material of the wick must be naturally absorbent or have high capillary action between non-absorbent fibres. Wick materials are mainly cotton and other natural fibres. However, non-combustible wicks have been developed using materials such as fiberglass, cement, plaster of paris, and Kevlar; although these are expensive and rarely used (“The Lamp Wick,” n.d.). The shape of the wick also varies. Some wicks used in the more advanced lamps can be tubular or even consist of two wicks of semi-circular shape. The oil lamp utilizes a cylindrical wick of woven cotton similar to a rope. The most common wicks however, are flat cotton wicks (see Figure 1b). These wicks are made from natural cotton, tightly weaved and oriented in a flat, rectangular shape. The width of these wicks varies depending on the size of the lamp.

Commercial Fuels

The fuel used in wick-feeding lamps is almost exclusively kerosene. Kerosene is a petroleum derived fuel containing hydrocarbons in the range of 6-16 carbons in length. It is obtained by the distillation of petroleum between 150-265 °C. The main components are straight chain alkanes and cycloalkanes (~70 vol. %), with aromatic hydrocarbons not

exceeding 25 vol. %. Olefins are present in small amounts (< 5 vol. %) (“Chemical and physical information,” 1989). See Table 1.2 for other liquid properties.

Another fuel available commercially and used mostly in recreational activities such as camping is branded as paraffin-based fuel. Paraffin in some areas is synonymous to kerosene, but in North America these paraffin based-fuels are a mixture of kerosene and other additives to enhance the fuel’s odour and appearances. These fuels come in colours such as red, blue, and yellow, and in scents such as “Cool Breeze,” “Pomegranate” and “Citronella.” Throughout this study these fuels will be referred to as Paraffin.

Table 1.2: Liquid Fuel Property Comparison of Kerosene and Soybean Oil

Property	Units	Kerosene	Soybean Oil
Dynamic Viscosity (25 °C)	cP	0.90 ¹	49.4 ¹
Density (20 °C)	g/cm ³	0.80 ¹	0.915 ¹
Flash Point	°C	60-80 ⁴	327 ²
LHV	MJ/kg	43.1 ⁴	37 ³
HHV	MJ/kg	46.2 ⁴	39.6 ³
Surface Tension	dyne/cm	26.41 ⁵	40.91 ⁵
Boiling Point	°C	150-275 ⁴	-
Pour Point	°C	-45 ⁴	-14 ²

¹ measurement obtained as per ASTM D 445, ² (Hammond, Johnson, Su, Wang, & White, 2003), ³ (Patzek, 2009), ⁴ (“Chemical and physical information,” 1989), ⁵ measurements as defined in Chapter 2.

Kerosene is a petroleum-derived fuel leading to its high price volatility. It is toxic to humans when ingested or inhaled. As previously stated this liquid represents a \$38 billion market contributing 260 MT of carbon dioxide emissions every year, for lighting needs alone. Knowing the detrimental impact of this fuel, many countries such as Nigeria are making significant efforts to reduce its consumption and move to cleaner fuels (Adejoro, 2014). Kerosene is a non-renewable fuel and a major contributor to GHG emissions. The need for an alternative is evident.

The only renewable lamp fuel currently in commercial production is produced by a company in Denmark called AGOWA. Its lack of toxicity and its reduced carbon footprint make this fuel very attractive in the marketplace. Primarily focusing on the café and restaurant market, as well as indoor and outdoor lighting applications in developed nations, this fuel has seen considerable success with annual revenues between \$2- 5 million USD. A recent partnership with EGO has led to development of clean burning, aesthetically pleasing lamps for primarily indoor use.

This fuel is comprised of various compositions of alkyl-esters of vegetable oil derivatives in the C₆-C₁₆ range. The majority of their feedstock is obtained from transesterified crop oils produced by Proctor and Gamble. The parent crops are a mixture of palm kernel and coconut oils. Subsequent to transesterification, the products are separated into three fractions: a light, middle, and heavy fraction. The heavy fraction is used primarily for biodiesel. The middle fraction is used in soaps and shampoos applications, and the light fraction is acquired by AGOWA to produce the lamp fuel. This fraction is typically only 10-12% of the original crop oil (Moller & Pederson, 2010). The acceptable properties of this fuel are given in Table 1.3.

Table 1.3: Liquid Fuel Properties of AGOWA Lamp Oil

Property	Units	AGOWA Lamp Oil ¹
Dynamic Viscosity (25 °C)	cP	1-3
Flash Point	°C	< 100
Surface Tension	dyne/cm	< 30
Melting Point	°C	< 0

¹obtained from (Moller & Pederson, 2010)

²measurements at 20 °C

The combustion of lamp fuel can be split into two processes: the supply of fuel up the wick, and the combustion of fuel to produce light. To produce the flame, the liquid fuel is supplied via the wick through capillary action towards the top surface of the wick. As the fuel reaches the surface, evaporation occurs providing a gas phase reactant for

combustion in air. The fuel vapour is required for combustion, and in turn the combustion provides heat feedback to the wick for vapourization. The evaporation of the fuel drives the capillary action by causing a saturation gradient (Raju & T'ien, 2008). Saturation is a measure of the fraction of voids in the wicking material that are occupied by liquid, on a volume/volume basis. Models have been proposed to explain this combustion process and rely on a number of factors including flame temperature, porosity, permeability, orientation, wick dimensions, fuel composition, and various liquid and gas properties. The supply process is equally important as it ensures that the saturation gradient remains at steady-state. As evaporation occurs decreasing the saturation of the wick, there must be an adequate supply of fuel to maintain saturation. If saturation reaches zero, the fuel supply is insufficient and the flame is extinguished.

As previously mentioned, crop oils have been used in lighting applications dating back many years. It has been clearly demonstrated that combustion of crop oils yields a bright flame. If the flame is supplied with the required volume of fuel for the given system, untreated crop oils can provide a viable light source. As seen in the two figures below, the flame shape, size, and brightness is similar in comparison to kerosene. The major difference is that the flame in Figure 3b, supplied by soybean oil, extinguished after a few seconds. The issue appears to be the supply of fuel. Therefore, the combustion process is assumed to be sufficient, shifting the focus of this study to the supply process. Specifically, wicking and its associated liquid properties require further investigation.

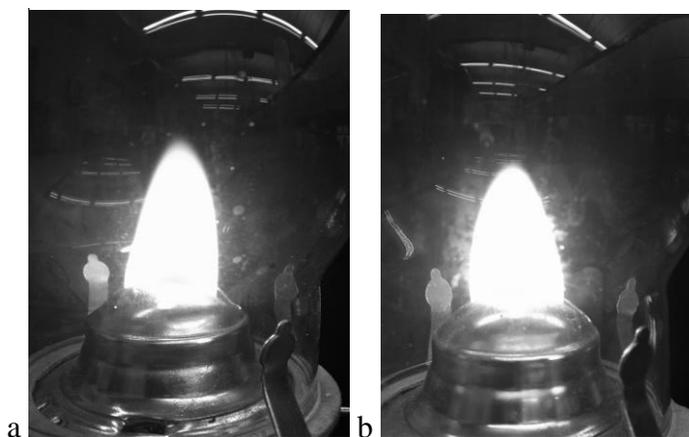


Figure 1.3: Flame comparison of a- kerosene and b- soybean oil fuel in traditional wick-based lamp

1.4 Wicking in Porous Media

Wicking is a physical phenomenon that, in the case of the lamp, allows for fuel to be automatically transported to the light-producing flame. Wicking, or spontaneous imbibition, is the displacement of a non-wetting fluid by a wetting, more viscous, immiscible fluid (Masoodi & Pillai, 2012a). In majority of cases, the non-wetting fluid being displaced is air.

Wicking and wetting applications can be found in processes such as oil recovery, resin transfer moulding, penetration of ink into paper, and absorption of water into paper towels. Due to this wide range of applications, extensive research has been undertaken on the subject (Masoodi & Pillai, 2012b).

The wicking of a fluid into a porous medium is a balance between cohesive and adhesive forces. Intermolecular forces, such as attractive forces between neighbouring water molecules, represent the cohesive forces. Surface tensions of both the liquid and the solid are the primary cohesive forces. Intermolecular forces between different molecules

represent the adhesive forces. Attractive forces between liquid molecules and cotton fibres for instance, account for adhesive forces in a cotton wick. Adhesive forces determine wettability in a system, an important property in wicking (Zhou, 2012). The simplest example of liquid rise due to this force balance is the rise of liquid in a glass capillary tube as seen in Figure 4. When the adhesive forces of the liquid are greater than the cohesive forces within the liquid, the liquid meniscus will rise up the glass tube. This is an example of the capillarity phenomenon. The height of rise of the liquid column (h) will vary dependent on parameters such as capillary radius, contact angle, as well as various other liquid properties explained later.

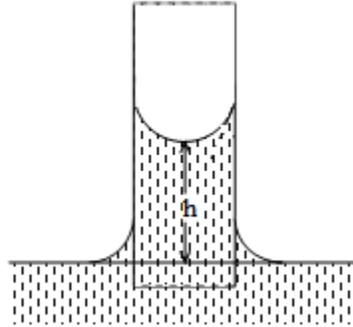


Figure 1.4: Liquid rise in capillary tube (Pillai & Hooman, 2012)

In 1805, two researchers by the name of Thomas Young and Pierre Simon de Laplace independently explained the value of the driving pressure known as capillary pressure. This is the pressure difference across the interface between the non-wetting and wetting fluids. The result of their findings is the well-known Young-Laplace equation (Equation 1.1) for capillary pressure (p_c) in a capillary tube, where σ is surface tension of the liquid, and R_c is capillary radius, and θ is contact angle.

$$p_c = \frac{2\sigma\cos\theta}{R_c} \quad [1.1]$$

When modelling a system of wicking through a porous medium, there are many different approaches that can be taken. These vary in complexity, with the simplest approach being

the assumption that the porous material acts as a bundle of aligned capillary tubes. This was first published by Lucas (1918) and Washburn (1921), independently (Masoodi & Pillai, 2012b). This model is based on the capillary model and uses momentum balance to derive an expression for meniscus height as a function of time in a capillary tube (Masoodi & Pillai, 2012a). This model neglected gravity and inertial effects. Since then, many modifications have been proposed to this model to account for neglected terms. Some other, more complex models include porous-continuum models, discrete models, and statistical models. These can give a more accurate picture of the process, but are less common due to increasing complexity.

The Lucas-Washburn model is used to describe wicking through porous media by balancing the Young-Laplace equation for capillary pressure (Equation 1.2) with the viscous force (friction) effects. This model considers the capillary pressure to be far greater than the hydrostatic pressure due to gravity, as well as the inertial forces. Neglecting gravity and inertial forces leads to the following pressure balance. The left side representing capillary pressure and the right side accounting for viscous forces.

$$\frac{2\sigma \cos \theta}{R_c} = \frac{8\mu h \dot{h}}{R_h^2} \quad [1.2]$$

where μ is dynamic viscosity of the liquid, \dot{h} is dh/dt , and R_h is hydraulic radius (Pillai & Hooman, 2012). Solving this equation using the initial condition $h(t=0) = 0$, yields the Lucas-Washburn equation seen below.

$$h = \sqrt{\frac{\sigma R_e \cos(\theta)}{2\mu} t} \quad [1.3]$$

where R_e is the effective capillary radius given by

$$R_e = \frac{R_h^2}{R_c} \quad [1.4]$$

From the Lucas-Washburn equation it can be seen that surface tension and viscosity are important liquid properties in wicking. Solid properties such as effective capillary radius, porosity, and permeability also influence the performance of wicking. The measurement of these properties is outside the scope of this report, and therefore the porous solid material properties will be kept constant to allow comparative wicking analysis of the liquid samples.

Applying this model to compare the wicking properties of kerosene to those of untreated soybean oil demonstrates the poor wickability of the untreated oil. Rearranging Equation 1.2 to isolate vertical penetration velocity yields Equation 1.5. Assumptions of this model include: a) gravity and inertial effects are negligible; b) saturation level is constant throughout h ; and c) physical properties of the liquid and the solid remain constant throughout the system

$$\dot{h} = \frac{dh}{dt} = \frac{2R_e\sigma \cos(\theta)}{8\mu h} \quad [1.5]$$

A ratio of the rise velocity of soybean oil to that of kerosene allows for a quick comparative analysis of the wicking properties of the two liquids. Assuming that both liquids completely wet the solid fibres and that both liquids are penetrating into identical porous solids (wicks), Equation the ratio simplifies to give Equation 1.6.

$$\frac{\dot{h}_s}{\dot{h}_k} = \frac{\sigma_s/\mu_s}{\sigma_k/\mu_k} \quad [1.6]$$

Substituting liquid property values as seen in Table 2, and solving gives

$$\frac{\dot{h}_s}{\dot{h}_k} \approx 0.027 \quad \text{or} \quad \frac{\dot{h}_k}{\dot{h}_s} \approx 37.5 \quad [1.7]$$

Therefore in a given wicking system, at a given height, soybean oil will climb the wick at a rate 2.7% of that of kerosene. It is clear that the feasibility of crop oils as fuel in wick-based lighting systems will depend on the improvement of wicking characteristics.

This is consistent with specifications of AGOWAs lamp fuel described above. As stated in their patent application, viscosity is the most controlled property for operation of AGOWA's green lamp fuel due to its effect on the wicking characteristics of the fuel (Moller & Pederson, 2010). Raw vegetable oil is too viscous to climb the wick at a rate sufficient for fuel consumption. Although different wick characteristics will vary the viscosity required, the maximum specification of AGOWA's lamp fuel viscosity is < 5 cP for outdoor lamps. This is drastically lower than crop oil viscosities, which range from 49.4 cP in the case of soybean oil to solid at room temperature in the case of palm kernel oil.

1.5 Conversion Technologies

The issue with untreated crop oils is their physical liquid properties. The viscous, high molecular weight compounds prevent the oil from being a viable fuel source in most applications. When considering kerosene lamps, the untreated vegetable oil displays poor wicking characteristics and is unable to climb the wick at a rate sufficient to fuel the flame. To meet the property requirements of this fuel, a number of methods were investigated.

1.5.1 Fractional crystallization

Fractional crystallization or dry fractionation is a common process used in refining vegetable oils. This technique, used mainly in the food industry, can separate TGs by their fatty acid profile. For instance, oils containing higher contents of saturated fatty acids, such as palm and palm kernel, have a wide array of TG combination resulting in broad melting intervals. This makes the oils unsuitable for retail use, and further processing is required. Liquid vegetable oils such as soybean and canola are typically refined and sold without any further processing (Bootello et al, 2011).

The mechanism behind this process relies on the differentiation of various melting points of species of TGs. As previously noted a TG contains three fatty acids. A species of TG that contains more saturated fatty acids such as tristearin will have a higher melting point than a TG species with mostly unsaturated acids such as trilinolein. Fractional crystallization is a multi-step process. Each crystallization step yields a solid phase (called the stearin) and a liquid phase (called the olein) (Bootello et al., 2011). These phases are separated through pressure filtration. Each phase can then be further separated at various temperatures, producing more valuable products with narrow melting ranges.

The basic steps in this process involve first heating the material to elevated temperatures (~80 °C) to destroy the crystal memory, this is called the melt. The melt is then sent to a cooling vessel, or crystallizer, where the material is cooled at predetermined rates resulting in crystallization. Crystallization is a phenomenon consisting of three stages: a) supercooling of the melt, b) crystal nucleation, and c) crystal growth. The rates of these stages and sizes and shapes of the crystals rely strongly on the conditions of the process.

Dry fractionation is a fairly efficient separation process with little impact on the environment. It is preferred over its counterpart of solvent extraction due to the avoidance of harmful solvents (Toro-Vazquez et al., 2002). However it becomes a very complex and difficult process as the desired melting point distribution narrows. The issue with this technology for the purpose of lamp fuel production is that the composition of the crop oils prevents its feasibility. Even in perfect separation of the individual TG species, the resultant product would not meet the lamp oil requirements. As seen in Table 1.4, TG species are too viscous for this application. Therefore conversion of the TGs is required.

Table 1.4: Pure Triglyceride Viscosities (Valeri & Meirelles, 1997)

Temperature (°C)	Viscosity (cSt)			
	Tricaprilin	Tripalmitin	Tristearin	Triolein
20				86.6958
30	17.3424			56.6127
40	12.3109			38.6284
50	9.1460			27.6632
60	7.1029			20.8588
70	5.6760	17.3069		15.3199
75		15.4161	18.7471	
80	4.7348	13.1755	16.3086	12.2278
85		11.6050	14.4477	
90	3.7795	10.3734	12.9165	9.9367

1.5.2 Transesterification

Transesterification is of fundamental importance in the biodiesel industry. Biodiesel as it is known today is defined as the fatty acid methyl esters obtained through transesterification of vegetable oils (Gerpen et al., 2004). This process reacts triglycerides of vegetable oils with an alcohol in the presence of a catalyst. The alcohol most commonly used is methanol due to its availability and low cost. The products of this reaction are alkyl esters (usually methyl esters) and glycerol. As seen in the figure below three moles of alcohol are required for every one mole of triglycerides. This results in production of three moles of alkyl ester (biodiesel) and one mole of glycerol (also known as glycerine). Glycerol in the past was considered a valued side product of this process, but due to the increased biodiesel production the supply of glycerol has become far greater than its demand. However, research is being undertaken to use this waste stream as feedstock for value-added chemicals such as propylene glycol (“A renewable future with biodiesel and glycerin,” n.d.).

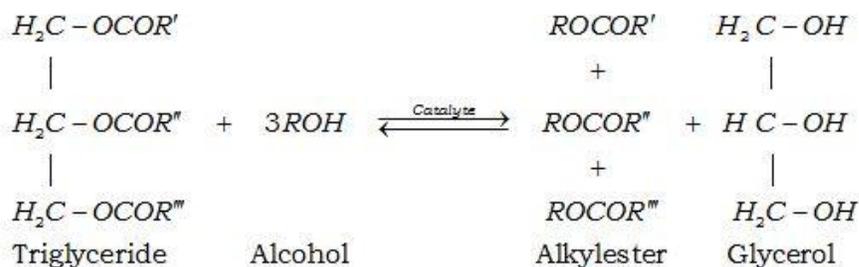


Figure 1.5: Transesterification of triglyceride molecule (“Biodiesel production and the transesterification process,” n.d.)

For this reaction to occur, it is common that 6 moles of alcohol are added for every one mole of triglycerides. As seen above, transesterification is a reversible reaction. Therefore excess methanol is added to shift the equilibrium of the reaction to the right, favouring biodiesel production. To obtain the biodiesel, product separation is carried out using water. The solubility difference of methyl ester and glycerine in water allow physical separation of the streams. This results in high volumes of wastewater to be treated.

In addition, this process requires the presence of catalysts. Base catalysts such as NaOH (sodium hydroxide) and KOH (potassium hydroxide) are used. Acid catalysts can also be used but it has been shown that base catalysts are superior for this process. Catalysts such as NaOH and KOH are inorganic compounds with dangerous impacts on both humans and the natural environment. NaOH for instance is strongly corrosive a powerful irritant to humans in all routes of exposure. It is also designated as a hazardous substance under the Federal Water Pollution Control Act stating its negative impact in both water pollution and air pollution (Gerpen et al., 2004). Due to the combination of alcohol requirements, catalyst requirements, and wastewater generation this process was not considered in this study. Considering the remote location of the target population for this technology, a simple, safe, and environmentally friendly approach was desired. Furthermore, the properties of biodiesel are not sufficient for operation in wick-feeding lamps. The viscosity is too high (~4.6 cSt at 40 °C) and wickability is not sufficient.

1.5.3 Visbreaking

Visbreaking is a process developed for the petrochemical industry with the objective of increasing yields of low molecular weight hydrocarbons. This process was developed in the 1930s to produce more valuable products. Viscous, high molecular weight liquids such as vacuum residues or oil sands bitumen are sent to the visbreaker where naphtha, as well as some kerosene and gas oil boiling range material are produced (Speight, 2012). The term visbreaking stems from ‘viscosity breaking’ or ‘viscosity reduction’ as the end product is much less viscous than the feedstock. In essence, it is a very mild form of thermal cracking, or slow pyrolysis, in that thermal cracking reactions are not allowed to proceed to completion.

There are two variations of the visbreaking process: coil and soaker (or pool). In coil visbreaking the feedstock material is passed through a high temperature coil, then immediately quenched, halting the cracking reactions. This process is characterized by higher temperatures of 455-510 °C and short residence times. Issues with coil visbreaking are coke deposits on the coil within the furnace. The need for de-coking is very frequent in relation to pool visbreaking. Accumulation of coke on the coil walls can lead to plugging and variation in residence time. This is especially evident in lab-scale reactors as coil diameters are smaller. The pool visbreaker achieves conversion by long residence times as opposed to high temperatures. Relatively low temperatures of 300-500 °C and long residence times in the order of hours are typical of this method. Advantages of this method include lower operating costs due to lower temperatures. Drawbacks of this method include longer processing times and more complex methods for coke removal (Joshi et al., 2008). At lab-scale operation, complex coke removal is not an issue.

When applied to triglycerides, the visbreaking process has the potential to reduce the viscosity of the oils by cracking the long-chain TG molecules. Visbreaking will be one of two conversion methods investigated in this study. This is a batch process where liquid

phase cracking occurs followed by a subsequent quench of the vapours. Differing from the petroleum process, vapours leave the reactor volume as they are produced (destructive distillation). Therefore residence time will refer to the liquid phase only. Process parameters include reaction temperature, residence time, and pressure. This study will focus solely on atmospheric pressure operation.

1.5.4 Pyrolysis

Pyrolysis is a form of thermochemical treatment which chemically decomposes organic materials through the addition of heat in the absence of oxygen (Sťávoová, Stahl, Seames, & Kubátová, 2012). Materials such as TGs can be pyrolyzed to produce hydrocarbon rich liquid products. Pyrolysis, or thermal cracking, of vegetable oils represents an alternative method of producing renewable liquid products for use in fuel applications. The main advantage pyrolysis possesses over transesterification is that the final product(s) can be altered dependent on reaction conditions. This allows for a process able to tailor the products towards certain applications by tuning various process parameters. Additional advantages over transesterification include lower processing costs, compatibility with infrastructure, and feedstock flexibility (Stumborg et al., 1996). Environmental benefits include the absence of harmful catalysts and wastewater treatment.

Dependent on the residence time of the reactant, pyrolysis can be divided into three subclasses: slow pyrolysis, quick pyrolysis, and flash pyrolysis (Maher & Bressler, 2007). These subclasses can be used to adjust the solid, liquid, or gas phase yields. The effect of temperature also influences selectivity towards certain phases. The yields of these phases are heavily dependent on the pyrolysis conditions. For example, a long residence time at low temperature will favour char production while a short residence time at high temperature will produce more organic liquid product. The majority of research on pyrolysis surrounds the use of solid biomass. When applying pyrolysis to the case of vegetable oils, products are materials resulting from simple cracking of the

molecules and possible reforming of the primary products to secondary products dependent on the conditions (Frey et al., 2011).

1.6 Present thesis work

The current market for fuel-based lighting is large and increasing annually. High price instability and poor social and environmental impacts of commercial fossil fuels presents an opportunity for biofuel development with the objective of reduction and/or replacement of petroleum kerosene in wick-based lighting systems. Energy-dense, easily transportable triglycerides of various crop oils indicate a potential feedstock for this application. Current biofuel competition in the market space is low. Existing commercial, renewable lamp oils exhibit very low yields from the original feedstock and require the use of harmful solvents and wastewater treatment. Thermochemical processes such as pyrolysis and visbreaking are possible conversion technologies exhibiting higher yields with improved social and environmental factors.

The aim of this study is to assess the feasibility of thermochemical conversion of crop oils for the production of renewable lamp fuel to replace traditional, petroleum-based derivatives. This thesis aims to gain a better understanding of the effects of operating conditions for the optimization of liquid product properties. Objectives of this study include developing a simple process for utilizing the high-energy triglycerides of crop oils for use in non-modified, wick-feeding lamps. Specifically this includes reduction of viscosity and improvement of wickability in a traditional cotton wicking system. Two processes will be analyzed and optimized with respect to liquid fuel characteristics. Visbreaking and pyrolysis are thermochemical processes resulting in the decomposition through thermal cracking of the parent vegetable oils. Product blending with traditional commercial fuels will also be investigated for the determination of optimal fuel blending ratios for successful operation in a wick-feeding lamp. Liquid properties of successful

blends will be analyzed to gain understanding of minimum property requirements of lamp fuels.

This thesis is divided into three major sections. The first section covers the batch visbreaking of soybean oil and analysis and optimization of product fuel characteristics. The second looks at the application of the pyrolysis technology in continuous operation with the same objectives and feedstock as the first section. Finally, the third section applies the optimized pyrolysis conditions to feedstocks of various triglyceride profiles and degrees of saturation.

1.7 References

A renewable future with biodiesel and glycerin. *Ontario Bioauto Council*.

Adejoro, L. (2014). Kerosene Scarcity: NNPC Concludes Plans to Increase Domestic Consumption of Cooking Gas. *Daily Times NG*.

Biodiesel production and the transesterification process. *Bioenergynet.com*. Retrieved April 30, 2014, from <http://www.bioenergynet.com/>

Bootello, M. a., Garcés, R., Martínez-Force, E., & Salas, J. J. (2011). Dry Fractionation and Crystallization Kinetics of High-Oleic High-Stearic Sunflower Oil. *Journal of the American Oil Chemists' Society*, 88(10), 1511–1519.

Chemical and physical information. (1989). Retrieved May 01, 2014, from <http://www.atsdr.cdc.gov/toxprofiles/tp75-c3.pdf>

Demirbas, a. (2009). Recovery of gasoline range fuels from vegetable oils. *Energy Sources, Part A*, 31(5), 420–426.

- Dupain, X., Costa, D., & Schaverien, C. (2007). Cracking of a rapeseed vegetable oil under realistic FCC conditions. *Applied Catalysis*, 72(1-2), 44–61.
- Fletcher, S. (2013). Energy consumption to escalate. *Oil & Gas Journal*.
- Frey, R., Da Graca C Da Rocha, M., Brandao, S. T., Pontes, L. a M., Padilha, J. F., Borges, L. E. P., & Gonzalez, W. a. (2011). Cracking and Hydrocracking of Triglycerides for Renewable Liquid Fuels: Alternative Processes to Transesterification. *Journal Of The Brazilian Chemical Society*, 22(7), 1206–1220.
- Gerpen, J. Van, Shanks, B., Pruszko, R., & Clements, D. (2004). Biodiesel Production Technology. *NREL*, (July).
- Hammond, E. G., Johnson, L. A., Su, C., Wang, T., & White, P. J. (2003). Soybean Oil. History of Kerosene Lamps. Retrieved April 24, 2014, from <http://www.historyoflamps.com>
- Joshi, J. B., Pandit, A. B., Kataria, K. L., Kulkarni, R. P., Sawarkar, A. N., Tandon, D., ... Kumar, M. M. (2008). Petroleum Residue Upgradation via Visbreaking: A Review. *Industrial & Engineering Chemistry Research*, 47(23), 8960–8988. Retrieved from <http://pubs.acs.org/doi/abs/10.1021/ie0710871>
- Kubičková, I., & Kubička, D. (2010). Utilization of Triglycerides and Related Feedstocks for Production of Clean Hydrocarbon Fuels and Petrochemicals: A Review. *Waste and Biomass Valorization*, 1(3), 293–308.
- Maher, K. D., & Bressler, D. C. (2007). Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresource Technology*, 98(12), 2351–68.
- Masoodi, R., & Pillai, K. (2012a). Introduction to Wicking in Porous Media. *Wicking in Porous Materials*, 1–12.

- Masoodi, R., & Pillai, K. (2012b). Traditional theories of wicking: capillary models. *Wicking in Prous Materials*, 31–54.
- Mills, E., & Ph, D. (2003). Technical and Economic Performance Analysis of Kerosene Lamps and Alternative Approaches to Illumination in Developing Countries.
- Moller, K., & Pederson, P. H. (2010). Fuel composition comprising alkyl ester. Canada, United States, Denmark.
- Nitske, R. W., & Wilson, C. M. (1965). *Rudolf Diesel, pioneer of the age of power* (1st ed., p. 318). Univeristy of Oklahoma Press.
- Patzek, T. W. (2009). A First Law Thermodynamic Analysis of Biodiesel Production From Soybean. *Bulletin of Science, Technology & Society*, 29(3), 194–204.
- Pillai, K., & Hooman, K. (2012). An Introduction to Modeling Flows in Porous Media. *Wicking in Porous Materials*, 55–96.
- Raju, M. P., & T'ien, J. S. (2008). Modelling of candle burning with a self-trimmed wick. *Combustion Theory and Modelling*, 12(2), 367–388.
- Speight, J. G. (2012). Visbreaking: A technology of the past and the future. *Scientia Iranica*, 19(3), 569–573.
- Sťávoová, J., Stahl, D. C., Seames, W. S., & Kubátová, A. (2012). Method development for the characterization of biofuel intermediate products using gas chromatography with simultaneous mass spectrometric and flame ionization detections. *Journal of Chromatography A*, 1224, 79–88.
- The Lamp Wick. *The Lampworks*. Retrieved April 24, 2014, from http://www.thelampworks.com/lw_wicks.htm
- Toro-Vazquez, J. F., Dibildox-Alvarado, E., Herrera-Coronado, V., & Charo-Alonso, M. (2002). Triacylglyceride Crystallization in Vegetable Oils. CRC Press.

Valeri, D., & Meirelles, A. J. a. (1997). Viscosities of fatty acids, triglycerides, and their binary mixtures. *Journal of the American Oil Chemists' Society*, 74(10), 1221–1226.

Zhou, J. (2012). Wettability and Its Role in Wicking. *Wicking in Porous Materials*, 13–30.

Chapter 2

2. VISBREAKING OF TRIGLYCERIDES OF SOYBEAN OIL FOR THE PRODUCTION OF RENEWABLE LAMP FUEL

2.1 Introduction

Substituting fossil fuels with biofuels has become a topic of a high interest in the recent past. Environmental concerns of fossil fuel combustion coupled with their finite sources and a growing energy demand has led to significant growth in the biofuel community (Demirbas, 2009). Currently, the majority of fuels in the North America and Europe are blended with biofuel. It has been proven that biofuels possess the ability to replace petroleum-derived fuels; potentially not in capacity, but in properties and functionality. This applies also to lamp fuels for the fuel-based lighting market, and in one case, commercial-scale production of this fuel is underway (Moller & Pederson, 2010). Fuel-based lighting is a large sector of the energy market and although primitive, this technology is prevalent in many areas of the globe (Mills & Ph, 2003). The sole biofuel technology in this market space relies on a fixed feedstock and the transesterification process. This process exhibits very low yields (< 10 wt% of original feedstock), and requires harmful catalysts and expensive wastewater treatment, thus warranting the investigation of alternative technologies.

