University of Alberta

Thermal cracking of lipids to produce renewable fuels and platform chemicals

by

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A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Bioresource and Food Engineering

Department of Agricultural, Food and Nutritional Science

Spring 2014
Edmonton, Alberta

Abstract

There are increasing social and economic pressures to develop renewable alternatives to fossil derived fuels and chemicals as well as renewable and biodegradable industrial and consumer products and materials. This has led to renewed focus on converting agricultural and forestry feedstocks (biomass) into multiple renewable commodities. The conversion of vegetable oils and animal fats using thermal cracking reactions represents a very promising option for the production of renewable fuels and chemicals.

The first objective of this dissertation research was to study the pyrolysis behaviour of model unsaturated fatty acids with focus on identification of reaction products under different conditions. Oleic acid and linoleic acid were pyrolyzed in batch microreactors at 350 – 450 °C for reaction times 0.5 – 8 h under N_2 at atmospheric pressure. The results showed the production of a series of hydrocarbons in the liquid product with the *n*-alkane series being the most abundant. Low molecular weight fatty acids particularly C_9 and C_{10} carbon chains were also formed in the liquid product. The presence of the double bond resulted in simultaneous deoxygenation and cracking of the alkyl chain, particularly at the allylic carbon bond. Deoxygenation occurred through both decarboxylation and decarbonylation pathways, the predominance of which was temperature dependent.

The thermal cracking of oleic acid under light hydrocarbon gas atmosphere was conducted to study the effect on reaction product yields and composition. The results showed no significant influence of saturated light hydrocarbon gases compared to inert atmosphere. On the other hand the unsaturated light hydrocarbon gases resulted in significant increases in liquid product yield, conversion, deoxygenation and formation of branched hydrocarbon compounds.

The second objective was to study the thermal cracking of low cost inedible lipid feedstocks using a two-step thermal hydrolysis-pyrolysis process. Beef tallow, brown grease, yellow grease and cold pressed camelina oil were used as feedstocks. The result showed that the organic liquid product yields were not significantly affected by the feedstock source of origin. Fuel property testing of crude batch pyrolytic product revealed the organic liquid products was composed of approximately 30% gasoline boiling range and 50% in the diesel boiling range compounds.

Acknowledgements

I would like to express my heartfelt gratitude to Dr. David C. Bressler, for first of all accepting me to join his research team and for his invaluable mentorship, supervision and patience which enabled me to complete this project. Thank you Dave for being such a wonderful supervisor, I couldn’t have asked for a better supervisor.

A special thank you to Dr. Jonathan Curtis and Dr. Murray R. Gray for being on my supervisory committee and for their valuable feedback and advice during the course of my program. Many thanks to them for also making their laboratory infrastructure available to me when needed. I also want to thank Dr. Feral Temelli and Dr. Greg P. Dechaine for being on my examining committee and Dr. Jean-Michel Lavoie for being my external examiner.

I would like to thank Dr. Suresh Narine for initially accepting me as a PhD student in Department of Agricultural, Food and Nutritional Science at the University of Alberta, thereby giving me the opportunity that started it all.

Many thanks to Dr. Paolo Mussone for his help, advice, directions and for being there to talk to when you need him. I also want to thank Kelly Maher who was very helpful, particularly when I initially joined the group in getting me started and up to speed with many techniques. I would also like to thank Jingui Lan, Ereddad Kharraz and Dr. Kelvin Lien for their technical assistance. Thank you to Dr. Natisha Stashko for her help and advice.

During the course of my study I had the pleasure of joining a multicultural research group and getting to know some great individuals. Thank you to all my

lab mates and friends particularly Tizazu, Isabel, Yiqiong Michael, Erin, Emily, Allie, and Sergio for their support and help.

My thanks also go my parents and siblings for their help and support throughout my studies. I would also like to express my gratitude to Dr. Setorme Tsikata, Ben, Sena and Zanna for all their help support and encouragements during my study.

Finally, to my lovely wife Edem and my daughters Abby and Anna, I can’t thank you enough for the support and love during my time of study and for all the times I had to be away and grumpy during my study.

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List of abbreviations

ALF - aqueous liquid fraction

ASTM - American society for testing and materials

CGSB - Canadian general standards board

DAG - diacylglycerol

EU - European union

FAME - fatty acid methyl ester

FAO - food and agricultural organization

FCC - fluid catalytic cracking

FFA - free fatty acid

FID - flame ionization detector

GC - gas chromatography

HPLC - high performance liquid chromatography

MAG - monoacylglycerol

MS - mass spectrometer

OLF - organic liquid fraction

NIST - national institute of standards and testing

TAG - triacylglycerol

TCD - thermal conductivity detector

WHSV - weight hourly space velocity

1. Introduction

The development of alternative and renewable energy and chemicals has been on the rise over the past decades. The primary drivers have been problems associated with over-reliance on fossil derived fuels and chemicals as well as increased consumer awareness and demand for renewability and sustainability [1-3]. Lipid feedstocks have been considered as one of the biomass sources with the most potential for producing renewable liquid hydrocarbon products, which can be used as petroleum alternatives. The primary reason for this is the higher energy density [4, 5] and relatively simpler structure [6] compared to other biomass feedstock such as lignocellulose.

Several lipid feedstocks are available for conversion to renewable liquid fuels including refined vegetable oils and animal fats (food grade), inedible plant oils (eg. Castor oil and jatropha oil), and waste oils and fats such as brown grease, yellow grease and sewage sludge lipids. The ability to utilize non-food lipid feedstocks is important for process economics and commercial viability as feedstock cost accounts for anywhere between 40-80% of the production cost of renewable fuels [7-9]. Lipids in the form of vegetable oils and animal fats are composed predominantly of triacylglycerols (TAGs) with minor components being monoacylglycerols, diacylglycerols, free fatty acids, sterols and phospholipids. The content of the minor components is high in waste oils and fats such as brown grease and yellow grease, which have a relatively high free fatty acids content compared to virgin or refined oils and fats [10-12]. TAG is composed of three fatty acid molecules esterified to glycerol. A representative model TAG molecule is shown in Figure 1.1. The fatty acids can be separated from the TAG molecule through various hydrolysis techniques. Triacylglycerol hydrolysis procedures employing acids, bases or enzymes as catalysts as well as high temperature and high pressure can be used to achieve fatty acid liberation. High temperature and pressure hydrolysis is important because it does not employ a catalyst, which may require additional processing steps for removal, regeneration and recovery [13]. It was therefore chosen as the technique to be used in this research.

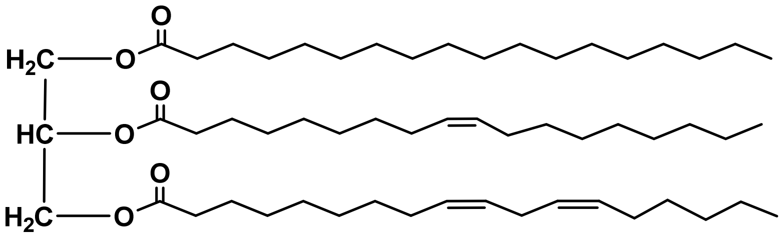

Figure 1.1. Model TAG molecule.

One of the most promising lipid conversion technologies is thermal cracking or pyrolysis; a high temperature reaction in the absence of oxygen. Pyrolysis is especially attractive in areas with developed oil and gas industry such as Alberta because it utilizes similar infrastructure and technologies. The thermal cracking of vegetable oils and animal fats in the form of TAGs has been the subject of many studies and literature is available. However, only limited studies have been reported on the thermal cracking of free fatty acids. The thermal cracking of model stearic acid (a saturated eighteen carbon free fatty acid) was studied by Maher et al. [14]. They found decarboxylation as the initial step of the thermal cracking resulting in the formation of *n*-heptadecane. Then, subsequent thermal cracking of *n*-heptadecane resulted in the production of low molecular weight *n*-alkanes and α-olefins as major products.

Natural vegetable oils and animal fats are however composed of a complex mixture of both saturated and unsaturated fatty acids. The earlier stearic acid study [14] provided valuable insight into the thermal cracking of saturated free fatty acids. There is however, the need to evaluate the thermal cracking of unsaturated free fatty acids to better understand the thermal cracking of free fatty acids produced from hydrolysis of natural vegetable oils and animal fats as vegetable oils especially often contain high levels of unsaturation. Also, a more detailed characterization of the products especially in the gas fraction is necessary to help shed more light on the fundamental reaction chemistry and the mechanism of the thermal cracking of these free fatty acids.

1.1. Hypotheses

- The presence of unsaturation (C=C) in the fatty acid chain will result in simultaneous cracking and deoxygenation compared to saturated fatty acids where deoxygenation precedes cracking.
- The use of unsaturated hydrocarbon gases instead of an inert atmosphere will affect product composition and distribution.

- Reaction temperature and time will impact reaction product composition by influencing particularly secondary reactions such as condensation, aromatization and coking.
- Composition of pyrolysis products of fatty acids hydrolyzed from triacylglycerol feedstocks will be different from model compounds due to heterogeneity in the fatty acids.
- Feedstock composition will significantly influence pyrolysis product properties.

1.2. Thesis objectives

The overall objective of this thesis research was to investigate the thermal non-catalytic conversion of lipids in the form of free fatty acids to renewable hydrocarbons for use as fuels and chemicals. The specific objectives were:

- To determine the effect of mono-unsaturation, temperature and time on fatty acid thermal cracking with respect to product composition and distribution (Chapter 3),
- To determine the effect of polyunsaturation temperature and time on fatty acid thermal cracking with respect to product composition and distribution (Chapter 4),
- To determine the effect of reaction atmosphere on product yield and distribution during the thermal cracking of fatty acids (Chapter 5) and

- To study the feasibility of utilizing inedible and waste vegetable and animal fats for production of liquid hydrocarbons using thermal hydrolysis and pyrolysis and characterizing the reaction products as well as testing fuel properties (chapter 6).

1.3. References

[1] A.E. Harman-Ware, T. Morgan, M. Wilson, M. Crocker, J. Zhang, K. Liu, J. Stork, S. Debolt, Microalgae as a renewable fuel source: Fast pyrolysis of Scenedesmus sp, Renewable Energy, 60 (2013) 625-632.

[2] A. Ajanovic, Renewable fuels - A comparative assessment from economic, energetic and ecological point-of-view up to 2050 in EU-countries, Renewable Energy, 60 (2013) 733-738.

[3] A.K. Azad, M.R. Islam, A renewable alternative bio-fuel source from Jatropha Curcus seeds oil: performance and emission study for DI diesel engine, International Journal of Advanced Renewable Energy Research, 1 (2012) 126-132.

[4] V.F. Luque, H.G. Soldevilla, C.G. Herrera, J.C. Martin, Renewable natural fats and their derivatives as source of fuels .1. Physical-properties of vegetable oil and farm engines diesel fuel mixtures, Grasas Y Aceites, 35 (1984) 300-305.

[5] V.F. Luque, H.G. Soldevilla, C.G. Herrera, J.C. Martin, Renewable natural fats and their derivatives as source of fuels .2. Relations between kinematic viscosity and temperature for vegetable oil and farm diesel fuel binary-mixtures, Grasas Y Aceites, 37 (1986) 39-41.

[6] P. Sergiy, K. Sandeep, S. Popov, S. Kumar, Renewable fuels via catalytic hydrodeoxygenation of lipid-based feedstocks, Biofuels, 4 (2013) 219-239.

[7] I.M. Atadashi, M.K. Aroua, A.R.A. Aziz, N.M.N. Sulaiman, Production of biodiesel using high free fatty acid feedstocks, Renewable & Sustainable Energy Reviews, 16 (2012) 3275-3285.

[8] J. Hill, E. Nelson, D. Tilman, S. Polasky, D. Tiffany, Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels, Proceedings of the National Academy of Sciences of the United States of America, 103 (2006) 11206-11210.

[9] J.M. Marchetti, V.U. Miguel, A.F. Errazu, Techno-economic study of different alternatives for biodiesel production, Fuel Processing Technology, 89 (2008) 740-748.

[10] X. Fan, R. Burton, G. Austic, The Enzymatic Conversion of Brown Grease to Biodiesel in a Solvent-free Medium, Energy Sources Part a-Recovery Utilization and Environmental Effects, 35 (2013) 1779-1786.

[11] E. Sari, C. DiMaggio, M. Kim, S.O. Salley, K.Y.S. Ng, Catalytic Conversion of Brown Grease to Green Diesel via Decarboxylation over Activated Carbon Supported Palladium Catalyst, Industrial & Engineering Chemistry Research, 52 (2013) 11527-11536.

[12] P.M.L. Ward, Brown and Black Grease Suitability for Incorporation into Feeds and Suitability for Biofuels, Journal of Food Protection, 75 (2012) 731-737.

[13] K.D. Maher, D.C. Bressler, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals, Bioresource Technology, 98 (2007) 2351-2368.

[14] K.D. Maher, K.M. Kirkwood, M.R. Gray, D.C. Bressler, Pyrolytic decarboxylation and cracking of stearic acid, Industrial & Engineering Chemistry Research, 47 (2008) 5328-5336.

2. Literature review [1]

2.1. The drive for renewable alternatives

The world's energy demand has been rising since the industrial revolution and is projected to continue rising for the foreseeable future driven largely by emerging economies as a result of strong long term economic growth and ever expanding populations [1-3]. The global energy demand has been projected to increase significantly by 56% by the year 2040 [2]. The vast majority of the current global energy is supplied by non-renewable resources in the form of petroleum, natural gas and coal, together accounting for more than 75% of the current energy needs [2, 4]. Petroleum derived fractions currently supply over 95% of the total energy needs of the transportation sector [2, 4, 5]. As well, petroleum serves as an important source of raw material for several chemical industries producing essential products such as solvents, lubricants, plastics and polymers etc. [6]. The current dependence on petroleum was fuelled by the relative ease of its discovery, transportation, processing and utilization [6].

Despite the importance of petroleum or fossil derived fuels in today's economy and energy needs, there are several issues associated with its use and overdependence. One of the major issues associated with petroleum use is its finite reserves and non-renewability. With a current total consumption of nearly 90 million barrels per day, the current proven reserves are expected to be depleted in about 50 years [2, 7]. The estimated depletion time did not take into account shale oil, which has been estimated to have current proven reserves of about 345

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[1] A version of this chapter has been prepared as review article for publication in the Journal Energy and Environmental Science.

billion barrels [8]. Another major issue with petroleum use is exhaust emissions from transportation vehicles that result in environmental pollution and greenhouse gas emission, which have been implicated in global warming [2, 9]. Another issue associated with petroleum use is localized nature of reserves with over 50% of the current proven reserves located in some of the most politically unstable countries/regions of the world. Additionally, petroleum suffers from price fluctuations and uncertainty and increasing environmental awareness. As a result of these issues, a considerable effort into research and development of renewable alternatives to petroleum has been made over several decades. There is also currently renewed interest in the development of alternative renewable fuels and chemicals, especially in the European Union, spurred by regulations and incentives from several governments mandating and promoting the development and use of renewable fuels and chemicals.

Several alternative and renewable energy technologies are being developed including solar power, wind power, wave power, geothermal energy, and biomass (including biofuels). The various alternative and renewable energy technologies have their advantages and drawbacks, which affect their large scale deployment and utilization. Biomass represents a renewable and alternative energy source that can meet our demand for carbon-based liquid transportation fuels and chemicals since it is the only renewable energy source that can yield solid, liquid and gaseous fuels [6, 10-13]. Additionally the exploitation of biomass also has the potential to return value to the agricultural and forestry sectors, both of which are seeking value-added opportunities in North America. The utilization of biomass will therefore play an important role in meeting our energy demands sustainably in the future.

Biomass contains a variety of components, some of which are readily accessible while others are much more difficult and costly to extract. Classification of biomass is not standardized; hence it is usually classified based on the context in which it is used. For the purposes of this review, biomass will be grouped into three broad classes based on composition namely: sugars and starches, lignocellulosics and lipids (oils and fats). Only lipids will be discussed further in this review.