Energy-rich crop oils present an attractive feedstock for the production of lamp fuels. Their liquid nature and high content of carbon and hydrogen provide an easily transportable, high-energy material. The triglycerides of crop oils represent the feedstock for biodiesel through transesterification, one of the leading biofuels globally. An alternative to transesterification of triglycerides for fuel applications is thermal treatment. Thermal treatment of triglycerides can be divided into two general processes, catalytic and non-catalytic. Due to the objectives of this research, non-catalytic processes will be the focus.

Studies involving non-catalytic thermal cracking of vegetable oils for fuel date back almost a century. Thermal cracking of cottonseed oil (Egloff & Morrell, 1932) and Alaskan fur seal oil (Egloff & Nelson, 1933) are examples of this. These processes were operating at moderately high temperatures (445–485 °C) and under pressure (0.93–1.3 MPa). Yields of 57–60 % gasoline range hydrocarbons were demonstrated. Years later, Tung oil was cracked on a large scale to produce motor fuels during the war (Chang and Wan, 1947). The process got its design from an American petroleum cracking process. Chang and Wang reported commercial crude oil yields of 70 % by volume. This crude then produced a 25 % yield of gasoline (by volume). In the 1980s, political and economic factors coupled with advances in instrumental and analytical techniques created a renewed interest in thermal conversion of vegetable oils for fuel production. This has allowed better characterization of reaction products and understanding of reaction mechanisms associated with the thermal decomposition of triglycerides (Maher & Bressler, 2007).

Maher and Bressler (Maher & Bressler, 2007) presented a review of the available literature on pyrolysis of triglyceride material such as crop oils. Concluding that research is lacking in comparison to lignocellulosic biomass pyrolysis, the group suggested areas needing improvement in the subject. These included, “optimization of reaction conditions to obtain specific reaction products, understanding the chemistry behind the pyrolysis reaction, and comprehensive evaluation of the final product properties.” In 2011, Frety et al. compiled a review of all studies performed by Brazilian researchers in the field of cracking pure or modified vegetable oils. Although this review carried an emphasis on catalytic processes, the conclusions were similar to Maher and Bressler in that a better understanding of the effects of reaction conditions is needed. These reviews also confirm the viability of alternative processes to transesterification for liquid fuel production, although much progress is still required.

The majority of recent pyrolysis studies have been carried out in batch reactors at atmospheric pressure and temperatures ranging from 300–500 °C. The relatively long residence times classify these processes as slow pyrolysis, and resemble the visbreaking process used in petroleum refining.

The Alencar et al. study from 1984 focused on the pyrolysis of babassu, piqui, and palm oils between 300 and 500 °C in a batch pyrolysis unit. The group also studied pyrolysis of oleic acid, one of the major moieties of the preceding feeds. 60-80 % liquid yields (volume basis) were obtained as condensed volatiles from the process. GC-MS analysis of the liquid products revealed mainly n-alkanes and 1-alkenes, with small quantities of cyclic hydrocarbons (Alencar et al., 1983). The feedstocks rich in oleic acid tend to produce higher concentrations of cyclic hydrocarbons. Effect of reaction conditions on products was not reported.

In 1988, Schwab et al. utilized destructive distillation in order to simultaneously crack and distil soybean and high oleic safflower oils. Liquid yields of 77 and 79 wt% were collected for soybean and high oleic safflower oils respectively. The primary constituents in the distillates were alkanes, alkenes, aromatics, and carboxylic acids with carbon numbers ranging from 4 to greater than 20. Low aromatic components of 1.9–2.3 % were detected and carboxylic acids ranged from 9.6–16.1 %. The process reduced viscosity and increased the cetane number of the liquid fuel, therefore improving the fuel characteristics in relation to the raw feedstocks (Schwab et al., 1988).

Lima et al. (2004) utilized soybean oil, castor oil and palm oil as feedstock. Pyrolysis temperatures were between 350 and 400 °C. The process was also batch destructive distillation of the vegetable oil. Equipment included a 5L homemade vessel equipped with electrical heating. After introducing the oil, the vessel was heated to desired temperature and vapours were condensed in water-cooled condenser. The condensate separated into an organic and an aqueous phase. The organic phase was then distilled into four fractions. The heaviest fraction (distillation temperature (T_d) > 200 °C) was stated to resemble diesel. This phase was the focus of the study. It was found that soybean oil vapours were formed at temperatures higher than 350 °C. At this temperature the

majority of the feed was cracked and distilled, leaving up to 2 wt% heavy residue in the reactor. Conversions were close to 100% from the original feedstock. Yields were highest for the heavy fraction at 60 %, with 10 % for $T_d < 80$ °C, 15 % for $80 < T_d < 140$ °C, and 15 % for $140 < T_d < 200$ °C. The pyrolysis of soybean and palm oils resulted in liquid fuel products that meet Brazilian standards for mineral diesel (Lima et al., 2004).

Doll et al. (2008) tested the properties such as kinematic viscosity, density and surface tension of green fuels obtained by pyrolysis. Pyrolysis was performed using refined soybean oil as well as soybean soapstock. Soapstock is the product obtained by alkali extraction of free fatty acids in the soybean oil. Analysis was done on the pyrolysis product as well as with green diesel- fossil diesel blends. Pyrolysis was carried out at 350 °C and atmospheric pressure. 2 L of feedstock was added to the reaction vessel and heated to 350 °C, producing vapours. Condensed vapours formed an organic phase and an aqueous phase. After separation of the organic phase the liquid was distilled, and the fraction with a boiling point greater than 200 °C was considered to be pyrolysis diesel. Table 2.1 shows the properties of the pyrolysis diesel. The study proved the suitability of both feedstocks for producing suitable diesel fuel additives through pyrolysis.

Table 2.1 Properties of Pyrolyzed Fuel Obtained from Soybean Oil¹

Kinematic Viscosity	6	cSt
Density	0.867	g/cm ³
Surface Tension	27.5	dyne/cm

¹. measurements taken at 20 °C

(Doll, Sharma, Suarez, & Erhan, 2008)

In 2010, Luo et al. examined the effect of various reaction parameters on cracking yields. This study performed in a batch system surveyed a series of reaction conditions to determine which produced attractive yields of valuable shorter chain hydrocarbons. Feedstock included soybean oil and soy methyl-esters. It was observed the reaction commenced at a liquid temperature of 370 °C. The maximum temperature tested was 440 °C with a residence time of 30 minutes. Single step pyrolysis was followed by distillation at a cut of $T_b < 300$ °C. Maximum OLP yields were reported at 76 wt%.

Increasing the pyrolysis temperature increased both the yield of organic liquid product) and its content in C₇-C₁₆. Temperature was reported to be the most important factor. Up to 50% yields of original feedstock were reported to resemble a fuel similar in properties to jet fuel. In addition, it was found that additional hydrogen is not required for formation of desired products as excess hydrogen is produced in thermal cracking reactions.

This group later published a study in 2011 on the optimization of the organic liquid yield. This batch process operated between 420-440 °C to maximize this yield. Significant cracking did not occur below 420 °C, the organic liquid yield stabilized between 420-440 °C, and decreased gradually above 420 °C (Kubátová et al., 2011). A Plackett-Burman design of experiment demonstrated temperature to be the only significant factor, whereas stirring rates, heating rates, reaction time, and initial pressure showed no significant impact.

These studies demonstrate that high conversions can be achieved from direct, batch pyrolysis of triglycerides. The majority of studies focus on the production of transportation fuels such green diesel and green gasoline. These show that moderate yields of green diesel and/or green gasoline (up to 60 %) can be obtained without the use of catalysts or any hazardous solvents. The most prominent experimental setup includes a batch, slow pyrolysis reactor followed by distillation of the organic liquid product. Three operating parameters in temperature, residence time, and pressure are used to control the process but few studies reported on the effects of reaction conditions on yields. These studies found temperature to be the only significant reaction parameter for the organic liquid yield. The feasibility of a slow pyrolysis process for the production of fuels from vegetable oils has been demonstrated but the literature is lacking in reporting effects of reaction parameters on product parameters besides the organic liquid yield.

The objective of this chapter is to investigate the use of slow pyrolysis, or visbreaking, of soybean oil for the production of lamp fuel. It focuses on the optimization of reaction conditions with respect to reaction product yields and fuel properties. Product blending with kerosene is studied to produce useable lamp fuel in traditional oil lamps.

2.2 Materials

2.2.1 Feedstock Selection

The feedstock employed in this study was commercially available, refined, bleached, and deodourized soybean oil obtained from Costco Wholesale. This feedstock was selected due to its availability and low cost in Ontario, Canada and around the world. The soybean crops are high in oil content, accounting for 20.1% of soybeans grown in Ontario (“Industrial Uses and Opportunities for Canadian Soybeans,” n.d.). As seen in Table 2.2, soybean oil is high in linoleic acid (C18:2) and oleic acid (C18:1).

Table 2.2: Fatty Acid Composition of Soybean Oil

Fatty Acid	Composition ¹	Fraction (wt%)
Palmitic acid	C16:0	11
Stearic acid	C18:0	4
Oleic acid	C18:1	24
Linoleic acid	C18:2	54
Linolenic acid	C18:3	7

¹C (carbon chain length): # C=C double bonds

It should be noted that the ideal feedstock for this technology is the most economical crop oil produced locally to the location of the treatment facility. The target population for lamp fuel for lighting applications is populations in remote areas and outside the reaches of electricity. Ontario-grown soybean oil may not be the most ideal feedstock for the application of this technology, but will serve however as a starting point in evaluating the viability of this process.

2.2.2 Commercial Fuels

Two commercial lamp fuels were utilized in this study for the purposes of comparison, analysis, and blending. Kerosene, the main fuel source for wick-based lighting, was obtained from Canadian Tire (Escort brand). Another popular fuel source in the more developed nations is Paraffin. This fuel is used primarily for recreational activities such as camping, and comes in various scents. The Escort Cool Water Paraffin was obtained for this study, also from Canadian Tire.

2.3 Methods

2.3.1 Equipment

The visbreaking process was carried out in a semi-batch mode stirred tank reactor. A schematic diagram of the reactor setup can be found below in Figure 2.1. The vessel was of cylindrical geometry having an inside diameter of 8.89 cm and a height of 12.7 cm. Total volume of the reactor was 788.31 cm³ with a loading capacity of 500 mL. It was made of carbon steel. The flanged tank equipped with a carbon steel lid and a graphite gasket provided an air-tight reactor. The agitation system comprised of a top-mounting electric motor driving a mixing apparatus. The mixer duplicated as a wall scraper ensuring no dead zones were present in the system, and preventing wall deposits. The good mixing and high wall to liquid heat transfer coefficient ensured that there were no hot spots.

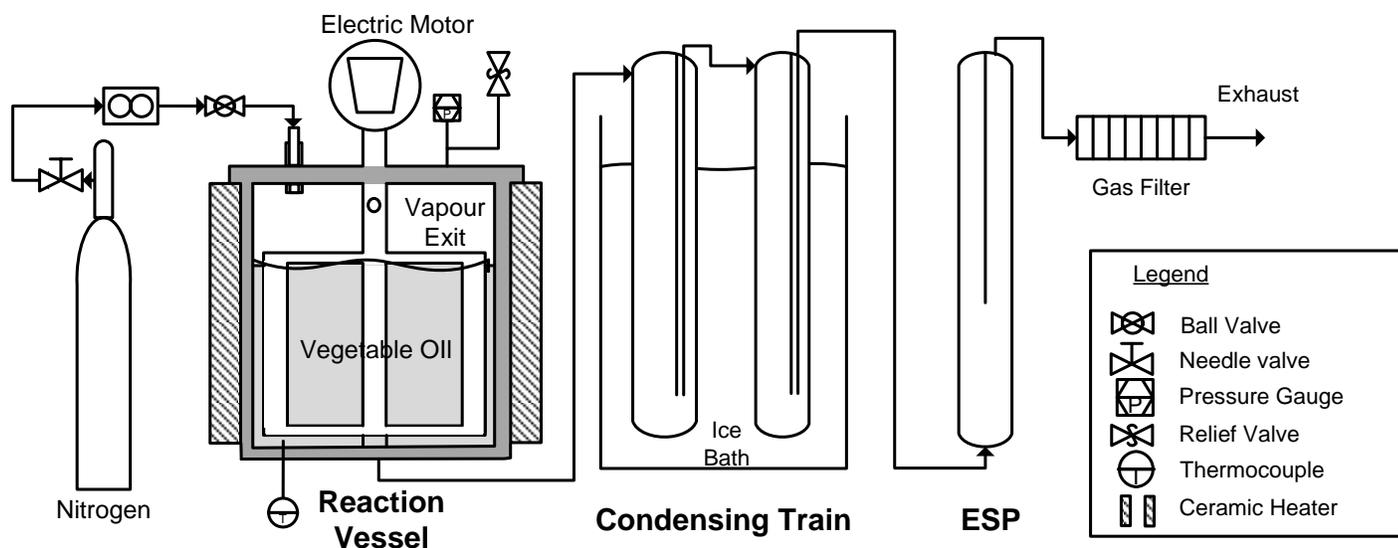


Figure 2.1: Process schematic of pool visbreaking unit

Heating was provided to the system by a ceramic electric resistance heater. The heater wrapped around the circumference of the reactor and covered the entire height. Electrical output was regulated by an Omega PID controller. The controller was tuned for optimal PID parameters for the given heating requirements of the system. This provided accurate temperature control resulting in temperature variances of $< \pm 5$ °C. RS-232 communication with the controller allowed for CPU programming and monitoring, as well as real-time data logging. The controlled process variable was obtained through a K-type thermocouple inserted into the bottom of the vessel in the liquid phase. Ceramic fiber provided insulation to the reactor, minimizing heat loss and maintaining uniform temperature distribution.

Nitrogen gas was also introduced to the top of the reactor during start-up conditions to flush out any oxygen. Its flow was controlled with a high-accuracy (± 1 %) Omega FMA flowmeter.

The condensing train consisted of two tube condensers in series followed by an electrostatic precipitator (ESP). Both tube condensers were of stainless steel construction. The first having a 3.51 cm ID and a 50 cm height, with a wall thickness of 0.36 cm. The second tube condenser was thinner for increased efficiency with an ID of 2.08 cm and a 40 cm height. Wall thickness of this condenser was 0.28 cm. The ESP consisted of a cylindrical aluminum tube with an ID of 5.08 cm and height of 30 cm. PVC caps were installed on each end to provide isolation. A copper electrode was positioned in the center of the tube with an applied DC voltage potential of 12.8 kV. Downstream from the ESP was a gas filter followed by an exhaust to the outside of the building.

Safety measures in the system include a pressure gauge and pressure relief valve. These allow for constant pressure monitoring and prevent pressurization and possible explosion hazard. The pressure relief valve was designed to relieve the pressure when the system exceeded 10 psig. The temperature controller was programmed with high temperature alarms set to prevent system temperature from reaching reactor design limitations. In the event of the process variable exceeding the alarm set point, a loud audio response is activated alerting the operator to the circumstances.

2.3.2 Experimental Procedure

Prior to operation the fresh soybean oil is loaded into the reactor. As the feed is heated, the vapours produced from the thermochemical reaction migrate to the top of the reaction chamber where they exit through the holes in the top of the mixing shaft. A subsequent quench to below 5°C causes vapours to condense and accumulate in two condensers in series. The ESP is downstream of the two ice bath condensers and this unit collects any remaining droplets in the vapour phase through induced electrostatic charge. The remaining non-condensable gases are sent through a gas filter followed by an exhaust line.

During a typical experimental run, 400 mL of fresh feed is loaded. Although the capacity of the reactor tank is 500 mL, 400 mL was used to ensure that the agitation does not lead to liquid escaping via the vapour outlet. Prior to operation, all components of the system were cleaned and weighed. The fresh soybean oil was then be loaded into the reactor and weighed. The system would then be assembled and insulated. As the controller was specifically tuned for the system it was important that the ceramic fiber insulation be installed in a similar manner for every run.

Following assembly of the unit, nitrogen gas was injected through the system to create an inert atmosphere. Nitrogen injection was done so at a rate of 1.45 SLPM. After assembly and weight measurements were complete, heating would commence. Nitrogen injection remained active until the liquid temperature reached 200 °C. At this temperature it is known that no transformations or reactions have occurred (Zhenyi, Xing, Shuyuan, & Li, 2004). Nitrogen flow was then shut off to prevent interference with produced vapours. All experiments operated at atmospheric pressure. A 20 minute cooling period was allowed after every run before collecting samples. Liquid and solid (residue) yields were determined through differential weight measurements of various sections of the unit. Gas yield was calculated based on closing the mass balance.

2.3.3 Experimental design

A three-factor, factorial design of experiments was employed to analyze the visbreaking process. Factorial experiments are when the effects of more than one factor are considered simultaneously. A factorial design allows for efficient analysis of the process factors and responses, and is the only effective way of examining interaction effects (“ANOVA,” 2009). The three factors were Temperature (A), Residence Time (B), and Mixing (C). Design of experiments analysis relates experimental factors to measured responses by fitting coefficients to a polynomial model using a regression approach. The three factors were evaluated with respect to five responses. Responses included: organic liquid yield, gas yield, residue yield, wax yield, viscosity, and surface tension.

Stat-Ease Design-Expert 9 software provided the statistical analysis of the model. The importance of each factor was determined from an analysis of variance (ANOVA). A three-way factorial ANOVA was used to determine the main effects of each factor and any interaction between factors (“ANOVA,” 2009). The experimental design consisted of 17 runs. Select runs were completed in duplicate to confirm repeatability. There are 7 levels of temperature (300-500 °C), four levels of residence time (60-300 min), and three levels of mixing (20-75 rpm). An outline of the experimental design can be found in Table 2.3.

Table 2.3: Experimental Design: Multi-level Three-Factor

Run #	A: Temperature (°C)	B: Residence time (min)	C: Mixing (rpm)
1	350	120	20
2	325	120	75
3	400	180	20
4	300	300	20
5	300	120	40
6	375	120	20
7	375	60	40
8	325	180	40
9	325	60	20
10	350	180	40
11	375	300	40
12	300	180	75
13	400	300	40
14	350	120	75
15	400	60	75
16	450	120	40
17	500	120	40

2.3.4 Product Analysis

2.3.4.1 Viscosity and Density Measurement

All samples obtained were analyzed for viscosity and density quantification. These measurements were performed by an Anton Paar SVM 300 Stabinger Viscometer. This device measures dynamic viscosity (η) and density (ρ) of liquids according to ASTM D7042. Kinematic viscosity (ν) is then automatically calculated and equivalent to ISO 3104 and ASTM D445. The relation between these three properties is seen in Equation 1. This viscometer allows for high accuracy measurements over a wide range of dynamic viscosities (0.2 to 20 000 cP) and densities (0.65 to 3 g/cm³).

$$[1] \quad \nu = \frac{\eta}{\rho}$$

The viscometer was equipped for temperature controlled measurements in the range of 15 to 105 °C. For this study, all measurements were taken at 25 °C to imitate conditions similar to lamp operation. Reproducibility and repeatability for the viscometer are displayed in Table 2.4.

Table 2.4: Viscometer Specifications

Anton Paar SVM 3000 Viscometer	
	Reproducibility
Viscosity	0.35%
Density	0.0005 g/cm ³
Temperature	0.02 °C

2.3.4.2 Wax Content

A side product from the reaction was the formation of wax, which was collected with the organic liquid. Centrifugation was used to recover the wax from the organic liquid, since the wax had a higher density than the liquid. After centrifugation for a time period of 30 minutes at a speed of 5000 rpm, the de-waxed organic liquid was decanted from the mixture, leaving a wax phase. In some cases the wax phase contained an aqueous fraction. Analysis of this fraction is outside the scope of this study, and is included in the wax content in terms of product yields.

2.3.4.3 Surface Tension

Surface tension, an important property in wicking, was measured based on the drop weight method. This is a modification to the Stalagmometer method in that direct calculation of surface tension is not performed. However, the liquids are fitted to a calibrated curve of liquids with known surface tensions. This method is based on mass per drop of the liquid for a given flow, dropping apparatus, and volume. As the liquid leaves the tip of the syringe, it slowly increases in mass and volume until the mass of the droplet exceeds the forces exerted by surface tension. At this point the liquid drop falls from the syringe.

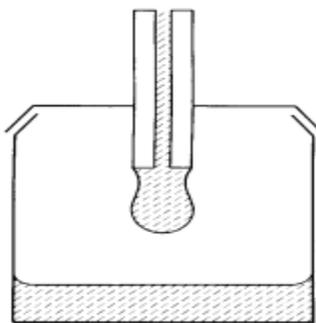


Figure 2.2: Liquid Droplet in Equilibrium with Surface Tension

(Methods of surface tension measurements, 2009)

In this method, drops of a fluid flow slowly in the downward vertical direction. The dropping apparatus contains a specially designed tip preventing drops from attaching to the outer surfaces of the tip, hence altering their drop properties. The dropping syringe was attached to a high-accuracy syringe dosing pump (New Era Pump Systems Inc.) to maintain a constant flow for each liquid. As the liquid escapes the syringe it forms droplets of constant size and mass. For a given volume, a liquid will produce a certain number of drops dependent on the surface tension of the fluid. For instance, a liquid with a high surface tension will form drops with higher mass per drop and therefore will result in less drops (Lee, Ravindra, & Chan, 2009).

Several liquids of known surface tensions (see Table 2.5) were tested with this apparatus and fitted to a curve of surface tension vs. droplet mass. Surface tensions of fitted liquids ranged from 18 to 73 dyne/cm, providing an accurate fit within the expected range of test samples. This resulted in a linear calibration curve exhibiting an R^2 value of 0.9921. The obtained linear equation from these liquids was applied to tested samples to obtain their respective surface tension values. Calibration figures can be found in Figure 6.1 in Appendix A.

Table 2.5: Surface Tensions of Known Liquids used in Method Calibration

Substance	(dyne/cm)
Water	73
Glycerol	64
Ethylene Glycol	48
Cyclopentanone	33
Acetone	25
Isopropyl Alcohol	22
Hexane	19

2.3.4.4 Wickability Testing

The test method for determining the wicking characteristics of the liquid samples as well as the commercial fuels and blends was a vertical penetration test. The test was a measure of the rate of rise of the liquid front over a given period of time. The solid wicking material was chosen to represent a traditional flat cotton wick. Heavy duty Scott Shop Towels (obtained from Canadian Tire) were selected as the cellulosic material mimicked similar wetting properties as cotton (Masoodi & Pillai, 2010). The blue hue of the towels also allowed for increased visual accuracy of the rising liquid front. By submersing a strip of the wicking material into a non-limiting volume of the liquid sample, a profile of penetration height over time was obtained. The Lucas-Washburn Equation (Equation 1.3) was used to describe the process. This model states that the height of penetration is proportional to the square root of time. The slope of the plot h vs. $t^{1/2}$ is therefore constant, and known as the wicking coefficient, W_c (Kamath, Hornby, Weigmann, & Wilde, 1994). W_c was calculated for each sample and provided a basis for comparative analysis of the samples (Kamath et al., 1994).

The Lucas-Washburn Equation is rearranged into Equation 2.2 as seen below, where h is height of rise of the liquid front, θ is contact angle, μ is dynamic viscosity, and R_e is effective capillary radius.

$$h^2 = \frac{\sigma R_e \cos\theta}{2\mu} t \quad [2.2]$$

Plotting h vs. $t^{1/2}$, and calculating slope yield W_c as seen in Equation 2.3

$$\text{Slope} = W_c = \left(\frac{\sigma R_e \cos\theta}{2\mu} \right)^{1/2} \quad [2.3]$$

Wicking strips were prepared by cutting the Scott Towel into strips 20 mm wide. Each strip was 300 mm x 20 mm x 1mm. The strips were also marked with ink to provide visual reference of scale. Strips were marked with a horizontal line every 10 mm in

vertical distance beginning 20 mm from the bottom of the strip since, during the test, 20 mm of the strip was submersed into the liquid. Ink was set to dry prior to testing to prevent contamination of the test sample.

High definition (HD) video recording captured the liquid rise over time. This minimized human error and allowed for visual alterations in contrast, brightness, and saturation of the picture to give a clear view of the rising front. Slow motion playback also enhanced accuracy for fast wicking rates such as those present at low heights. This test was able to measure up to 6 liquid samples simultaneously. A photo of the test as well as schematic of the setup can be seen in Figure 2.1a and 2.1b, respectively.

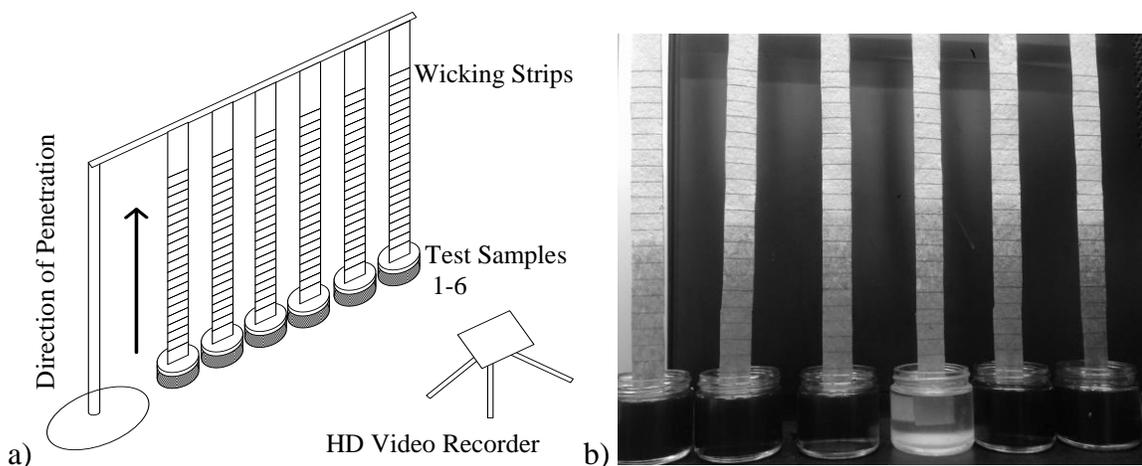


Figure 2.3: Wickability test. a- schematic, b- photo

The suitability of the wicking paper material as a cotton wick proxy was analyzed and presented in Figure 2.4. The wicking test was employed to compare the wicking rates of fuel in both the wicking strips and a typical cotton wick found in fuel-based lighting applications. To ensure accuracy of the test, a commercial fuel (paraffin), as well as an organic liquid product obtained from the thermal treatment of crop oils was used. As seen in the results of penetration test, the fuel samples wick upwards in both materials at very similar rates. Not only is the wicking speed similar, but the trend of the rate decreasing over time is also very similar. This test proves that the selected material for the wicking strips in the vertical penetration test is adequate in comparing wickability of various fuels for application in wick-based lighting.

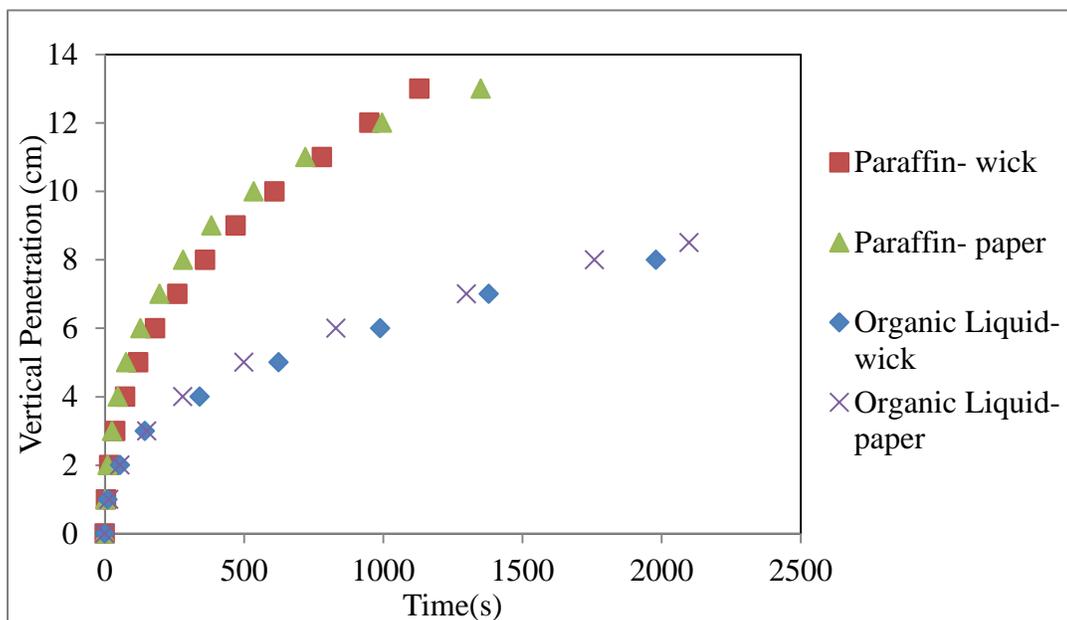


Figure 2.4: Vertical penetration of wicking paper vs. cotton wick. Organic liquid shown obtained from pyrolysis at T= 450 C.

2.3.4.5 Lamp Performance

The culmination of the above tests is the lamp performance test. Liquid samples were subjected to full-scale operation in a common kerosene wick-feeding lamp. The objective of this test is to determine a fuel's operational capabilities in a real lamp. It is a test with the simple binary results of success or fail. Failure of a single criteria results in complete operational failure for the fuel. Success was based on four criteria, each of which was measured by simple observation:

- The first was flammability of fuel. When put in contact with a source of flame, the wick must produce a flame, and it must be of similar size, shape, and brightness to that produced with kerosene. Note that these are observed qualitative requirements, not quantitative measurements.

- The second was sufficient fuel delivery. After producing a flame above the top of the wick, the flame must be supported for a minimum of twenty minutes. Although insufficient fuel supply usually extinguishes a flame in seconds, a large safety margin was employed to ensure adequate fuel supply.
- Thirdly, the burning fuel must not consume the wick. It has been shown by Mills et al. that a typical kerosene lamp consumes up to 0.06 cm/hr of wick length (Mills & Ph, 2003). Therefore, this test required that wick consumption is negligible after twenty minutes of operation.
- Finally, during the required twenty minutes of operation, the flame must not produce smoke or significant odour (after initial wick adjustment). A fuel resulting in the fulfillment of all of the above requirements is deemed successful in lamp operation.

As these requirements are not independent of each other, and the analysis is qualitative, the results of the test are given as successful or failed. Further analysis of lamp operation is planned in future work, and thus outside the scope of this study.

Prior to testing, the globe was cleaned of any soot or deposits from the previous test. Cleaning started with compressed air to remove loose debris, followed by soap and water. This ensured flame brightness of each test was not hindered by previous runs. Following globe cleaning, a new wick was installed and the test sample was loaded into the fuel reservoir. The wick was then submersed in the sample to saturate the wick with fuel. This was done to ensure a common starting point for fuel saturation within the wick. At this point the wick was inserted into the housing and the housing was screwed onto the reservoir. The wick was trimmed carefully leaving a straight, rectangular top. It should be noted that variations such as triangular and curved wick trimming is also used to manipulate the flame shape and fuel consumption (Mills & Ph, 2003). A flat top was selected as this geometry exhibits the highest fuel consumption and therefore the worst-case scenario for a poor-wicking fuel (“The Lamp Wick,” n.d.).

2.4 Results and Discussion

2.4.1 Design of Experiments Evaluation

The statistical evaluation of the design of experiments was aided by the use of Stat-Ease Design Expert 9 (DX-9) software. Where noted in this section, statistical values were generated by this software and detailed calculations are not shown. This section will present the interpretation of the data from the statistical analysis with the objective of identifying the significance of the three factors for each of the six responses. This will give a better understanding of the process parameters and confirm the validity of the experimental design.

The preliminary tool for identifying significant factors for a given response is the half-normal plot. This plot is graphical representation to help visually recognize the factors which have a significant effect on the response. The x-axis represents the standardized effects; a measure of the magnitude of the experimental effects. Standardized effects are given by the difference of the average response at the high factor level minus the average response at the low factor level. The y-axis is the half-normal probability. These values are not based on the experimental data, but represent the idealized values for the given number of effects and samples, as if they were drawn randomly from a half-normal distribution. The red line represents the level of non-significance on the design of experiments. Factors to right of this line are significant to the given response, whereas factors on or close to the line are insignificant. The further to the right of the line, the more significant the factor is.

As seen in Figure 2.4, Factor A, temperature, appears to be of the highest significance to the organic liquid yield. Factor B, residence time, could also display a small magnitude of effect on the response, but its proximity to the red line indicates the possibility of statistical insignificance. It is clear from this figure that Factor C, mixing, is insignificant to the response.

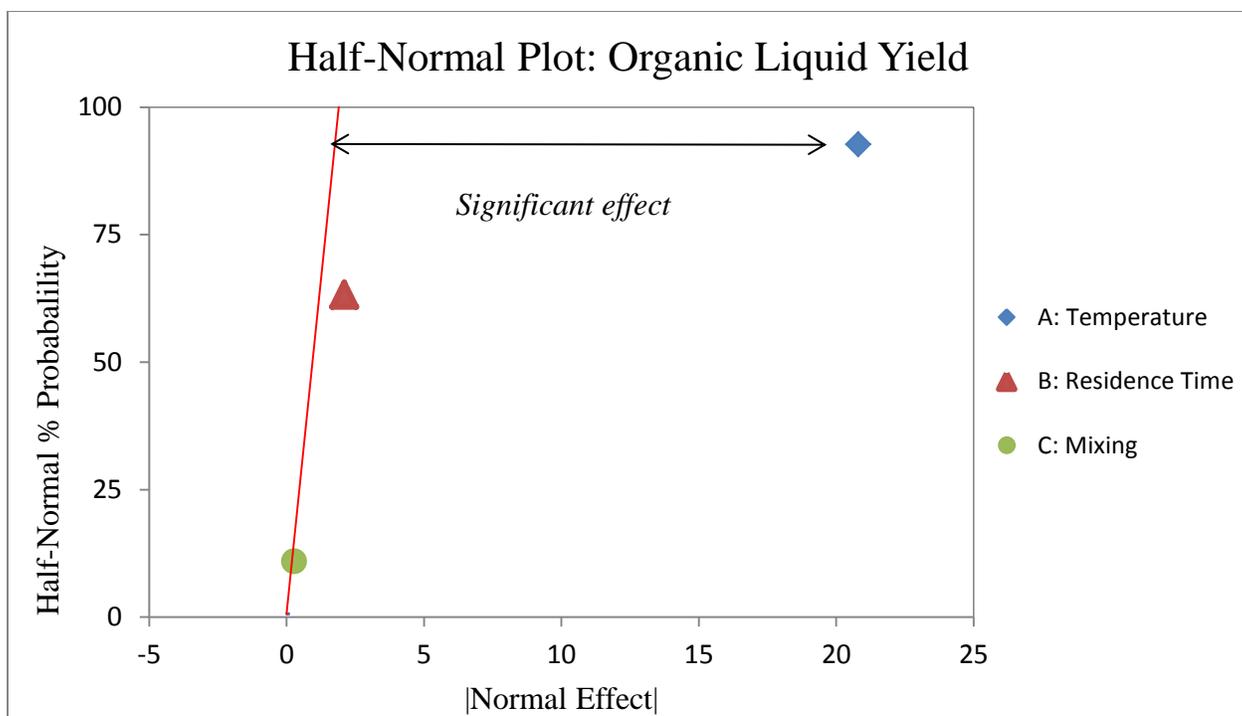


Figure 2.5: Half-Normal Plot for Organic Liquid Yield

To confirm the significance of each factor with respect to the organic liquid yield, the results of the ANOVA (analysis of variance) test can provide more specific determinations (“ANOVA,” 2009). The ANOVA test can also provide the significance of the model for each response. The factorial model developed in DX-9 utilized the classical sum of squares method (Type II), which is commonly accepted in statistical studies. A table of the ANOVA results can be seen below. The F Value represents a ratio of explained variance over unexplained variance (noise). This can also be seen as a ratio of variance between levels to variance within levels. Therefore a factor with an F value greater than one cannot be significant. The p value represents the probability that the effects of the parameter are due to noise. In the statistical community it is commonly accepted that a factor is significant if the p value is less than 0.05. That is, there is a 95% probability the factor has an effect on the model.

Table 2.6: ANOVA Values for Response 1- Organic Liquid Yield

Source	F value	<i>p</i> value
Model	54.038	< 0.0002
A-Temperature	77.045	< 0.0001
B-Residence Time	3.584	0.1083
C-Mixing	0.267	0.7762

The Model F-value of 54.04 implies the model is significant. There is only a 0.02% chance that an F-value this large could occur due to noise. In this case for Response 1- organic liquid yield, the only significant factor is A, which is temperature. This is consistent with the half-normal plot. Factor B, similar to the half-normal plot, is in close proximity to the insignificance cut-off, while Factor C is very clearly insignificant in this response. The insignificance of Factor C indicates that mixing was excellent in all experiments and provides sufficient wall heat transfer. The findings are consistent with literature (Kubátová et al., 2011)

In addition to determination of significant parameters for this response, the model itself must be accurate to confirm the validity of the experimental design and statistical results for factor significance. The *p* value of the model is < 0.0002 indicating the model is significant. The Adequate Precision is a measure of the signal to noise ratio. A value of greater than 4 is desirable for an accurate model. The value calculated for this model is 19.9 indicating the model is accurate and experimental noise is not affecting data. The R² value is 0.992 which also implies high accuracy in the fit of the model to the experimental data. Figure 2.6 shows a plot of predicted values vs. actual experimental values for organic liquid yields. It can be seen these values fit very closely to a line of unity slope, confirming the accuracy of the model. Therefore this model can be used to navigate the design space.

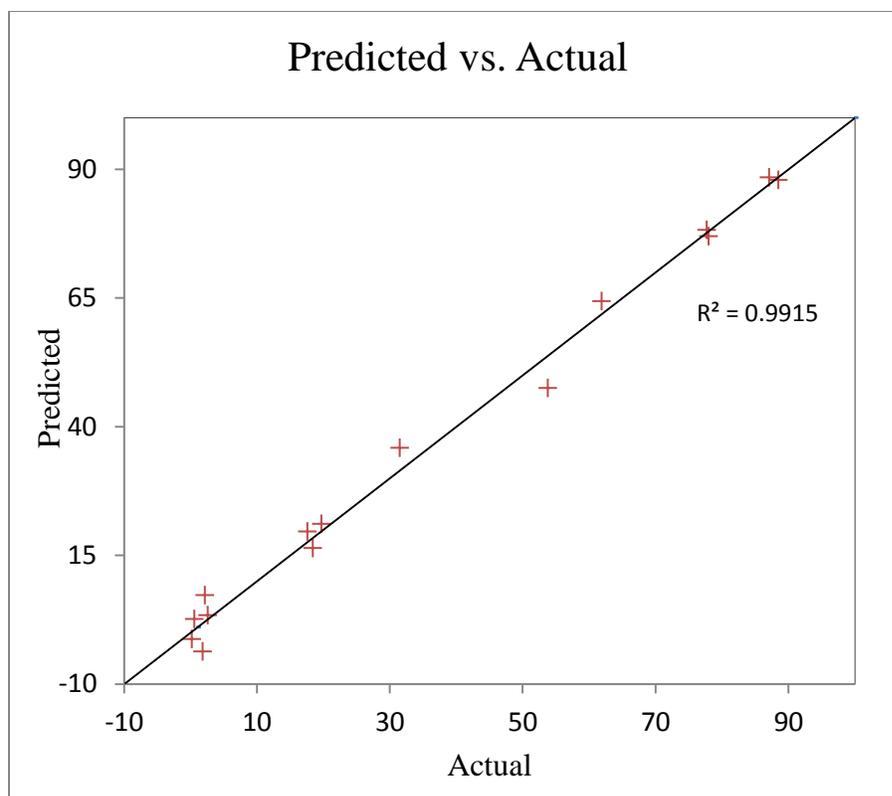


Figure 2.6: Predicted vs. Actual Values of Organic Liquid Yield

The same analysis was performed on Responses 2-6. Table 2.7 provides a summary of the p values for each response, with values less than 0.05 (indicating significance) in bold. From these values it can be seen that the only significant factor in the design of experiments is Factor A-Temperature. This is consistent through all responses. In the yield-related responses, it can be seen that Factor B- Residence Time is in close proximity to the insignificance cut-off. Therefore it may be possible to see minor effects by varying residence times. In terms of model significance, all responses with the exception of surface tension are within the specified range of significance. This states that the models presented are accurate in predicting various effects and can be used to navigate the design space. In the case of surface tension, the model has a p value of 0.073 indicating it is neither significant nor non-significant. The decreased accuracy of this model could be attributed to measurement error due to the small range of surface tension measurements (29.5-33 dyne/cm) of the samples. It could also indicate the three factors

do not display any significant relation to the changes in surface tension of the product, within the design space.

Table 2.7: Summary of p- values for Responses and Model

Response	A: Temperature	B: Residence Time	C: Mixing	Model
Organic Liquid Yield	< 0.0001	0.1083	0.7762	0.0002
Gas Yield	< 0.0001	0.3035	0.8738	< 0.0001
Residue + Wax Yield	< 0.0001	0.0979	0.7895	0.0001
Viscosity	< 0.0001	0.6768	0.087	< 0.0001
Surface Tension	0.0341	0.6348	0.7147	0.0729

*bold value indicates significant

2.4.2 Phase Yields

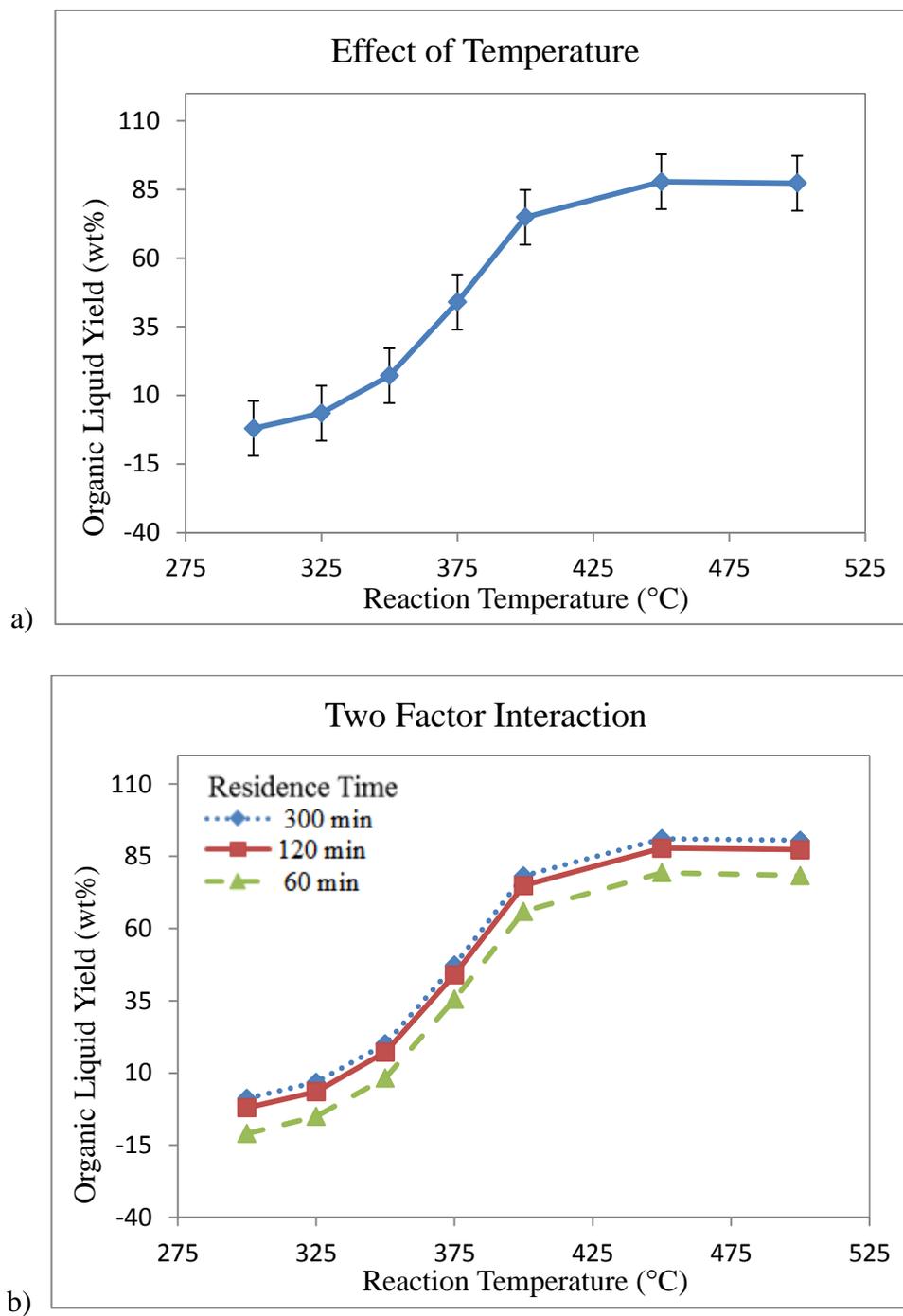
Responses 1-4 of the design of experiments represent the phase yields of the visbreaking process. It has been demonstrated that the effect of temperature is significant in the design space. The following section will present the effects of reaction temperature on the yields of the various fractions generated in the visbreaking process. In addition, the interaction effects will be presented and analyzed for effects on the specific responses.

Organic Liquid Yield

The effects of temperature and the factor interaction effects on organic liquid yield are given in Figures 2.6a and 2.6b, respectively. Figure 2.6a is plot of the effects of reaction temperature on organic liquid yield, at average value of residence time and mixing. It can be seen that the lowest yield (0.2 wt%) is generated at a reaction temperature of 300 °C, which is the minimum temperature tested for this process. This indicates that no significant cracking reactions are occurring at this temperature, at any given residence times or mixing rates. This also confirmed that tests at temperatures below those outlined in the design of experiments are unnecessary. As the severity of the conditions increase, the organic liquid yield also increases, with the maximum yield (~88 wt%) experienced at 450 °C. Temperatures beyond 450 °C indicate no further increase in organic liquid yield.

Due to the destructive distillation nature of the process, this indicates there is no remaining liquid in the reactor after 450 °C.

Figure 2.6b shows the interaction of temperature and residence time and their combined effect on organic liquid yield. The curves represent the effect of temperature on organic liquid yields at the three levels of residence time. It can be seen that although not deemed a significant factor, the increases in residence time have a positive impact on organic liquid yield. This increase has greater magnitude as the residence time is increased from 60 to 120 minutes. The increase from 120 to 300 minutes has little effect. Depending on the economics of the process, this increase in energy requirements is likely not beneficial for the resulting marginal increase in yield. Similarly, mixing has no effect on organic liquid yield and should be set to a minimum to minimize energy usage. Therefore, the optimal conditions for maximizing organic liquid yield are 450 °C, 120 minutes, and 40 rpm for temperature, residence time, and mixing rate, respectively.



**Figure 2.7: Factor effects on visbreaking liquid yield. a) one factor (Temperature).
b) two factor interaction**

Gas Yield

The gas yield represents the non-condensable gases which passed uncollected through the condensing train and ESP. Corresponding figures to those of organic liquid yield presented above can be found in Appendix A. It can be seen that at relatively low reaction temperatures, the gas yield is close to zero. As reaction temperature is increased, the gas yield gradually increases up to a temperature of 375 °C. The increasing severity of the reaction conditions leads to initial decomposition of triglycerides producing low molecular weight gases. At 400 °C, the gas yield spikes to 15 wt%. Interestingly, this yield decreases at temperatures above 400 °C to 6 wt% where it remains stable at temperatures increasing to 500 °C. The interaction effects of residence time and temperature on gas yields can be seen in Figure 6.2 in Appendix A. No interaction effects are present for this phase yield. Increasing or decreasing the residence time at a given temperature has negligible impact on the amount of gas produced.

Wax/Residue Yield

The wax yield represents the waxy fraction separated from the organic liquid fraction. This fraction is combined with the heavy residue fraction resulting in a waste stream. Temperature was shown to be the only significant factor on this response. Figure 6.3a and b in Appendix A present the effect of temperature, and the interaction effects of temperature with residence time, respectively. At a reaction temperature of 300 °C, this fraction is near 100 %. This indicates cracking reactions are not occurring. The general trend of this fraction is a decrease with increasing temperature. A minimum is reached at 400 °C. Similar, but inversely, to organic liquid yield, the yield of this fraction gradually decreases with increasing temperature from 300- 350 °C, followed by a steep decrease from 350- 400 °C, and finally stabilizing around 6 wt.% at temperatures above 450 °C. This 6 % is only wax and indicates all material has been vapourized and exited the reactor. Interaction effects are also inversely similar to organic liquid yield, in that an initial increase in residence time gives a decrease in residue, for given temperatures. Residence times in excess of 120 minutes provide negligible decreases in this fraction. Mixing has no effect on this fraction. Therefore to minimize this waste stream, optimal

conditions are 450 °C, 120 minutes, and 40 rpm for temperature, residence time, and mixing rate, respectively.

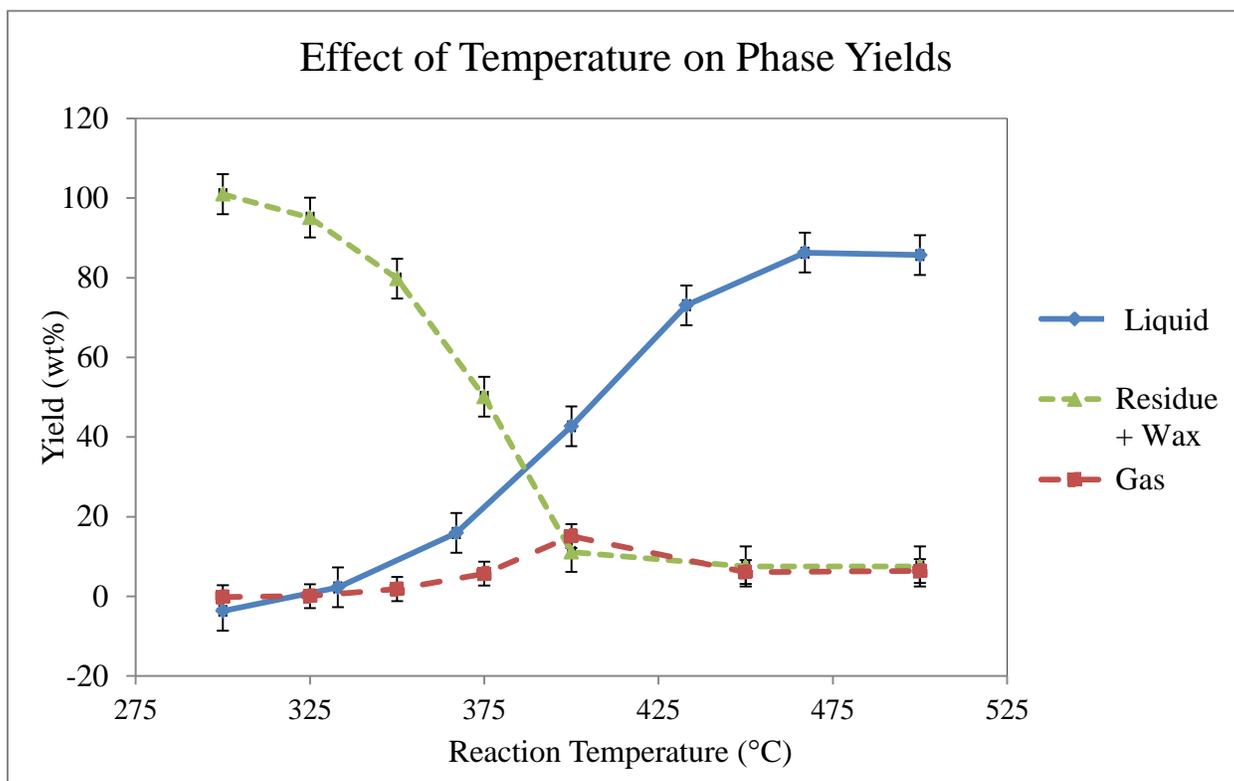


Figure 2.8: Effect of temperature on visbreaking phase yields

A summary of the effect of temperature on the yields of the four fractions is presented in Figure 2.8. The summation of wax yield and residue yield is presented in this figure as they are currently waste streams. It should be noted however that the wax stream could be further refined producing a second product from the process. It was concluded by Zhenyi et al. (2004) that initial decomposition of the triglycerides occurs at 288 °C, where the C-O bond is cleaved. The breaking of this bond separates fatty acids from the glycerol moiety. The remaining glycerol is rapidly decomposed to form low-molecular weight

gases such as acrolein (Zhenyi et al., 2004). As the reaction temperature is increased, it is possible that distillation of the various fatty acid molecules is occurring, resulting in increased organic liquid yield with increased temperatures.

It can be seen that organic liquid collection begins at temperatures approaching 325 °C. This is expected as the flash point of soybean oil is 315 °C, indicating initial degradation of the oil (Hammond et al., 2003). At 400 °C, the residue fraction approaches zero. At this temperature, the gas phase peaks, while organic liquid yield also rises sharply. Beyond this temperature the thermal cracking of the fatty acids may be occurring. This is consistent with studies by Zhenyi et al. who calculated that 400 °C is the temperature at which the C=C bond is cleaved. This is also similar to Kubataova et al. stating significant cracking occurs above 420 °C.

2.4.3 Liquid Properties

The following section provides the remaining responses in the design of experiments. The responses are the liquid properties of the organic liquid fraction. It was found that temperature is the only significant factor for these responses. The effect of temperature on each response will be presented as well as the interaction of temperature and residence time, and their impact on liquid properties.

Viscosity

The effect of temperature on liquid viscosity of the organic liquid is given in Figure 2.9a. Figure 2.9b represents the interaction effects. It can be seen that viscosity is at a minimum at 300 °C. An increase in viscosity is experienced as the reaction temperature is increased. As the temperature rises, the heavier compounds are vaporized thus increasing the condensate viscosity. The maximum viscosity (15 cP) is reached at the maximum temperature of 500 °C. The rate of increase trend is similar, although not in magnitude, to that of organic liquid yield. As this property is desired at minimum values, the increase in yield is a trade-off for the increase in viscosity of the liquid product. Interaction effects

are negligible in this response, indicating increased residence times have no benefit to the process for this property. Therefore minimum residence times (60 min) are optimal to reduce energy needs.

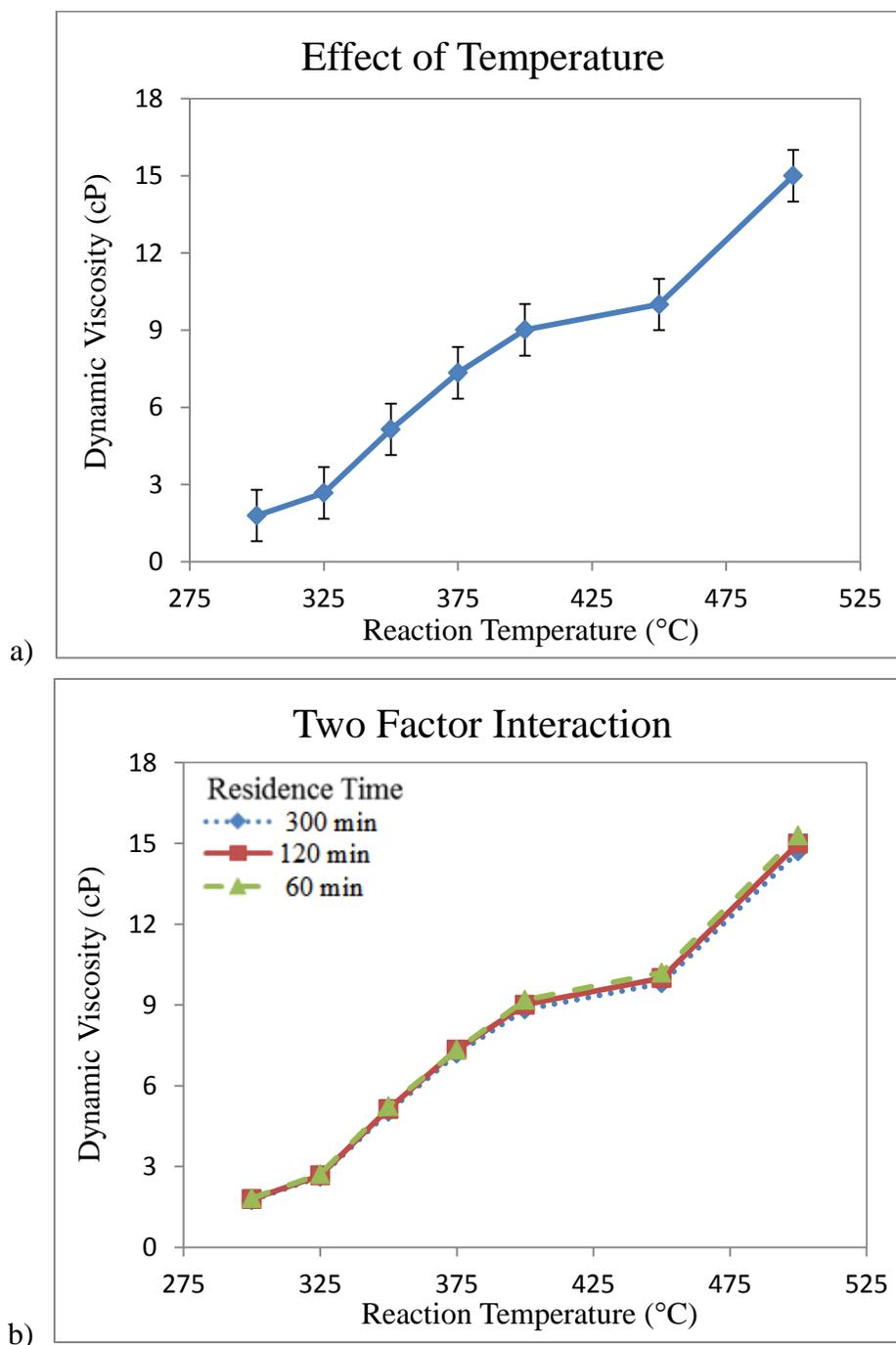


Figure 2.9: Factor effects on dynamic viscosity of visbreaking liquid products. a) one factor (Temperature). b) two factor interaction

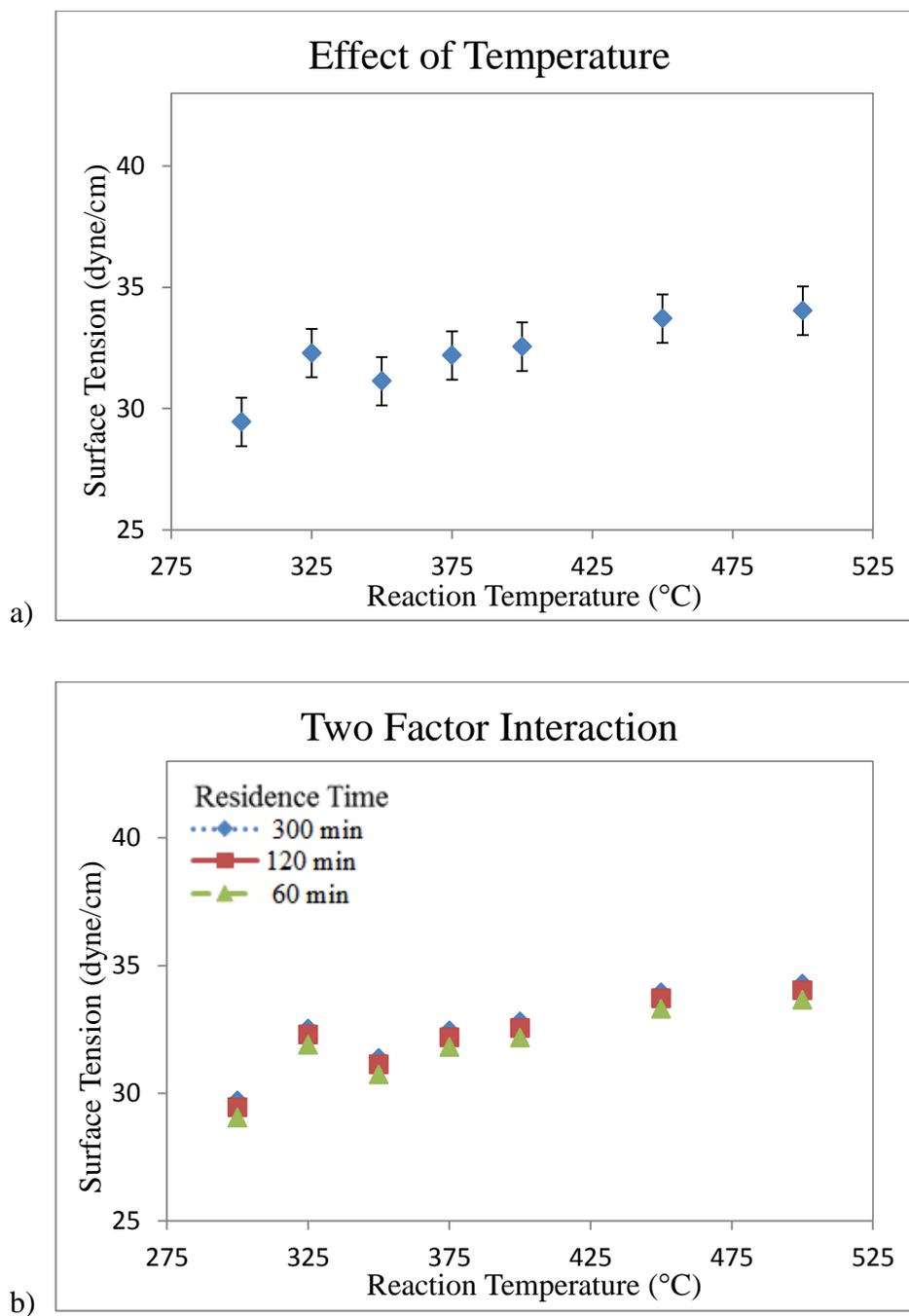
Surface Tension

Figure 2.10: Factor effects on surface tension of visbreaking liquid products. a) one factor (Temperature). b) two factor interaction

Figures 2.10a and 2.10b present the effect of temperature and temperature- residence time interaction, respectively, on liquid product surface tension. It can be seen that varying reaction temperature has little impact on liquid surface tension. In addition, the interaction effects are negligible. This is consistent with the design of experiments analysis above, stating the model for surface tension is not significant in the design space. The minor differences in the surface tension values in the above figures could be attributed to noise within the measured response or experimental error in measurement. The pyrolysis process significantly decreased the surface tension from the untreated oil, but among the pyrolysis products the surface tensions are very similar. A comparison of surface tensions can be found in Table 2.9. The process decreases the surface tension an average of 23% from the feedstock oil, resulting in a fuel with slightly higher surface tension than kerosene.