2.1.1. Lipid (fats and oils) resources

Fats and oils are water insoluble, hydrophobic substances in plants and animals that are primarily made up of three fatty acid molecules esterified to glycerol, commonly referred to as TAGs [14]. Unprocessed fats and oils are composed almost exclusively of triacylglycerols (TAGs) with minor components being monoacylglycerols, diacylglycerols, free fatty acids, phospholipids and sterols [15, 16]. The possibility of using vegetable TAGs as a source of energy was demonstrated over a century ago when Rudolf Diesel used peanut oil to run one of his engines [17]. The main advantage of fats and oils over the other biomass sources is its higher energy density, which is more than double the energy density of sugar and starches or lignocellulosics [16, 18-20]. Fats and oils have been estimated to contain as much as 90% of the energy content of conventional petroleum derived diesel [21, 22]

There are a variety of fats and oils sources that can be utilized as renewable feedstocks for the production of petroleum derived alternatives. These sources have been divided into four main groups, including vegetable oils (canola oil, soybean oil, olive oil, palm oil, etc.), animal fats (lard, tallows, fish oils etc.), waste cooking oils (yellow grease, brown grease etc.) and nonedible oils (castor oil, jatropha oil, rubber seed oil etc.) [9, 23, 24]. The availability and production of the various fats and oils vary significantly between regions. Table 2.1 show the total world production of some edible fats and oils in 2011 along with the top 5 producers who together produced between 70 and 97% of the respective fats and oils. The oils produced in the largest quantities are palm, soybean and canola oils. The widespread availability and variability in the location of the largest producers shows the potential of using fats and oils as feedstock in different parts of the world.

Data on the world production of non-edible oils are not as readily available as that of the edible oils. Total castor oil seeds production for the year 2011 was estimated to be 2.8 million tonnes [25] and according to Gui et al. [23] the oil yield of castor oil seeds is 53%. Thus, by calculation, the 2011 castor oil production would amount to 1.5 million tonnes. Other non-edible oils which have been reported in the literature but production quantity information is not available are jatropha, karanja seed, rubber seed oil, carinata oil etc. [26-29]. Because these oils do not compete directly with food and feed applications, their use as feedstock for biofuels is thought to be more desirable. However, land use considerations, both direct and indirect, must be equally considered.

Table 2.1. Total world production of fats and oils and top 5 producers (data source [25])

Fat and oil	Top 5 producers	2011 world production (million tonnes)
Palm oil	Indonesia, Malaysia, Thailand, Colombia, Nigeria	47.7
Soybean oil	China, USA, Brazil, Argentina, India	41.6
Canola/rapeseed oil	China, Canada, Germany, India, France	22.8
Coconut oil	Philippines, Indonesia, India, Vietnam, Mexico	3.3
Peanut oil	China, India, Nigeria, Myanmar, Senegal	5.8
Corn oil	USA, China, Japan, Brazil South Africa	2.4
Cotton seed oil	China, India, USA, Pakistan, Brazil	5.2
Sunflower oil	Ukraine, Russia, Argentina Turkey, China	13.4
Olive oil	Spain, Italy, Greece, Syria, Turkey	3.0
Safflower oil	India, USA, Mexico, Argentina, Kazakhstan	0.13
Lard	China, Germany, Brazil, USA, Russia	5.8
Tallow	USA, Brazil, Australia, Canada, France	6.7

Another important source of fat and oil feedstock is waste fats and oils, including brown grease, due to their worldwide availability. The use of these types of lipid feedstocks does not negatively impact the food and feed industry [30, 31]. Waste fats and oils are also important because of their relatively low cost compared to refined fats and oils and therefore their use as feedstock would help positively improve the process economics [30, 32-35]. Table 2.2 shows the available quantities of waste fats and greases as well as potential quantities of fats and greases and lipids from sewage sludge. The potential lipids from sewage sludge was calculated based on potential sewage sludge quantities of 12 million tonnes in the European Union (EU) and 6.2 million tonnes in the US [30, 36-38] and reported sewage sludge lipids content of between 15-20% [39-42]. Since sewage sludge is readily available in most municipalities, the use of lipids from sewage sludge as renewable feedstock for chemicals and fuels will be important as new and low cost feedstocks are researched.

2.2. Lipid conversion technologies

Fats and oils have long been recognized as potential liquid fuel for use in automotive vehicles [32]. They are especially important as feedstock for liquid fuel generation because of their high energy content compared to other biomass resources and their relatively simpler structure, much closer to that of n-alkanes, compared to starches or lignocellulosic biomass [14]. Development of alternative fuel from lipids, particularly vegetable oil, became urgent in the late 1970s as a result of the short supply and high prices of crude oil [17, 43] and research into renewable alternative fuels has been renewed in the past decade.

Table 2.2. Current and potential waste fats and oils (adapted from [30])

Product	Quantity (million tonnes/yr)	
	US	EU 25
Waste fats and greases -Rendered	2.88	3.96
Inedible tallow	1.51	0.90
Lard	0.14	1.06
Poultry fat	0.61	0.81
Yellow grease	0.61	1.20
Waste fats and greases - Potential	4.92	4.44
Sewage sludge lipids- Potential	1.24	2.40

Fat and oil conversions have primarily focused on the production of fatty acid alkyl esters usually methyl esters commonly referred to as biodiesel. Biodiesel has been suggested as a direct replacement for petroleum-derived diesel [17, 32, 44, 45]. Another alternative conversion technology for fats and oils is thermochemical conversion predominantly pyrolysis to convert fats and oils and their derivatives to liquid hydrocarbons. These lipid conversion technologies will be discussed further in the subsections below.

2.2.1. Chemical conversion (Biodiesel)

The chemical conversion of vegetable oil and animal fat TAGs to fatty acid methyl esters (FAMEs) through transesterification reactions is currently the most applied conversion technology for lipid feedstocks for fuel applications. World biodiesel production and consumption in 2011 was 160 million barrels [46]. The term biodiesel was previously used to describe different renewable liquid fuels including vegetable oils and their blends with petroleum derived fuel fractions [6, 17]. Biodiesel has now been formally defined by the American Society for Testing and Materials (ASTM) International as “fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100” (ASTM D6751-12) [47]. A similar definition is used by the European Committee for standardization in the specification EN14214-13 [48].

The transesterification of vegetable oils and animal fats to produce biodiesel involves the reaction of the fat or oil with a primary or secondary aliphatic alcohol with or without the use of a catalyst [24]. Stoichiometrically, one mole of vegetable oil or animal fat TAG reacts with three moles of alcohol resulting in the production of three moles of alkyl esters and one mole of glycerol. The most used alcohols are by far methanol and ethanol. Several catalysts have been investigated for applicability in the transesterification reaction including strong acids and bases, metal alkoxides, and enzymes (lipases). However, most of the current commercial biodiesel plants employ the use of strong base (NaOH or KOH) as catalyst [49-52]. Non-catalyzed transesterification reactions include the use of supercritical methanol [45, 53-55] and the use of co-solvents such as in the BIOX® process which occurs at atmospheric pressure and near ambient temperatures [4, 56].

The current commercial base catalyzed biodiesel production in the US requires the use of high quality vegetable oils and animal fats that have been estimated to account for up to 88% of the production cost [34, 35, 57]. The high cost of the feedstock makes the process uneconomical without government incentives. As a result there have been research efforts into developing biodiesel processes that are capable of utilizing low quality feedstocks such as yellow grease and brown grease. Reviews of these approaches are available elsewhere in the literature [23, 30, 51, 58-62].

In addition to the high cost of current biodiesel commercial production, the use of biodiesel as petroleum diesel alternative has some disadvantages. Poor cold flow properties limits the use of biodiesel in cold temperature regions during winter as it results in engine performance issues and increased NO_x emissions [63-65]. Another disadvantage of the use of biodiesel as petroleum derived alternative is the long term instability of biodiesel due to hydrolytic and oxidative reactions [66]. Biodiesel use also has other disadvantages over petroleum-derived diesel such as lower energy content, lower engine speeds and power, and injector choking etc. [67].

2.2.2. Thermochemical conversion (pyrolysis)

Pyrolysis is a thermochemical conversion technique that is utilized to produce mostly liquid product in addition to non-condensable gaseous products with solid “coke” being an unwanted by-product [68]. In the case of lipids conversion, pyrolysis results in a fuel that has a high fuel-to-feed ratio making the process the most efficient and promising lipid conversion technology, capable of directly competing with petroleum derived fuels [69-71]. Pyrolysis is the thermochemical decomposition of carbonaceous materials occurring in the absence of oxygen or reduced oxygen [12, 69, 72]. The product distribution and composition is influenced by the reaction conditions employed as well as the feedstock composition. Products from vegetable oil and animal fat pyrolysis are generally composed of hydrocarbons, carboxylic acids, alcohols, and carbonyl compounds.

Lipid pyrolysis has several advantages over chemical conversion into biodiesel including compatibility with infrastructure, feedstock flexibility and product composition similar to petroleum derived fractions [73, 74]. The subsequent section will review the literature on pyrolysis of vegetable oil and animal fat TAGs and their derivatives with a focus on thermal and thermo-catalytic studies.

2.3. Pyrolysis (thermal cracking) of TAGs and derivatives

Studies involving the thermal degradation or cracking of TAG and derivatives such as fatty acids and fatty acid soaps have been reported in the literature over the past century. Model lipid compounds as well as lipids from vegetable oils and animal fats have been investigated by several research teams. Some initial studies mainly focused on studying quality changes associated with the use of lipids such as during frying [75-77] whereas others studied the conversion of lipids for the production of fuels and chemicals from lipids [78-80]. Developments in analytical techniques such as gas chromatography and mass spectrometry has led to better product characterization and mechanism elucidation of thermal degradation and cracking of lipids. The following subsections will take an in-depth look at thermal cracking and degradation of TAGs and its derivatives such as fatty acids and fatty acid soaps and the mechanisms proposed to account for the degradation or cracking.

2.3.1. Pyrolysis of TAGs

Several studies investigating the thermal cracking of different TAG feedstocks from vegetable oils and animal fats as well as model TAGs have been reported in recent literature. Conditions employed ranged from 300 to 1000 °C, with reaction times ranging from a few seconds to hours at either atmospheric, reduced pressure or at elevated pressures with the aim of producing renewable hydrocarbons. Fabbri et al. [81] studied the conversion of the model TAGs trilinolein, triolein and tristearin at 1000 °C for 60 s using a pyroprobe at a heating rate of 20 °C ms^{-1}. They reported that each of the model TAGs produced a unique pattern of pyrolysis products, with trilinolein and triolein producing mostly alkadienes ranging in carbon number from C10 to C17 and higher as the major products. On the other hand pyrolysis of tristearin resulted in the production of α-olefins and *n*-alkanes with carbon numbers from C10 to C17 and higher as the main products. Aromatic compounds formation was significantly higher in the trilinolein pyrolysis product compared to triolein or tristearin. Their study also reported that the thermal degradation of the hydrocarbon chain was not affected by the nature of the carboxyl moiety as similar results were obtained when sodium salts or glycerol carbonate esters of the fatty acids were pyrolyzed under similar conditions.

Soybean oil was pyrolyzed by Doll et al. [82] at temperatures between 350-400 °C following the approach reported earlier by Lima et al. [83] in the pyrolysis of other vegetable oils. They reported the production of two liquid fractions; an aqueous fraction and an organic liquid fraction. The organic liquid fraction from the soybean oil was distilled and the fraction that distilled above 200 °C was analyzed and compared to high sulphur and low sulphur petroleum diesel. They found that the density and the surface tension of the distilled fraction was comparable to that of the high sulphur diesel whereas the viscosity was relatively higher in the distilled fraction when compared to petroleum diesel. They concluded that the distilled fraction could be a viable alternative to petroleum diesel or it could be blended with petroleum diesel to overcome the high viscosity. In a similar study, Prado and Filho [84] pyrolyzed soybean oil in a batch system at 380-400 °C under atmospheric pressure using both simple pyrolysis and fractionated pyrolysis. They obtained a 93% conversion in the simple pyrolysis with 84% liquid product yield of which 1% was aqueous fraction. The non-condensable gas fraction accounted for 9% with a coke yield of 7%. The primary products were *n*-alkanes, alkenes, carboxylic acids, alcohols and ketones. The hydrocarbon had carbon numbers from C4 to C30 and the oxygenated compounds had carbon numbers from C2 to C20.

In another study of the batch thermal cracking of TAGs, soybean and canola oils were pyrolyzed at 350-400 °C with a starting pressure of 3 kPa vacuum or 2000 kPa pressurized with hydrogen, a heating rate of 2 °C/min and a residence time of 30 min was conducted by Luo et al. [85]. They reported organic liquid product yield of 76% and 64% for reactions conducted under vacuum and pressurised hydrogen respectively, at 440 °C for soybean oil. A similar observation was made with canola oil cracking at 430 °C. They further observed that external source of hydrogen was not required to facilitate the formation of the products if the initial process step is thermal cracking of the TAGs. The main products in the organic liquid were alkanes and short chain fatty acids with minor concentrations of alkenes and aromatic compounds. In a follow up study, Kubatova et al. [86] performed batch thermal cracking of canola oil and soybean oil at 420-440 °C, for reaction times of 10-30 min and starting pressure of 3 kPa vacuum and 2200 kPa pressurized hydrogen. They obtained organic liquid product yield of approximately 70% for both canola oil and soybean oil with the main compounds being alkanes from C3 to C26, fatty acids from C1-C18, alkenes, monoaromatic and polyaromatic compounds, and ketones. In support of the earlier work, they confirmed that under the conditions employed (temperature > 400 °C), external hydrogen source did not significantly impact the organic liquid product yield or composition of the compounds of interest in the organic liquid fraction.

The studies mentioned so far involved the use of refined vegetable oils which are high value commodities in other markets such as the food and feed industries making the processes uneconomical. The use of low value feedstocks is one of the important ways of improving the process economics. Santos et al. [87] studied the batch pyrolytic conversion of beef tallow, a relatively low cost lipid feedstock from the rendering industry [88] at temperatures of 350-400 °C at a heating rate of 4 °C/min and atmospheric pressure. They reported 56% organic liquid fraction as well as residue of 36% and 8% non-condensable gases. The organic liquid fraction was distilled into four fractions and the heavy fraction (distillation temperature > 200 °C) was characterized. The main compounds were hydrocarbons (alkanes, alkenes alkadienes and alkynes) with carbon number C8-C20 and carboxylic acids with carbon numbers C6-C18 and minor compounds being alcohols and esters. Fuel property testing following ASTM methods revealed the distillate conformed to the Brazilian diesel fuel specification with the exception of Acid index which was significantly higher than the maximum recommended. Studies by Ito et al. [89] evaluated the pyrolysis of beef tallow and waste cooking oil at 360-420 °C for reaction time of 0-120 min at the reaction temperature and a starting pressure of 490 kPa. They reported a hydrocarbon fraction yield of 60% at 420 °C and 120 min reaction time together with a fatty acid yield of 15% under the same conditions. The hydrocarbons had carbon numbers ranging from C8-C19. The hydrocarbon fraction was reported to have a distillation temperature range of 100 to 550 °C. However, the researchers did not indicate how the fatty acids were separated from the hydrocarbons. Biswas and Sharma [26] pyrolyzed the inedible jatropha oil in a batch system at 300-375 °C for reaction times of 2-10 min at atmospheric pressure. At 375 °C, they reported 100% conversion with 73% liquid, 26% gaseous and less than 1% char production. Compounds in the liquid product included alkanes, alkenes, cycloalkanes and carboxylic acids.

Another means of improving process economics is the use of continuous systems as batch processes have some drawbacks for large scale operations, such as low throughput and clean-up after each operation. Wiggers et al. [90] studied the thermal conversion of soybean oil in a pilot scale tubular flow reactor. Operation conditions were 450-600 °C, at atmospheric pressure, a feed mass flow rate of 3.06 kg/h and residence time between 10 and 37 s. The effect of steam was investigated at a water to feed ratio of 0:10 to 1:9. Results showed that liquid product yields ranged from 34-88% and gas product yields were 12-66% and were dependent on the operating conditions employed. The liquid bio-oils were fractionated into light bio-oil and heavy bio-oil to represent gasoline and diesel fraction, respectively. Distillation curves of the bio-oils together with petroleum derived gasoline and diesel showed the respective bio-oils to have good similarity to the petroleum derived gasoline and diesel fractions. In other studies, Wiggers et al. [91] and Wisniewski et al. [92] studied the pyrolysis of waste fish oil in a similar pilot scale tubular flow reactor at 525 °C and atmospheric pressure, feed mass flow rate of 3.21 kg/h and residence time of 17 s. Product distribution was

73% liquid, 16% gas and 11% coke. The liquid product was fractionated into light and heavy bio-oils and characterized. They reported carbon numbers of C5-C12 in the light bio-oil and C10-C26 in the heavy bio-oil fraction. The compounds identified in the bio-oils were alkanes, alkenes, aromatics and carboxylic acids. The authors studied the conversion of waste cooking oils in the same pilot plant tubular flow reactor at temperatures of 475-500 °C at atmospheric pressure and residence times of 15-70 s and feed mass flow rate of 0.78-3.65 kg/h [93]. Similar results as reported in the previous studies utilizing waste fish oils and soybean oil were reported.