Table 2.8: Surface Tension Comparison

Surface Tension (cP)	
Untreated Oil	41
Pyrolysis Products (avg)	32
Kerosene	28

2.4.4 Wickability

The wickability test demonstrates the capability to transport fuel up the wick. As shown in Chapter 1, the liquid physical properties, presented above, impact the wickability of the fuel. In addition to physical properties, the wickability test incorporates liquid-solid interaction. Although these properties, such as contact angle, are not individually quantified, the wickability test ultimately demonstrates the wicking performance of the fuel. The results of the vertical penetration test, measuring the height climbed by the liquid over time, are presented in Figure 2.11. The solid lines represent the organic liquid samples obtained from the visbreaking process, at various reaction temperatures. It can be seen that the visbreaking process has provided improvement to wickability of the oil. The wicking performance of the optimal pyrolysis sample is much greater than the feedstock oil, however still less than the commercial fuel. The effect of temperature on wickability

is given in Figure 2.12. The products obtained at lower reaction temperatures demonstrate higher wicking performance. This is expected as low reaction temperatures yield less viscous organic liquid product.

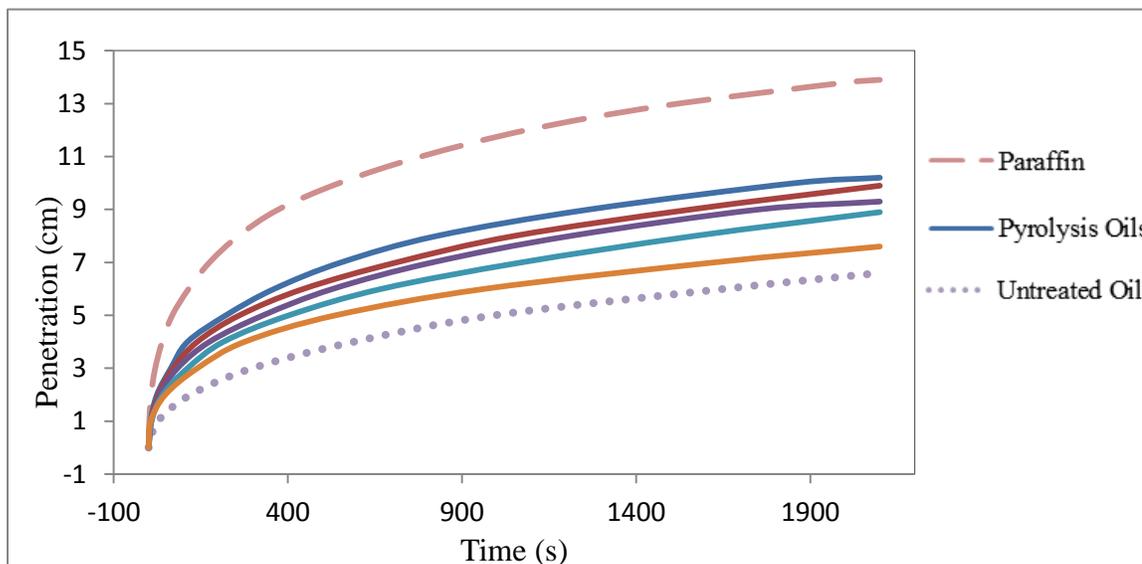


Figure 2.11: Wickability test of visbreaking samples

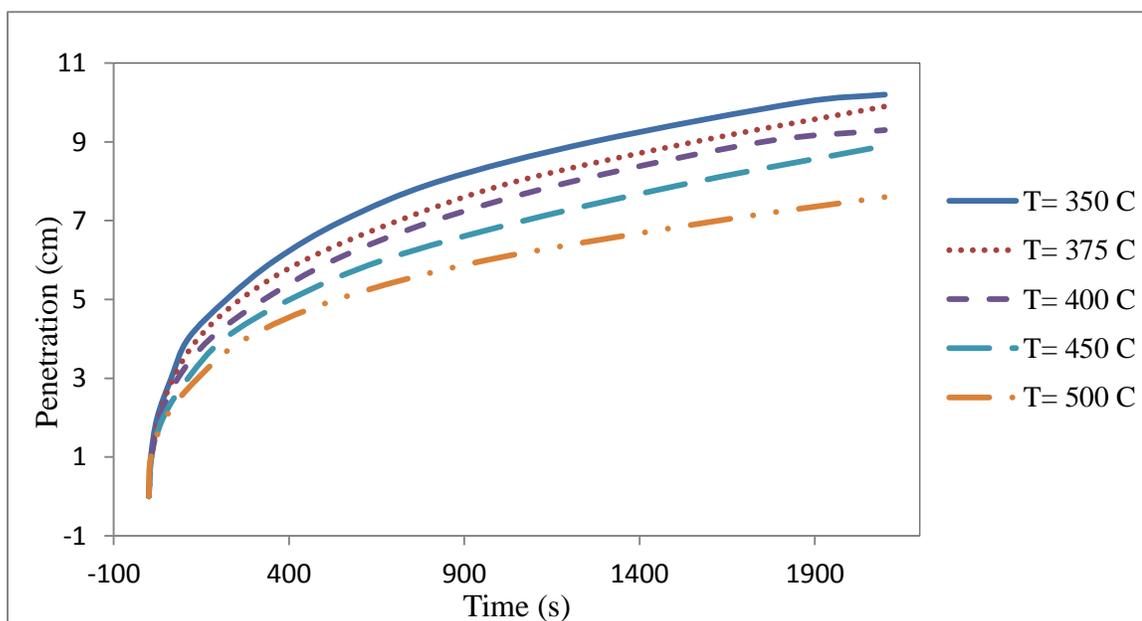


Figure 2.12: Effect of visbreaker temperature on wickability of visbreaking liquid products

To quantify the results of the vertical penetration test, the data was linearized according to the procedure in Section 2.3.4. This was performed on all organic liquid samples, allowing for calculation of the wicking coefficient (W_c). This coefficient has been used in literature to quantify the wicking of liquids in porous materials (Kamath et al., 1994). W_c represents the slope of the linearized vertical penetration curve. A sample plot of the linearized curve is given in Figure 2.13. The visbreaking process has shown to improve the wicking coefficient by as much as 67% from the untreated oil. Table 2.9 shows a comparison of W_c values.

Table 2.9: Wicking Coefficients of Untreated Oil, Visbreaking Products, and Kerosene

Sample	W_c
Untreated Oil	0.15
Visbreaking Products	0.19 - 0.25
Kerosene	0.44

Reaction temperature was the only factor to impact the wicking coefficient of the resultant organic liquid. The effect of temperature on W_c is given in Figure 2.14. It can be seen that increasing reaction temperature has a negative effect on wicking coefficient. That is, the maximum wicking rates are given by fuels from low reaction temperatures. This is expected as low reaction temperatures yield low viscosity fuels. In terms of optimization, this suggests that lower temperatures are desired, however the decreased organic liquid yields at low temperatures must be considered.

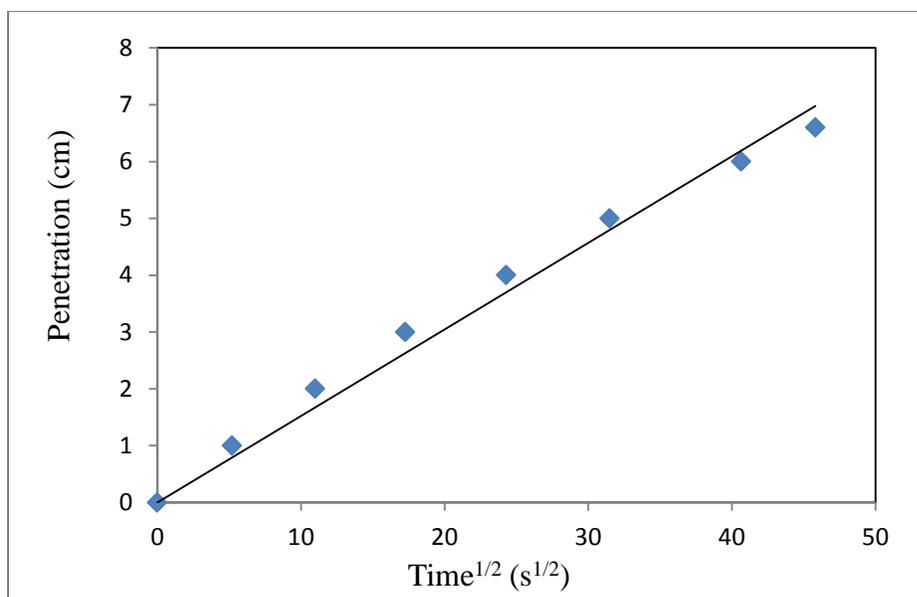


Figure 2.13: Linearized plot of penetration test. ($T = 450\text{ C}$, $W_c = 0.254\text{ cm/s}^{1/2}$)

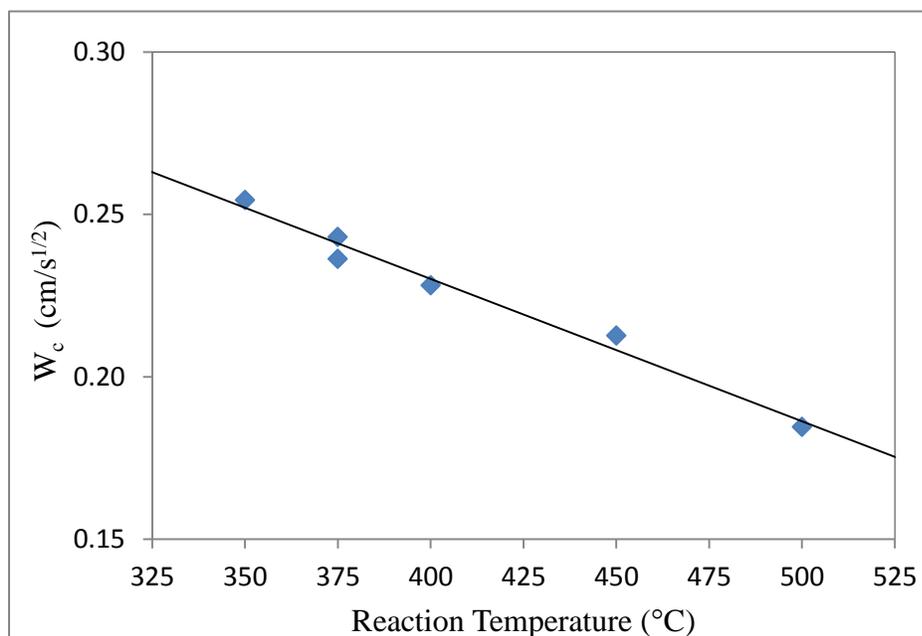


Figure 2.14: Effect of temperature on wicking coefficient (W_c) of visbreaking liquid products

2.4.5 Lamp Performance

The final indicator of the viability of a fuel as a lamp fuel was the lamp performance test. Successful operation in the lamp performance test indicates a successful lamp fuel in terms of the functionality of a lamp.

The results from this test on the visbreaking products indicated no successful lamp fuels. Each sample was tested at 100% pyrolysis oil. It was found that none of the oils produced from the visbreaking process of soybean oil passed the lamp performance test. As previously mentioned, this test has the binary results of pass or fail. The following figures (Figure 2.15 and Figure 2.16) demonstrate the typical outcomes of a failed fuel.



Figure 2.15: Wick consumption with inadequate fuel. . Visbreaking sample obtained at 450 C, t= 120 min.

Figure 2.15 shows the excessive wick consumption demonstrated by the pyrolysis fuels. During the twenty minute run, a commercial fuel such as kerosene will consume about 0.06 cm of the wick (Mills & Ph, 2003). It is clear from the figure above that lamp operation with this pyrolysis- derived fuel is not feasible. The second issue with many of the pyrolysis fuels was the insufficient fuel supply. In this case, the flame, when ignited, was initially bright but soon dwindled and extinguished in a matter of seconds. An image of this behavior is given in Figure 2.16.

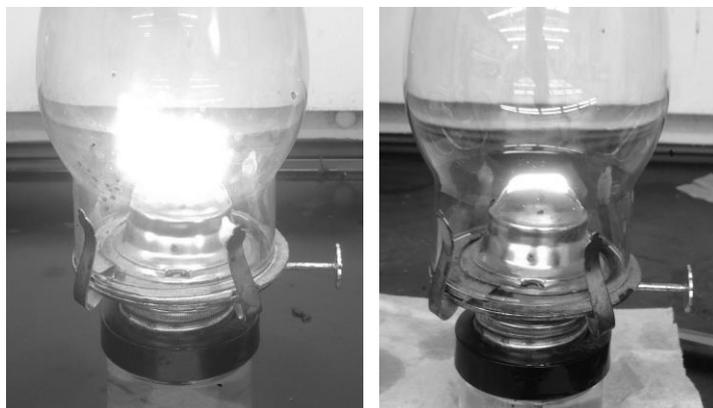


Figure 2.16: Insufficient fuel supply in a traditional wick lamp. (left) initial ignition, (right) flame diminishing. Visbreaking sample obtained at 450 C, t= 120 min.

2.4.6 Product Blending

In order to obtain a fuel with the correct properties for successful lamp operation, the visbreaking fuels were blended with commercial kerosene. Blending percentages are based on the minimum fraction of kerosene required to obtain a successful lamp fuel. This was determined by a trial and error approach utilizing the lamp performance test as a measure of fuel adequacy. The solubility of the organic liquid product in kerosene results in a homogeneous fuel. No phase separation occurred during the testing period ensuring kerosene separation was not providing misleading data. It was assumed that this homogeneous state was also present in the wicking material, and that the solution composition remained constant over the volume of the wicking material.

Kerosene blending ranged from 40-65 wt% for pyrolysis fuels, while untreated oil required over 95 wt% kerosene loading. This indicates the visbreaking process upgraded the fuel from its parent oil. The liquid properties of the visbreaking fuel impacted the kerosene loading required for lamp operation.

The effect of reaction temperature on required kerosene loading can be seen in Figure 2.17. The trend is very similar to that of viscosity and inversely similar to that of W_c . The less viscous, faster wicking fuels require lower kerosene loading. The relation between

wicking coefficient (of the visbreaking oil prior to blending) and kerosene loading is given in Figure 2.18. It can be seen that wicking rate displays a direct linear relation to kerosene loading indicating the importance of wicking in the oil lamp system. Higher values of W_c lead to lower kerosene requirements. In terms of optimization of process conditions, one must consider the low yields experienced at conditions producing faster wicking fuels. Economic factors such as the price of feedstock and kerosene, as well as production costs will affect the optimal conditions for the process.

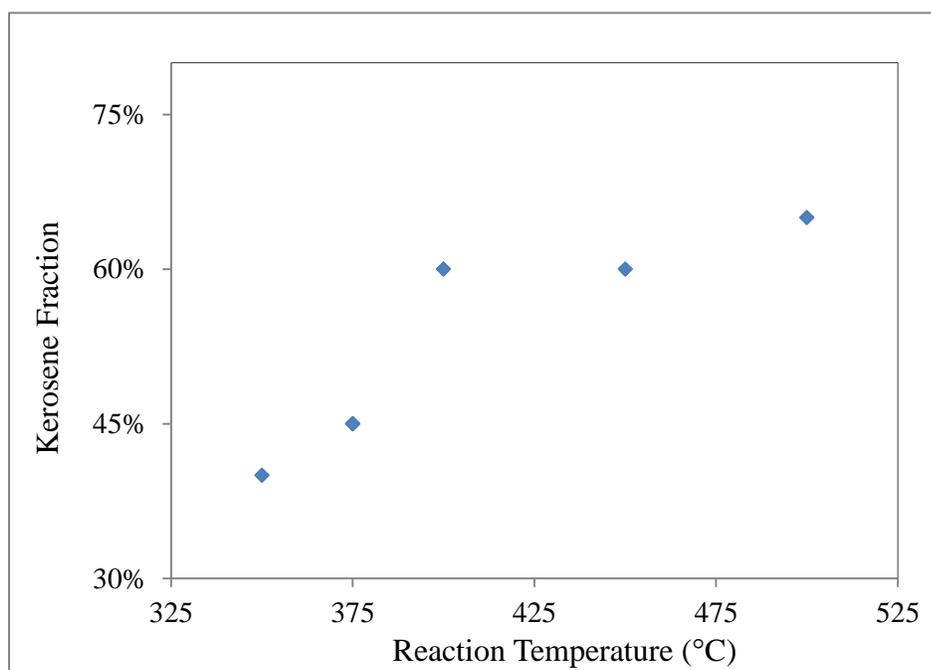


Figure 2.17: Effect of reaction temperature on kerosene loading required for successful lamp operation

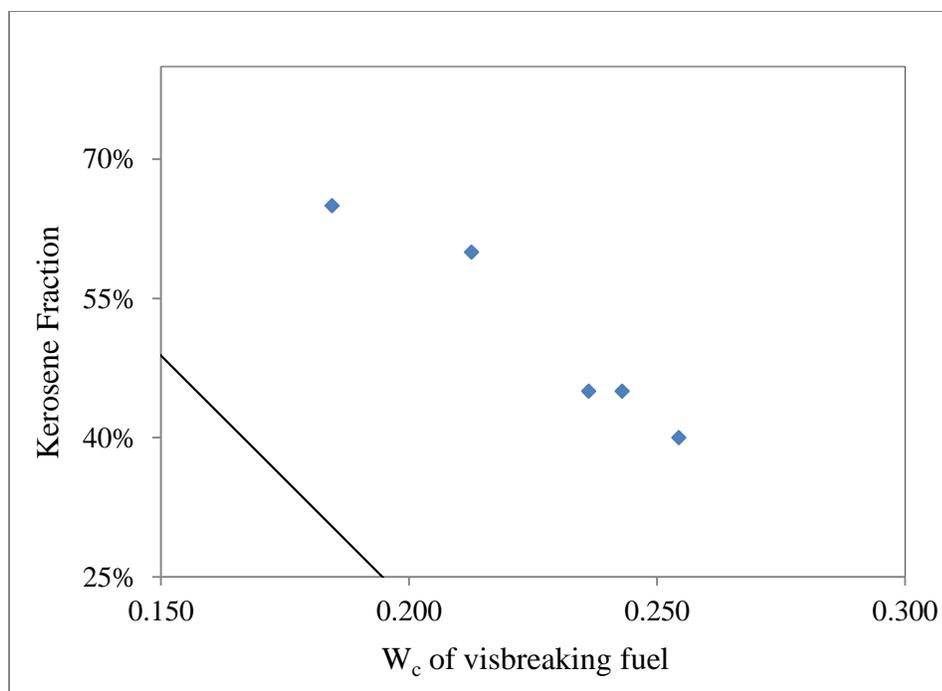


Figure 2.18: Kerosene loading vs. wicking coefficient of visbreaking fuel

Properties of Successful Blends

After obtaining the kerosene- pyrolysis oil blends, measurements of liquid fuel properties were taken and can be seen in Table 2.10. These ranges represent the minimum requirements of a successful lamp fuel. The values obtained are also within AGOWA's acceptable fuel properties outlined in their patent (Moller & Pederson, 2010).

Table 2.10: Liquid Properties of Successful Fuels

	Blends	Kerosene	Paraffin
Dynamic Viscosity (cP)	2.0 - 2.9	0.89	2.68
Density (g/cm ³)	0.82 - 0.83	0.78	0.79
Surface Tension (dyne/cm)	27.12 - 27.85	26.5	27.7
W _c	0.38 - 0.40	0.44	0.38
HHV (MJ/kg)	43.5 - 44.7	45.8	43.6

2.5 Conclusions and Recommendations

The visbreaking process was observed to upgrade soybean oil into a lamp fuel additive. Although unsuccessful in producing pure lamp fuel, up to 60% blends can provide a useable lamp fuel. It was determined that reaction conditions heavily impact the yields of the process, as well as the organic liquid fuel properties. Statistical analysis based on design of experiments concluded that the reaction temperature is the only significant factor for the given responses. The interaction effects with residence time, in some cases, can be used to provide marginal improvements in responses such as organic liquid yield, wax yield, and residue yield. In terms of organic liquid yield, increases in reaction temperature lead to increased yields. These increased yields were accompanied by increases in liquid viscosity and decreases in wicking coefficient, leading to higher kerosene loading requirements for lamp operation. Therefore the optimization of this process is highly dependent on economic conditions such as feedstock, heating, and kerosene costs. The high flexibility of this process allows for implementation in a variety of economic landscapes. The ability to fine tune reaction conditions to achieve desired product yields and properties is ideal for lamp fuel applications considering the high instability of kerosene prices.

The next chapter of this study will investigate higher severity reaction conditions. The low severity visbreaking process provided higher viscosity, poorer wicking fuels as reaction severity increased. This is contrary to some literature studies on vegetable oil cracking. It is possible that sufficient cracking is not occurring and that the longer chain molecules are being distilled prior to undergoing cracking reactions. Along with investigating high severity processes, improvements to the visbreaking process could also be studied. Research is recommended in areas such as the distillation and characterization of the produced liquid. Finer control of the distillation temperatures could allow for more accurate control of condensed organic liquid properties. In addition, research in the utilization of wax and heavy residues may be beneficial in increasing yields or adding additional value streams.

2.6 References

- Alencar, J., Alves, P., & Craveiro, A. (1983). Pyrolysis of tropical vegetable oils. *Journal of Agricultural and ...*, 1268–1270. Retrieved from <http://pubs.acs.org/doi/abs/10.1021/jf00120a031>
- ANOVA. (2009). *Explorable.com*. Retrieved June 17, 2014, from <https://explorable.com/anova>
- Demirbas, a. (2009). Recovery of gasoline range fuels from vegetable oils. *Energy Sources, Part A*, 31(5), 420–426.
- Doll, K., Sharma, B., Suarez, P., & Erhan, S. (2008). Comparing Biofuels Obtained from Pyrolysis, of Soybean Oil or Soapstock, with Traditional Soybean Biodiesel: Density, Kinematic Viscosity, and Surface Tensions. *Energy & Fuels*, 257(2), 2061–2066.
- Egloff, G., & Morrell, J. C. (1932). The cracking of cottonseed oil. *Ind. Eng. Chem.*, 24, 1426–1427.
- Egloff, G., & Nelson, E. F. (1933). Cracking Alaskan fur-seal oil. *Ind. Eng. Chem.*, 25, 386–387.
- Hammond, E. G., Johnson, L. A., Su, C., Wang, T., & White, P. J. (2003). Soybean Oil.
- Kamath, Y. K., Hornby, S. B., Weigmann, H. D., & Wilde, H. F. (1994). Wicking of Spin Finishes and Related Liquids into Continous Filament Yarns. *Textile Research Journal*, 64, 33–40.
- Kubátová, A., Luo, Y., Šťávoová, J., Sadrameli, S. M., Aulich, T., Kozliak, E., & Seames, W. (2011). New path in the thermal cracking of triacylglycerols (canola and soybean oil). *Fuel*, 90(8), 2598–2608.

- Lee, B.-B., Ravindra, P., & Chan, E.-S. (2009). New drop weight analysis for surface tension determination of liquids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 332(2-3), 112–120.
- Lima, D. G., Soares, V. C. D., Ribeiro, E. B., Carvalho, D. a., Cardoso, É. C. V., Rassi, F. C., ... Suarez, P. a. Z. (2004). Diesel-like fuel obtained by pyrolysis of vegetable oils. *Journal of Analytical and Applied Pyrolysis*, 71(2), 987–996.
- Maher, K. D., & Bressler, D. C. (2007). Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresource Technology*, 98(12), 2351–68.
- Masoodi, R., & Pillai, K. M. (2010). Darcy ' s Law-Based Model for Wicking in Paper-Like Swelling Porous Media, 56(9).
- Methods of surface tension measurements*. (2009). Lublin. Retrieved from <http://www.umcs.pl/pl/>
- Mills, E., & Ph, D. (2003). Technical and Economic Performance Analysis of Kerosene Lamps and Alternative Approaches to Illumination in Developing Countries
- Moller, K., & Pederson, P. H. (2010). Fuel composition comprising alkyl ester. Canada, United States, Denmark.
- Schwab, A. W., Dykstra, G. J., Selke, E., Sorenson, S. C., & Pryde, E. H. (1988). Diesel fuel from thermal-decomposition of soybean oil. *Journal of American Oil Chemists' Society*, 65(11), 1781–1786.
- The Lamp Wick. (n.d.). *The Lampworks*. Retrieved April 24, 2014, from http://www.thelampworks.com/lw_wicks.htm
- Zhenyi, C., Xing, J., Shuyuan, L., & Li, L. (2004). Thermodynamics calculation of the pyrolysis of vegetable oils. *Energy Sources*, 26(9), 849–856.

Chapter 3

3. PYROLYSIS OF TRIGLYCERIDES OF SOYBEAN OIL FOR PRODUCTION OF RENEWABLE LAMP FUEL

3.1 Introduction

The widespread growth of energy demand in the world market has provided advances in the research of alternative fuels (Daniel & Garc, 2013). In an attempt to minimize dependency on fossil fuels, many biofuels are being researched and developed globally. Traditionally, hydrocarbon based fuels are obtained from fossil fuel refining (Meyers, 2003). It has been demonstrated that the thermal treatment of triglycerides present in crop oils can produce hydrocarbon-rich fuels suitable for various applications.

One of the potential thermal processes for conversion of triglycerides to alternative fuels is pyrolysis. Pyrolysis is a form of thermochemical treatment which chemically decomposes organic materials through the addition of heat in the absence of oxygen (Střávořová et al., 2012). Materials such as TGs can be pyrolyzed to produce hydrocarbon rich liquid products. Pyrolysis, or thermal cracking, of vegetable oils represents an alternative method of producing renewable liquid products for use in fuel applications. Currently, transesterification is the leading process converting crop oils to fuels. The main advantage pyrolysis possesses over transesterification is that the final product(s) can be altered dependent on reaction conditions. This allows for a process able to tailor the products towards certain applications by tuning various process parameters. Additional advantages over transesterification include lower processing costs, compatibility with infrastructure, and feedstock flexibility (Stumborg et al., 1996). Environmental benefits include the absence of harmful catalysts and wastewater treatment.

Dependent on the residence time of the reactant, pyrolysis can be divided into three subclasses: slow pyrolysis, quick pyrolysis, and flash pyrolysis (Maher & Bressler, 2007). These subclasses can be used to adjust the solid, liquid, or gas phase yields. The effect of temperature also influences selectivity towards certain phases. The yields of these phases are heavily dependent on the pyrolysis conditions. For example, a long residence time at low temperature will favour char production while a short residence time at high temperature will produce more organic liquid product. The majority of research on pyrolysis surrounds the use of solid biomass. When applying pyrolysis to the case of vegetable oils, products are materials resulting from simple cracking of the molecules and possible reforming of the primary products to secondary products dependent on the conditions (Frey et al., 2011).

Many previous studies focused on batch operation, including the visbreaking study in Chapter 2. Continuous operation presents an attractive option. Batch processes can be impractical in larger scale operations (Maher & Bressler, 2007). Cleaning and recharging is required after each run. They also exhibit low throughputs and experience frequent interruptions (Idem et al., 1996). The literature contains few studies on continuous operation of thermal treatment of vegetable oils for fuel.

In 1996, Iden et al. published a study using a flow-type reactor with a fixed bed of inert materials. The cracking of vegetable oil in this reactor was carried out at operating temperatures between 300–500 °C, at atmospheric pressure, with gas hourly space velocities (GHSV) ranging from 3.3–640 h⁻¹ (Idem, Katikaneni, & Bakhshi, 1996). Results of this work shows conversions ranging from 54- 100%, which were very sensitive to operating variables. Product obtained was comprised of C4 and C5 hydrocarbons, aromatic and C6 aliphatic hydrocarbons, and C2–C4 olefins as well as a diesel like fuel and hydrogen (Idem et al., 1996). The liquid product consisted of 26% C6–C12, non-aromatic hydrocarbons. No aromatic compounds were detected in the liquid fraction (Idem et al., 1996). Following this study, the group shifted towards catalytic processes publishing their work in 1998 (Idem et al., 1998).

In 1999, Fortes and Baugh studied the cracking of crop oils in a process representative of fast pyrolysis. The majority of pyrolysis studies involving vegetable oils do not achieve fast pyrolysis due to their lower temperatures and relatively long residence times (Maher & Bressler, 2007). Fast pyrolysis is generally characterized by temperatures around 500 °C and reaction times in the order of seconds. This research looked at the fast pyrolysis of macuba fruit oil. The main products were aldehydes, alkenes and carboxylic acids, and the secondary products consisted of alkanes, cycloalkanes and unknowns.

Limited research has been undertaken on the cracking of vegetable oil in fluidized beds, Dupain et al. published a study on cracking of rapeseed oil performed in a laboratory-scale once-through micro riser to mimic the design of an FCC reactor (Dupain et al., 2007). In this study the decomposition of the triglyceride was reported to occur within the first 50 ms, followed by step-wise cracking of the fatty acids. Triglycerides conversions as high as 95% were observed. Products consisted of fatty acids, reaction intermediates, diesel and gasoline boiling range products, and light gases.

This literature review provides supporting evidence that pyrolysis is a potential process for the production of lamp fuel from crop oils. The objective of this chapter is to investigate the use of fast pyrolysis of soybean oil for the production of lamp fuel. The effect of an increased severity process and a continuous operation will be analyzed. The area of focus is on the optimization of reaction conditions with respect to reaction product yields and fuel properties. Product blending with kerosene is studied to produce useable lamp fuel in traditional oil lamps. Comparative analysis of the pyrolysis process and the visbreaking process is performed to determine the optimal technology for this application.

3.2 Materials

3.2.1 Feedstock Selection

Refer to Chapter 2 for description of feedstock.

3.2.2 Commercial Fuels

Refer to Chapter 2 for description of commercial fuels.

3.2.3 Bed Material

The bed material utilized in this study was SiO_2 , or silica sand. The sand was obtained was Opta Mineral Barco Silica Sand size 42, with a sauter-mean diameter of 0.425 mm. These inert particles provided good heat transfer and were non-reactive with the feedstock.

3.3 Methods

3.3.1 Equipment

Fast pyrolysis was carried out in a mechanically fluidized reactor (MFR). The unit was of cylindrical geometry having an inside diameter of 8.89 cm and a height of 12.7 cm. Total volume of the reactor was 788.31 cm^3 with an effective capacity of 600 mL. A diagram of the MFR is given in Figure 3.1. The reactor was made of carbon steel. The flanged tank equipped with carbon steel lid and graphite gasket provided the seal from atmospheric air. The mechanical fluidization system comprised of a top-mounting electric motor driving a mixing apparatus. Mechanical mixing provided mimicked fluidization of the bed material, giving uniform heat transfer and excellent mixing. The mixer duplicated as a wall scraper ensuring no dead zones were present in the system, and preventing wall deposits.

The reactor included a high temperature filter immediately downstream of the MFR. The high temperature filter was of cylindrical tube geometry and of stainless steel construction. Dimensions were a diameter of 5 cm, and a length of 13 cm resulting in a

total volume of 255 cm³. The internals of the tube included a stainless steel mesh filter. The filter was also cylindrical in shape as seen in Figure 3.1. The mesh size was 10 microns.

Heating was provided to the MFR and the high temperature filter by two independently controlled ceramic fiber heaters. Each heater was equipped with an Omega PID controller. Controllers were independently tuned for optimal PID parameters for the given heating requirements. This provided accurate temperature control resulting in temperature variances of $< \pm 5^{\circ}\text{C}$. Each controller was equipped with RS-232 communication for CPU programming and monitoring. The MFR was controlled based on a temperature measurement taken at the bottom of the vessel in the fluidized sand bed. Heating of the high temperature filter was controlled by a vapour phase temperature measurement in the center of the vessel. Both measurements were obtained with K-type thermocouples. Ceramic fiber insulation was installed on both units to minimize heat loss, maximize efficiency, and prevent condensation between units.

Continuous feeding of oil was provided by a syringe dosing pump (New Era Pump Systems Inc.) which maintained a constant flowrate of feedstock with very high accuracy. Fresh feed entered the top of the MFR unit. A constant flow of nitrogen gas was also introduced to the top of the MFR and was controlled by a high-accuracy ($\pm 1\%$) Omega FMA flowmeter.

The condensing train consisted of two tube condensers in series followed by an electrostatic precipitator (ESP). Both tube condensers were of stainless steel construction. The ESP consisted of a cylindrical aluminum tube with a diameter of 5 cm and height of 20 cm. A copper electrode was positioned in the center of the tube and supplied with 12 kV. End caps of the ESP were constructed of PVC to provide electrical isolation. Downstream from the ESP was a cotton gas filter followed by an exhaust to atmosphere.

Safety measures in the system included a pressure gauge and pressure relief valve. These allowed for constant pressure monitoring and prevented pressurization and possible explosion hazard. The pressure relief valve was designed to relieve the pressure when the system exceeded 10 psi. Both PID temperature controllers were programmed to set off an

alarm when the temperature of the system exceeded its maximum design specifications. This would result in a loud audio response alerting the operator to the circumstances.

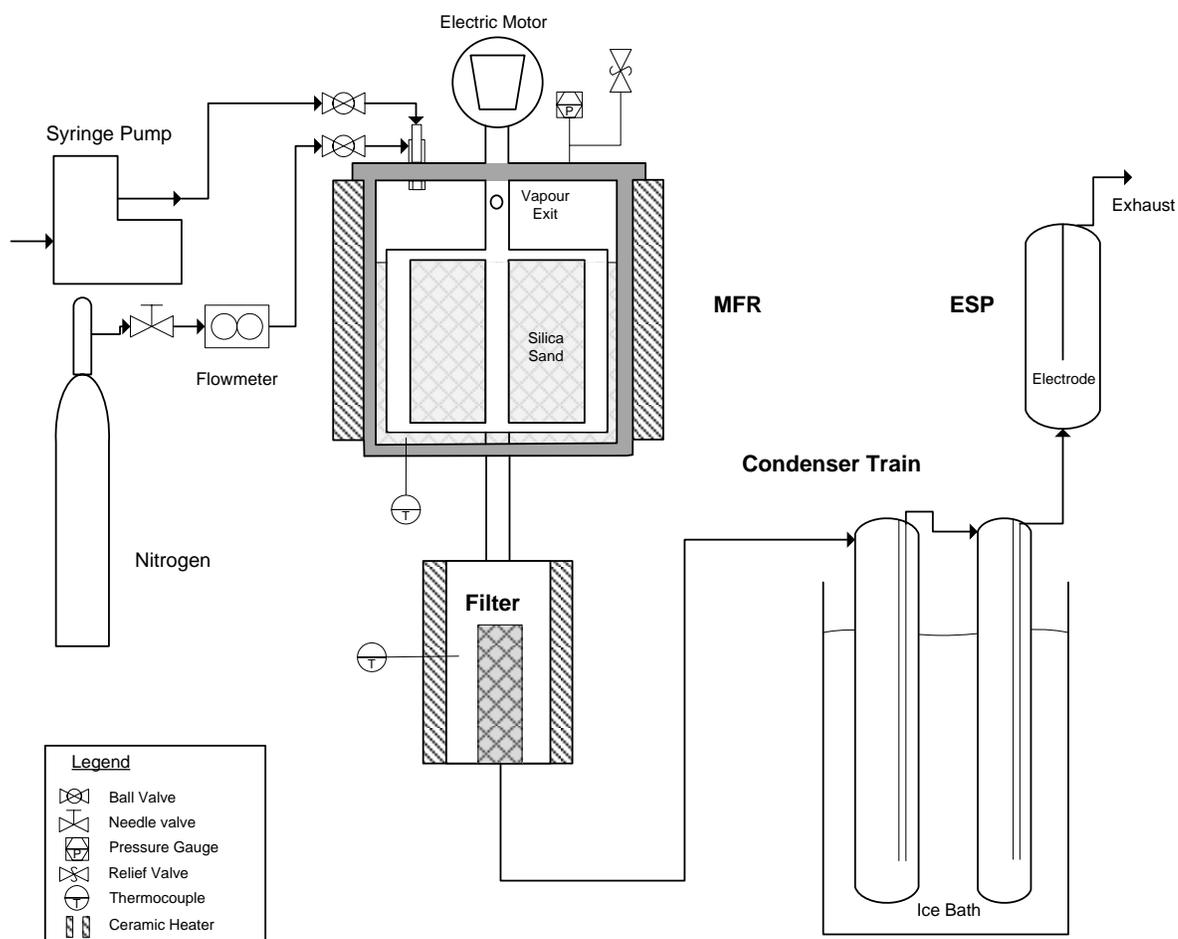


Figure 3.1: Fast pyrolysis schematic

During operation, the fresh vegetable oil enters the MFR from the top, where it drops into the high temperature sand bed. The vapours produced from the thermochemical reaction then migrate to the top of the MFR chamber where they exit through the holes in the top of the mixing shaft. The vapours then proceed downward to the high temperature filter where additional vapour phase cracking occurs and any escaping particulates are captured. A subsequent quench to a temperature of $< 5^{\circ}\text{C}$ causes vapours to condense and be collected in two condensers in series. The ESP recovers any remaining droplets from

the gas exiting the condensing train through induced electrostatic charging and collection. The remaining non-condensable gases are exhausted through a gas filter and a line.

3.3.2 Experimental Procedure

During a typical experimental run, between 170-230 g of fresh feed would be consumed. Prior to injection all pieces of the system would be cleaned and weighed, and 600 g of fresh silica sand would be loaded into the MFR. The system would then be assembled and insulated. As the controllers were specifically tuned for the system it was important that insulation be installed in a similar manner for every run. Following assembly of the unit, the nitrogen, mixing and heating would be initiated. Mixing speeds ranged from 20 to 144 rpm and nitrogen flowrates were 0-2 SLPM. Feed injection began after system had reached and maintained target conditions for both MFR and filter. Liquid injection was controlled by the syringe pump. Typically 3-4 60 mL syringes of fresh feed would be injected. A feed rate of 4 mL/min was selected for this study. All experiments operated at atmospheric pressure. A 20 minute cooling off period was allowed after every run before collecting samples. Liquid and solid (residue) yields were determined through weight measurements of various sections of the unit. Gas yield was calculated based on closing the mass balance.

3.3.3 Product Analysis

3.3.3.1 Viscosity and Density Measurement

Refer to Chapter 2 for description of viscosity and density measurement.

3.3.3.2 Surface Tension

Refer to Chapter 2 for description of surface tension measurement.

3.3.3.3 Wickability Testing

Refer to Chapter 2 for description of wickability testing.

3.3.3.4 Lamp Performance

Refer to Chapter 2 for description of lamp performance testing.

3.4 Results and Discussion

3.4.1 Effect of Reaction Parameters

Based on the conclusions of Chapter 2, the primary reaction parameter investigated was reaction temperature. As demonstrated in Chapter 2, and confirmed in literature (Kubičková & Kubička, 2010b), the temperature is the most significant parameter in the reaction with respect to both phase yields and product properties. This was also true for the pyrolysis process, as demonstrated in the following sections. It should be noted however that vapour residence time was not investigated in this study.

Due to the high mixing rates involved in the mimicked fluidization of the bed material, the effect of mixing was also investigated. It was shown that an increase in mixing results in an increase in liquid yield. However, the increase in mixing reaches a point after which no further increase in liquid yield is experienced. This is consistent with other studies in our group which utilized this equipment (Stanlick, 2014), and is related to the breakup of liquid-solid agglomerates and the resulting increase in heat transfer experienced at increased mixing speeds. The point at which the curve reaches its maximum is 100 rpm. Beyond this mixing speed, no further increase in yield is experienced. Therefore the optimal mixing speed is 100 rpm and all further experiments were run at this speed to prevent unnecessary attrition of the sand bed and reduce energy consumption.

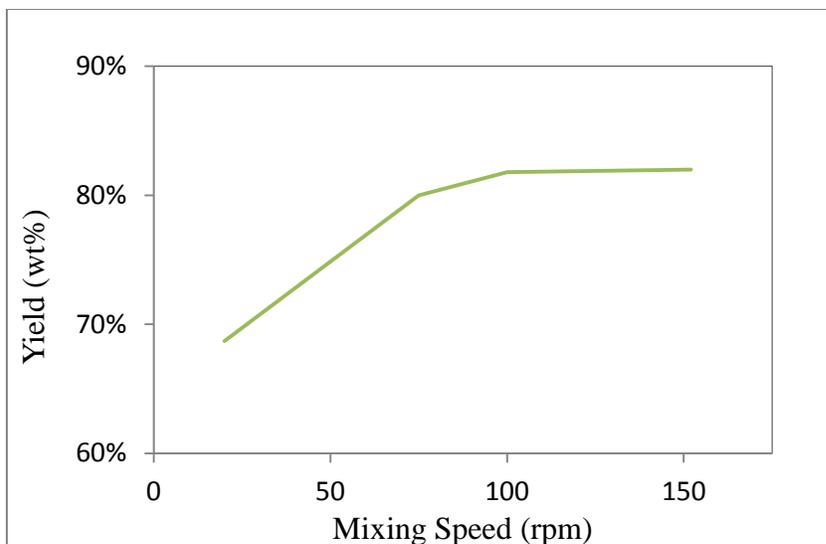


Figure 3.2: Effect of mixing speed on pyrolysis liquid product yield

3.4.2 Phase Yields

The following section will present the effects of reaction temperature on the yields of the various fractions generated in the pyrolysis process. Collected phases include organic liquid, gas, and heavy residues.

Organic Liquid Yield

The results of the pyrolysis experiments in terms of organic liquid yield are presented in Figure 3.3. It can be seen that a maximum liquid yield of 93 wt% is experienced at a reaction temperature of 450 °C. Beyond this temperature the yield of organic liquid decreases linearly at approximately $-0.33 \text{ wt\% / } ^\circ\text{C}$ until a minimum of 23 wt% is reached at 650 °C. Therefore no further experiments were performed above a reaction temperature of 650 °C as the resulting liquid yield was insufficient.

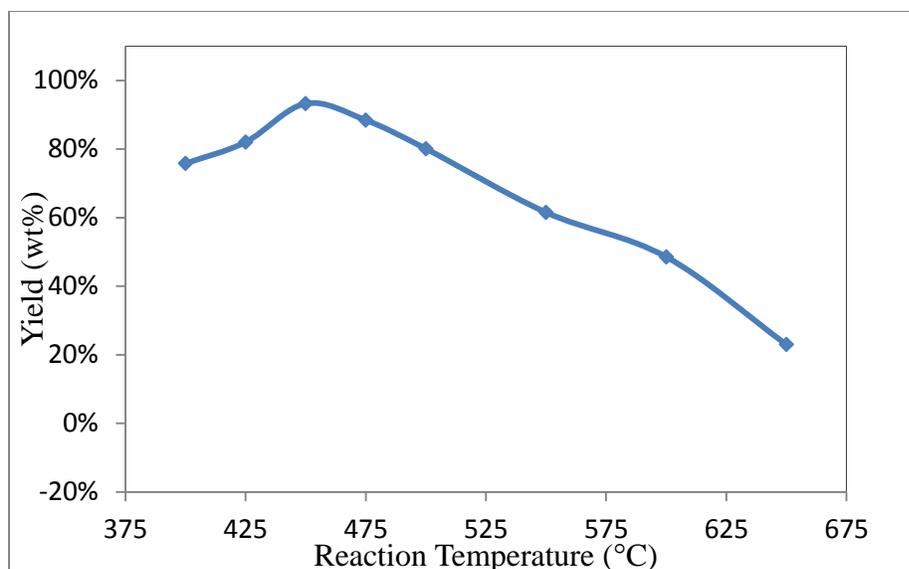


Figure 3.3: Effect of temperature on pyrolysis liquid product yield

Gas Yield

The gas yield represents the non-condensable gases which passed uncollected through the condensing train and ESP. Figure 3.5 displays the effect of reaction temperature on this quantity. It can be seen that at relatively low reaction temperatures, the gas yield is below 10%. Beginning at a reaction temperature of 450 °C (the maximum for organic liquid yield, and minimum for gas yield), the gas yield increases linearly with temperature until reaching a maximum value of 77 % at 650 °C. This is inversely similar to the trend of organic liquid yield. This demonstrates that as the severity of the reaction increases, the magnitude of molecular cracking also increases. The long-chain, high molecular weight molecules are decomposing to form smaller molecules which remain in the gas phase even at low temperatures present in the collection train. The effect of increased cracking translates into the organic liquid properties and is discussed in the following section.

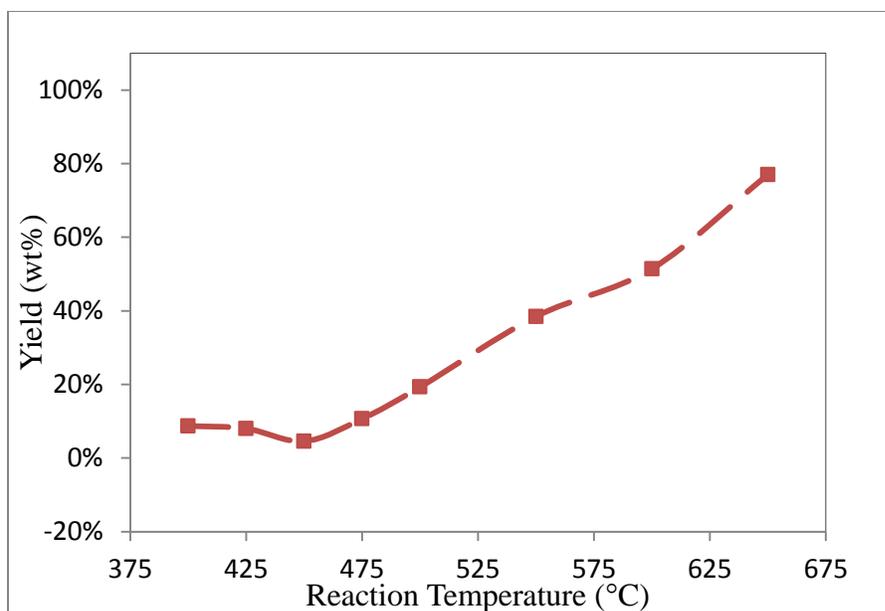


Figure 3.4: Effect of temperature on pyrolysis gas product yield

Residue Yield

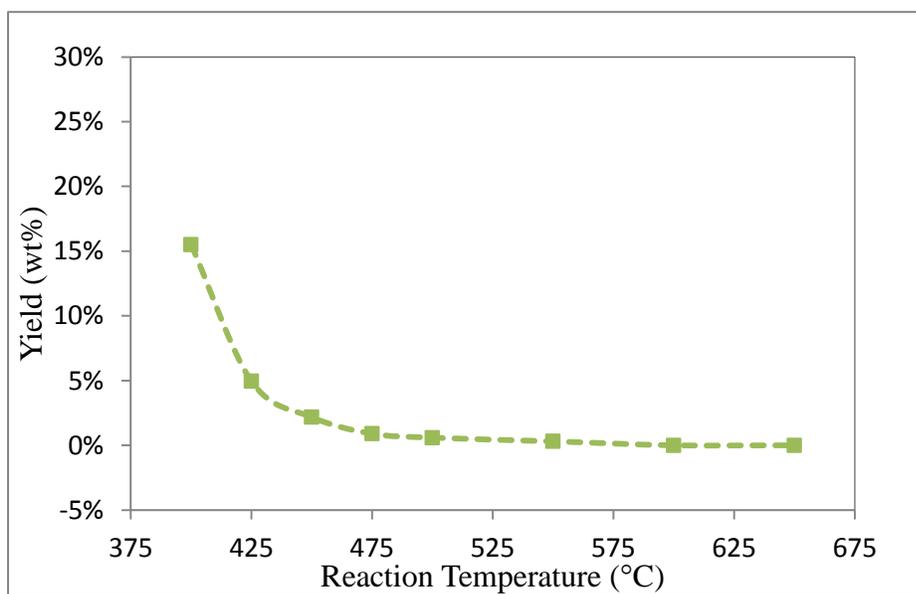


Figure 3.5: Effect of temperature on pyrolysis residue yield

The residue is the heavy liquid remaining in the reactor upon process completion. Figure 3.5 displays the effects of reaction temperature on this yield. At a reaction temperature of 400 °C, the residue fraction is near 15 wt%. Increasing the reaction temperature beyond 400 °C caused a steep decrease in the residue yield. At temperatures of 475 °C and above, the residue is essentially nil. This indicates that all liquid has escaped the reactor at temperatures above 475 °C.

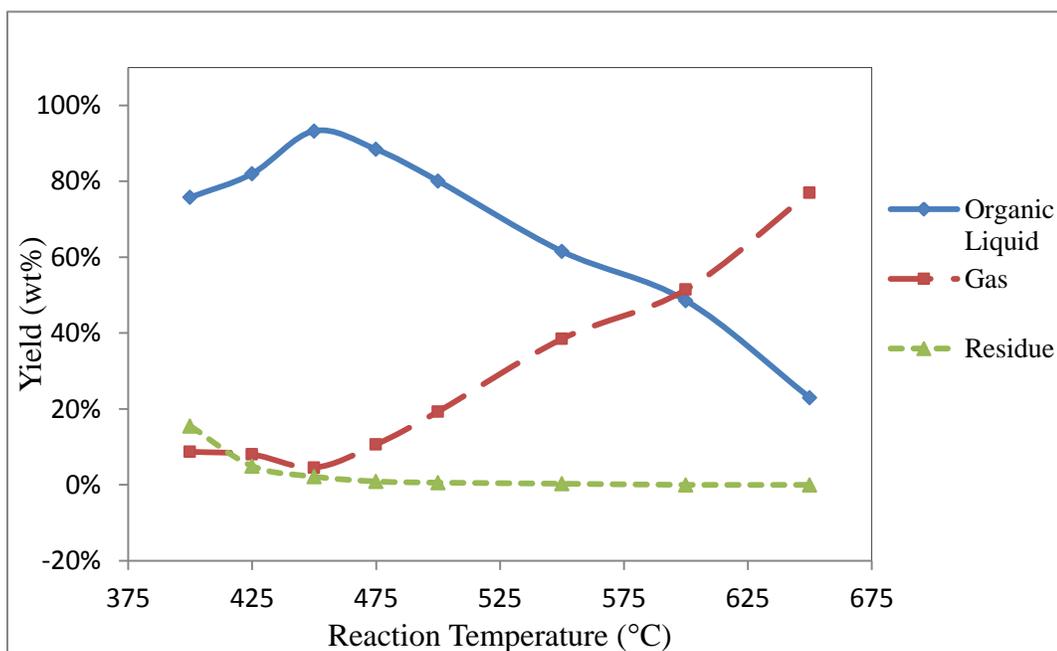


Figure 3.6: Effect of temperature on pyrolysis product phase yields

A summary of the effect of temperature on the yields of the three fractions is presented in Figure 3.6. It was demonstrated that as the reaction temperature is increased initially from 400 to 450 °C, an increase in organic liquid yield is experienced, along with a decrease in residue. This is likely due to the increased amount of distillation of the heavier molecules. As the reaction temperature is increased further the residue approaches zero, while the organic liquid decreases proportionally to the increase in gas yield. This indicates that as the severity of the reaction is increased, the organic liquid is thermally cracking, producing lighter compounds, and increasing the fraction of non-condensable gases. This behavior coincides with what has been reported in the literature in that significant

cracking does not occur until reaction temperatures of at least 420 °C (Kubičková & Kubička, 2010b). The optimal conditions of this process are dependent on the resulting liquid properties. In terms of yield optimization, the maximum yield is experienced between 425-500 °C.

3.4.3 Liquid Properties

Liquid properties refer to the measured properties of the obtained organic liquid in the pyrolysis reaction. Similar to phase yields, and also to the visbreaking reactions, the only significant reaction parameter is reaction temperature. The effect of reaction temperature on liquid properties is given in this section. The influence of phase yields on liquid properties is also investigated. It should be noted that vapour residence time was not considered in this study and may potentially have an effect on the process.

Viscosity

It has been demonstrated that viscosity is a crucial property in the success of liquid lamp fuels. Low viscosities are desired in this application as lower viscosities increase wickability in fuel lamp systems. The thermal cracking process was able to reduce the viscosity of the parent oil by as much as 96 %.

The resulting viscosity of the organic liquid produced at each reaction temperature is shown below in Figure 3.7. The trend of liquid viscosity vs. reaction temperature is similar to that of organic liquid yield vs. temperature. It can be seen that the viscosity of the liquid increases with temperature from 400 to 450 °C. At this temperature range it was shown that residue decreases and organic liquid yield increases with increasing temperature. At 450 °C, the viscosity reaches a maximum value of 14.8 cP. This is the same temperature at which the organic liquid yield was at a maximum. The trend of increasing organic liquid yield and viscosity in this temperature range is further indication that distillation is the main contributing process at temperatures below 450 °C. As temperature is increased beyond 450 °C, the viscosity of product decreases. This is

opposite to what is expected in distillation and indicates that thermal cracking is occurring.

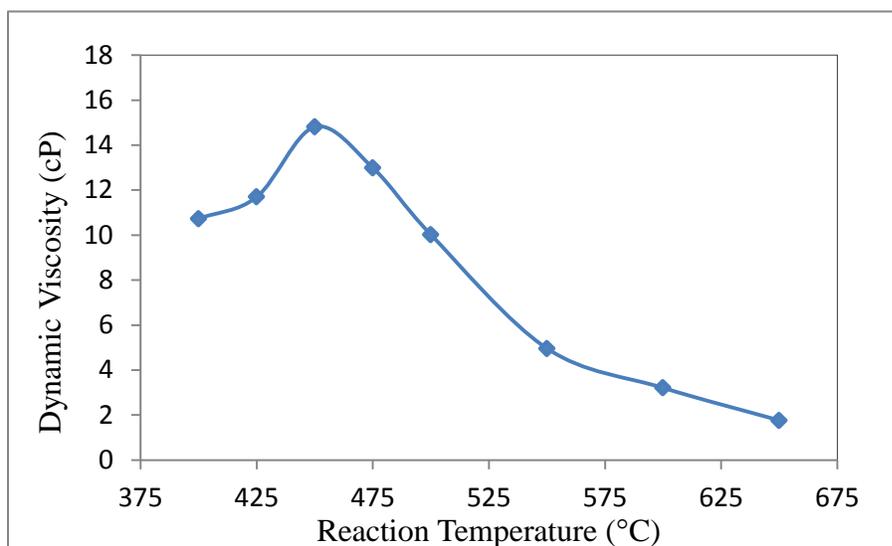


Figure 3.7: Effect of reaction temperature on dynamic viscosity of pyrolysis liquid products

Surface Tension

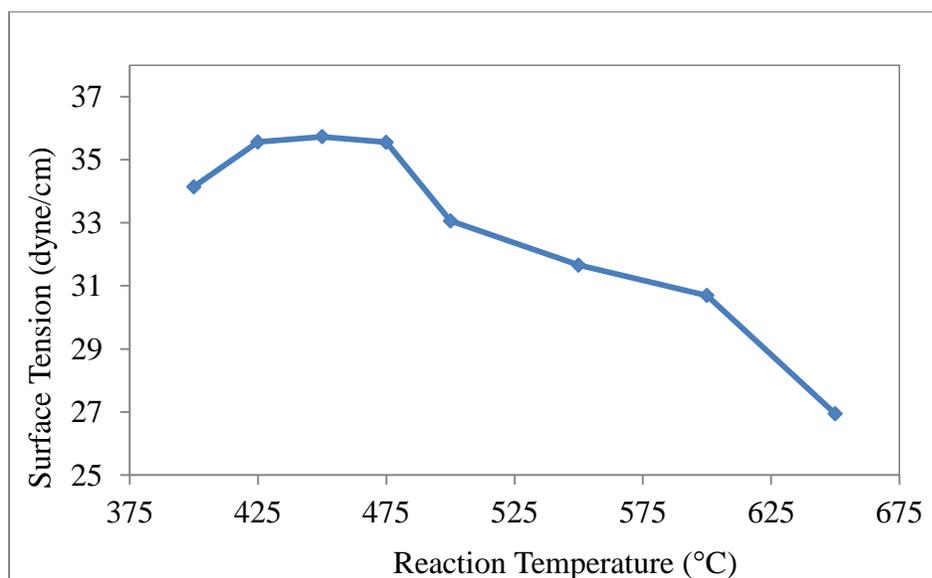


Figure 3.8: Effect of reaction temperature on surface tension of pyrolysis liquid products

Similarly to the visbreaking process, the thermal cracking process can decrease the surface tension of the untreated oil by an average of 20 %. The effect of the reaction temperature on this parameter is given in Figure 3.8. The surface tension experiences a similar trend to both organic oil yield, and viscosity. Upon increasing the temperature from 400 - 450 °C, the value rises, reaching its maximum at 450 °C. A further increase in reaction severity due to temperature rise results in the decrease of the organic liquid surface tension. The maximum temperature of 650 °C results in the minimum surface tension of 26.94 dyne/cm. This is a close match to that of the commercial kerosene-based fuel at 27.7 dyne/cm.

Figure 3.9 displays a map of two important wicking characteristics in surface tension and viscosity. This plot demonstrates the ability of this process to tailor product characteristics towards those of commercial lamp fuel.

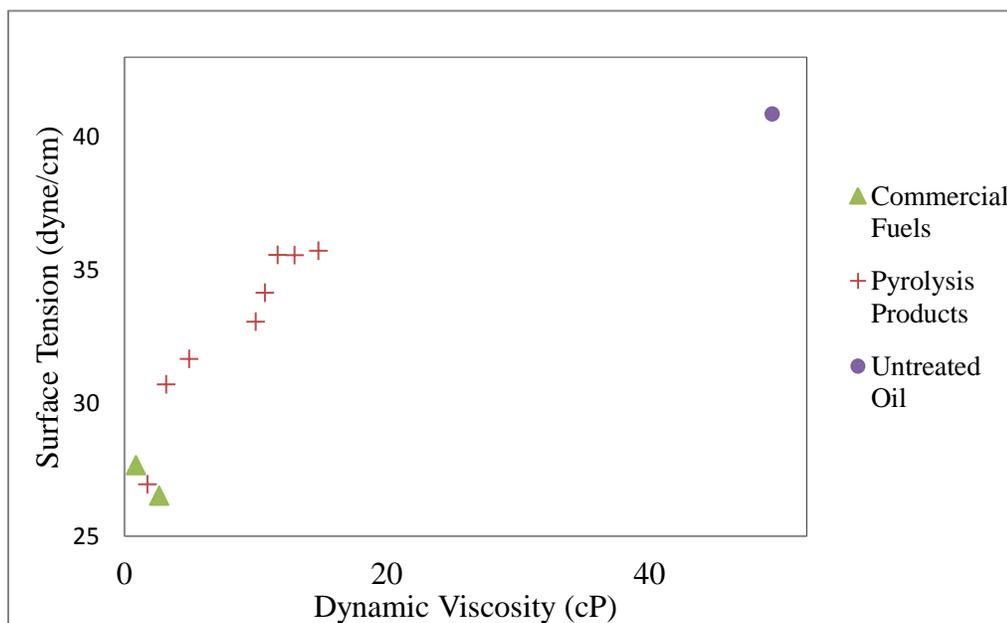


Figure 3.9: Surface Tension vs. Viscosity map of various pyrolysis liquids, untreated oil, and commercial fuels

3.4.4 Wickability

The wickability test demonstrates the capability to transport fuel up the wick of an oil lamp. As shown in Chapter 1, the liquid physical properties, presented above, impact the wickability of the fuel. In addition to physical properties, the wickability test incorporates liquid-solid interaction. Although these properties, such as contact angle, are not individually quantified, the wickability test ultimately demonstrates the wicking performance of the fuel. The results of the vertical penetration test, measuring the height climbed by the liquid over time, are presented in Figure 3.10. The solid lines represent the organic liquid samples obtained from the pyrolysis process, at various reaction temperatures. It can be seen that the thermal process has provided improvement to the wickability of the oil. The wicking performance of the optimal pyrolysis sample is much greater than the feedstock oil, however still less than the commercial fuel. The effect of temperature on wickability is given in Figure 3.11. The products obtained at higher reaction temperatures demonstrate higher wicking performance. This is contrary to the results in Chapter 2 where low temperatures yielded higher wicking rates. It is likely that the severe nature of the pyrolysis process provided enhanced molecular cleavage compared to that of visbreaking. The larger molecules are decomposing to form smaller molecules prior to escaping the reaction zone. Further molecular analysis should be carried out to confirm this.