2.3.2. Pyrolysis of fatty acids and fatty acid soaps

The pyrolysis of lipids in the form of TAGs have been extensively studied. However, the pyrolysis of other lipid derivatives such as free fatty acids or salts of fatty acids have received very little attention. Soaps are fatty acid salts which are formed either by reaction of free fatty acids with an alkali and the reaction of TAG based oil or fat with an alkali. The latter proceeds through hydrolysis of the fatty acid acylglycerol before the alkali reaction with the fatty acid formed to produce soaps. Soaps are also produced during the neutralization step of the oil refining process for edible purposes [94].

Hartgers et al. [95] studied the pyrolysis of model sodium salts of palmitic, oleic acid and linoleic acids using a pyroprobe at 770 °C for 10 s. They reported the formation of *n*-alk-1-enes and *n*-alkanes, ranging in carbon number up to C15 in the case of palmitic acid sodium salt as the main compounds. The pyrolysis products of the oleic acid and linoleic acid sodium salts were characterized by the formation of linear alkenes up to C11 and linear alkadienes from C11-C17. No aromatic compounds were detected in the pyrolysis product of the palmitic acid sodium salt whereas trace amounts of aromatic compounds were reported for the sodium salts of oleic and linoleic acids. In a similar study, Lappi and Alen [96] studied the pyrolysis of the sodium salts of stearic, oleic acid linoleic acids at 450-600 °C for 20-80 s using a pyroprobe. They reported similar results to those obtained by Hartgers et al. [95] as the primary products. However, they also reported the formation of oxygenated as well as aromatic compounds when the saturated salt was pyrolyzed. This could be due to the longer reaction time used in their study. In a follow up study, Lappi and Alen [97] studied the pyrolysis of the sodium salts of palm, olive, rapeseed and castor oils at 750 °C for 20 s using a pyroprobe. They reported that products in the petroleum-derived gasoline and diesel range were formed along with undesirable oxygenated compounds. Santos et al. [87] pyrolyzed soybean soapstock at 350-400 °C at atmospheric pressure. They reported 30% organic liquid product, 30% gas product and 16% residue. The organic liquid product was distilled and the fraction with distillation temperature greater than 200 °C analyzed. They reported the fraction had properties similar to those outlined for diesel fuel in Brazil with the exception of acid index and carbon residue which were slightly higher than the specified maximum. A similar observation was made by Doll et al. [82] who also pyrolyzed soybean soapstock.

Dupain et al. [98] carried out thermal cracking of oleic acid in a continuous reactor at 525 °C for 2.9 s at atmospheric pressure. They reported a conversion of 19% and the fatty acid was largely unaffected by the reaction conditions used. Maher et al. [99] on the other hand studied the batch thermal cracking of stearic acid at 350-500 °C for reaction times of 0.5 to 8h at starting pressure of atmospheric pressure. Conversions of 32 to 97 weight % of feed which were highly dependent on the reaction conditions were reported. Main products were *n*-alkanes and alkenes as well as low molecular weight saturated and unsaturated carboxylic acids and eventually aromatic compounds as temperature and reaction times increased.

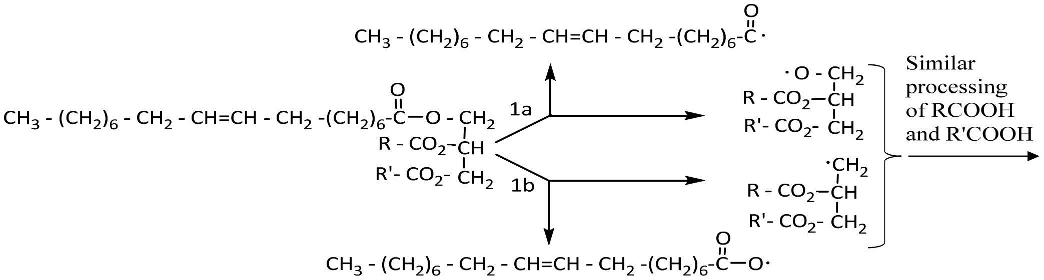
2.3.3. Reaction mechanisms

The thermal cracking of TAGs has been studied for decades and several researchers have proposed mechanisms to account for the reactions occurring. The thermal decomposition is thought to proceed through either a free radical mechanism or through carbonium ion mechanism [100, 101]. Chang and Wan [80] proposed a mechanism for the thermal decomposition of TAGs involving sixteen reaction types. Alencar et al. [102] and Schwab et al. [100] proposed mechanisms to account for the thermal decomposition of saturated and unsaturated TAG moieties, respectively. Later, Idem et al. [103] built on the previous mechanisms and proposed a more detailed mechanism for the thermal decomposition of TAGs. The above mechanism has been thoroughly reviewed by Maher and Bressler [6].

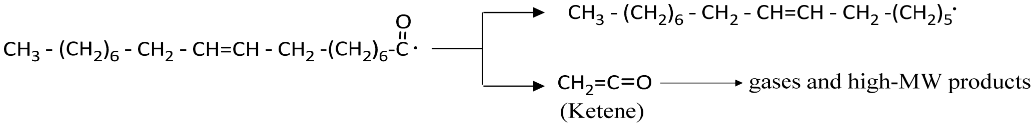
Kubatova et al. [86] proposed primary reactions in the general mechanism for the thermal TAG cracking shown in Figure 2.1. The proposed mechanism build on those proposed by earlier researchers to account for the formation of branched hydrocarbons (equation 7) as well fatty acids cracking (equation 11). The thermolysis of the TAG ester bond to produce carboxyl radical (equation 1a) or a carbonyl radical (equation 1b) is thought to be the initial reaction. Alkanes and alkenes are then formed though decarboxylation and the carboxyl radical (equation 3) and deketenization of the carbonyl radical (equation 2).

The branched hydrocarbons are thought to be formed through the direct isomerization of radicals to more stable forms (equation 7a) and the reaction of radicals with double bonds. The presence of double bonds results in an enhancement of the cleavage at the allylic position (β- to the double bond). This reaction is predominant when the fatty acid moieties are unsaturated due to the lower bond dissociation energy of the allylic C-C bond compared to saturated C-C bonds or the C-C bond adjacent to the carboxyl group [86, 95, 104, 105].

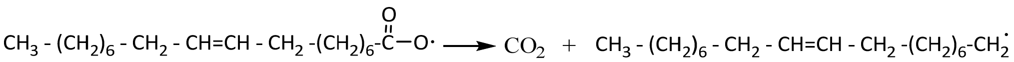
(1) Thermolysis of the triacylglycerol ester bond



(2) Deketenization (continuation of reaction 1a)

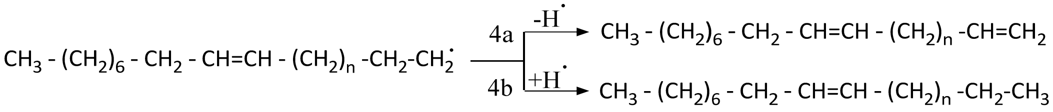


(3) Decarboxylation (continuation of reaction 1b)

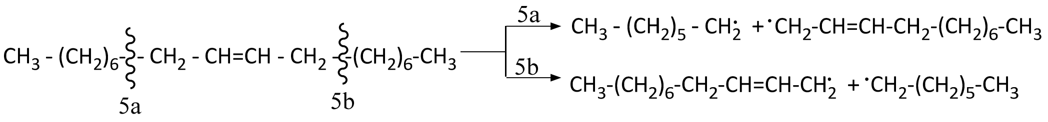


$$CH_3-(CH_2)_6-CH_2-CH{=}CH-CH_2-(CH_2)_6-\overset{O}{\overset{\|}{C}}-O\cdot \longrightarrow CO_2 + CH_3-(CH_2)_6-CH_2-CH{=}CH-CH_2-(CH_2)_6-CH_2^{\bullet}$$

(4) Stabilization of radicals



(5) Cracking of unsaturated hydrocarbons (shown for predominant allyl position)



(6) Splitting Decomposition of paraffins

(6a) Moving the double bond

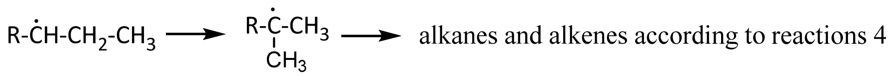
$$CH_3-(CH_2)_6-CH_2-CH{=}CH-CH_2-CH_2-(CH_2)_n-CH{=}CH_2 \longrightarrow CH_3-(CH_2)_6-CH_2-CH{=}CH-CH{=}CH-(CH_2)_n-CH_2-CH_3$$

(6b) Forming more stable radicals

$$CH_3-(CH_2)_n-CH_2-CH_2^{\bullet} \longrightarrow CH_3-(CH_2)_n-\dot{C}H-CH_3$$

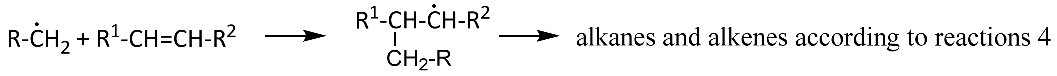
(7) Formation of branched radicals

(7a) Direct isomerization to form more stable radicals



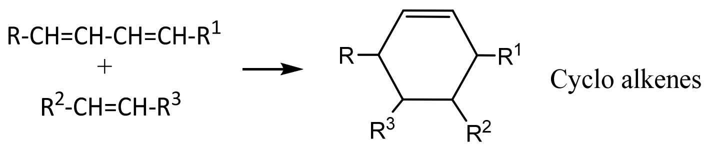
$$R\text{-}\dot{C}H\text{-}CH_2\text{-}CH_3 \longrightarrow R\text{-}\underset{CH_3}{\overset{\bullet}{C}}\text{-}CH_3 \longrightarrow \text{alkanes and alkenes according to reactions 4}$$

(7b) Reactions of radicals with double bonds

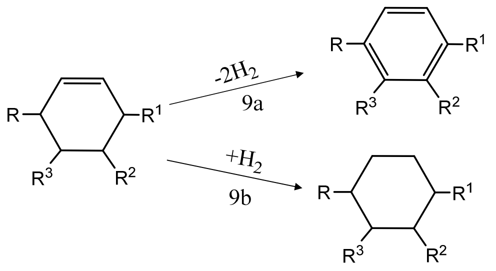


$$R\text{-}\dot{C}H_2 + R^1\text{-}CH{=}CH\text{-}R^2 \longrightarrow R^1\text{-}\underset{CH_2\text{-}R}{CH}\text{-}\dot{C}H\text{-}R^2 \longrightarrow \text{alkanes and alkenes according to reactions 4}$$

(8) Diels-Alder reaction



(9) Hydrogen abstraction and dehydrogenation



(10) Termination

$$R\text{-}\dot{C}H_2 \;+\; R^1\text{-}\dot{C}H_2 \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}R^2$$

(11) Fatty acid cracking

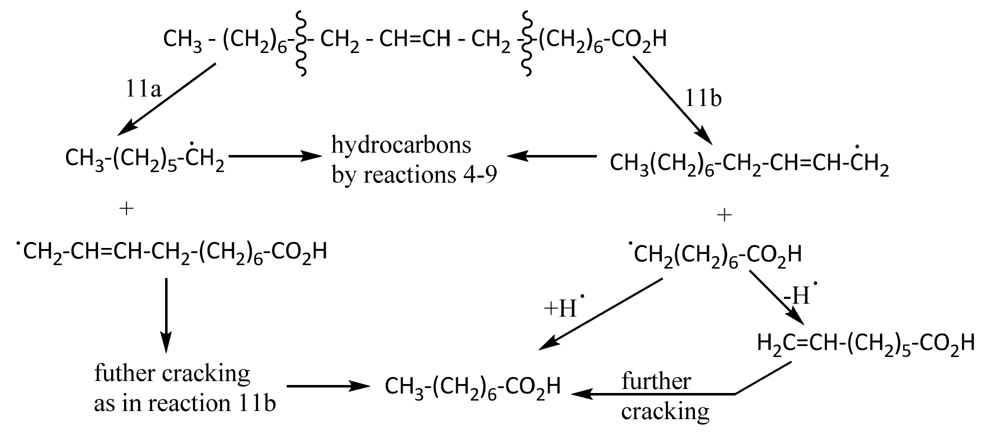


Figure 1.1. Primary reactions involved in the general mechanism of TAG cracking (reprinted with permission [86])

The formation of cyclic compounds especially six membered structures are generally accepted to be due to the Diels-Alder reaction of a diene with a dienenophile [103]. However, a new mechanism has recently been postulated by Kubatova et al. [106] as shown in Figure 2.2. The formation of cyclic compounds as proposed by the researchers involves the intramolecular cyclization of alkenyl radicals with terminal double bonds. Cyclopentanes and cyclopentenes are formed from the endo-cyclization of alkenyl radicals with radical at the γ-position to the double bond (equation 1) and exo-cyclization of alkenyl radicals with the radical at the δ-position to the double bond (equation 2). Cyclohexanes and cyclohexenes on the other hand are formed through endo-cyclization of alkenyl radical with radical at the δ-position and the exo-cyclization of alkenyl radical with the radical at the ε-position to the double bond (equations 2 and 3).

Monoaromatic compounds are formed through dehydrogenation of cyclohexanes and cyclohexenes as shown in Figures 2.3 and 2.4 [100, 103, 106-108]. Polyaromatic compounds are then formed through the polymerization and dehydrogenation of monoaromatic compounds. Another route for the formation of polyaromatic hydrocarbon (PAH) products has been suggested by Kubatova et al. [106] as shown in Figure 2.3. The mechanism involves the intramolecular cyclization of cyclic six membered alkenyl radicals and subsequent free radical reactions.