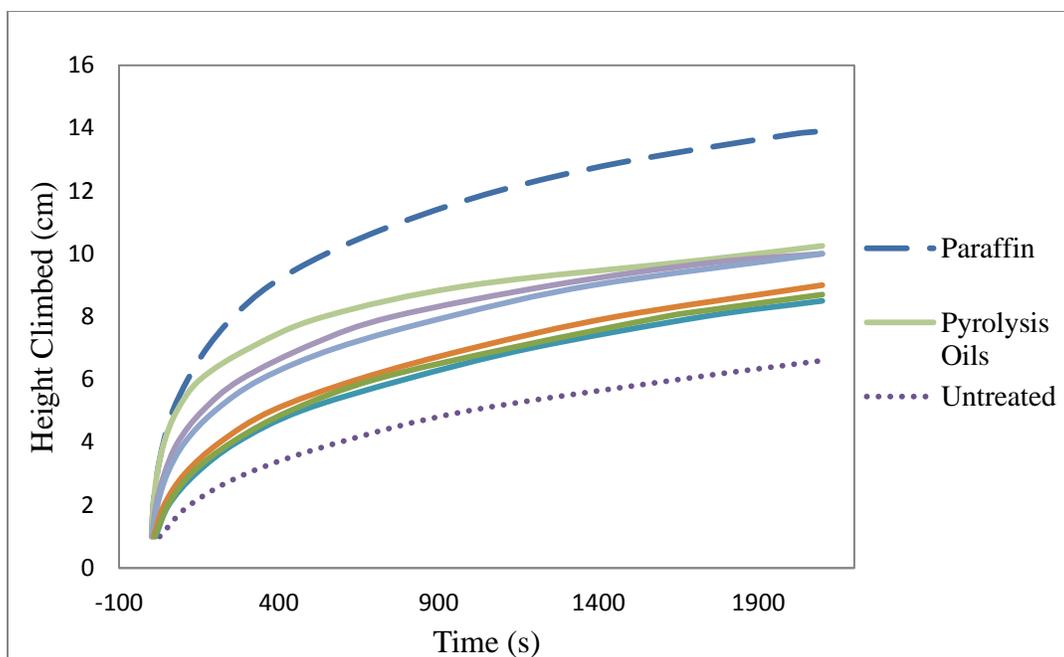


Figure 3.10: Wickability test of paraffin, pyrolysis liquid products, and untreated oil.

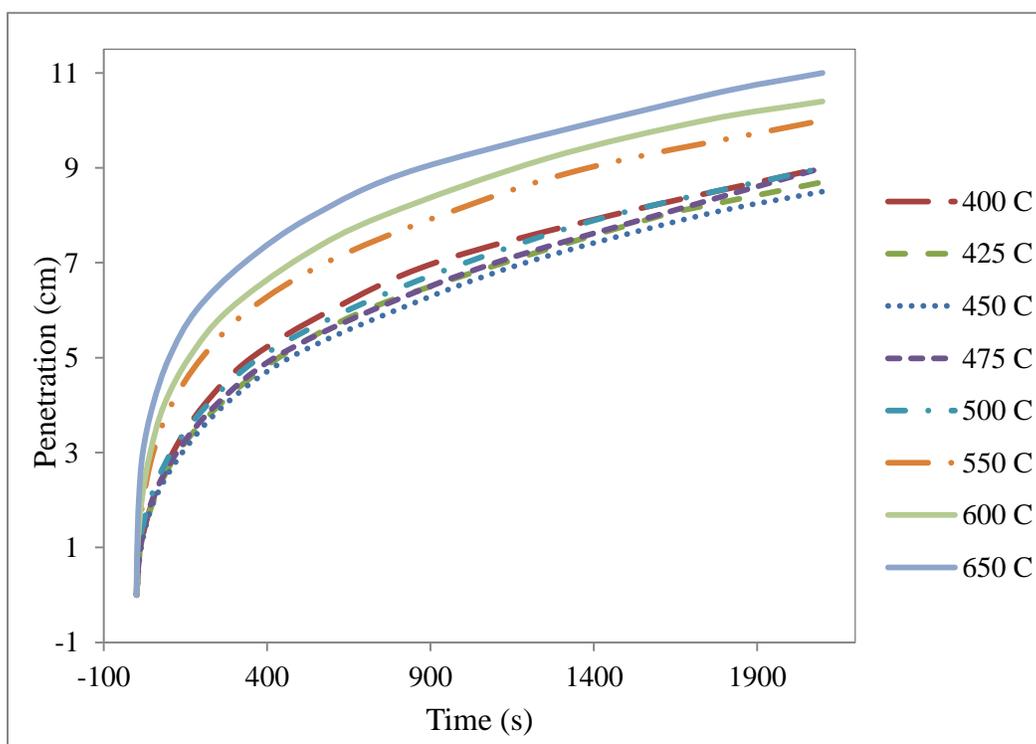


Figure 3.11: Effect of pyrolysis temperature on wicking of pyrolysis liquid products

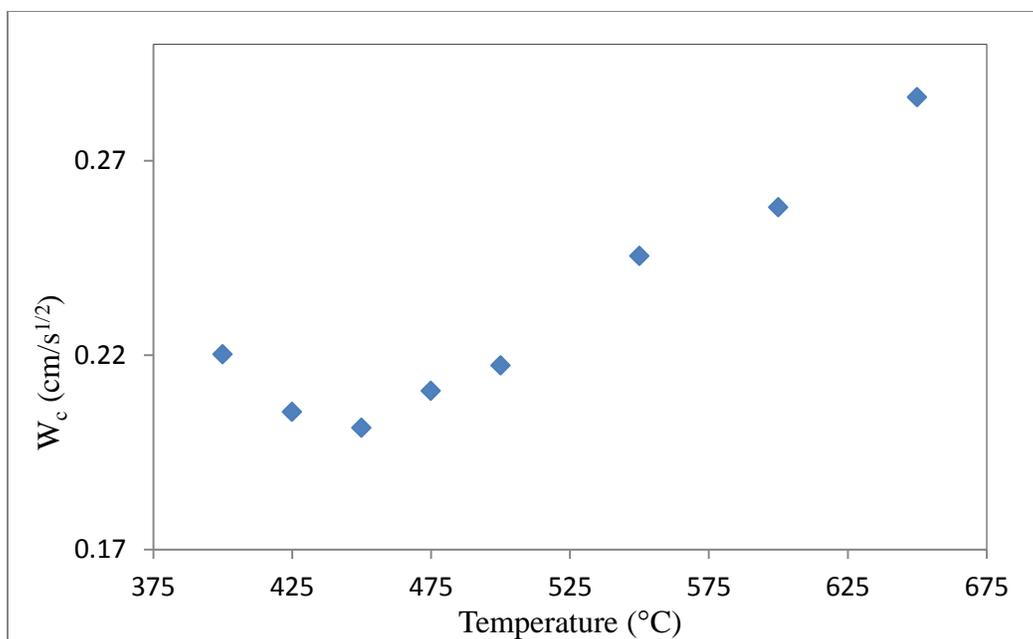


Figure 3.12: Effect of temperature on wicking coefficient (W_c) of pyrolysis liquid products

To quantify the results of the vertical penetration test, the data was linearized according to the procedure in Section 2.3.4. This was performed on all organic liquid samples, allowing for calculation of the wicking coefficient (W_c). This coefficient has been used in literature to quantify the wicking of liquids in porous materials (Kamath et al., 1994). W_c represents the slope of the linearized vertical penetration curve. A sample plot of the linearized curve was given in Chapter 2. The pyrolysis process has shown to improve the wicking coefficient by as much as 91% from the untreated oil. Table 3.1 shows a comparison of W_c values.

Table 3.1: Wicking Coefficients of Untreated Oil, Pyrolysis Products, and Kerosene

Sample	W_c (cm/s ^{1/2})
Untreated Oil	0.15
Pyrolysis Products	0.20 - 0.29
Kerosene	0.44

The effect of temperature on W_c is given in Figure 3.12. It can be seen that increasing the reaction temperature has a positive effect on the wicking coefficient. That is, the maximum wicking rates are given by fuels from high reaction temperatures. This is expected as high reaction temperatures yield low viscosity fuels. In terms of optimization, this suggests that higher temperatures are desired, however the decreased organic liquid yields at high temperatures must be considered.

3.4.5 Lamp Performance

The lamp performance testing was carried out in an identical procedure to that of the visbreaking analysis in Chapter 2. Successful operation in the lamp performance test indicates a successful lamp fuel in terms of the functionality of a lamp.

Similarly to the visbreaking process, the results of the lamp performance test revealed none of the pure products were performing as successful lamp fuels. Each sample was tested with 100 % pyrolysis oil. It was found that none of the oils produced from the pyrolysis process of soybean oil passed the lamp performance test. The failure of the test was due to similar contributors as the visbreaking fuels. The combination of wick consumption and flame loss resulted in an unsuccessful lamp fuel. These outcomes are displayed in Figure 3.13 and Figure 3.14, respectively.



Figure 3.13: Wick consumption with inadequate fuel. Pyrolysis sample obtained at 450 C



Figure 3.14: Insufficient fuel supply in a traditional wick lamp. (left) initial ignition, (right) flame diminishing. Pyrolysis sample obtained at 450 C

During the twenty minute run duration of the test run, all organic liquid samples exhibited one or both of these outcomes. In order to obtain a successful fuel for lamp operation, blending with traditional fuels was investigated.

3.4.6 Product Blending

It has been demonstrated that the addition of commercial fuels, such as kerosene and paraffin, to the organic liquid product can result in a successful lamp fuel. The blending of kerosene with the resultant organic liquid product of the pyrolysis process is discussed below. The kerosene blending percent represents the minimum weight fraction of kerosene (wt%) that when blended with pyrolysis product results in successful lamp operation. Successful lamp operation is determined by the Lamp Performance Test described in Section 2.3.4.5.

The high miscibility of the organic liquid product with kerosene results in a homogeneous fuel. No phase separation occurred during the testing period. It was assumed that this homogeneous state was also present in the wicking material, and that the solution composition remained constant over the volume of the wicking material.

The effect of reaction temperature on the required kerosene blending is shown in Figure 3.15. It can be seen that the trend is similar to that of Viscosity vs. Temperature. The initial increase in temperature from 400 - 450 °C results in an increase in kerosene requirement. Beyond 450 °C the increased severity results in products more suitable for lamp fuel, requiring less kerosene blending. This is further demonstrated in Figure 3.16 which displays the kerosene requirements for various pyrolysis product viscosities. The trend is fairly linear and signifies lower product viscosities result in lower kerosene requirement. This trend further confirms the importance of fuel viscosity in lamp fuel systems.

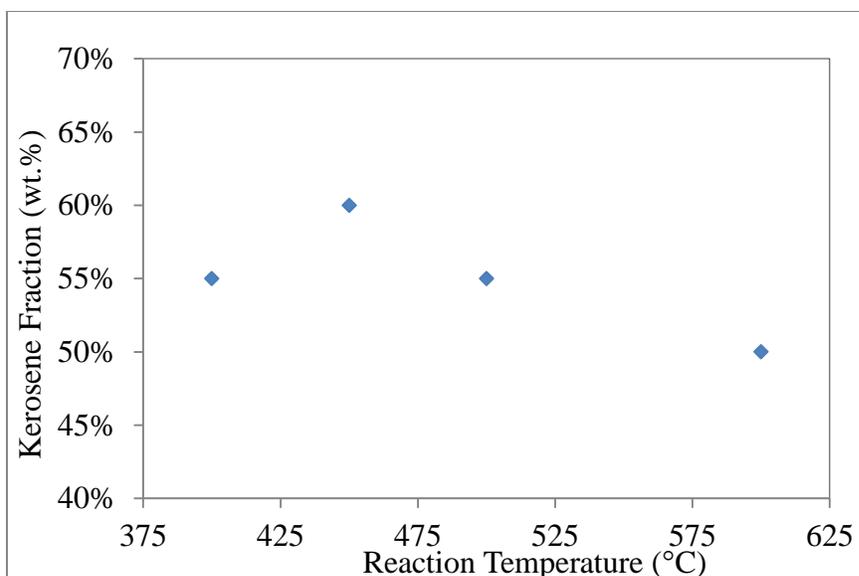


Figure 3.15: Effect of reaction temperature on required kerosene fraction of kerosene- pyrolysis oil fuel mixture for successful lamp operation

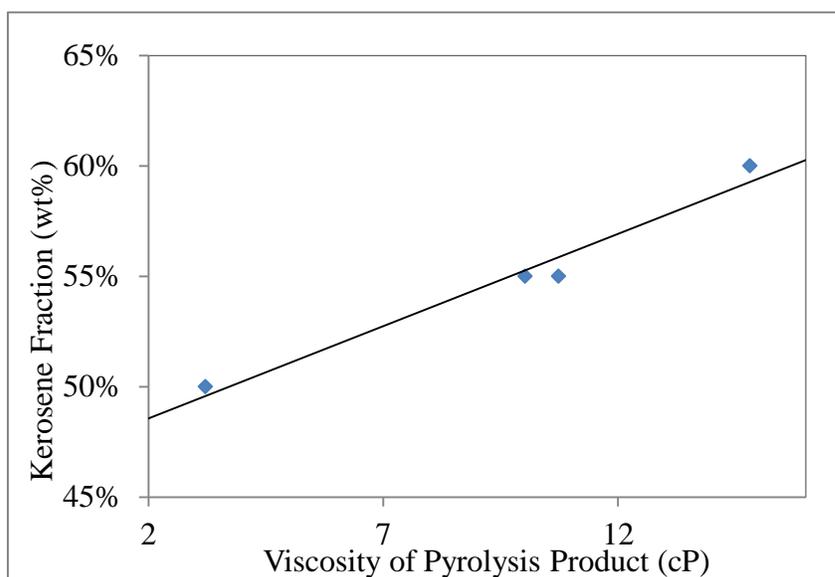


Figure 3.16: Effect of pyrolysis product viscosity on required kerosene fraction of kerosene- pyrolysis oil fuel mixture for successful lamp operation

Figure 3.17 is a plot earlier described in Section 3.4.3, with the addition of successful blends. It can be seen that in this system, a desired combination of viscosity and surface tension ranges (indicated by red circle) result in a successful lamp fuel. However, the single pyrolysis product falling within the red circle represents an unsuccessful fuel. This sample was taken at 650 °C and failed not due to fuel supply, but due to excessive smoke production. As mentioned previously, this sample was extremely degraded. Although suitable in terms of wicking and fuel supply, the very low yields and excessive smoke production made it unsuitable for lamp fuel applications.

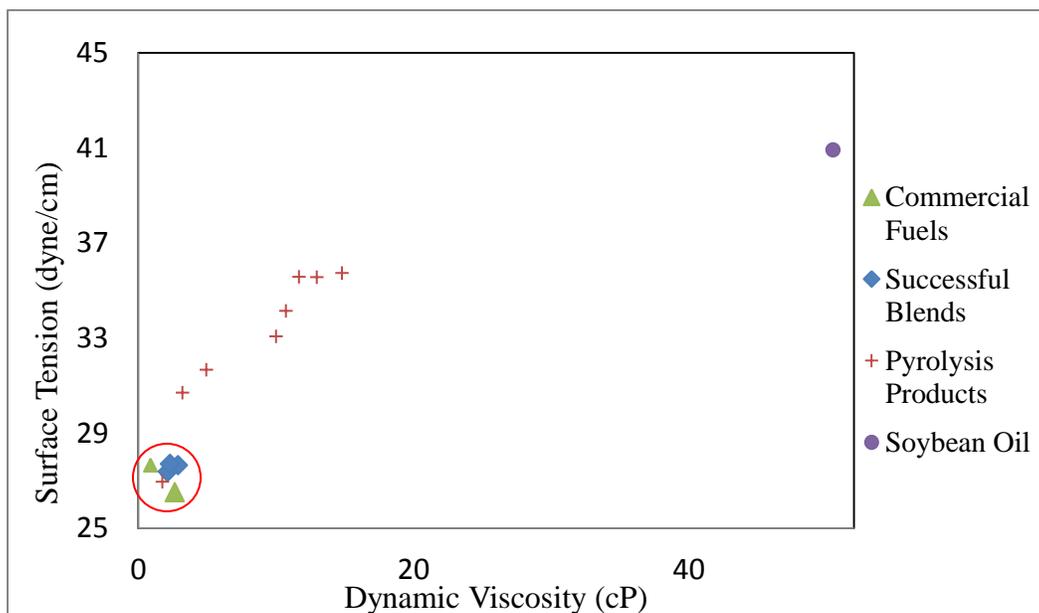


Figure 3.17: Surface tension vs. viscosity map of successful fuel blends, pyrolysis liquid products, and untreated oil

3.4.7 Pyrolysis vs. Visbreaking

The low-severity, batch visbreaking process and the high-severity, continuous pyrolysis process both improve the fuel characteristics of the parent crop oil, in terms of lamp fuel application. Each process was sensitive to reaction conditions, however, the effect of reaction conditions and therefore the optimization of each process varied.

The visbreaking process was low-severity in comparison to the pyrolysis process. The low-severity of this process likely resulted in decreased cracking of larger molecules. Therefore the gas production was very low and the yield increased with increasing temperature. The viscosity also increased with temperature due to the vapourization of viscous, high molecular weight compounds. The wicking coefficient, and therefore the fuel's wickability decreased with increasing temperatures. Overall, the optimization of this process with respect to fuel characteristics favoured lower reaction temperatures. The balance between optimizing both yield and fuel characteristics is dependent on market conditions.

The higher severity pyrolysis process increased the thermal cracking of the long-chain triglycerides. In contrast to visbreaking, and displayed in Figure 3.18, it can be seen that at increased temperatures the organic liquid yield is decreased and the gas yield is increased. This trend suggests cleavage of larger compounds into smaller, non-condensable gases. The optimization of the pyrolysis process, with respect to fuel characteristics, favoured high temperatures. The increased temperatures resulted in increased wicking coefficient, and decreased kerosene blending amounts. Inversely to visbreaking, the increase in temperature led to a decrease in organic liquid yield. The balance of organic liquid yield and fuel characteristics must be considered for process optimization.

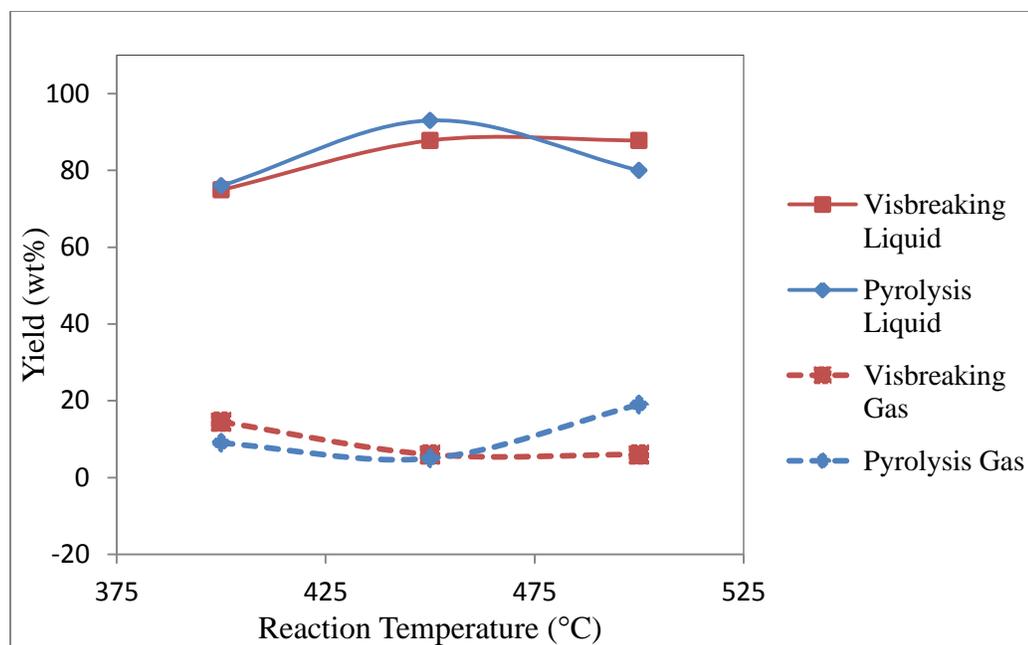


Figure 3.18: Effect of temperature on phase yields of visbreaking and pyrolysis processes

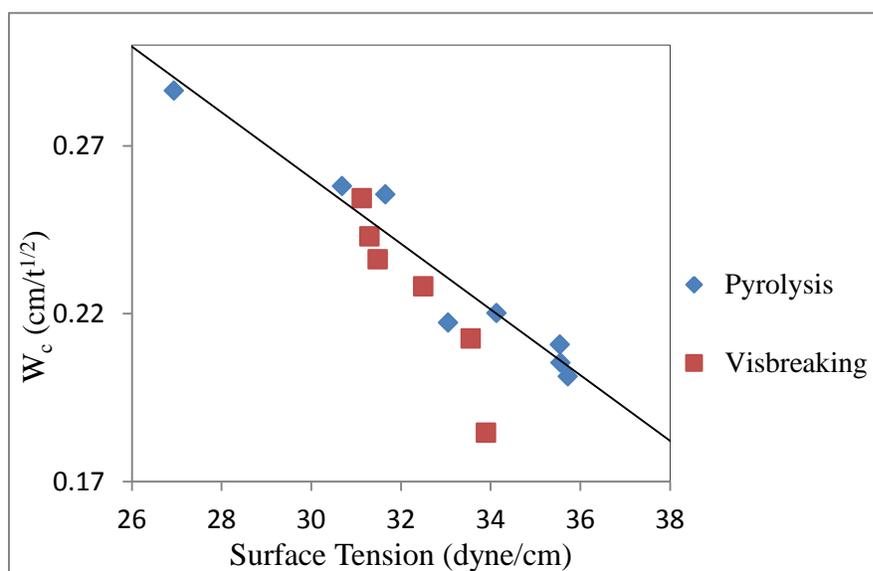


Figure 3.19: Wicking coefficient vs. surface tension for visbreaking and pyrolysis products

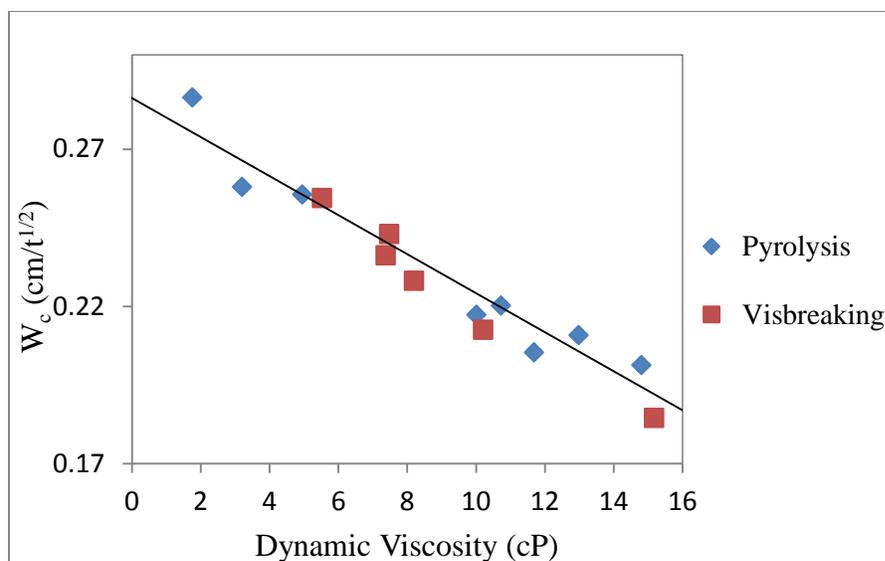


Figure 3.20: Wicking coefficient vs. viscosity for visbreaking and pyrolysis products

Figure 3.19 and Figure 3.20 show the relationship between wicking coefficient and surface tension, and wicking coefficient and viscosity, respectively. The organic liquid product from both visbreaking and pyrolysis processes exhibit decreasing wickability with increasing viscosity and surface tension. While both trends are linear, the W_c vs. Viscosity trend exhibits a better fit and a larger range of values. This displays both the flexibility of these processes as well as the importance of viscosity as a performance indicator in optimization.

Process Performance Comparison

To determine the optimal process for the production of lamp fuel from crop oils, many factors must be considered. Two important indicators for the performance of each process are organic liquid yield and wicking performance, which is quantified by the wicking coefficient (W_c). Figure 3.21 plots these two metrics allowing for a direct comparison between the two thermal processes. It is clear that for the majority of data points, pyrolysis produces faster wicking fuels, at a higher yield.

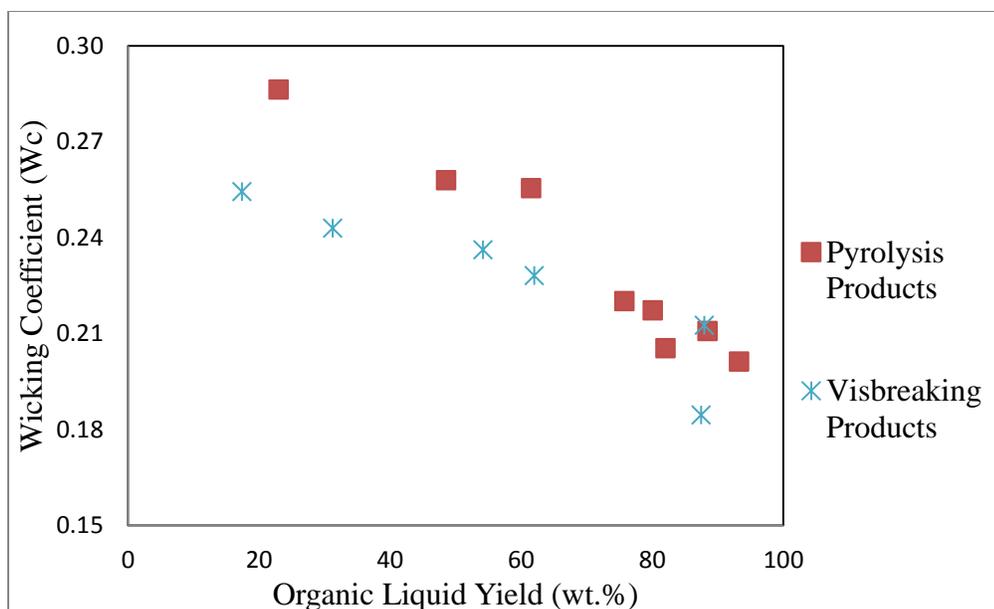


Figure 3.21: Performance comparison between visbreaking and pyrolysis- Wicking Coefficient vs. Liquid Product Yield

Table 3.2: Optimal Visbreaking and Pyrolysis Conditions

Operation	Visbreaking		Pyrolysis	
	Batch	Batch	Continuous	Continuous
Reaction Temperature (°C)	375	400	450	500
Viscosity (cP)	7	9	15	10
Surface Tension (dyne/cm)	32	32	35	33
Organic Liquid Yield (wt%)	54	78	93	88
Wicking Coefficient (cm/s ^{1/2})	0.24	0.22	0.20	0.22
Blending (wt% Kerosene)	45	55	60	55

Table 3.2 lists the two optimal conditions for both the pyrolysis and the visbreaking process. These optimal conditions were based on maximizing yield and wicking coefficient, while minimizing the required kerosene blending amount. It should be noted that these optimal conditions may change based on the economic analysis surrounding

feedstock and kerosene pricing, as well as energy costs in local regions of implementation. The flexibility of the processes allows for tailoring to specific and variable market conditions.

As seen in Table 3.2, the pyrolysis process exhibits much higher yields with similar wicking coefficients and blending amounts. The drawback is the increase in reaction temperature resulting in increased energy requirements. As seen in bold, the pyrolysis process has yields of organic liquids of 93 and 88 wt%, at 450 and 500 °C, respectively. When considering equal kerosene blending amounts, the pyrolysis process produces over 10 wt% higher yield compared to the visbreaking process.

In addition to the performance indicators discussed above, advantages exist in the operational methods of the pyrolysis process. As previously mentioned, the continuous process is more practical in scaling up operations, more efficient in maintenance requirements and is typically capable of processing higher throughputs than batch operation.

3.5 Conclusions and Recommendations

This study has demonstrated that thermal processes such as visbreaking and thermal cracking have the capability to improve fuel characteristics of crop oils for applications in fuel-based lighting. It has also been demonstrated that these processes can produce organic liquids able to comprise as much as 60 wt% of useable lamp fuel. The thermal cracking process is a higher severity process in relation to visbreaking, operating at higher temperatures and more rapid heating rates. It was demonstrated that the increased severity of the pyrolysis process resulted in increased thermal cracking leading to less viscous products and higher gas production at elevated temperatures. The optimization of the process based on organic liquid product fuel characteristics favours high reaction temperatures. Similarly to visbreaking, the product properties and yields are very sensitive to reaction temperature. An increase in reaction temperature results in a decrease in product viscosity and surface tension, leading to an increase in wickability.

The increase in fuel quality at high temperature is accompanied by decreases in liquid yield. The balance between fuel characteristics and liquid yield is important in process optimization and optimal conditions will be dependent on market conditions.

A comparison between visbreaking and pyrolysis processes yields pyrolysis as the optimal process for the given application. The pyrolysis process exhibits superior performance producing faster wicking products at higher liquid yields compared to those of the visbreaking process. The continuous operation of the pyrolysis process also provides advantages over the batch method of visbreaking.

The next chapter of this study will investigate the potential of alternate crop oils in the production of lamp fuel via the continuous pyrolysis method described in this chapter. Crop oils vary in saturation levels and composition. In addition, some crop oils have lower costs and do not compete in the edible oil market. The opportunity exists to reduce feedstock costs and potentially utilize saturation levels and composition changes to improve product quality. Further research in the pyrolysis of soybean oil is also recommended in the areas of product analysis and energy efficiency. The waste gas phase in the pyrolysis process has potential to provide heat back to the pyrolysis reaction, thus increasing the energy efficiency and reducing the environmental impact of the process.

3.6 References

- Daniel, J., & Garc, R. (2013). Fuel Properties of Tire Pyrolysis Liquid and Its Blends with Diesel Fuel.
- Dupain, X., Costa, D., & Schaverien, C. (2007). Cracking of a rapeseed vegetable oil under realistic FCC conditions. *Applied Catalysis B: ...*, 72(1-2), 44–61.
- Frey, R., Da Graca C Da Rocha, M., Brandao, S. T., Pontes, L. a M., Padilha, J. F., Borges, L. E. P., & Gonzalez, W. a. (2011). Cracking and Hydrocracking of Triglycerides for Renewable Liquid Fuels: Alternative Processes to Transesterification. *Journal Of The Brazilian Chemical Society*, 22(7), 1206–1220.
- Idem, R. O., Katikaneni, S. P. R., & Bakhshi, N. N. (1996). Thermal Cracking of Canola Oil: Reaction Products in the Presence and Absence of Steam. *Energy & Fuels*, 10(6), 1150–1162. Retrieved from <http://pubs.acs.org/doi/abs/10.1021/ef960029h>
- Kamath, Y. K., Hornby, S. B., Weigmann, H. D., & Wilde, H. F. (1994). Wicking of Spin Finishes and Related Liquids into Continuous Filament Yarns. *Textile Research Journal*, 64, 33–40.
- Katikaneni, S. P. R., Adjaye, J. D., Idem, R. O., & Bakhshi, N. N. (1998). Performance studies of various cracking catalysts in the conversion of canola oil to fuels and chemicals in a fluidized-bed reactor. *Journal of the American Oil Chemists' Society*, 75(3), 381–391.
- Kubičková, I., & Kubička, D. (2010). Utilization of Triglycerides and Related Feedstocks for Production of Clean Hydrocarbon Fuels and Petrochemicals: A Review. *Waste and Biomass Valorization*, 1(3), 293–308.
- Maher, K. D., & Bressler, D. C. (2007). Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresource Technology*, 98(12), 2351–68.

- Meyers, R. (2003). *Handbook of petroleum refining processes*. McGraw-Hill. Retrieved from <http://library.pvu.vn/handle/123456789/891>
- Stanlick, C. (2014). *Effects of mixing and vapor residence time on the thermal cracking performance of fluidized beds*. The University of Western Ontario.
- Sťávoová, J., Stahl, D. C., Seames, W. S., & Kubátová, A. (2012). Method development for the characterization of biofuel intermediate products using gas chromatography with simultaneous mass spectrometric and flame ionization detections. *Journal of Chromatography A*, 1224, 79–88.

Chapter 4

4. PYROLYSIS OF VARIOUS CROP OILS FOR PRODUCTION OF RENEWABLE LAMP FUEL

4.1 Introduction

Vegetable oils are comprised almost completely of triglycerides. These materials are rich in carbon and hydrogen and can provide an energy rich feedstock for the production of alternative fuels (Maher & Bressler, 2007). Vegetable oils, or crop oils, are produced globally and available in a very wide range of sources. There are over 350 oil-bearing crops currently identified (Dupain et al., 2007). The majority of vegetable oil feedstocks are not completely saturated. Unsaturated fatty acids are present in the triglyceride-rich liquids. Depending on the crop from which the oil was harvested, the saturation level will differ substantially. Literature studies have identified that the saturation level of a crop oil has a large impact on its thermal cracking, or pyrolysis (Maher & Bressler, 2007). A wide spectrum of these oils has been tested in varying reactor conditions and designs.

Feedstock oils include tung oil (Chang and Wan, 1947), sunflower oil (Schwab et al., 1988), safflower oil (Schwab et al., 1988), canola oil (Idem et al., 1996), soybean oil (Lima et al., 2004), palm oil (Lima et al., 2004), macauba fruit oil (Fortes and Baugh, 1999, 2004), used cooking oil (Dandik and Aksoy, 1998a), castor oil (Lima et al., 2004), and various tropical vegetable oils (Alencar et al., 1983).

In 1983, Alencar et al. investigated the cracking of palm, babassu, and piqui oils in a pyrolysis process at temperatures between 300 and 500 °C. They found the major products to consist primarily of n-alkanes and 1-alkenes. The differences in composition between the three feeds were attributed to variation in saturation levels. The group stated the increase in unsaturated acids leads to an increase in volatiles. A reaction scheme was proposed based on these findings (Alencar et al., 1983).

In 1988, Schwab et al. utilized destructive distillation to convert soybean and safflower oil into liquid fuels. They found that the primary products consisted of alkanes, alkenes, aromatics, and carboxylic acids. Carbon chains ranged from 4 to 20+. Higher yields were

seen with safflower oil than those of soybean oil. In addition the fuel properties were analyzed and it was determined that pyrolysis upgraded the oils from their parent oil resulting in decreased viscosities and increased cetane values (Schwab et al., 1988).

In 2004, Lima et al. investigated the pyrolysis of soybean, palm, and castor oils at temperatures of 350- 400 °C. The organic phase was separated by distillation into four fractions: F1 < 80 °C, 80 < F2 < 140 °C, 140 < F3 < 200 °C and F4 > 200 °C. The F4 fraction was shown to be composed of olefins, paraffins, carboxylic acids and aldehydes. This fraction was most similar to fossil diesel (Lima et al., 2004). The F4 fraction of castor oil pyrolysis also presented a higher concentration of compounds with a high chain length in both hydrocarbons (C₁₅-C₁₆) and fatty acids (C₁₁-C₁₂) compared with the two other oils with (C₁₁-C₁₄) and (C₇-C₁₁) respectively (Frey et al., 2011). The pyrolysis of soybean and palm oils resulted in liquid fuel products that meet Brazilian standards for mineral diesel fuel (Lima et al., 2004).

The above studies were conducted in batch reactors. In 1996, Idem et al. produced a study on the cracking of canola oil in a flow type reactor at temperatures of 300-500 °C. Conversions of the oil ranged from 54 to 100 %, and were heavily reliant on operating conditions. A diesel-like fuel was obtained from the condensate.

Fresh, refined vegetable oils are not the only feedstock to be considered when reviewing this technology. In fact, the relatively high cost of these feedstocks can make up as much as 70% of the total product costs. An attractive alternative may be used cooking oil or other waste oils. The conversion of used cooking oil to fuel and chemical feedstock through use of a fractionating pyrolysis reactor has been investigated (Dandik & Aksoy, 1998). The pyrolysis of used cooking oil was carried out at 400 and 420 °C for 180 minutes. The liquid product was analyzed. It consisted of a variety of hydrocarbons in the C₅-C₁₇ including paraffins, olefins and their isomers, aromatics, cycloparaffins, and cycloolefins (Dandik & Aksoy, 1998). It was found that it was possible to produce high concentrations of liquid hydrocarbons in the gasoline boiling range in high conversions, without the aid of a catalyst.

It has been demonstrated in previous chapters that the pyrolysis of soybean oil can provide significant improvements in the fuel characteristics desired in lamp fuels. The objective of this chapter is to investigate the use of a pyrolysis of various crop oils for the production of lamp fuel. Five crop oils will be tested as feedstocks, including soybean oil, canola oil, safflower oil, palm oil, and palm kernel oil. This mix represents a wide spectrum of oils with varying saturation level and composition. The results of the preceding chapter determined the process to be utilized for thermal cracking of the various crop oils. The increased performance of the continuous pyrolysis process led to its selection over the less severe visbreaking process. See Chapter 3 for details on the performance of pyrolysis compared to that of visbreaking of soybean oil. It was assumed that the variance of oil compositions present in the feedstock for this chapter would not affect the process superiority of pyrolysis for this application. The area of focus is on the optimization of reaction conditions with respect to reaction product yields and fuel properties. Product blending with kerosene is studied to produce useable lamp fuel in traditional oil lamps. Comparative analysis of the feedstock effect on the pyrolysis process is performed to determine the optimal feedstock for this application.

4.2 Materials

4.2.1 Feedstock

Five feedstocks were tested in this study, representing a spectrum of the available crop oils globally. The five oils were canola oil, safflower oil, soybean oil, palm oil, and palm kernel oil. Each oil was commercially available and a treated form of the raw oil. Prior to commercial sale, the oils are refined, bleached, and deodourized. Oils of high purity were obtained from Candora Soap and Soap Supplies in London, Ontario.

Table 4.1: Fatty Acid Composition of Various Crop Oils(wt%)

Vegetable Oil	Caprylic C8	Capric C10	Lauric C12	Myristic C14	Palmitic C16	Stearic C18	Oleic C18:1	Linoleic C18:2	Linolenic C18:3
Canola					4	2	56	26	10
Safflower					7	3	14	75	
Soybean					11	4	24	54	7
Palm				1	44	4	40	10	
Palm Kernel	3	3	48	16	8	3	15	2	

These oils were selected as they represent a broad spectrum of fatty acid profiles and degree of saturation. For example, canola oil is comprised of 92% unsaturated fatty acids, while palm kernel oil is 82% saturated fatty acids. In addition, the oils vary greatly in composition. Safflower oil is very high in polyunsaturated acids such as linoleic acid (75%). Canola oil contains majority oleic acid which is a monounsaturated acid. Soybean oil is high in both mono-and polyunsaturated acids with oleic and linoleic acids accounting for 78%. Palm oil contains almost equal amounts of saturated and unsaturated fatty acids with palmitic acid (44%) and oleic acid (40%) accounting for the majority of the oil. Finally, palm kernel, a highly saturated oil, contains greater fractions of smaller chain saturated acids (C₈-C₁₆) such as lauric (C₁₂) in comparison to other oils. Table 4.1 and Table 4.2 represent fatty acid compositions and degree of saturation, respectively, of the five feedstock crop oils.

Table 4.2: Saturation of Various Crop Oils

Vegetable Oil	Total Saturated	Total Unsaturated
Canola	6%	92%
Safflower	10%	89%
Soybean	14%	81%
Palm	49%	50%
Palm Kernel	82%	18%

Table 4.3: Feedstock Viscosities (cP)

Canola	61.7
Safflower	68.3
Soybean	53.9
Palm	n/a ¹
Palm Kernel	n/a ¹

¹Oils are solid at room temperature

Table 4.3 shows the viscosities of the five feedstock oils. Palm and palm kernel oil represent the most viscous feedstocks as they are solid at room temperatures. This can be attributed to their high saturated fatty acid composition. The high composition of lauric acid and palmitic acid in palm kernel and palm oil, respectively, lead to a more crystalline, and therefore more viscous compound. This trait is utilized by many processes in the food industry such as producing margarine through the saturation (hydrogenation) of crop oils. The three oils liquid at room temperature, in order of increasing viscosity are soybean, canola, and safflower oil. In terms of surface tension of the feedstocks, all liquid oils are very similar. The variance between oils is less than 1% with an average of 39.9 dyne/cm.

4.2.2 Commercial Fuels

Refer to Chapter 3 for description of commercial fuels.

4.2.3 Bed Material

Refer to Chapter 3 for description of bed material.

4.3 Methods

4.3.1 Equipment

Equipment used in this study was identical to that of Chapter 3, with one addition. Due to the higher melting points of some of the crop oils, a silicone resistance heating tape (obtained from McMaster-Carr) was installed on the feed line. This was installed in the case where palm oil or palm kernel oil was injected as feedstock. The feed pre-heating effectively prevented line plugging due to solidification.

Refer to Chapter 3 for further description of equipment.

4.3.2 Experimental Procedure

During a typical experimental run, between 170-230 g of fresh feed would be consumed. Prior to injection all pieces of the system would be cleaned and weighed. 600 g of fresh silica sand was loaded into the MFR each run. The system was then be assembled and insulated. As the controllers were specifically tuned for the system, it was important that insulation be installed in a similar manner for every run. Following assembly of the unit, the nitrogen, mixing and heating would be initiated. The heating tape was set to 70 °C in the case of palm oil and palm kernel oil. Mixing speeds ranged from 20 to 144 rpm and nitrogen flowrates were 0-2 SLPM. Feed injection began after the system had reached and maintained target conditions for both MFR and filter. Liquid injection was controlled by the syringe pump. Typically three to four 60 mL syringes of fresh feed would be injected. A feed rate of 4 mL/min was selected and remained constant for all experiments of this study. All experiments were conducted at atmospheric pressure. A 20 minute cooling off period was allowed after every run before collecting samples. Liquid and solid (residue) yields were determined through weight measurements of various sections of the unit. The gas yield was estimated based on closing the mass balance, as an accurate value would not be crucial to the success of the process.

4.3.3 Product Analysis

4.3.3.1 Viscosity and Density Measurement

Refer to Chapter 2 for description of viscosity and density measurement.

4.3.3.2 Surface Tension

Refer to Chapter 2 for description of surface tension measurement.

4.3.3.3 Wickability Testing

Refer to Chapter 2 for description of wickability measurement.

4.3.3.4 Lamp Performance

Refer to Chapter 2 for description of lamp performance testing.

4.4 Results and Discussion

The learnings from the previous two chapters were employed in this chapter to focus the testing on the most promising range of operating conditions. It was demonstrated that reaction temperature is the most significant factor with respect to the product quality. Therefore, only the effect of reaction temperature on phase yields and liquid product characteristics is analyzed. It should be noted that the potential impact of vapour residence time was not investigated in this study and the analysis of its effect on the product quality is recommended for future studies.

4.4.1 Phase Yields

Figure 4.1 displays the effect of reaction temperature on the resulting phase yields. Similar to that of soybean oil feedstock, the canola oil feedstock produces its maximum organic liquid yield at 450 °C. This maximum liquid yield is 84 wt%, which is lower than that of soybean oil, resulting in a greater gas fraction. The trend is also similar to soybean oil feedstock in that as temperature is increased beyond 450 °C, the liquid yield fraction decreases, increasing the gas phase yield. This suggests thermal cracking of the condensable vapours is occurring due to increased reaction severity. The residue fraction decreased with increasing temperature, reaching approximately zero at 500 °C.

Figure 4.2 shows the effect of reaction temperature on the pyrolysis yields with safflower oil as feedstock. It can be seen that at the given temperature range both the gas phase and liquid phase increase with increasing temperature, but only marginally. The increased temperature leads to a decrease in residue yield reaching approximately zero at 450 °C.

The effect of reaction temperature on phase yields of palm kernel oil pyrolysis is presented in Figure 4.3. It can be seen that the minimum temperature in the plot is 450 °C. At temperatures below 450 °C, no condensed liquid product was collected. Although some material was vapourized and collected in the condensers, the product collected was solid at room temperature and therefore non-usable as lamp fuel in wicking lamps. The liquid yield obtained at temperatures ranging from 450-500 °C remained fairly constant at 84-87 wt%. The residue reached a minimum of 6 wt% at 500 °C, which is a greater residue yield than all feedstocks discussed above.

Figure 4.4 represents the effect of reaction temperature on the pyrolysis of palm oil. Palm oil pyrolysis did not produce a condensed liquid products at temperatures below 500 °C. For this reason, the temperature range that was investigated was increased to 500-600 °C. It can be seen that significant cracking is occurring in this temperature range as the liquid yield decreases sharply, leading to greater gas fractions than liquid fractions at 600 °C. The maximum liquid yield is 81 wt% which is produced at 500 °C.

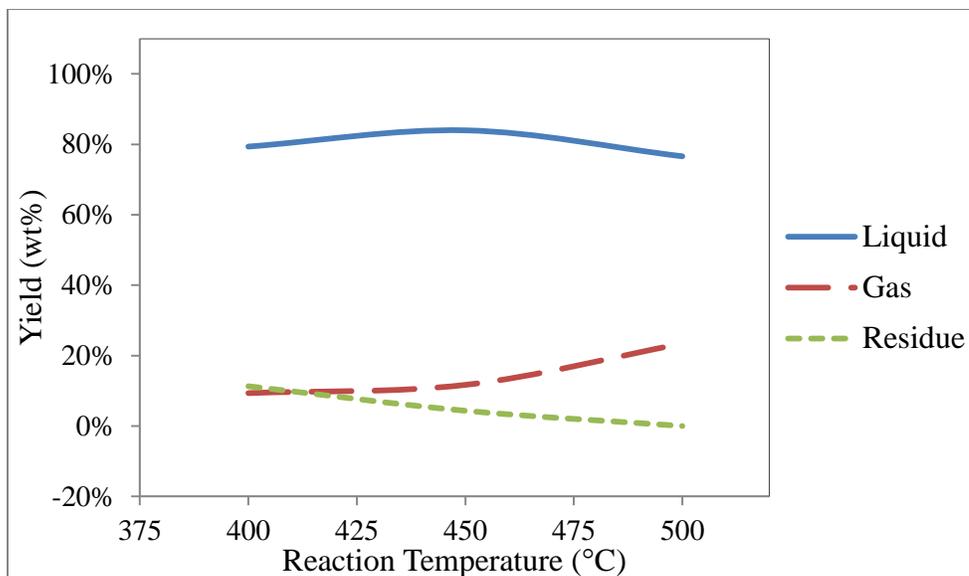


Figure 4.1: Effect of temperature on pyrolysis phase yields (Canola Oil)

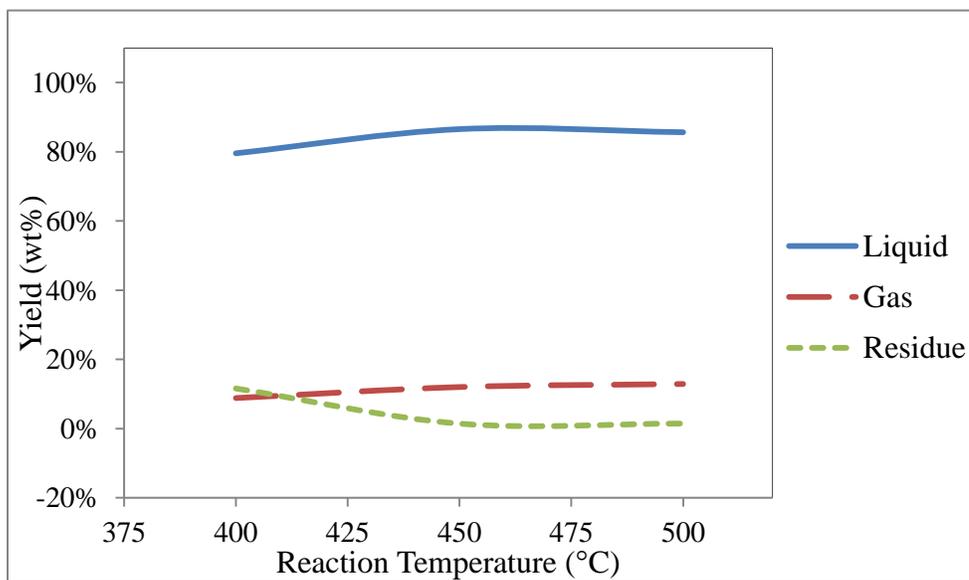


Figure 4.2: Effect of temperature on pyrolysis phase yields (Safflower Oil)

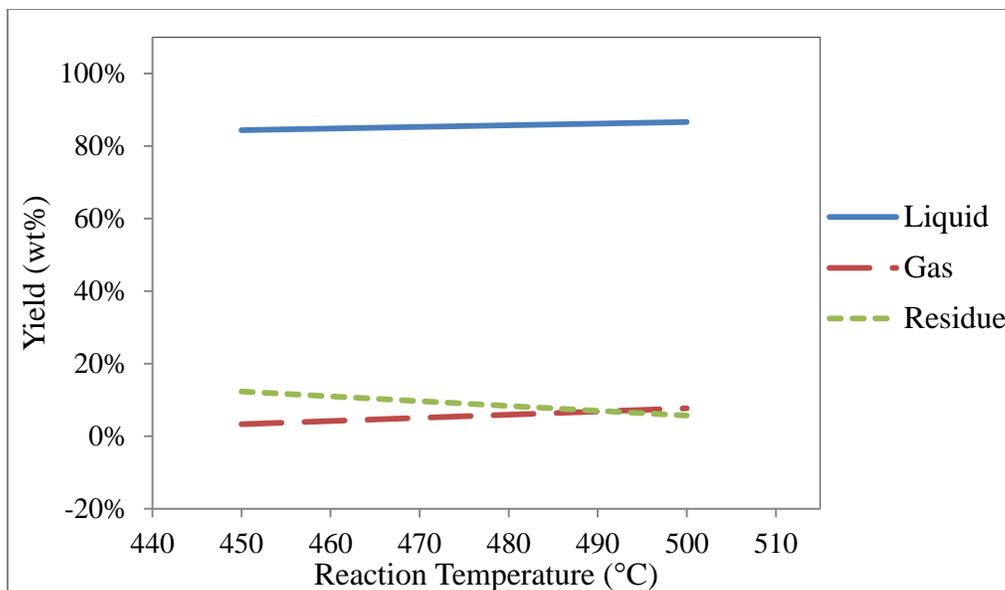


Figure 4.3: Effect of temperature on pyrolysis phase yields (Palm Kernel Oil)

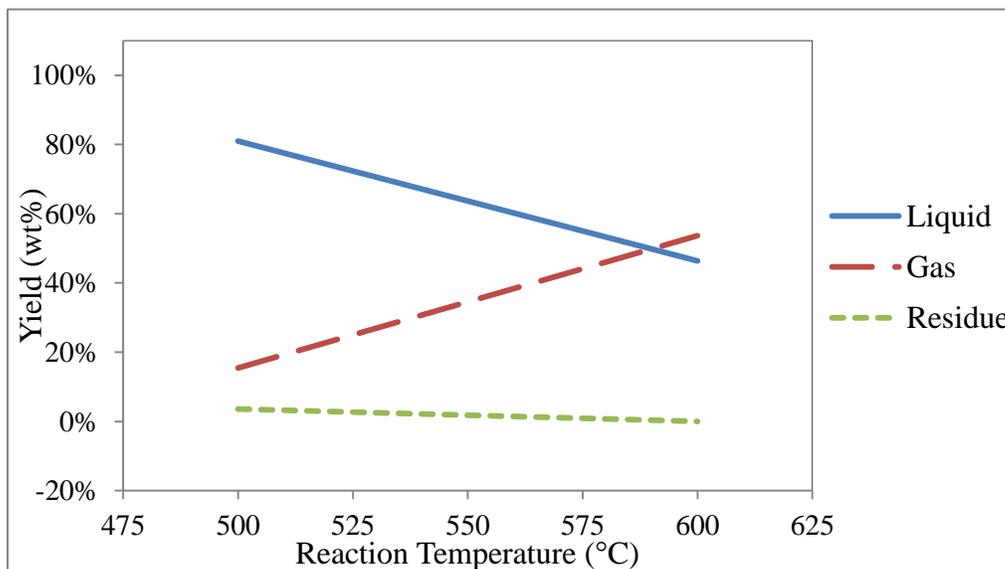


Figure 4.4: Effect of temperature on pyrolysis phase yields (Palm Oil)

The degree of saturation present in crop oil compositions is known to have a large impact on the thermal behavior of the oil. This is evidenced in that the highly saturated feedstocks of palm and palm kernel oil are solid at room temperature. It is also argued in

literature that the saturation levels and the number of unsaturated sites have an impact on the thermal molecular cleavage reaction at high temperatures (Maher & Bressler, 2007). The unsaturated sites of a triglyceride molecule enhance thermal cleavage and thermal cleavage is a dominant reaction (Bressler et al., 2014).

Table 4.4 shows the saturation level of each feedstock. It was demonstrated above that canola oil and soybean oil exhibit similar trends with increasing temperatures. Soybean oil however, has higher liquid yields and lower gas yields. It is possible that the increased fraction of unsaturated molecules present in canola oil is contributing to higher cracking and increased gas production at constant temperatures. In addition, the pyrolysis of safflower oil produces greater liquid yields than canola oil, but less than soybean oil. This aligns with the unsaturation level of safflower in relation to that of canola and soybean oil.

Palm and palm kernel oils are the two feedstocks with high saturation levels. These oils are both solid at room temperature. The increased temperature requirement of these oils further demonstrates the effect of saturation level on the pyrolysis reaction. The high fraction of saturated triglycerides leads to decreased cracking. It is possible that a large portion, if not all of the saturated fraction is vapourizing without cracking, and being collected in the condensing train. Although further analysis is required and recommended to confirm this, the results directionally align with literature findings.

Table 4.4: Feedstock Saturation Levels

	Saturated (wt%)	Unsaturated (wt%)
Soybean	15	85
Canola	6	94
Safflower	10	90
Palm	49	51
Palm Kernel	82	18

In terms of optimization of the process conditions for favourable liquid yields, each feedstock varies significantly. The highly saturated oils such as palm and palm kernel require increased reaction temperatures of 500 °C or greater to provide liquid product. The three oils with the higher unsaturation level produce optimal yields below 500 °C.

The maximum liquid yield experienced among the five feedstocks was produced from soybean oil at 450 °C and resulted in 93 wt% liquid yield. It can be seen in Figure 4.5 that the increased saturation level of the parent oil results in decreased liquid yields.

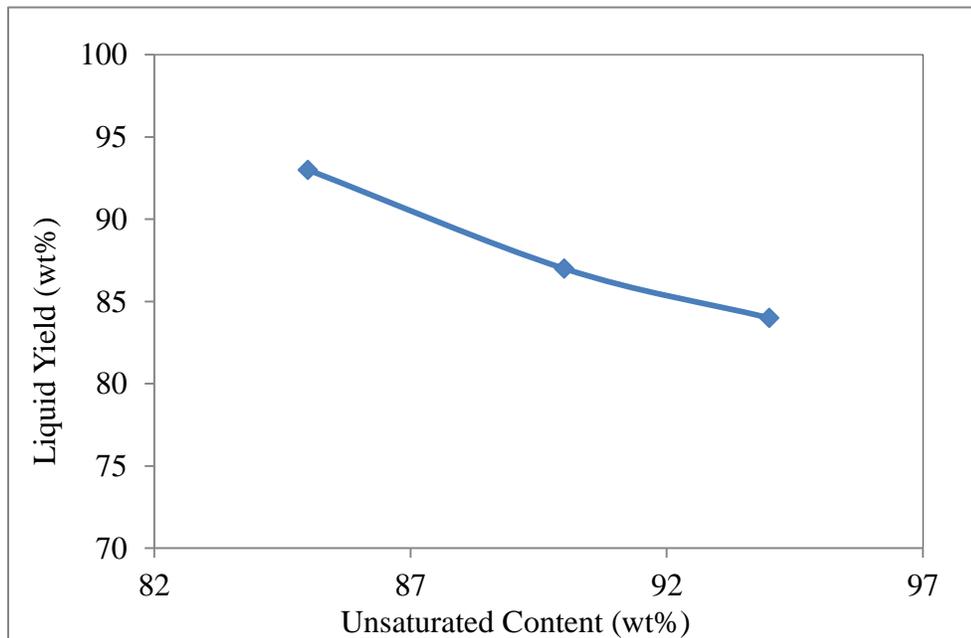


Figure 4.5: Effect of saturation on pyrolysis liquid product yield of varying unsaturated contents (Soybean, Safflower, Canola)

4.4.2 Liquid Properties

The following section provides the effect of reaction temperature on the properties of the liquid product obtained from the pyrolysis of the various feedstock oils. Palm oil is not included in this analysis as the organic liquid from the pyrolysis of palm oil was too viscous to obtain measurements. Among the range of temperatures tested, palm oil was unable to produce a liquid suitable for lamp fuel or fuel blending. Therefore, the investigation of pyrolysis of palm oil for use as a lamp fuel is not carried out any further. The same was true for palm kernel oil, with the exception of one reaction temperature. Therefore palm kernel oil produced at a reaction temperature of 500 °C is the only sample of this feedstock which is tested further.

Viscosity

It has been demonstrated that viscosity is a crucial property in the success of liquid lamp fuels. Low viscosities are desired in this application as lower viscosities increase wickability in fuel lamp systems. The thermal cracking process was able to significantly reduce the viscosity of each of the parent feedstock oils.

The viscosity of the organic liquids produced at various reaction temperatures are shown below in Figure 4.6. It can be seen that at temperatures above 450 °C, the viscosity trend with increasing temperature is very similar among the feedstocks. At lower temperatures such as 400 °C, the viscosities vary. At these low temperatures, the products obtained from safflower oil are the most viscous, followed by those from canola oil, and finally the soybean oil-derived liquid is the least viscous. This is the same ranking order as for the viscosity of the parent crop oil. In addition, it was found that significant cracking of triglycerides does not occur at these lower temperatures. It is possible that the variance in viscosity at low temperatures is attributed to the variance in viscosities of the parent crop oil. These conditions are likely causing influence from distillation to be greater than that of thermal cracking. As the severity of the reaction increases the liquids obtained from each of the feedstocks possess very similar viscosities. The lowest viscosity was obtained with the canola oil feedstock at 500 °C, resulting in liquid product viscosity of 9.2 cP. The optimal liquid with respect to viscosity is the canola-derived liquid produced at 500 °C. This is only the case when solely considering viscosity. As in previous chapters the optimal conditions and in this case feedstock, is reliant on many factors such as yield, wickability, and kerosene requirements, as well as market conditions.

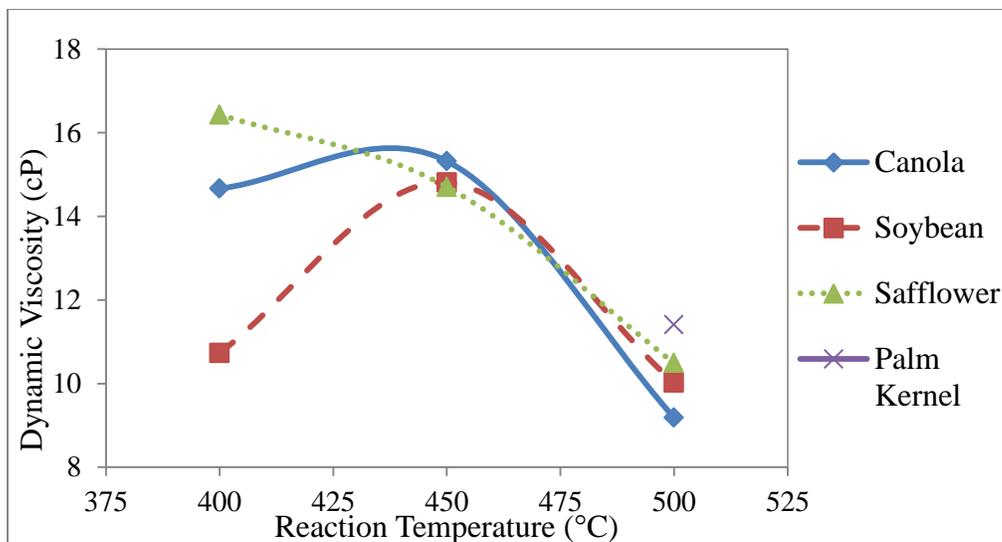


Figure 4.6: Viscosities of organic liquids from pyrolysis of various crop oils

Surface Tension

Similarly to the visbreaking process, the thermal cracking process can decrease the surface tension of the untreated oil by approximately 20 %. The effect of the reaction temperature on this parameter is given in Figure 4.7. The trend of each feedstock is similar to that of viscosity vs. reaction temperature. The minimum surface tension is exhibited at the highest temperature. The minimum surface tension experienced was that of the palm kernel oil- derived liquid at 32.3 dyne/cm. The variance among surface tension values between feedstocks as well as reaction temperatures is small. After the initial decrease from the parent oil surface tension, the effect of reaction temperature influences the surface tension by a maximum of 7 % (Soybean oil-derived fuels).

Figure 4.8 displays a map of two important wicking characteristics in surface tension and viscosity. This plot demonstrates the ability of this process to tailor product characteristics towards those of commercial lamp fuel.