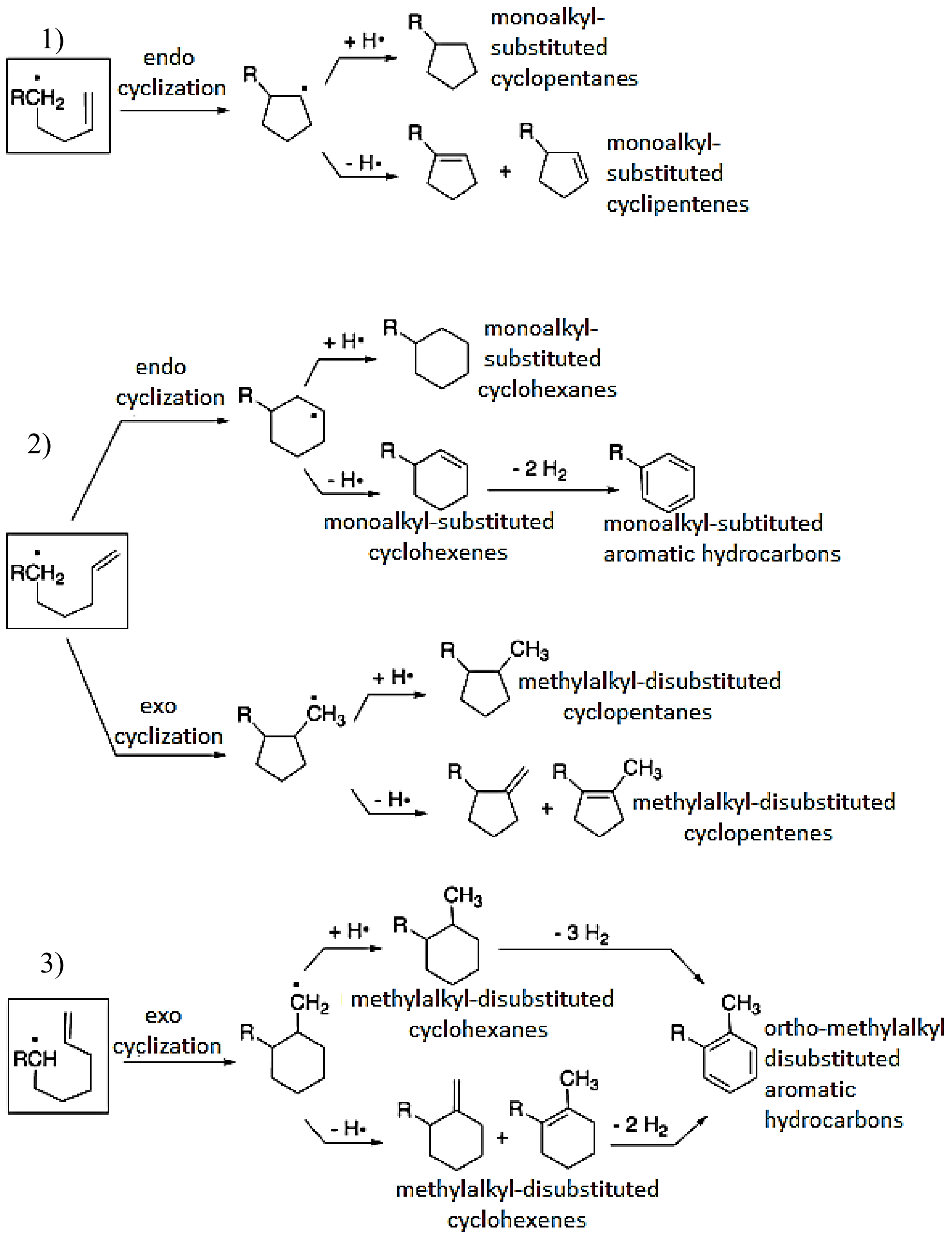


Figure 2.2. Intramolecular radical cyclization mechanism to produce monocyclic hydrocarbons (reprinted with permission [106])

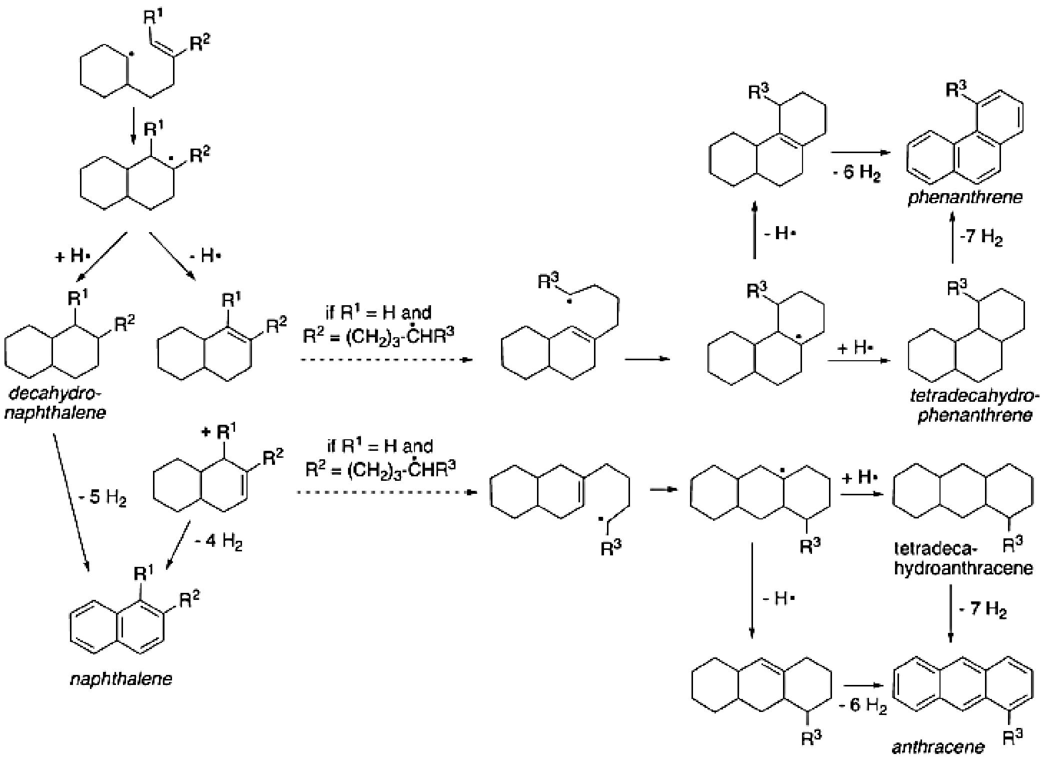


Figure 2.3. Six-membered PAH formation via intramolecular radical cyclizations (reprinted with permission [106])

A mechanism for the thermal cracking of stearic acid has been proposed by Maher et al. [99] and is shown in Figure 2.4. The mechanism involves the initial decarboxylation of the fatty acid to form *n*-heptadecane, which then undergo cracking reactions to produce low molecular weight alkanes and alkenes. Secondary reactions such as addition, isomerization and aromatization are responsible for high molecular weight hydrocarbon and aromatic compounds formation.

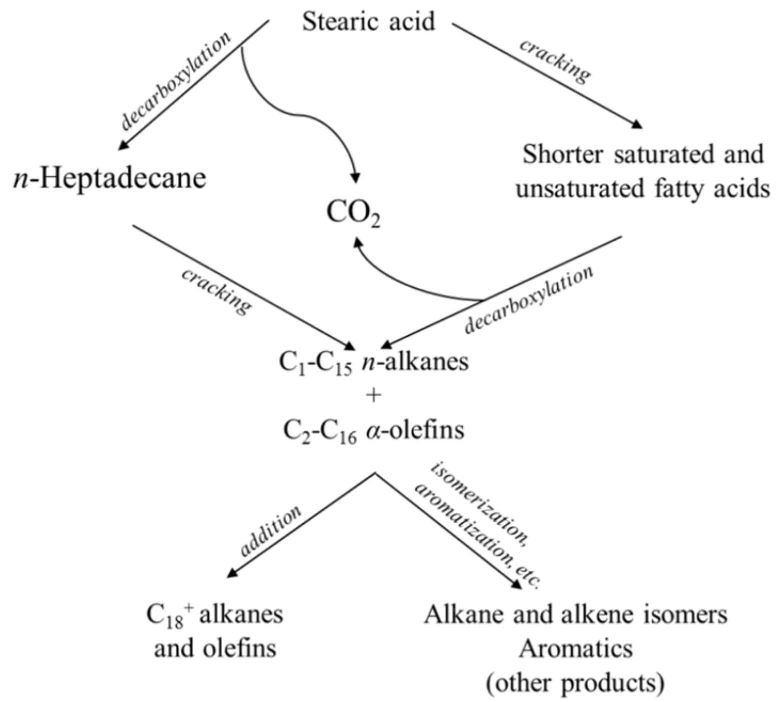


Figure 2.4. Proposed reaction scheme for the pyrolysis of stearic acid (reprinted with permission [99]).

2.4. Thermo-catalytic conversion of TAGs and derivatives

The thermo-catalytic conversion of TAG materials has been widely studied and a wealth of literature is available in this area. Thermo-catalytic conversion has the advantage of requiring lower reaction temperatures when compared to thermal cracking as well as the higher selectivity of reaction products in the case of thermo-catalytic cracking [9, 109-111]. Catalytic cracking of vegetable oils and animal fats can generally be classified into two categories; in the absence of hydrogen and in the presence of hydrogen (referred to as hydroprocessing or hydrotreating). Catalytic cracking of vegetable oils and animal fats in the absence of hydrogen are aimed primarily at producing hydrocarbons in the gasoline range whereas hydrotreating aims to produce hydrocarbons in the diesel range [112]. The initial work on the catalytic conversion of TAG materials into hydrocarbons has been reported by Rao [113]. One of the first studies dealing with the thermo-catalytic cracking of vegetable oils to hydrocarbons is the work by Weisz et al. [114]. They reported yields of 42-78% paraffins, olefins and aromatics using HZSM-5 catalyst. Several thermo-catalytic studies have been reported in the literature following the initial work by the authors. The next subsections will review the current literature on the thermo-catalytic conversion of TAGs and their derivatives with and without hydrogen (hydrotreating).

2.4.1. Catalytic conversion of TAG and derivatives

Catalytic conversion of TAG materials in the absence of hydrogen has been carried out mostly with HZSM-5, β, USY and MSM-41 zeolite materials and their composites. Zeolites belong to a wider group of aluminosilicates referred to as molecular sieves [115]. They are porous solids with pore sizes between 2-10 Å which is described by IUPAC as microporous. The crystalline aluminosilicate materials of zeolites have rigid honeycomb-like pore structures which are three dimensional network of AlO_4 and SiO_4 tetrahedrally linked through oxygen anions (Campbell, 1983). The widespread use of zeolites as catalysts, catalyst support and adsorbent are the result of their tuneable acidic properties, high surface area, thermal stability and well-defined microporosity properties [116-118].

Between 1995 and 1999, a group of Canadian scientists extensively studied the catalytic cracking of canola oil using HZSM-5 and various hybrids of it as well as aluminophospate systems (SAPO-5, SAPO-11 and MgAPO-36) [119-126]. The effect of reaction conditions were also studied with temperatures between 300-500 °C under inert atmosphere at atmospheric pressure and weight hourly space velocity (WHSV) ranging from 1.8-3.6 h^{-1}. They reported very high yields especially in the case of HZSM-5 catalysts (up to 100%) and high aromatic compound yields of up to 63%. The aluminophosphate systems had the lowest liquid product yields of about 48% of the feed.

Ooi and Bhatia [127] studied the conversion of waste used palm oil to hydrocarbons using aluminum-containing mesoporous materials (SBA-15 and AL-SBA-15) in a fixed-bed microreactor at 450 °C and WHSV of 2.5 h^{-1} at atmospheric pressure. They reported products consisting mainly of liquid organic product, gaseous product, water and coke. The conversion was between 50-72 wt % of feed after 5 h of reaction. They also reported a decrease in the yield with time and attributed it to catalyst deactivation due to coke formation. Increasing the initial catalyst loading resulted in an increase in conversion to between 75-95% after 6.4 h reaction. The desired gasoline fraction of the liquid product ranged from 23-40% after 6.4 h reaction.

The catalytic conversion of chicken fat, palm oil and soybean oil was studied in a riser fluid catalytic cracking (FCC) reactor using a mixture of USY and ZSM-5 catalysts [128]. They reported a conversion of 97% for chicken fat, 98% for palm oil and 96% for soybean oil with gasoline fraction of 34%, 42% and 36%, respectively, for chicken fat, palm oil and soybean oil. In another study, Bielansky et al. [129, 130] studied the catalytic conversion of rapeseed, soybean and palm oils in a riser FCC at 500 °C and feed rate of 3 L/h at atmospheric pressure using a REUSY-catalyst which was partially coated with ZSM-5. They reported conversions of up to 80% for the various oils with gasoline fraction staying constant between 40-43%. They also reported that the oxygen in the oils was converted predominantly to water.

Studies involving the use mesoporous catalysts such as MCM-41 have received a great deal of attention in recent literature due to the higher selectivity for the desirable liquid product over gaseous product [6, 131, 132]. Lu et al. [133] studied the conversion of rubber seed oil to liquid hydrocarbons in a batch glass reactor at 400-440 °C at a heating rate of 20 °C/min and atmospheric pressure using mesoporous MCM-41 with different base sites. They reported conversions of 80% without the use of catalyst and 82-92% with the use the MCM-41 with base sites. The highest conversion was achieved with K_2O/Ba-MCM-41 whereas the lowest conversion was achieved with Si-MCM-41 catalyst. The bio-oil yields followed a similar trend with the conversion with K_2O/Ba-MCM-41 catalyst giving the highest yield of 72%.

Ramya and Sivakumar [134] studied the pyrolysis of jatropha oil in a fixed-bed flow reactor at 400 °C, WHSV of 4.6 h^{-1} and reaction time of 1 h using ALMCM-41with different Si/Al ratios. The results showed conversion of 55-65% which were heavily dependent on the Si/Al ratio of the catalyst. The lower the Si/Al ratio the higher was the conversion. Similarly, the bio-oil yield was influenced by the Si/Al ratio with lower ratios favouring higher bio-oil yield. The observed trend was explained in terms of decreasing acidity with increasing Si/Al ratio. In a follow up study, Ramya et al. [135] studied the pyrolysis of jatropha oil under similar condition using a similar reactor with HZSM-5, AlMCM-41 and composite of HZSM-5 and AlMCM-51 catalysts. The results showed similar conversion when HZSM-5 or ALMSM-41 was used (approximately 65%). However, AlMCM-41 had a higher bio-oil yield compared to HZSM-5. A composite of 5% or 10% AlMCM-41 over HZSM-5 resulted in a significant increase in conversion of 94% and 99% respectively. Bio-oil yields were also significantly increased to 70%.

The reaction mechanisms for the catalytic conversion of TAGs are complex but can be classified into primary and secondary reactions. A general reaction mechanism for the catalytic cracking of TAG molecules is shown in Figure 2.5. The mechanism is thought to involve the thermal and catalytic cracking of the TAG molecule to produce heavy hydrocarbons and oxygenated compounds on the surface of the catalyst [109, 136]. Once the TAG molecule has been primarily decomposed to less bulky compounds such as free fatty acids, ketones, aldehydes and esters, their transformation into different products starts by breaking the C–O and C–C bonds by β-scission reactions. The presence of double bonds influences the preferential breaking of the C-C beta to the double bond over the C-C bond adjacent to the carboxyl or carbonyl group [95, 103, 136-138]. Secondary reactions include the formation of cyclic compounds and subsequent aromatization of six membered ring structures through dehydrogenation and further to coke formation through polymerization and dehydrogenation of monoaromatic compounds (Figure 2.5).

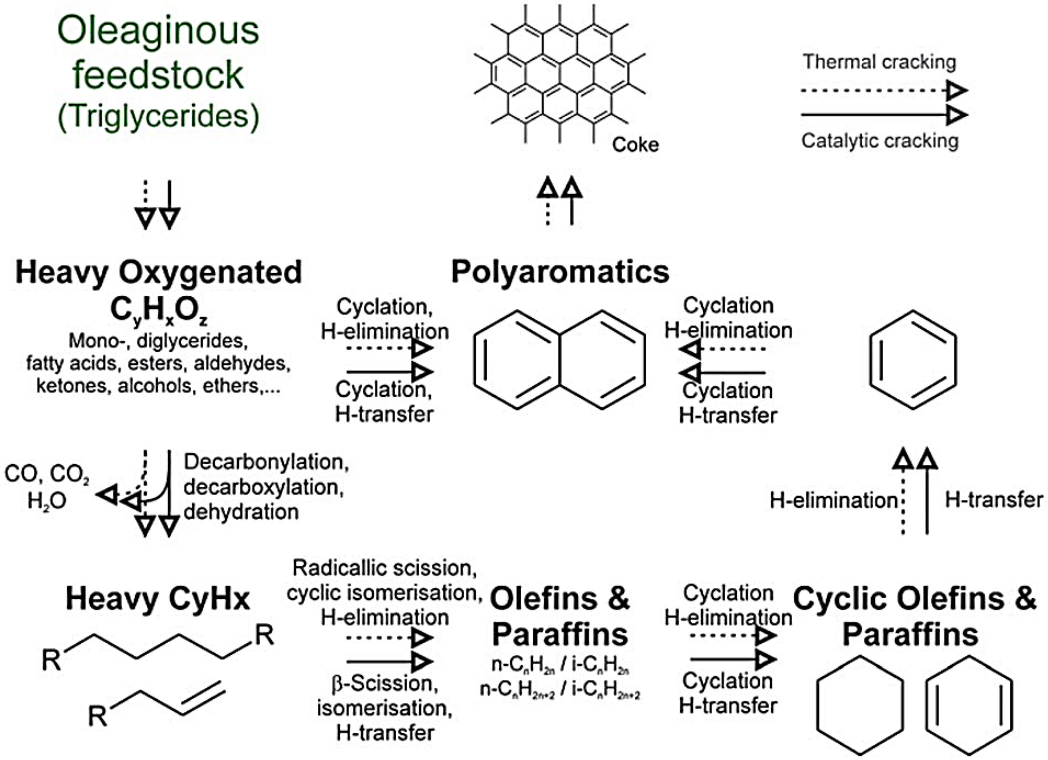


Figure 2.5. Proposed **r**eaction mechanism for the catalytic cracking of TAG molecules (reprinted with permission [136]).

2.4.2. Hydrotreating of TAG and derivatives

There is renewed interest in the hydrotreating of TAGs to produce renewable hydrocarbons. Hydrotreating is used extensively in the petroleum refinery industry to remove sulphur, nitrogen and metals from petroleum-derived feedstocks such as heavy oils and vacuum-gas oil [139]. Hydrotreating of TAG materials has several advantages including compatibility with current petroleum infrastructure, production of deoxygenated hydrocarbon products which can be hydroisomerized to high quality diesel or hydrocracked to kerosene, stability of products and low sulphur and nitrogen content [139-142]. Several studies involving the hydrotreating of vegetable oils have been reported in the literature. Studies involving the use of model compounds such as fatty acids and model TAGs [143-150], as well as vegetable oils and animal fats [151-158] and inedible and waste oils and fats [139, 159-165] are available in the literature. There have been several recent reviews of the hydrotreating of TAG material and detailed information on the feedstocks, catalysts as well as reaction conditions effect is available [109, 112, 136, 140, 166-168].

There are several commercial plants in operation that employ the hydroprocessing of TAG materials for the production of renewable hydrocarbons. Neste Oil company has commercialized the hydrotreating of vegetable oils and animal fats to produce hydrocarbon fuels, the NExtBTL (next generation biomass to liquid). The biofuel obtained from NExtBTL process has high cetane index (84-99) and does not contain oxygen or nitrogen. The diesel can be blended with petroleum-derived diesel from 0-100%. There are currently four commercial plants with a combined output of 2 million tonnes per year [169]. Another commercial example of hydrotreating of vegetable oils and animal fats is the UOP/Eni Ecofining technology for converting TAG based feedstocks into high cetane diesel fuels [170]. The hydrocarbons produced are 100% compatible with existing petroleum infrastructure with high diesel yields (88-99% by volume) [112].

2.5. Co-processing of TAG and derivatives with petroleum fractions

An area of research that is becoming increasingly important is the co-processing of vegetable oils and animal fats with petroleum fractions such as vacuum-gas oil and heavy oil. Co-processing has several advantages the most important of which is the use of existing petroleum infrastructure with little or no modification thereby eliminating the cost of setting up a new processing unit [159, 171-173]. Other advantages include compatibility with automotive engines, feedstock flexibility, increase in cetane number and reduction in sulphur content [140, 174].

Huber et al. [174] studied the co-processing of sunflower oil and heavy vacuum-oil in a fixed bed reactor with conventional hydrotreating catalyst (sulphided $NiMo/Al_2O_3$) at 300-450 °C, 50 bar (5000 kPa), liquid hourly space velocity (LHSV) of 4.97 h^{-1} and hydrogen to feed ratio of 1600 mL H_2/mL liquid feed. They reported that the reaction pathway involves the hydrogenation of the double bonds in the vegetable oil followed by the production of alkanes through three different mechanisms; decarboxylation, decarbonylation and hydrodeoxygenation. They further observed that the addition of sunflower oil to hydrotreating reactions of heavy vacuum-oil did not affect the hydrodesulphurization of the heavy vacuum-oil indicating addition of sunflower oil did not inhibit the hydrotreating of heavy vacuum-oil. They postulated that the observation indicates the hydrotreating of sunflower oil and hydrodesulphurization probably occur on different catalytic sites. In another study, Donnis et al.[175] made a similar hydrodesulphurization observation when rapeseed oil (15-25%) was co-processed with light gas oil at 350 °C using commercial hydrotreating catalyst. They also reported complete conversion of the rapeseed oil feed which resulted in a high yield of diesel product though the overall yield was lower than when 100% light gas oil was hydrotreated. The observed lower overall yield was attributed to the formation of water, propane and CO_2 from the hydrotreating of the TAGs in the rapeseed oil.

Melero et al. [108] studied the co-processing of soybean oil, palm oil, inedible animal fats and waste cooking oil with vacuum gas oil in a FCC at the 30% mass of the vacuum gas oil. The reaction conditions employed were 565 °C for 12 s contact time with an industrial FCC equilibrium catalyst. Similar to the previous co-processing studies, they also reported complete conversion of the TAG feeds to a mixture of hydrocarbons, CO_2, CO and water. They also reported a reduction in the liquid hydrocarbon yield and an increase in coke and gas yield with the TAG feedstocks. Aromatic compounds formation was enhanced especially with the highly unsaturated TAG feedstocks (soybean oil and waste cooking oils). The decrease in the liquid product yield was attributed to the deoxygenation of the TAG feeds as well as increased coke formation due to the increased aromatic compounds formation. Similarly, Bielansky et al. studied the co-processing of rapeseed oil [130] and soybean and palm oil [129] in a FCC pilot plant. They reported no effect of the triacyglycerol feedstock on the gasoline yield although total fuel yield decreased which was attributed to oxygen removal. However, unlike the study by Melero et al. [139] they reported no influence on coke formation with the addition of the TAG feed. The level of unsaturation of the TAG feed was also found to influence the aromatic compound formation, with higher degree of unsaturation promoting aromatic compounds formation. Bezergianni et al. [142] studied the co-processing of sunflower oil with vacuum gas oils in a FCC pilot plant using commercial hydrocracking catalysts. Unlike the other studies which reported no effect on the hydrodesulphurization of the vacuum gas oil, they reported an inhibition of sulphur and nitrogen removal with the addition of sunflower oil to vacuum gas oil at 10 and 30% mass of the vacuum gas oil. The observed inhibition is due to the use of hydrocracking catalyst instead of hydrotreating catalysts, which are designed purposely for the removal of sulphur from the feed.

In other studies the researchers assessed the potential of co-processing of rapeseed oil [176], waste soybean oil [159, 172, 177], canola oil [178] and sunflower, rapeseed, mustard seed and palm oils [179] with vacuum gas oil using commercial hydrotreating catalysts. The TAG feedstocks were blended at levels of up to 40% of the mass of the vacuum gas oil. They all reported complete conversion of the TAGs into hydrocarbons, CO_2, CO and water. They further reported that the co-processing of the vacuum gas oil with the vegetable oil feedstock did not impact the hydrodesulphurization of the vacuum gas oil. Thus the deoxygenation of the vegetable oils and the hydrodesulphurization of the vacuum gas oil are not competing reactions and may be occurring at different sites of the catalysts. An increase in the gasoline and aromatic compound yields were also reported.

2.6. Oils and fats hydrolysis

Vegetable oils and animal fats are composed predominantly of TAGs, which consists of glycerol esterified to three fatty acids. In this research, the pyrolysis study will be carried out using protonated free fatty acids. Thus, the vegetable oil and animal fat feedstocks have to be hydrolyzed to release the fatty acids. High temperature and high pressure hydrolysis has been the commonly most used industrial fat splitting/hydrolysis process. The most widely used processes are the Twitchell process involving the use of acid (H_2SO_4) to catalyze the conversion of TAGs to fatty acids and glycerol [180] and the Colgate-Emry process [181, 182] involving high temperature high pressure splitting under conditions usually referred to as subcritical.

Thermal hydrolysis of vegetable oils and animal fats have been reported in the literature at temperatures ranging from 240-350 °C and 10-20 MPa pressure with complete conversion of the TAGs to free fatty acids [182-184]. The reaction has been reported to involve three stepwise reversible reactions as shown in Figure 2.6. The reaction is thought to be first order reaction occurring in the oil phase [185]. The reaction can be driven to completion with increasing temperature and water to oil ratio as well as reaction pressure [182].

$$\text{TAG} + H_2O \rightleftharpoons \text{DAG} + \text{FFA} \qquad \text{Step 1}$$

$$\text{DAG} + H_2O \rightleftharpoons \text{MAG} + \text{FFA} \qquad \text{Step 2}$$

$$\text{MAG} + H_2O \rightleftharpoons \text{Glycerol} + \text{FFA} \qquad \text{Step 3}$$

Figure 2.6. Reaction scheme for the hydrolysis of TAG

2.7. Conclusions

There has been renewed interest in the last decades in the research and development of renewable alternatives to petroleum-derived fuels and chemicals. Of the various renewable biomass being explored for production of liquid fuel and chemical alternatives to petroleum, lipids in the form of vegetable oils and animal fats are the most promising due to their high energy content, relatively simple structure and lower oxygen content. Vegetable oil and animal fat conversion to biodiesel has been researched and currently being produced commercially. However, biodiesel has some drawbacks such as lower energy density and poor cold flow properties compared to conventional diesel. The use of pyrolysis or thermal cracking to convert oils and fats to renewable hydrocarbon free of oxygen hold one the most potential for producing liquid petroleum fuel alternatives. Research has mainly focused on the pyrolysis of whole vegetable oils and animal fats that are composed predominantly of TAG. Only limited studies have been reported on the thermal conversion or pyrolysis of free fatty acids that can be readily obtained from TAG feedstocks through hydrolysis. There is therefore the need to better understand the mechanism and primary reaction products of thermal cracking of free fatty acids. The understanding of these mechanisms and product formation will help evaluate the potential feasibility of converting TAG feeds to hydrocarbons through hydrolysis followed by pyrolysis of the fatty acids.

2.8. References

[1] P.A.Z. Suarez, A.L.F. Santos, J.P. Rodrigues, M.B. Alves, Oils and fats based biofuels: technological chalendges, Quimica Nova, 32 (2009) 768-775.

[2] U.S. Energy Information Administration, International Energy Outlook 2013, in, 2013. Available online at http://www.eia.gov/forecasts/ieo/pdf/0484(2013).pdf. last accessed October, 2013.

[3] M. Arend, T. Nonnen, W.F. Hoelderich, J. Fischer, J. Groos, Catalytic deoxygenation of oleic acid in continuous gas flow for the production of diesel-like hydrocarbons, Applied Catalysis a-General, 399 (2011) 198-204.

[4] A. Abbaszaadeh, B. Ghobadian, M.R. Omidkhah, G. Najafi, Current biodiesel production technologies: A comparative review, Energy Conversion and Management, 63 (2012) 138-148.

[5] S.P.A. Brown, H.G. Huntington, Assessing the US oil security premium, Energy Economics, 38 (2013) 118-127.

[6] K.D. Maher, D.C. Bressler, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals, Bioresource Technology, 98 (2007) 2351-2368.

[7] US Energy Iinformation Administration, The Availability and Price of Petroleum and Petroleum Products Produced in Countries Other Than Iran. Washington, DC, 2013.

[8] US Energy Information Administration, Technically Recoverable Shale Oil and Shale Gas Resources: An Assessment of 137 Shale Formations in 41 Countries Outside the United States, in, 2013. Available online at http://www.eia.gov/analysis/studies/worldshalegas/pdf/fullreport.pdf Last accessed Dec. 2013.

[9] N. Taufiqurrahmi, S. Bhatia, Catalytic cracking of edible and non-edible oils for the production of biofuels, Energy & Environmental Science, 4 (2011) 1087-1112.

[10] A.V. Bridgwater, G.V.C. Peacocke, Fast pyrolysis processes for biomass, Renewable & Sustainable Energy Reviews, 4 (2000) 1-73.

[11] A.V. Bridgwater, Renewable fuels and chemicals by thermal processing of biomass, Chemical Engineering Journal, 91 (2003) 87-102.

[12] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass & Bioenergy, 38 (2012) 68-94.

[13] S. Uçar, S. Karagöz, The slow pyrolysis of pomegranate seeds: The effect of temperature on the product yields and bio-oil properties, Journal of Analytical and Applied Pyrolysis, 84 (2009) 151-156.

[14] N.O.V. Sonntag, Structure and composition of fats and oils, 4th ed., John Wiley and Sons, New York, 1979, pp 1-19..

[15] A. Demirbas, Biorefineries: Current activities and future developments, Energy Conversion and Management, 50 (2009) 2782-2801.

[16] N.O.V. Sonntag, Structure and composition of fats and oils, 4th ed., John Wiley and Sons, New York, 1979, pp 34-55.

[17] J. van Gerpen, Biodiesel from vegetable oils, in: A.A. Vertes, N. Qureshi (Eds.) Biomass to Biofuels, John Wiley and Sons Ltd., Chichester, West Sussex, UK, 2010, pp. 141-163.

[18] A. Demirbas, Diesel fuel from vegetable oil via transesterification and soap pyrolysis, Energy Sources, 24 (2002) 835-841.

[19] A. Demirbas, M.F. Demirbas, Importance of algae oil as a source of biodiesel, Energy Conversion and Management, 52 (2011) 163-170.

[20] A. Demirbas, Progress and recent trends in biofuels, Progress in Energy and Combustion Science, 33 (2007) 1-18.

[21] F. Karaosmanoglu, E. Tetik, E. Gollu, Biofuel production using slow pyrolysis of the straw and stalk of the rapeseed plant, Fuel Processing Technology, 59 (1999) 1-12.

[22] F. Karaosmanoglu, Vegetable oil fuels: A review, Energy Sources, 21 (1999) 221-231.

[23] M.M. Gui, K.T. Lee, S. Bhatia, Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock, Energy, 33 (2008) 1646-1653.

[24] A. Demirbas, Progress and recent trends in biodiesel fuels, Energy Conversion and Management, 50 (2009) 14-34.

[25] U.N. Food and Agricultural Organization, Crops Production, in, 2013.

[26] S. Biswas, D.K. Sharma, Studies on cracking of Jatropha oil, Journal of Analytical and Applied Pyrolysis, 99 (2013) 122-129.

[27] M. Cardone, M.V. Prati, V. Rocco, M. Seggiani, A. Senatore, S. Vitolo, Brassica carinata as an alternative oil crop for the production of biodiesel in Italy: Engine performance and regulated and unregulated exhaust emissions, Environmental Science & Technology, 36 (2002) 4656-4662.

[28] M.Y. Koh, T.I.M. Ghazi, A review of biodiesel production from jatropha curcas L. oil, Renewable & Sustainable Energy Reviews, 15 (2011) 2240-2251.

[29] B.K. De, D.K. Bhattacharyya, Biodiesel from minor vegetable oils like karanja oil and nahor oil, Fett-Lipid, 101 (1999) 404-406.

[30] J. Iglesias, G. Morales, Biodiesel from waste oils and fats, Advances in Biodiesel Production: Processes and Technologies, (2012) 154-178.

[31] M. Canakci, The potential of restaurant waste lipids as biodiesel feedstocks, Bioresource Technology, 98 (2007) 183-190.

[32] M. Canakci, H. Sanli, Biodiesel production from various feedstocks and their effects on the fuel properties, Journal of Industrial Microbiology & Biotechnology, 35 (2008) 431-441.

[33] H.J. Kim, H. Hilger, S. Bae, NiSO4/SiO2 Catalyst for Biodiesel Production from Free Fatty Acids in Brown Grease, Journal of Energy Engineering-Asce, 139 (2013) 35-40.

[34] M.J. Haas, A.J. McAloon, W.C. Yee, T.A. Foglia, A process model to estimate biodiesel production costs, Bioresource Technology, 97 (2006) 671-678.

[35] M. Kim, C. DiMaggio, S.L. Yan, H.L. Wang, S.O. Salley, K.Y.S. Ng, Performance of heterogeneous ZrO2 supported metaloxide catalysts for brown grease esterification and sulfur removal, Bioresource Technology, 102 (2011) 2380-2386.

[36] S. Dufreche, R. Hernandez, T. French, D. Sparks, M. Zappi, E. Alley, Extraction of lipids from municipal wastewater plant microorganisms for production of biodiesel, Journal of the American Oil Chemists Society, 84 (2007) 181-187.

[37] C. Pastore, A. Lopez, V. Lotito, G. Mascolo, Biodiesel from dewatered wastewater sludge: A two-step process for a more advantageous production, Chemosphere, 92 (2013) 667-673.

[38] I. Fonts, G. Gea, M. Azuara, J. Abrego, J. Arauzo, Sewage sludge pyrolysis for liquid production: A review, Renewable & Sustainable Energy Reviews, 16 (2012) 2781-2805.