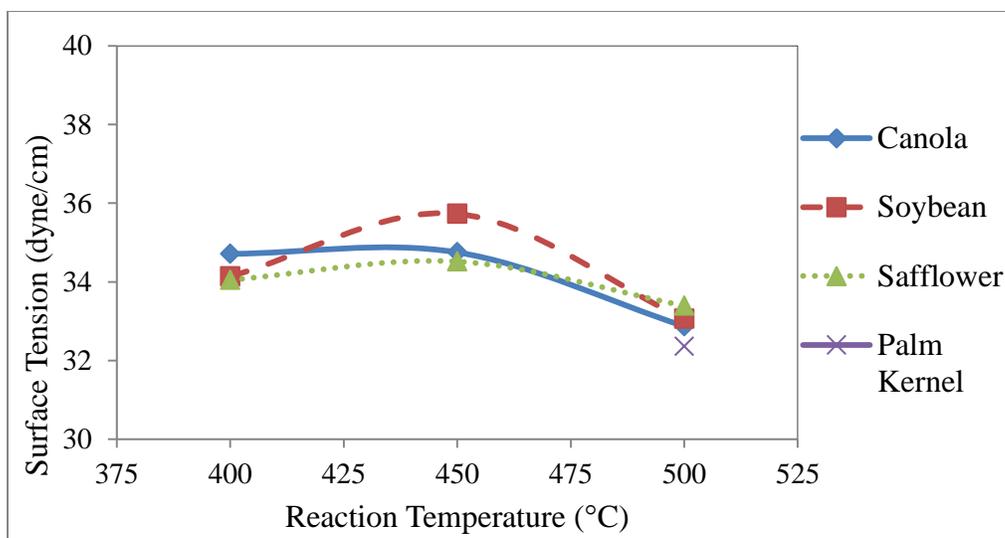


Figure 4.7: Surface tension of organic liquids from pyrolysis of various crop oils

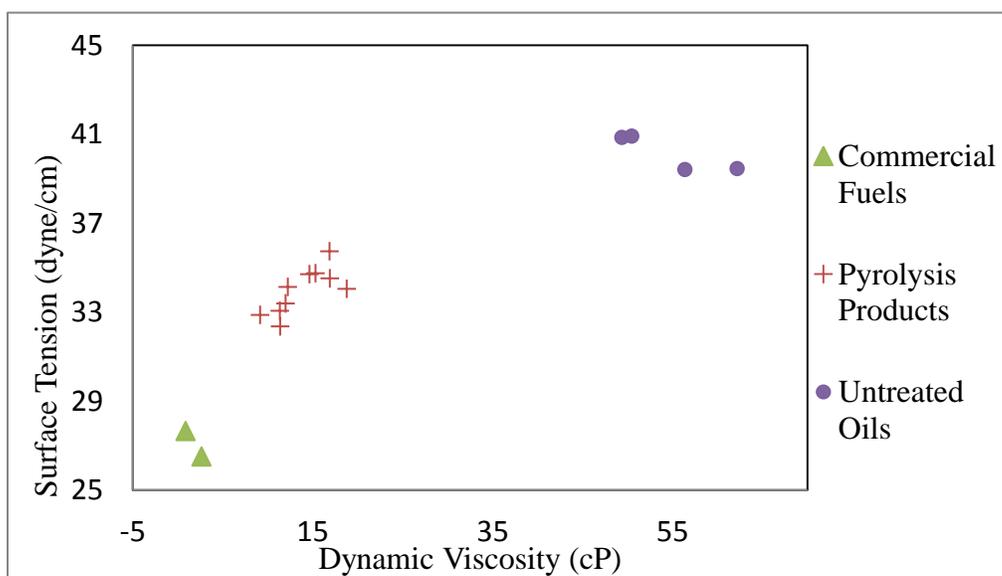


Figure 4.8: Surface Tension vs. Viscosity map of commercial fuels, pyrolysis liquid products, and untreated crop oils

4.4.3 Wickability

The wickability test demonstrates the capability to transport fuel up the wick of an oil lamp. As shown in Chapter 1, the liquid physical properties, presented above, impact the wickability of the fuel. In addition to physical properties, the wickability test incorporates liquid-solid interaction. Although these properties, such as contact angle, are not

individually quantified, the wickability test ultimately demonstrates the wicking performance of the fuel. The results of the vertical penetration test, measuring the height climbed by the liquid over time, are utilized to determine the wicking coefficient (W_c).

To quantify the results of the vertical penetration test, the data was linearized according to the procedure in Section 2.3.4. This was performed on all organic liquid samples, allowing for calculation of the wicking coefficient (W_c). This coefficient has been used in literature to quantify the wicking of liquids in porous materials (Kamath et al., 1994). W_c represents the slope of the linearized vertical penetration curve. A sample plot of the linearized curve was given in Chapter 2. The pyrolysis process has shown to improve the wicking coefficient by as much as 91% from the untreated oil. Table 4.5 shows a comparison of W_c values.

Table 4.5: Wicking Coefficient Comparison of Various Liquids

Sample	W_c (cm/s ^{1/2})
Untreated Oil	0.14 - 0.15
Pyrolysis Products	0.19 - 0.23
Kerosene	0.44

It can be seen that the thermal process has provided improvement to the wickability of the oil. The wicking performance of the optimal pyrolysis sample is greater than the feedstock oil, however still less than the commercial fuel.

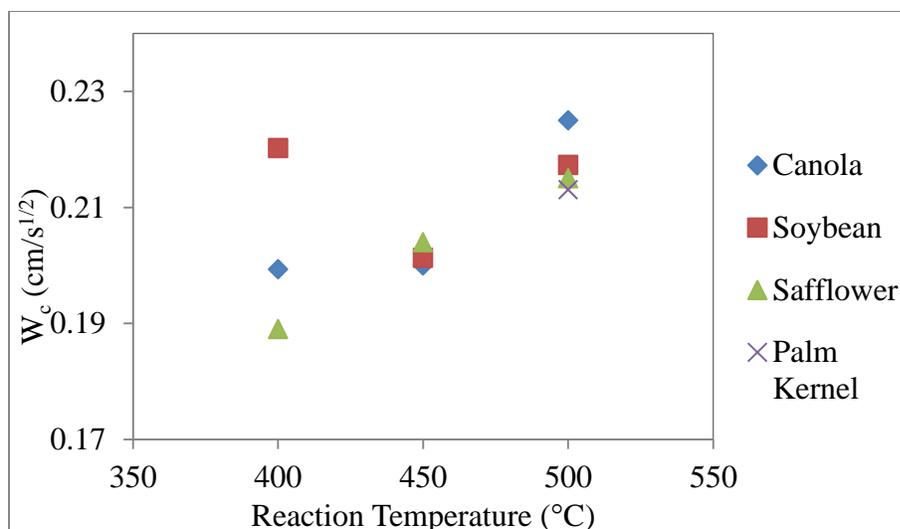


Figure 4.9: Wicking coefficient of liquid product from various feedstocks

The effect of temperature on W_c is given in Figure 4.9. It can be seen that increasing the reaction temperature has a positive effect on the wicking coefficient. That is, the maximum wicking rates are obtained with fuels from high reaction temperatures. This is expected as high reaction temperatures yield low viscosity fuels. Similarly to the viscosity analysis, the wicking coefficients of the three feedstocks vary significantly at lower temperatures. This is likely due to the variance in viscosities at this reaction temperature. The trend of W_c with increasing temperature is also similar, but inversely proportional to that of viscosity with increasing temperature. As the temperature is increased, the wicking coefficients of the various feedstocks become similar, generally increasing with reaction temperature. In terms of optimization, this suggests that higher temperatures are desired, however the decreased organic liquid yields at high temperatures must be considered. The feedstock that generated the fastest wicking fuel was canola oil, resulting in a W_c of $0.225 \text{ cm/s}^{1/2}$ for product obtained at a reactor temperature of $500 \text{ }^\circ\text{C}$.

4.4.4 Lamp Performance

The lamp performance testing was carried out in an identical procedure to that of the pyrolysis analysis outlined in Chapter 3. Successful operation in the lamp performance test indicates a successful lamp fuel in terms of the functionality of a lamp.

Similarly to both methods of treating soybean oil discussed in previous chapters, the pyrolysis of the four alternate feedstocks did not yield a successful lamp fuel in its pure form. Each sample was tested at 100% pyrolysis oil, with the exception of palm oil derived fuels as these were solid at room temperature. All palm oil derived fuels were deemed unsuccessful in previous sections. It was found that none of the oils produced from the pyrolysis of the various crop oils passed the lamp performance test. The failure of the test was due to similar contributors as were seen with the thermally treated soybean oil. The combination of wick consumption and flame loss resulted in an unsuccessful lamp fuel. These outcomes are displayed in Figure 3.13 and Figure 3.14, respectively.

During the twenty minute run duration of the test run, all organic liquid samples exhibited one or both of these outcomes. In order to obtain a successful fuel for lamp operation, blending with traditional fuels was investigated.

4.4.5 Product Blending

It has been demonstrated that the addition of commercial fuels, such as kerosene and paraffin, to the organic liquid product can result in a successful lamp fuel. The blending of kerosene with the resultant organic liquid product of the pyrolysis process is discussed below. The kerosene blending percent represents the minimum weight fraction of kerosene (wt%) that when blended with pyrolysis product results in successful lamp operation. Successful lamp operation is determined by the Lamp Performance Test described in Section 2.3.4.5.

The high miscibility of the organic liquid product with kerosene results in a homogeneous fuel. No phase separation occurred during the testing period. It was

assumed that this homogeneous state was also present in the wicking material, and that the solution composition remained constant over the volume of the wicking material.

The effect of reactor temperature on the required kerosene blending is shown in Figure 4.10. This relationship is given for each feedstock oil. It can be seen that the trend is similar to that of Viscosity vs. Reactor Temperature, and inversely similar to that of W_c vs. Reactor Temperature. At relatively low reactor temperatures, the kerosene requirements vary significantly among the three feedstock oils. As the severity is increased, the viscosities and wicking coefficients converge among feedstocks and this is also seen in the kerosene blending amounts. At 450 °C, all three feedstocks require 60 wt% kerosene to produce a successful fuel. Beyond 450 °C, the increased severity results in products more suitable for lamp fuel, requiring less kerosene blending. The fuel produced from the pyrolysis of canola oil at 500 °C was the optimal fuel in this regard, requiring only 50 wt% kerosene to produce a successful fuel. This coincides with the optimal fuel in terms of both viscosity and W_c in this chapter. Although the fuel characteristics resulting from these conditions are superior, the low yields at this temperature must also be considered. The feedstocks of palm kernel and safflower oil both exhibit liquid yields about 10 % greater than canola oil at these conditions. Dependent on market conditions, these feedstocks may prove to be the optimal selection even with the increased kerosene requirements.

Figure 4.11 is a plot earlier described in Section 4.4.3, with the addition of successful blends. It can be seen that in this system, a desired combination of viscosity and surface tension ranges (indicated by red circle) result in a successful lamp fuel. The properties desired in the successful blends are consistent with both Chapter 2 and Chapter 3 studies. This plot demonstrates the capability of the pyrolysis process to improve fuel characteristics of a wide variety of feedstocks towards those of commercial lamp fuels. This feedstock flexibility presents a great advantage of this process for the application of this technology in varying market conditions.

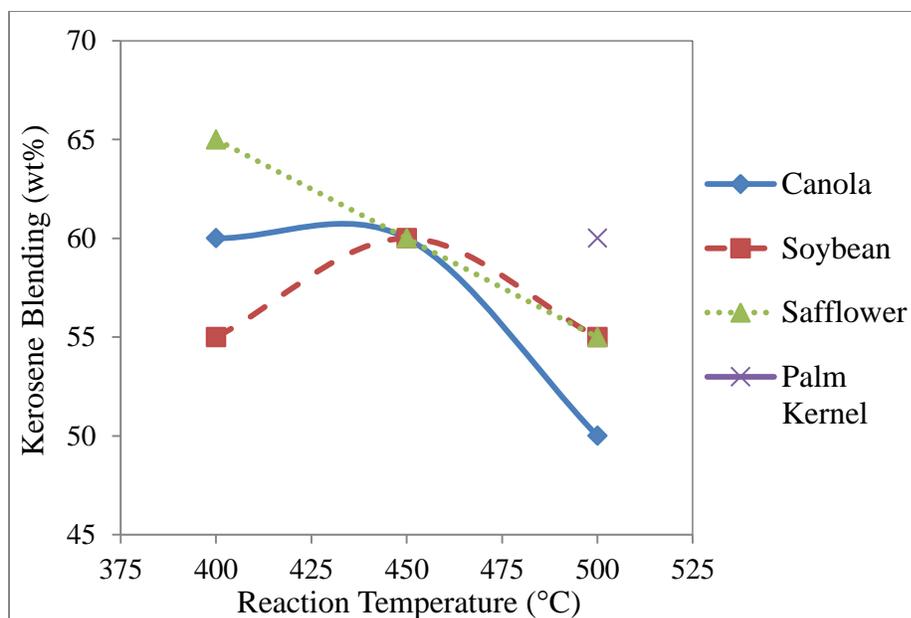


Figure 4.10: Effect of reaction temperature on kerosene blending (multiple feedstocks)

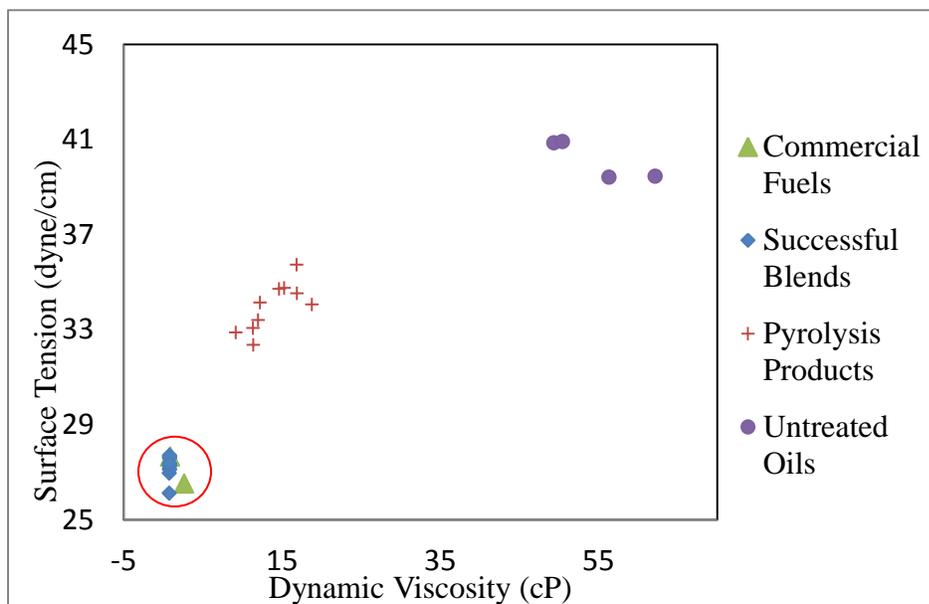


Figure 4.11: Surface tension vs. viscosity map of successful fuel blends (multiple feedstocks)

4.5 Conclusions and Recommendations

This study has demonstrated that thermal processes such as pyrolysis have the capability to improve fuel characteristics of a variety of crop oils for applications in fuel-based lighting. The pyrolysis process was applied to a range of crop oils varying in composition and saturation level. The degree of saturation had a great influence on the performance of the pyrolysis process at relatively low temperatures. The predominately saturated crop oils were unable to produce liquid fuels below 500 °C. It is recommended that greater temperatures be applied and investigated with these oils. Overall, the increase in unsaturation enhanced the cracking reaction. The pyrolysis of these feedstocks led to a significant upgrade over the parent oils with respect to lamp fuel properties. Liquid yields, viscosities, and wicking coefficients were similar to those of Chapter 3, and demonstrate the feedstock flexibility of this process. The flexibility of the process presents an advantage in the ability to adapt to changing market conditions and requirements. The optimization of the process based on organic liquid product fuel characteristics favours high reaction temperatures. An increase in reaction temperature results in a decrease in product viscosity and surface tension, leading to an increase in wickability. The increased severity however can lead to increased cracking and decreased liquid yields. The balance between fuel characteristics and liquid yield is important in process optimization and optimal conditions will be dependent on market conditions.

In addition to those stated in previous chapters, further research in the refining and separation of products is recommended. The single-step operation currently under investigation presents advantages in its simplicity, though the refining of the liquid product could provide increased flexibility and fuel improvement. A compositional analysis is recommended to gain a better understanding of the reactions taking place and the composition of the liquid fuel. This analysis would provide insight into the need of further refining or separation of the products.

4.6 References

- Alencar, J., Alves, P., & Craveiro, A. (1983). Pyrolysis of tropical vegetable oils. *Journal of Agricultural and ...*, 1268–1270. Retrieved from <http://pubs.acs.org/doi/abs/10.1021/jf00120a031>
- Asomaning, J., Mussone, P., & Bressler, D. C. (2014). Two-stage thermal conversion of inedible lipid feedstocks to renewable chemicals and fuels. *Bioresource Technology*, 158, 55–62.
- Dandik, L., & Aksoy, H. A. (1998). Converting used oil to fuel and chemical feedstock through a fractionating pyrolysis reactor. In *Proceedings of the World Conference on Oilseed and Edible Oil Processing, Istanbul, Turkey*.
- Dupain, X., Costa, D., & Schaverien, C. (2007). Cracking of a rapeseed vegetable oil under realistic FCC conditions. *Applied Catalysis B: ...*, 72(1-2), 44–61.
- Kamath, Y. K., Hornby, S. B., Weigmann, H. D., & Wilde, H. F. (1994). Wicking of Spin Finishes and Related Liquids into Continuous Filament Yarns. *Textile Research Journal*, 64, 33–40.
- Lima, D. G., Soares, V. C. D., Ribeiro, E. B., Carvalho, D. a., Cardoso, É. C. V., Rassi, F. C., ... Suarez, P. a. Z. (2004). Diesel-like fuel obtained by pyrolysis of vegetable oils. *Journal of Analytical and Applied Pyrolysis*, 71(2), 987–996.
- Maher, K. D., & Bressler, D. C. (2007). Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresource Technology*, 98(12), 2351–68.
- Schwab, A. W., Dykstra, G. J., Selke, E., Sorenson, S. C., & Pryde, E. H. (1988). Diesel fuel from thermal-decomposition of soybean oil. *Journal of American Oil Chemists' Society*, 65(11), 1781–1786.

5. Conclusions and Future Outlook

The preceding chapters have demonstrated the capability of thermal processes such as visbreaking and pyrolysis to improve fuel characteristics of crop oils for applications in fuel-based lighting. It has also been demonstrated that these processes can produce organic liquids able to comprise as much as 60 wt% of useable lamp fuel. A comparison between visbreaking and pyrolysis processes yields continuous pyrolysis as the optimal process for the given application. The continuous pyrolysis process exhibits superior performance producing less viscous, faster wicking products at higher liquid yields compared to those of the visbreaking process. The continuous operation of the pyrolysis process also provides advantages over the batch method of visbreaking.

The pyrolysis process also proved capable of processing a variety of crop oil feedstocks. The oils tested represented a wide spectrum in terms of oil composition and degree of saturation. It was demonstrated that increased saturation is unfavourable in this process at lower reaction temperatures. The unsaturated sites enhanced the cracking reaction and produced less viscous, faster wicking fuels. The optimization of the pyrolysis process is highly dependent on reaction temperature. The reaction temperature was the only significant parameter in the process with respect to obtaining desired liquid product characteristics and maximum liquid yields.

The flexibility of this process and the ability to tailor the product properties through the control of reaction temperature presents a great advantage in this application. The process is able to adapt to the instability of kerosene pricing and variable market conditions to provide the optimal balance. Due to this, process optimization is highly dependent on market conditions such as feedstock, kerosene, and energy pricing as well as local fuel requirements.

The pyrolysis process developed in this study is able to produce liquid fuels from the triglycerides of crop oils. This simple, one-step process results in upgraded liquid fuels, which can replace up to 60 wt% of kerosene in a wick-feeding lamp fuel. As mentioned previously the market for kerosene in wick-based lighting is very large. The opportunity

exists to provide an alternative option resulting in potential social, environmental, and financial benefits.

Recommendations for Future Work

There are many areas of focus that could potentially bring advancements to this study. The following recommendations are a short list of potential areas to investigate to further benefit this process:

- Product characterization: The quantification and identification is recommended for the product stream in these processes. The above study optimizes conditions on the basis of improving fuel characteristics. It would be beneficial to gain a better understanding of the composition of the products allowing for more detailed analysis going forward.
- Additional process parameters such as vapour residence time should be analyzed. The analysis and optimization of vapour residence time could provide further flexibility and product refinement.
- Product refining and separation: Further refining and/or separation of the product streams could allow for more precise tailoring of the product fuel characteristics. This could potentially reduce the amount of kerosene blending required.
 - In addition, the recycling of separated heavier fraction back into the process could potentially lead to increased light yields
- Energy utilization: The study of energy utilization/recovery including potential usage of current waste streams could reduce the energy efficiency of this process, resulting in increased environmental and financial benefit.

6. Appendix A

The following plot presents the calibration curve utilized in the measurement of surface tension. This method was similar for all 3 studies.

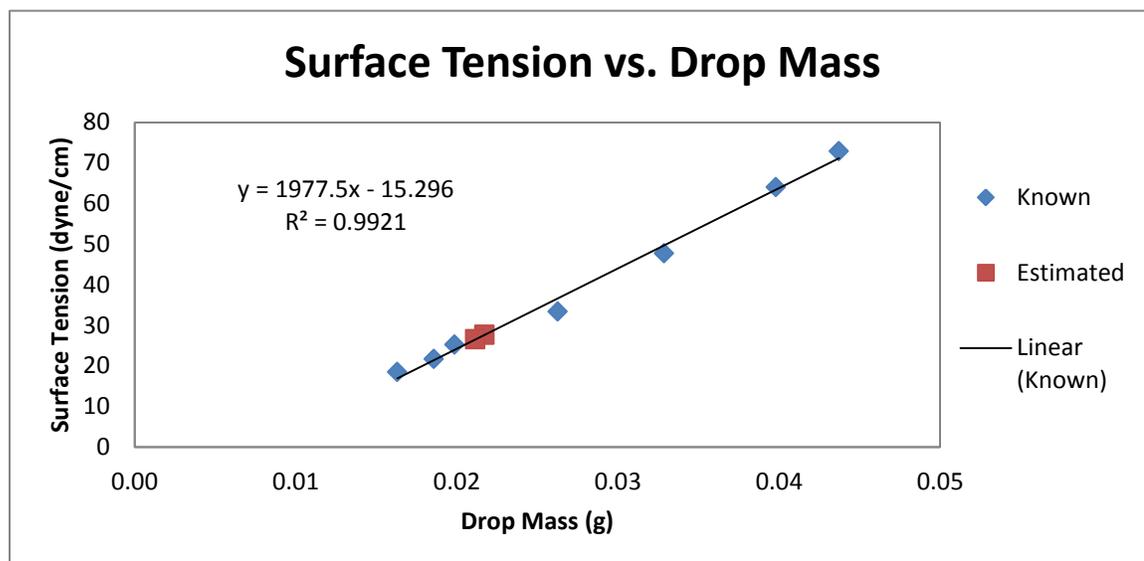


Figure 6.1: Surface tension drop mass calibration curve

Chapter 2

Figures 6.2 to 6.4 represent the effect of temperature and the interactions effects of temperature and residence time on various phase yields. These results were obtained from Chapter 2: Visbreaking of triglycerides of soybean oil for the production of lamp fuel.

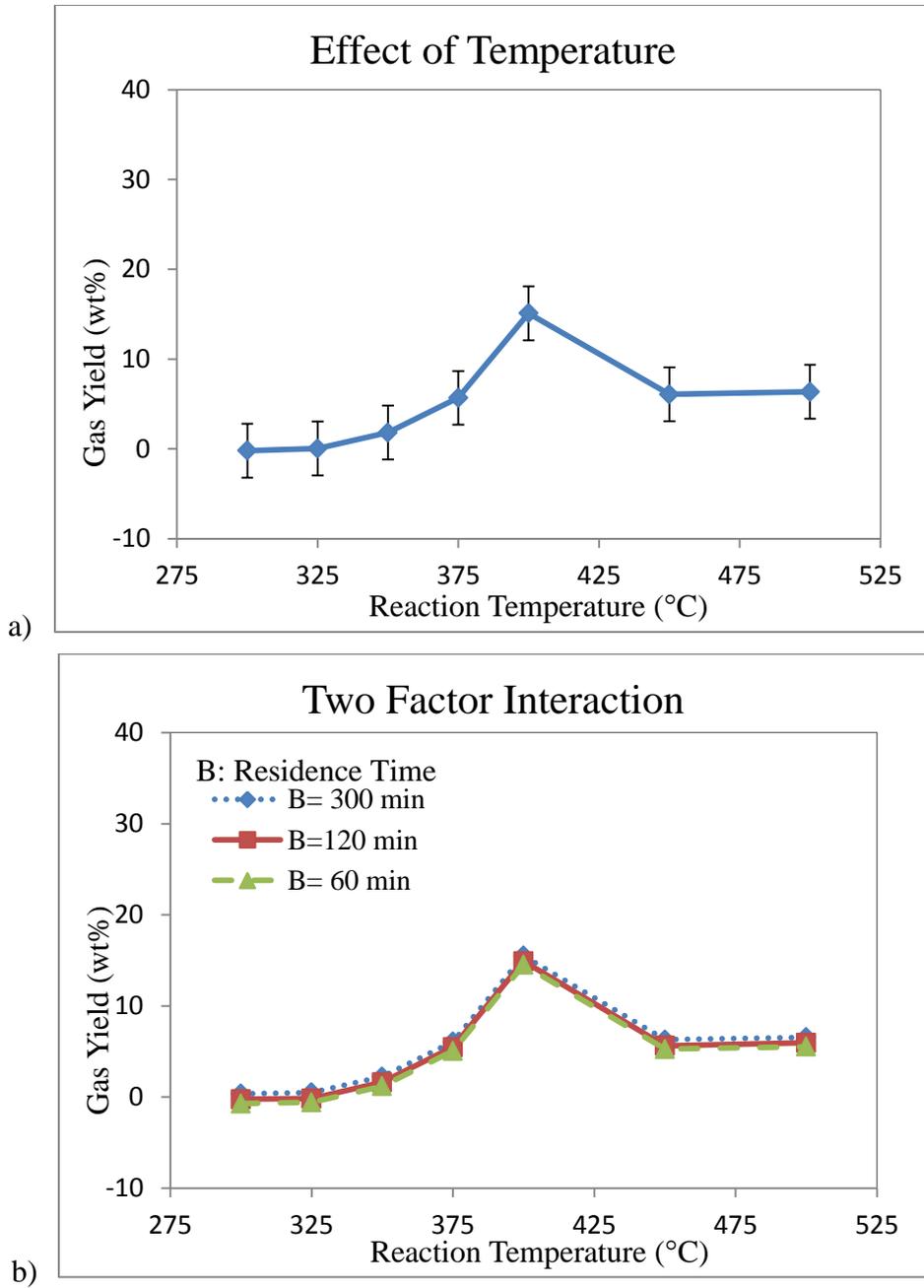


Figure 6.2: Factor effects on Gas Yield. a) one factor (Temperature). b) two factor interaction

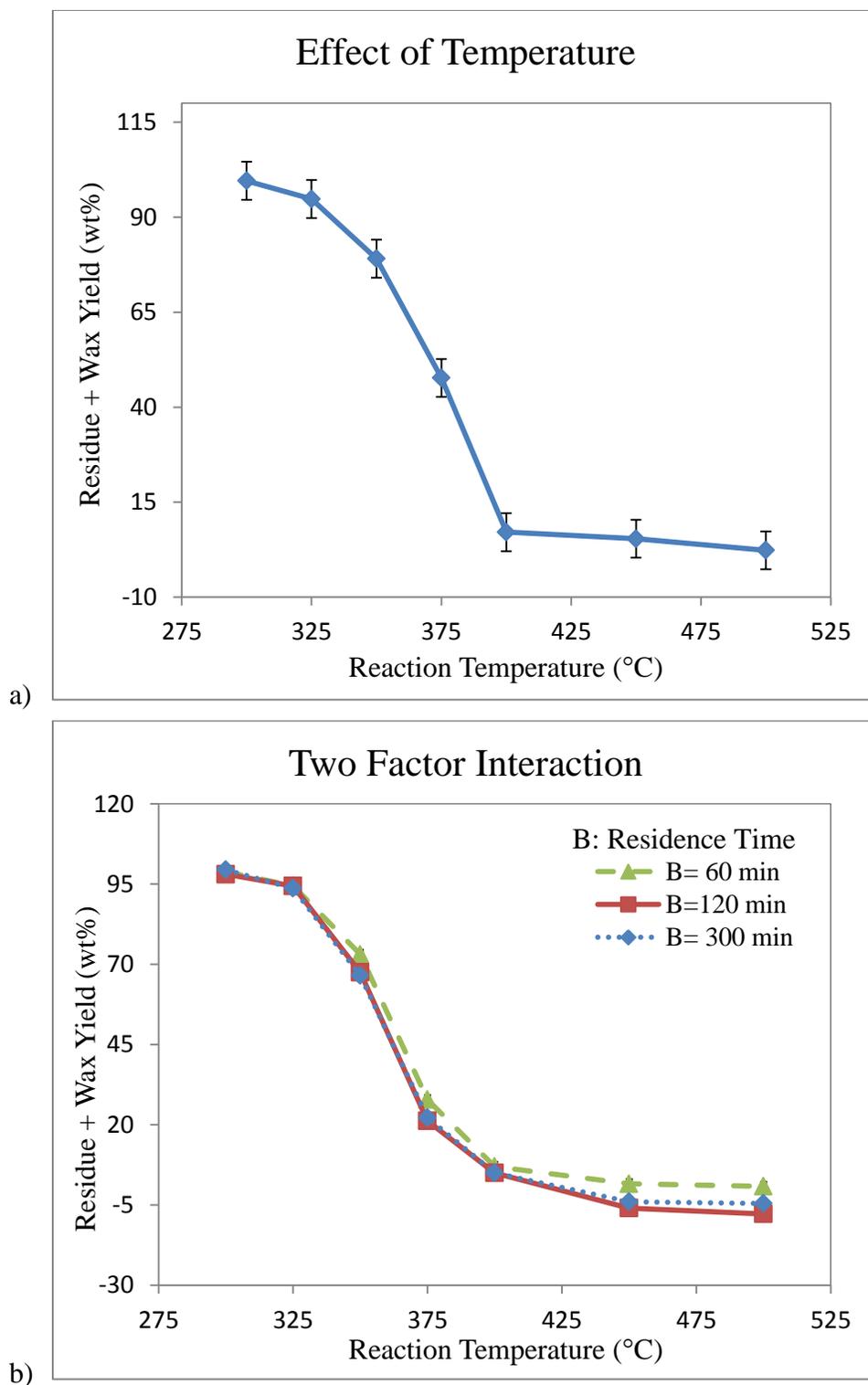


Figure 6.3: Factor effects on Residue + Wax Yield. a) one factor (Temperature). b) two factor interaction

Curriculum Vitae

Name: Jamie Gregory

**Post-secondary
Education and
Degrees:** The University of Western Ontario
London, Ontario, Canada
2008-2012 BESC

The University of Western Ontario
London, Ontario, Canada
2012-2014 MESC

**Honours and
Awards:** Queen Elizabeth Scholarship
Dean's Honour List 2009-2012
University of Western Ontario Scholarship