[39] I. Fonts, M. Azuara, G. Gea, M.B. Murillo, Study of the pyrolysis liquids obtained from different sewage sludge, Journal of Analytical and Applied Pyrolysis, 85 (2009) 184-191.

[40] E.E. Kwon, S. Kim, Y.J. Jeon, H. Yi, Biodiesel Production from Sewage Sludge: New Paradigm for Mining Energy from Municipal Hazardous Material, Environmental Science & Technology, 46 (2012) 10222-10228.

[41] D. Fytili, A. Zabaniotou, Utilization of sewage sludge in EU application of old and new methods - A review, Renewable & Sustainable Energy Reviews, 12 (2008) 116-140.

[42] E. Revellame, R. Hernandez, W. French, W. Holmes, E. Alley, Biodiesel from activated sludge through in situ transesterification, Journal of Chemical Technology and Biotechnology, 85 (2010) 614-620.

[43] M. Canakci, J. Van Gerpen, Biodiesel production from oils and fats with high free fatty acids, Transactions of the Asae, 44 (2001) 1429-1436.

[44] A.K. Agarwal, Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines, Progress in Energy and Combustion Science, 33 (2007) 233-271.

[45] K. Bunyakiat, S. Makmee, R. Sawangkeaw, S. Ngamprasertsith, Continuous production of biodiesel via transesterification from vegetable oils in supercritical methanol, Energy & Fuels, 20 (2006) 812-817.

[46] US Energy Iinformation Administration, World Biodiesel production in 2011, 2013. Available online at http://www.eia.gov/cfapps/ipdbproject/iedindex3.cfm?tid=79&pid=81&aid=1&cid=regions&syid=2007&eyid=2011&unit=TBPD Last accessed Dec. 2013..

[47] ASTM International, Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, Annual Book of ASTM Standards, ASTM, Philadelphia, PA, USA, 2012.

[48] E.C. Standardization, Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods, in, European Committee for Standardization, Brussels, Belgium, 2013.

[49] A. Demirbas, Biofuels securing the planet's future energy needs, Energy Conversion and Management, 50 (2009) 2239-2249.

[50] I.M. Atadashi, M.K. Aroua, A.A. Aziz, Biodiesel separation and purification: A review, Renewable Energy, 36 (2011) 437-443.

[51] I.M. Atadashi, M.K. Aroua, A.R.A. Aziz, N.M.N. Sulaiman, Production of biodiesel using high free fatty acid feedstocks, Renewable & Sustainable Energy Reviews, 16 (2012) 3275-3285.

[52] G. Knothe, "Designer" biodiesel: Optimizing fatty ester (composition to improve fuel properties, Energy & Fuels, 22 (2008) 1358-1364.

[53] A. Demirbas, Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification, Energy Conversion and Management, 50 (2009) 923-927.

[54] Y. Warabi, D. Kusdiana, S. Saka, Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols, Bioresource Technology, 91 (2004) 283-287.

[55] D. Kusdiana, S. Saka, Methyl esterification of free fatty acids of rapeseed oil as treated in supercritical methanol, Journal of Chemical Engineering of Japan, 34 (2001) 383-387.

[56] BIOX, available oinline at http://www.bioxcorp.com/production-process/ last accessed Sept. 2013.

[57] C.V. McNeff, L.C. McNeff, B. Yan, D.T. Nowlan, M. Rasmussen, A.E. Gyberg, B.J. Krohn, R.L. Fedie, T.R. Hoye, A continuous catalytic system for biodiesel production, Applied Catalysis a-General, 343 (2008) 39-48.

[58] V.G. Gude, G.E. Grant, Biodiesel from waste cooking oils via direct sonication, Applied Energy, 109 (2013) 135-144.

[59] J.F. Puna, M.J.N. Correia, A.P.S. Dias, J. Gomes, J. Bordado, Biodiesel production from waste frying oils over lime catalysts, Reaction Kinetics Mechanisms and Catalysis, 109 (2013) 405-415.

[60] K. Ramachandran, T. Suganya, N.N. Gandhi, S. Renganathan, Recent developments for biodiesel production by ultrasonic assist transesterification using different heterogeneous catalyst: A review, Renewable & Sustainable Energy Reviews, 22 (2013) 410-418.

[61] Z. Yaakob, M. Mohammad, M. Alherbawi, Z. Alam, K. Sopian, Overview of the production of biodiesel from Waste cooking oil, Renewable & Sustainable Energy Reviews, 18 (2013) 184-193.

[62] B.L. Salvi, N.L. Panwar, Biodiesel resources and production technologies – A review, Renewable and Sustainable Energy Reviews, 16 (2012) 3680-3689.

[63] G. Knothe, Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, Fuel Processing Technology, 86 (2005) 1059-1070.

[64] G. Knothe, C.A. Sharp, T.W. Ryan, Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine, Energy & Fuels, 20 (2006) 403-408.

[65] M. Canakci, NOx emissions of biodiesel as an alternative diesel fuel, International Journal of Vehicle Design, 50 (2009) 213-228.

[66] G. Knothe, Some aspects of biodiesel oxidative stability, Fuel Processing Technology, 88 (2007) 669-677.

[67] M. Canakci, A. Erdil, E. Arcaklioglu, Performance and exhaust emissions of a biodiesel engine, Applied Energy, 83 (2006) 594-605.

[68] S. Yaman, Pyrolysis of biomass to produce fuels and chemical feedstocks, Energy Conversion and Management, 45 (2004) 651-671.

[69] A.A. Lappas, E.F. Iliopoulou, K. Kalogiannis, S. Stefanidis, Conversion of biomass to fuels and chemicals via thermochemical processes, in: F. Dumeignil, A. Dibenedetto, M. Aresta (Eds.) Biorefinery : From Biomass to Chemicals and Fuels, [Walter] de Gruyter, Berlin, Germany, 2012, pp. 333-363.

[70] I. Demiral, A. Eryazici, S. Sensoz, Bio-oil production from pyrolysis of corncob (Zea mays L.), Biomass & Bioenergy, 36 (2012) 43-49.

[71] S. Sensoz, M. Can, Pyrolysis of pine (Pinus Brutia Ten.) chips: 1. Effect of pyrolysis temperature and heating rate on the product yields, Energy Sources, 24 (2002) 347-355.

[72] M. Balat, Mechanisms of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis, Energy Sources Part a-Recovery Utilization and Environmental Effects, 30 (2008) 620-635.

[73] G. Knothe, Biodiesel and renewable diesel: A comparison, Progress in Energy and Combustion Science, 36 (2010) 364-373.

[74] M. Stumborg, A. Wong, E. Hogan, Hydroprocessed vegetable oils for diesel fuel improvement, Bioresource Technology, 56 (1996) 13-18.

[75] C. Buziassy, W.W. Nawar, Specificity in thermal hydrolysis of triglycerides, Journal of Food Science, 33 (1968) 305-307.

[76] W.W. Nawar, Thermal degradation of lipids . A review, Journal of Agricultural and Food Chemistry, 17 (1969) 18-21.

[77] A. Crossley, T.D. Heyes, B.J.F. Hudson, Effect of heat on pure triglycerides, Journal of the American Oil Chemists Society, 39 (1962) 9-14.

[78] G. Egloff, J.C. Morrell, The cracking of cottonseed oil, Industrial and Engineering Chemistry, 24 (1932) 1426-1427.

[79] G. Egloff, E.F. Nelson, Cracking Alaskan fur-seal oil, Industrial and Engineering Chemistry, 25 (1933) 386-387.

[80] C.C. Chang, S.W. Wan, Chinas motor fuels from tung oil, Industrial and Engineering Chemistry, 39 (1947) 1543-1548.

[81] D. Fabbri, V. Bevoni, M. Notari, F. Rivetti, Properties of a potential biofuel obtained from soybean oil by transmethylation with dimethyl carbonate, Fuel, 86 (2007) 690-697.

[82] K.A. Doll, B.K. Sharma, P.A.Z. Suarez, S.Z. Erhan, Comparing biofuels obtained from pyrolysis, of soybean oil or soapstock, with traditional soybean biodiesel: Density, kinematic viscosity, and surface tensions, Energy & Fuels, 22 (2008) 2061-2066.

[83] D.G. Lima, V.C.D. Soares, E.B. Ribeiro, D.A. Carvalho, E.C.V. Cardoso, F.C. Rassi, K.C. Mundim, J.C. Rubim, P.A.Z. Suarez, Diesel-like fuel obtained by pyrolysis of vegetable oils, Journal of Analytical and Applied Pyrolysis, 71 (2004) 987-996.

[84] C.M.R. Prado, N.R. Antoniosi Filho, Production and characterization of the biofuels obtained by thermal cracking and thermal catalytic cracking of vegetable oils, Journal of Analytical and Applied Pyrolysis, 86 (2009) 338-347.

[85] Y. Luo, I. Ahmed, A. Kubatova, J. St'avova, T. Aulich, S.M. Sadrameli, W.S. Seames, The thermal cracking of soybean/canola oils and their methyl esters, Fuel Processing Technology, 91 (2010) 613-617.

[86] A. Kubatova, Y. Luo, J. Stavova, S.M. Sadrameli, T. Aulich, E. Kozliak, W. Seames, New path in the thermal cracking of triacylglycerols (canola and soybean oil), Fuel, 90 (2011) 2598-2608.

[87] A.L.F. Santos, D.U. Martins, O.K. Iha, R.A.M. Ribeiro, R.L. Quirino, P.A.Z. Suarez, Agro-industrial residues as low-price feedstock for diesel-like fuel production by thermal cracking, Bioresource Technology, 101 (2010) 6157-6162.

[88] A.O. Adebanjo, A.K. Dalai, N.N. Bakhshi, Production of diesel-like fuel and other value-added chemicals from pyrolysis of animal fat, Energy & Fuels, 19 (2005) 1735-1741.

[89] T. Ito, Y. Sakurai, Y. Kakuta, M. Sugano, K. Hirano, Biodiesel production from waste animal fats using pyrolysis method, Fuel Processing Technology, 94 (2012) 47-52.

[90] V.R. Wiggers, H.F. Meier, A. Wisniewski, Jr., A.A. Chivanga Barros, M.R. Wolf Maciel, Biofuels from continuous fast pyrolysis of soybean oil: A pilot plant study, Bioresource Technology, 100 (2009) 6570-6577.

[91] V.R. Wiggers, A. Wisniewski, Jr., L.A.S. Madureira, A.A. Chivanga Barros, H.F. Meier, Biofuels from waste fish oil pyrolysis: Continuous production in a pilot plant, Fuel, 88 (2009) 2135-2141.

[92] A. Wisniewski, Jr., V.R. Wiggers, E.L. Simionatto, H.F. Meier, A.A.C. Barros, L.A.S. Madureira, Biofuels from waste fish oil pyrolysis: Chemical composition, Fuel, 89 (2010) 563-568.

[93] V.R. Wiggers, G.R. Zonta, A.P. Franca, D.R. Scharf, E.L. Simionatto, L. Ender, H.F. Meier, Challenges associated with choosing operational conditions for triglyceride thermal cracking aiming to improve biofuel quality, Fuel, 107 (2013) 601-608.

[94] B.K. De, J.D. Patel, Refining of rice bran oil by neutralization with calcium hydroxide, European Journal of Lipid Science and Technology, 113 (2011) 1161-1167.

[95] W.A. Hartgers, J.S.S. Damste, J.W. Deleeuw, Curie-point pyrolysis of sodium-salts of functionalized fatty-acids, Journal of Analytical and Applied Pyrolysis, 34 (1995) 191-217.

[96] H. Lappi, R. Alen, Production of vegetable oil-based biofuels-Thermochemical behavior of fatty acid sodium salts during pyrolysis, Journal of Analytical and Applied Pyrolysis, 86 (2009) 274-280.

[97] H. Lappi, R. Alen, Pyrolysis of vegetable oil soaps-Palm, olive, rapeseed and castor oils, Journal of Analytical and Applied Pyrolysis, 91 (2011) 154-158.

[98] X. Dupain, D.J. Costa, C.J. Schaverien, M. Makkee, J.A. Moulijn, Cracking of a rapeseed vegetable oil under realistic FCC conditions, Applied Catalysis B-Environmental, 72 (2007) 44-61.

[99] K.D. Maher, K.M. Kirkwood, M.R. Gray, D.C. Bressler, Pyrolytic decarboxylation and cracking of stearic acid, Industrial & Engineering Chemistry Research, 47 (2008) 5328-5336.

[100] A.W. Schwab, G.J. Dykstra, E. Selke, S.C. Sorenson, E.H. Pryde, Diesel fuel from thermal-decomposition of soybean oil, Journal of the American Oil Chemists Society, 65 (1988) 1781-1786.

[101] B.S. Greensfelder, H.H. Voge, G.M. Good, Catalytic and thermal cracking of pure hydrocarbons - mechanisms of reaction, Industrial and Engineering Chemistry, 41 (1949) 2573-2584.

[102] J.W. Alencar, P.B. Alves, A.A. Craveiro, Pyrolysis of tropical vegetable-oils, Journal of Agricultural and Food Chemistry, 31 (1983) 1268-1270.

[103] R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Thermal cracking of Canola oil: Reaction products in the presence and absence of steam, Energy & Fuels, 10 (1996) 1150-1162.

[104] A. Osmont, L. Catoire, I. Gokalp, M.T. Swihart, Thermochemistry of C-C and C-H bond breaking in fatty acid methyl esters, Energy & Fuels, 21 (2007) 2027-2032.

[105] A. Osmont, L. Catoire, I. Gokalp, Thermochemistry of methyl and ethyl esters from vegetable oils, International Journal of Chemical Kinetics, 39 (2007) 481-491.

[106] A. Kubatova, J. St'avova, W.S. Seames, Y. Luo, S.M. Sadrameli, M.J. Linnen, G.V. Baglayeva, I.P. Smoliakova, E.I. Kozliak, Triacylglyceride Thermal Cracking: Pathways to Cyclic Hydrocarbons, Energy & Fuels, 26 (2012) 672-685.

[107] J.A. Melero, G. Vicente, G. Morales, M. Paniagua, J. Bustamante, Oxygenated compounds derived from glycerol for biodiesel formulation: Influence on EN 14214 quality parameters, Fuel, 89 (2010) 2011-2018.

[108] J.A. Melero, M.M. Clavero, G. Calleja, A. Garcia, R. Miravalles, T. Galindo, Production of Biofuels via the Catalytic Cracking of Mixtures of Crude Vegetable Oils and Nonedible Animal Fats with Vacuum Gas Oil, Energy & Fuels, 24 (2010) 707-717.

[109] Y.K. Ong, S. Bhatia, The current status and perspectives of biofuel production via catalytic cracking of edible and non-edible oils, Energy, 35 (2010) 111-119.

[110] N. Taufiqurrahmi, A.R. Mohamed, S. Bhatia, Production of biofuel from waste cooking palm oil using nanocrystalline zeolite as catalyst: Process optimization studies, Bioresource Technology, 102 (2011) 10686-10694.

[111] B.X. Peng, C. Zhao, S. Kasakov, S. Foraita, J.A. Lercher, Manipulating Catalytic Pathways: Deoxygenation of Palmitic Acid on Multifunctional Catalysts, Chemistry-a European Journal, 19 (2013) 4732-4741.

[112] A.V. Lavrenov, E.N. Bogdanets, Y.A. Chumachenko, V.A. Likholobov, Catalytic processes for the production of hydrocarbon fuels from oils and fatty raw materials: contemporary approaches, Catalysis in Industry, 3 (2011) 250-259.

[113] K.V.C. Rao, Production of hydrocarbons by thermolysis of vegetable oils, US patent US4102938A, USPTO, USA, 1978, 260/676 R; 260/682.

[114] P.B. Weisz, W.O. Haag, P.G. Rodewald, Catalytic production of high-grade fuel (gasoline) from biomass compounds by shape-selective catalysis, Science, 206 (1979) 57-58.

[115] M.A. Morris, Production of bio-oils via catalytic pyrolysis, in: R. Luque, J. Campelo, J. Clark (Eds.) Handbook of biofuels production: processes and technology, Woodhead Publishing Ltd, Cambridge, UK, 2011, pp. 349-389.

[116] S. Ordonez, D. Eva, Basic Zeolites: Structure, preparation and environmental applications, in: T.W. Wong (Ed.) Handbook of Zeolites: structure, properties and applications, Nova Science Publishers, Inc., New York, USA, 2009, pp. 51-66.

[117] H. Hattori, Heterogeneous basic catalysis, Chemical Reviews, 95 (1995) 537-558.

[118] M. Guisnet, Influence of zeolite composition on catalytic activity, in: D.C. Sherrington, A.P. Kybett (Eds.) Supported Catalysts and their Applications, The Royal Society of Chemistry, Cambridge, UK, 2001, pp. 55-67.

[119] J.D. Adjaye, S.P.R. Katikaneni, N.N. Bakhshi, Catalytic conversion of a biofuel to hydrocarbons: Effect of mixtures of HZSM-5 and silica-alumina catalysts on product distribution, Fuel Processing Technology, 48 (1996) 115-143.

[120] R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Catalytic conversion of canola oil to fuels and chemicals: Roles of catalyst acidity, basicity and shape selectivity on product distribution, Fuel Processing Technology, 51 (1997) 101-125.

[121] S.P.R. Katikaneni, J.D. Adjaye, N.N. Bakhshi, Catalytic conversion of canola oil to fuels and chemicals over various cracking catalysts, Canadian Journal of Chemical Engineering, 73 (1995) 484-497.

[122] S.P.R. Katikaneni, J.D. Adjaye, N.N. Bakhshi, Performance of aluminophosphate molecular-sieve catalysts for the production of hydrocarbons from wood-derived and vegetable-oils, Energy & Fuels, 9 (1995) 1065-1078.

[123] S.P.R. Katikaneni, J.D. Adjaye, N.N. Bakhshi, Studies on the catalytic conversion of canola oil to hydrocarbons - influence of hybrid catalysts and steam, Energy & Fuels, 9 (1995) 599-609.

[124] S.P.R. Katikaneni, J.D. Adjaye, R.O. Idem, N.N. Bakhshi, Catalytic conversion of Canola oil over potassium-impregnated HZSM-5 catalysts: C-2-C-4 olefin production and model reaction studies, Industrial & Engineering Chemistry Research, 35 (1996) 3332-3346.

[125] S.P.R. Katikaneni, R.O. Idem, N.N. Bakhshi, Catalytic conversion of a biomass-derived oil using various catalysts, 1997.

[126] S.P.R. Katikaneni, J.D. Adjaye, N.N. Bakhshi, Conversion of canola oil to various hydrocarbons over Pt/HZSM-5 bifunctional catalyst, Canadian Journal of Chemical Engineering, 75 (1997) 391-401.

[127] Y.S. Ooi, S. Bhatia, Aluminum-containing SBA-15 as cracking catalyst for the production of biofuel from waste used palm oil, Microporous and Mesoporous Materials, 102 (2007) 310-317.

[128] H. Tian, C.Y. Li, C.H. Yang, H.H. Shan, Alternative processing technology for converting vegetable oils and animal fats to clean fuels and light olefins, Chinese Journal of Chemical Engineering, 16 (2008) 394-400.

[129] P. Bielansky, A. Weinert, C. Schoenberger, A. Reichhold, Catalytic conversion of vegetable oils in a continuous FCC pilot plant, Fuel Processing Technology, 92 (2011) 2305-2311.

[130] P. Bielansky, A. Reichhold, C. Schoenberger, Catalytic cracking of rapeseed oil to high octane gasoline and olefins, Chemical Engineering and Processing, 49 (2010) 873-880.

[131] F.A. Twaiq, N.A.M. Zabidi, A.R. Mohamed, S. Bhatia, Catalytic conversion of palm oil over mesoporous aluminosilicate MCM-41 for the production of liquid hydrocarbon fuels, Fuel Processing Technology, 84 (2003) 105-120.

[132] J.A. Melero, A. Garcia, M. Clavero, Production of biofuels via catalytic cracking, 2011.

[133] L. Li, K.J. Quan, J.M. Xu, F.S. Liu, S.W. Liu, S.T. Yu, C.X. Xie, B.Q. Zhang, X.P. Ge, Mesoporous molecular sieves K2O/Ba(Ca or Mg)-MCM-41 with base sites as heterogeneous catalysts for the production of liquid hydrocarbon fuel from catalytic cracking of rubber seed oil, Green Chemistry, 15 (2013) 2573-2578.

[134] G. Ramya, T. Sivakumar, Catalytic Cracking using Nanoporous AIMCM-41 for the Production of Green Fuel, Transactions of the Indian Ceramic Society, 70 (2011) 149-152.

[135] G. Ramya, R. Sudhakar, J.A.I. Joice, R. Ramakrishnan, T. Sivakumar, Liquid hydrocarbon fuels from jatropha oil through catalytic cracking technology using AlMCM-41/ZSM-5 composite catalysts, Applied Catalysis a-General, 433 (2012) 170-178.

[136] J.A. Melero, J. Iglesias, A. Garcia, Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges, Energy & Environmental Science, 5 (2012) 7393-7420.

[137] T.L. Chew, S. Bhatia, Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery, Bioresource Technology, 99 (2008) 7911-7922.

[138] T.L. Chew, S. Bhatia, Effect of catalyst additives on the production of biofuels from palm oil cracking in a transport riser reactor, Bioresource Technology, 100 (2009) 2540-2545.

[139] S. Bezergianni, A. Dimitriadis, A. Kalogianni, K.G. Knudsen, Toward Hydrotreating of Waste Cooking Oil for Biodiesel Production. Effect of Pressure, H-2/Oil Ratio, and Liquid Hourly Space Velocity, Industrial & Engineering Chemistry Research, 50 (2011) 3874-3879.

[140] J.K. Satyarthi, T. Chiranjeevi, D.T. Gokak, P.S. Viswanathan, An overview of catalytic conversion of vegetable oils/fats into middle distillates, Catalysis Science & Technology, 3 (2013) 70-80.

[141] S. Bezergianni, A. Kalogianni, Hydrocracking of used cooking oil for biofuels production, Bioresource Technology, 100 (2009) 3927-3932.

[142] S. Bezergianni, A. Kalogianni, I.A. Vasalos, Hydrocracking of vacuum gas oil-vegetable oil mixtures for biofuels production, Bioresource Technology, 100 (2009) 3036-3042.

[143] M. Snare, I. Kubickova, P. Maki-Arvela, D. Chichova, K. Eranen, D.Y. Murzin, Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons, Fuel, 87 (2008) 933-945.

[144] S. Lestari, P. Maki-Arvela, I. Simakova, J. Beltramini, G.Q.M. Lu, D.Y. Murzin, Catalytic Deoxygenation of Stearic Acid and Palmitic Acid in Semibatch Mode, Catalysis Letters, 130 (2009) 48-51.

[145] P.T. Do, M. Chiappero, L.L. Lobban, D.E. Resasco, Catalytic Deoxygenation of Methyl-Octanoate and Methyl-Stearate on Pt/Al2O3, Catalysis Letters, 130 (2009) 9-18.

[146] M. Chiappero, P.T.M. Do, S. Crossley, L.L. Lobban, D.E. Resasco, Direct conversion of triglycerides to olefins and paraffins over noble metal supported catalysts, Fuel, 90 (2011) 1155-1165.

[147] S. Lestari, P. Maki-Arvela, H. Bernas, O. Simakova, R. Sjoholm, J. Beltramini, G.Q.M. Lu, J. Myllyoja, I. Simakova, D.Y. Murzin, Catalytic Deoxygenation of Stearic Acid in a Continuous Reactor over a Mesoporous Carbon-Supported Pd Catalyst, Energy & Fuels, 23 (2009) 3842-3845.

[148] S. Lestari, P. Maki-Arvela, J. Beltramini, G.Q.M. Lu, D.Y. Murzin, Transforming Triglycerides and Fatty Acids into Biofuels, Chemsuschem, 2 (2009) 1109-1119.

[149] S. Lestari, P. Maki-Arvela, K. Eranen, J. Beltramini, G.Q.M. Lu, D.Y. Murzin, Diesel-like Hydrocarbons from Catalytic Deoxygenation of Stearic Acid over Supported Pd Nanoparticles on SBA-15 Catalysts, Catalysis Letters, 134 (2010) 250-257.

[150] P. Maki-Arvela, B. Rozmyslowicz, S. Lestari, O. Simakova, K. Eranen, T. Salmi, D.Y. Murzin, Catalytic Deoxygenation of Tall Oil Fatty Acid over Palladium Supported on Mesoporous Carbon, Energy & Fuels, 25 (2011) 2815-2825.

[151] B. Veriansyah, J.Y. Han, S.K. Kim, S.A. Hong, Y.J. Kim, J.S. Lim, Y.W. Shu, S.G. Oh, J. Kim, Production of renewable diesel by hydroprocessing of soybean oil: Effect of catalysts, Fuel, 94 (2012) 578-585.

[152] P. Simacek, D. Kubicka, G. Sebor, M. Pospisil, Hydroprocessed rapeseed oil as a source of hydrocarbon-based biodiesel, Fuel, 88 (2009) 456-460.

[153] P. Simacek, D. Kubicka, G. Sebor, M. Pospisil, Fuel properties of hydroprocessed rapeseed oil, Fuel, 89 (2010) 611-615.

[154] G.W. Huber, S. Iborra, A. Corma, Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering, Chemical Reviews, 106 (2006) 4044-4098.

[155] G.W. Huber, P. O'Connor, A. Corma, Processing biomass in conventional oil refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures, Applied Catalysis a-General, 329 (2007) 120-129.

[156] G.W. Huber, L. Sauvanaud, P. O'Connor, A. Corma, Processing of biomass-derived feedstocks in a petroleum refinery: Catalytic cracking of biomass-derived feedstocks, Abstracts of Papers of the American Chemical Society, 234 (2007).

[157] R. Nava, B. Pawelec, P. Castano, M.C. Alvarez-Galvan, C.V. Loricera, J.L.G. Fierro, Upgrading of bio-liquids on different mesoporous silica-supported CoMo catalysts, Applied Catalysis B-Environmental, 92 (2009) 154-167.

[158] R. Sotelo-Boyas, Y.Y. Liu, T. Minowa, Renewable Diesel Production from the Hydrotreating of Rapeseed Oil with Pt/Zeolite and NiMo/Al2O3 Catalysts, Industrial & Engineering Chemistry Research, 50 (2011) 2791-2799.

[159] R. Tiwari, B.S. Rana, R. Kumar, D. Verma, R. Kumar, R.K. Joshi, M.O. Garg, A.K. Sinha, Hydrotreating and hydrocracking catalysts for processing of waste soya-oil and refinery-oil mixtures, Catalysis Communications, 12 (2011) 559-562.

[160] M. Toba, Y. Abe, H. Kuramochi, M. Osako, T. Mochizuki, Y. Yoshimura, Hydrodeoxygenation of waste vegetable oil over sulfide catalysts, Catalysis Today, 164 (2011) 533-537.

[161] C. Liu, J. Liu, G. Zhou, W.Q. Tian, L. Rong, A cleaner process for hydrocracking of jatropha oil into green diesel, Journal of the Taiwan Institute of Chemical Engineers, 44 (2013) 221-227.

[162] C. Templis, A. Vonortas, I. Sebos, N. Papayannakos, Vegetable oil effect on gasoil HDS in their catalytic co-hydroprocessing, Applied Catalysis B-Environmental, 104 (2011) 324-329.

[163] S. Gong, A. Shinozaki, M. Shi, E.W. Qian, Hydrotreating of Jatropha Oil over Alumina Based Catalysts, Energy & Fuels, 26 (2012) 2394-2399.

[164] S. Kovacs, T. Kasza, A. Thernesz, I.W. Horvath, J. Hancsok, Fuel production by hydrotreating of triglycerides on NiMo/Al2O3/F catalyst, Chemical Engineering Journal, 176 (2011) 237-243.

[165] M. Krar, S. Kovacs, D. Kallo, J. Hancsok, Fuel purpose hydrotreating of sunflower oil on CoMo/Al2O3 catalyst, Bioresource Technology, 101 (2010) 9287-9293.

[166] A.K. Hossain, P.A. Davies, Pyrolysis liquids and gases as alternative fuels in internal combustion engines - A review, Renewable & Sustainable Energy Reviews, 21 (2013) 165-189.

[167] R. Frety, M.D.C. da Rocha, S.T. Brandao, L.A.M. Pontes, J.F. Padilha, L.E.P. Borges, W.A. Gonzalez, Cracking and Hydrocracking of Triglycerides for Renewable Liquid Fuels: Alternative Processes to Transesterification, Journal of the Brazilian Chemical Society, 22 (2011) 1206-1220.

[168] T.V. Choudhary, C.B. Phillips, Renewable fuels via catalytic hydrodeoxygenation, Applied Catalysis a-General, 397 (2011) 1-12.

[169] Neste Oil NExtBTL, available oinline at http://www.nesteoil.com/default.asp?path=1,41,11991,12243 last accessed Sept. 2013.

[170] UOP Honeywell, available online at http://www.uop.com/processing-solutions/biofuels/green-diesel/ last accessed Sept. 2013.

[171] R. Kumar, B.S. Rana, R. Tiwari, D. Verma, R.K. Joshi, M.O. Garg, A.K. Sinha, Hydroprocessing of jatropha oil and its mixtures with gas oil, Green Chemistry, 12 (2010) 2232-2239.

[172] B.S. Rana, R. Kumar, R. Tiwari, R.K. Joshi, M.O. Garg, A.K. Sinha, Transportation fuels from co-processing of waste vegetable oil and gas oil mixtures, Biomass & Bioenergy, 56 (2013) 43-52.

[173] A.K. Sinha, M. Anand, B.S. Rana, R. Kumar, S.A. Farooqui, M.G. Sibi, R.K. Joshi, Development of Hydroprocessing Route to Transportation Fuels from Non-Edible Plant-Oils, Catalysis Surveys from Asia, 17 (2013) 1-13.

[174] G.W. Huber, A. Corma, Synergies between bio- and oil refineries for the production of fuels from biomass, Angewandte Chemie-International Edition, 46 (2007) 7184-7201.

[175] B. Donnis, R.G. Egeberg, P. Blom, K.G. Knudsen, Hydroprocessing of Bio-Oils and Oxygenates to Hydrocarbons. Understanding the Reaction Routes, Topics in Catalysis, 52 (2009) 229-240.

[176] J. Walendziewski, M. Stolarski, R. Luzny, B. Klimek, Hydroprocesssing of light gas oil - rape oil mixtures, Fuel Processing Technology, 90 (2009) 686-691.

[177] P. Simacek, D. Kubicka, Hydrocracking of petroleum vacuum distillate containing rapeseed oil: Evaluation of diesel fuel, Fuel, 89 (2010) 1508-1513.

[178] J.W. Chen, H. Farooqi, C. Fairbridge, Experimental Study on Co-hydroprocessing Canola Oil and Heavy Vacuum Gas Oil Blends, Energy & Fuels, 27 (2013) 3306-3315.

[179] V.P. Doronin, O.V. Potapenko, P.V. Lipin, T.P. Sorokina, Catalytic cracking of vegetable oils and vacuum gas oil, Fuel, 106 (2013) 757-765.

[180] N.O.V. Sonntag, Fat splitting, Journal of the American Oil Chemists Society, 56 (1979) A729-A732.

[181] H.L. Barnebey, Continuous fat splitting plants using the colgate-emery process, Journal of the American Oil Chemists Society, 25 (1948) 95-99.

[182] R.L. Holliday, J.W. King, G.R. List, Hydrolysis of vegetable oils in sub- and supercritical water, Industrial & Engineering Chemistry Research, 36 (1997) 932-935.

[183] R. Alenezi, G.A. Leeke, R.C.D. Santos, A.R. Khan, Hydrolysis kinetics of sunflower oil under subcritical water conditions, Chemical Engineering Research & Design, 87 (2009) 867-873.

[184] J.W. King, R.L. Holliday, G.R. List, Hydrolysis of soybean oil in a subcritical water flow reactor, Green Chemistry, 1 (1999) 261-264.

[185] T.A. Patil, D.N. Butala, T.S. Raghunathan, H.S. Shankar, Thermal hydrolysis of vegetable-oils and fats .1. Reaction-kinetics, Industrial & Engineering Chemistry Research, 27 (1988) 727-735.

3. Thermal deoxygenation and pyrolysis of oleic acid [1]

3.1. Introduction

The global development of renewable energy solutions is accelerating, driven by a variety of socio-economic and environmental reasons. Technology platforms for the conversion of biomass into energy, fuels, chemicals and a host of other bioproducts have been developed [1-6] with several focused on demonstrating novel chemical and thermochemical pathways [7-10].

Triacylglycerols (TAGs) are a good starting material for conversion to chemicals and fuels used as petroleum alternatives because of their high energy content compared to other biomass sources [10-12]. In this context, a potential feedstock is beef tallow, a low-cost by-product from animal rendering plants composed primarily of TAG molecules that consist of three fatty acid chains esterified to glycerol [11]. This material lost a substantial amount of its market value as a result of new regulations and classifications implemented in response to the recent outbreaks of bovine spongiform encephalopathy across Canada and the US.

Pyrolysis is one of the most extensively studied pathways to convert TAGs to hydrocarbons. Several studies involving the pyrolysis of TAGs with and without catalysts have been reported and a comprehensive review has been reported in the literature [13, 14].

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[1] A version of this chapter has been published. J. Asomaning, P. Mussone, D.C. Bressler, Thermal Deoxygenation and Pyrolysis of Oleic Acid, Journal of Analytical and Applied Pyrolysis, 105 (2014) 1-7. DOI: http://dx.doi.org/10.1016/j.jaap.2013.09.005.

The pyrolysis of TAG results in oxygenated products as a result of complex free radical reactions [13]. On the other hand, the pyrolysis of free fatty acids produced from TAG through various hydrolysis techniques, has received little attention and little work has been reported. While thermo-catalytic deoxygenation [15-19] and hydrothermal deoxygenation [20-22] of fatty acids are well documented in the literature, thermal deoxygenation and cracking of free fatty acids have received only limited attention.

Previous work in our laboratory demonstrated that pyrolytic processing of stearic acid proceeds through a complex sequence of reactions starting with decarboxylation and proceeding with cracking resulting in a series of *n*-alkanes and 1-alkenes with a shift towards lower carbon numbers as temperature and time increased [23]. Longer reaction times and/or severe pyrolytic conditions eventually produced aromatic compounds and insoluble solids.

Lipid feeds such as animal tallow and vegetable oils consist of a mixture of fatty acids of varying chain length and degrees of unsaturation. The primary objective of this work was to investigate pyrolysis of oleic acid, a dominant mono unsaturated free fatty acid present in animal and plant lipids, as feedstock to produce deoxygenated liquid hydrocarbons for applications as chemicals and fuels.

3.2. Materials and methods

3.2.1. Materials

The feedstock for this work, oleic acid (≥99%), internal standard for gas chromatography (GC) analysis of liquid product, nonadecanoic acid methyl ester (≥99 %), pentane (≥99%), diethyl ether (≥99%), carbon monoxide standard (≥99%), gaseous alkane and alkene standards (C_1-C_4) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Diazomethane for derivatization of fatty acids was prepared using a Diazald kit (Sigma-Aldrich, St. Louis, MO, USA) following the manufacturer's procedures.

3.2.2. Pyrolysis reactions

Pyrolysis reactions were conducted in 15 mL batch microreactors constructed with stainless steel Swagelok fittings and tubing (0.75-inch) and heated in a Techne SBS-4 fluidized bed sand bath and TC-D8 controller (Burlington, NJ, USA) as previously described in detail for the pyrolysis of stearic acid [23]. Similar microreactors have also been used in previous studies [24-27]. Pictures of the reactor, sand bath system and purging unit as well as schematic diagrams of the sand bath, purging unit and microreactors have been provided in Appendix, Figures A1-A5.

Approximately 1g of oleic acid was weighed into a clean and dry microreactor which was then closed, checked for leaks, purged with nitrogen (99.998 %) (Praxair, Mississauga, ON, Canada) and sealed. The microreactor was heated at the desired temperature (350 to 450 °C) under constant agitation for the desired length of time (0.5 to 8 h) and then reaction was quenched by cooling in water at room temperature (approximately 22 °C). The outside of the microreactor was then cleaned and dried using compressed air to ensure the microreactor was clean of sand from the sand bath. All pyrolysis reactions were carried out in triplicates at each of the conditions studied.

3.2.3. Analytical methods - gas product analysis

The weight of the gas fraction produced was determined by weighing the microreactors before and after venting of the gas product in the microreactor using an analytical balance capable of weighing up to 620 g with a precision of 0.1 mg (Sartorius Extend ED623S, Sartorius AG, Goettingen, Germany). To sample the gas product for GC analysis, a 0.25 inch stainless steel Swagelok tube fitted with a septum was screwed onto the microreactor above the closed valve. Then using either a 50 µL or a 250 µL Hamilton gas tight micro syringe and syringe guide (Hamilton Co., Reno, NV, USA), the gas product was directly sampled from the microreactor by inserting the syringe's needle through the septum and opening the reactor valve. The gas product sample was then directly injected manually onto the GC.

CO_2 analysis was conducted on a Hewlett Packard (HP) Series II 5890 GC equipped with a thermal conductivity detector (TCD) with an Agilent HP-PLOT Q column (30 m x 0.56 mm, film thickness of 40 µm) (Agilent Technologies, Santa Clara, CA, USA). The injector and detector temperatures were kept constant at 170 °C and the GC oven temperature program was 60 °C for 2 min and then increased at 10 °C min^{-1} to 200 °C and held for an additional 4 min to achieve a total run time of 20 min. This was to ensure that all analytes in the gas sample were eluted to avoid contamination of succeeding runs. Helium was used as carrier gas with a constant pressure of 12 psi (82.7 kPa) and the injection volume was 50 μL.

N_2 and CO analysis was carried out by using a similar instrument and conditions as in CO_2 analysis butwith an Agilent HP-Molsieve column (30 m x 0.32 mm, film thickness of 12 μm). The GC oven temperature program was set out at 40 °C for 3 min and then increased at 10 °C min^{-1} to 200 °C and held for an additional 1 min to achieve a total rum time of 20 min. The injection volume was 150 μL. H_2 analysis was conducted using the same equipment and parameters but the carrier gas was changed from helium to argon.

Alkanes and alkenes in the gas product were analyzed on a Varian 3400 GC equipped with a flame ionization detector (FID) (Varian Inc., Palo Alto, CA, USA) and an Agilent CP-Al_2O_3/Na_2SO_4 column (50 m x 0.32 mm, film thickness 5 μL). The injector and detector temperatures were kept constant at 170 °C and 230 °C respectively and GC oven temperature program was set to 70 °C for 0.1 min and then increased at 3 °C min^{-1} to 170 °C and held for an additional 26 min to achieve a total run time of 60 min. Helium was used as carrier gas with a constant pressure of 20 psi (137.9 kPa) and injection volume was 250 μL.

3.2.4. Analytical methods - liquid product analysis

After venting, the microreactor was opened to recover the product. Recovery was carried out by adding 10 mL of pentane with approximately 1 mg/mL of nonadecanoic acid methyl ester as internal standard to the content of the microreactor. After carefully mixing with a spatula, samples were allowed to stand for 15 min and the content poured into sample vials and capped with Teflon® lined screw cap. The recovered samples were stored at 4 °C prior to analysis. Any solid material left in the reactor after the recovery with pentane was considered as pentane insoluble residue. Mass determination of the pentane insoluble residue was conducted by allowing the microreactors to stand in a fume hood until all the solvent has evaporated. The microreactor was then weighed before and after thoroughly cleaning the inside of the microreactor.

The pentane extracts were derivatized with diazomethane to convert fatty acids into their methyl ester derivatives allowing greater GC resolution and analyzed on an Agilent 6890N GC-FID with Agilent 7683 series autosampler and injector with an Agilent HP-5ms column (30 m x 0.32 mm, film thickness 0.25 μm) (Agilent Technologies, Santa Clara, CA, USA). The injector and detector temperatures were kept constant at 300 °C and 350 °C respectively and the GC oven temperature program was initially at 35 °C for 0.1 min and then increased at 10 °C min^{-1} to 280 °C and held for an additional 5.4 min for a total run time of 30 min. The carrier gas was helium at a constant flow rate of 1 mL min^{-1}. A 1:30 split injection with a volume of 1 μL was used.

GC with mass spectrometric detection (GC-MS) analysis was conducted on an Agilent GC 6890N coupled to an Agilent 5975B EI/CI MS instrument operated in electron ionization (EI) mode. The column and conditions used in the GC-MS was similar to the GC-FID as described above. The temperature of the GC-MS interface was kept constant at 320 °C.

3.2.5. Products identification and quantification

Compounds in the gas product (CO, CO_2 and H_2) were identified by comparing their retention times with the retention times of known standards and quantified using the pure compounds as external standards. Hydrocarbons in the gas phase identified using retention times of known standards and they were quantified using methane as external standard. Liquid products were identified based on retention times of known standards and by comparison of the mass spectra to the National Institute of Standards and Testing (NIST) 2011 mass spectral library and recognition of the fragmentation pattern of the mass spectra. Only quality matches of 90% and greater were regarded as identified products. Quantification of the compounds in the pentane extract was done semi-quantitatively by comparing the peak areas of the compounds with the peak area of the known concentration of the nonadecanoic acid methyl ester internal standard. Data in all tables and figures represent mean ± standard deviation of triplicate experiments, unless otherwise indicated. Statistic tests were performed using ANOVA or T-test to determine significant differences in data at the 95% confidence level.

3.3. Results and discussion

3.3.1. Gas hydrocarbon products

The pyrolysis of oleic acid under all conditions tested resulted in the formation of gaseous products. A typical GC-FID chromatogram of the gas product hydrocarbons is shown in Figure 3.1. Hydrocarbon molecules ranging from C_1 (methane) to as high as C_7 (heptane) were observed in the gas product analysis. In all the reaction conditions tested the most abundant hydrocarbon products in the gas fraction were C_1 to C_3 alkanes and alkenes. The amount of saturated hydrocarbon in the gas product was higher than the unsaturated hydrocarbons under all condition tested (Figure 3.1 and Table 3.1), suggesting that saturation/hydrogenation occurred during pyrolysis. It is important to observe the presence in the gas hydrocarbon fraction of branched alkanes and alkenes as well as alkadienes which are important precursors in the formation of cyclic compounds and subsequent aromatic compounds formation through dehydrogenation [10, 13, 28, 29].

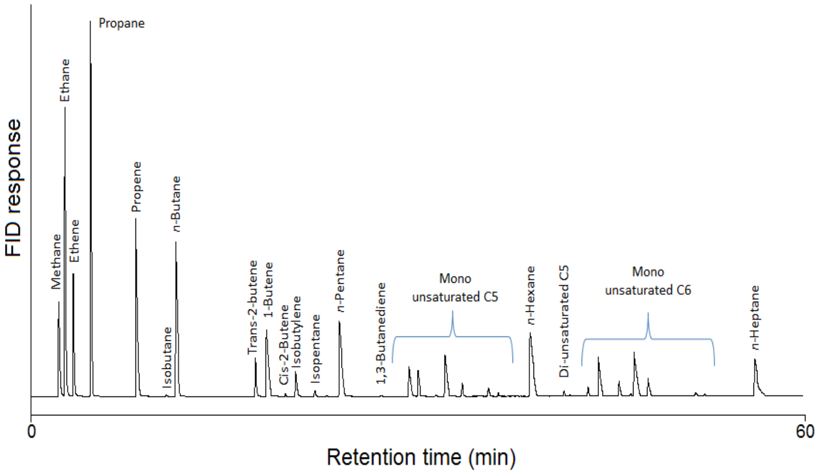

Figure 3.1. Representative GC-FID chromatogram showing the occurrence of hydrocarbons in the gas fraction of oleic acid pyrolysis product.

Table 3.1. Material balance of select oleic acid pyrolysis product.

	weight % of feed	
Gas fraction	390°C 4 h	450°C 4 h
C_1 to C_4 alkanes	2.33 ± 0.19	17.73 ± 1.89
C_2 to C_4 alkenes	0.98 ± 0.33	3.84 ± 0.42
C_5+ alkanes and alkenes	1.22 ± 0.26	1.53 ± 0.56
CO_2	1.51 ± 0.18	3.26 ± 1.17
CO	2.56 ± 0.20	2.34 ± 1.28
Balance (Unidentified)	2.63 ± 0.23	8.10 ± 1.06
Hydrogen (% volume of gas)[a]	**0.21 ± 0.03**	**2.73 ± 0.80**
Liquid fraction		
C_6 to C_{20} n-alkanes	19.62 ± 1.05	15.17 ± 1.53
C_6 to C_{17} 1-alkenes	2.50 ± 0.40	2.71 ± 0.41
C_6 to C_{17} internal alkenes	10.41 ± 0.20	3.58 ± 0.51
Cyclic + branched hydrocarbons	1.42 ± 0.14	3.60 ± 0.74
C_4 to C_{18} fatty acids	8.65 ± 1.44	0.65 ± 0.11
Aromatic	0.41 ± 0.04	8.94 ± 0.30
Unreacted feed + isomers	7.12 ± 1.13	ND
Pentane insoluble residue	ND	5.56 ± 0.71
Balance (Unidentified)	38.64 ± 1.74	22.99 ± 1.96

a – unit is % volume of gas as the amount was too low when calculated in wt % of feed.
ND – not detected.

The molar yields of the hydrocarbons in the gas fraction of select runs are shown in Table 3.2. The saturated hydrocarbon gases (methane, ethane and propane) showed substantial increases in molar yield as temperature increased from 350 °C to 450 °C. The unsaturated hydrocarbon gases on the other hand had mixed results with ethene being generally unaffected by temperature whereas propene showed an increase in molar yield with increasing temperature.

Table 3.2. Molar yields of hydrocarbons in the gas fraction at different temperatures for 4 h reaction tine

Compound	Molar yield* (mol/mol of feed) x 10^{-3} at 4 h reaction time			
	350 °C	390 °C	410 °C	450 °C
Methane	31 ± 8	100 ± 4	257 ± 24	785 ± 51
Ethane	40 ± 11	105 ± 10	257 ± 28	623 ± 37
Ethene	29 ± 6	28 ± 2	28 ± 7	33 ± 6
Propane	37 ± 8	78 ± 5	137 ± 18	218 ± 17
Propene	33 ± 9	54 ± 5	54 ± 7	162 ± 14
C_4 Hydrocarbons	41 ± 6	55 ± 4	73 ± 11	159 ± 15
C_5+ Hydrocarbons	109 ± 21	70 ± 8	41 ± 5	53 ± 11

The results also show the saturated hydrocarbon gases had relatively higher molar yields compared to the unsaturated hydrocarbon gases. This may be explained in terms of the relative increased reactivity of double bonds due to the presence of the pi bond electrons. The molar yield of the C_4 alkane and alkene gases also increased with increasing temperature whereas the molar yield of the C_5 and higher alkane and alkene in the gas fraction decreased with increasing temperature.

3.3.2. Deoxygenation and hydrogen formation

Carbon dioxide and carbon monoxide were detected in the gas product under the reaction conditions tested and the general trend of formation is shown in Figure 3.2. This is representative of the general trends observed under all the reaction conditions. Previous studies have described the formation of these species through decarboxylation and decarbonylation, respectively, of fatty acids [8, 19, 28, 30, 31]. Several researchers have also reported the presence of both CO and CO_2 in the gas fraction of thermal and catalytic pyrolysis of fats and oils as well as model TAGs [1, 28, 32-36].

For reactions conducted at temperatures lower than 430 °C decarbonylation is predominant because there is substantially more CO than CO_2 on a mass basis. Under severe reaction conditions, the amount of CO_2 increases while the amount of CO remains relatively constant and then decreases as temperature and time increases, suggesting that decarboxylation is favoured at higher reaction temperatures. As decarbonylation results in the formation of water

[19], a product incompatible with fuel formulations, reaction temperature and time should be selected to minimize its production. However, as previously noted, higher temperature also promote the formation of aromatic compounds which are responsible for coke formation, another undesirable reaction product. Therefore, the reaction conditions should be carefully chosen to minimize both decarbonylation and aromatization and maximize decarboxylation and organic hydrocarbon yield.

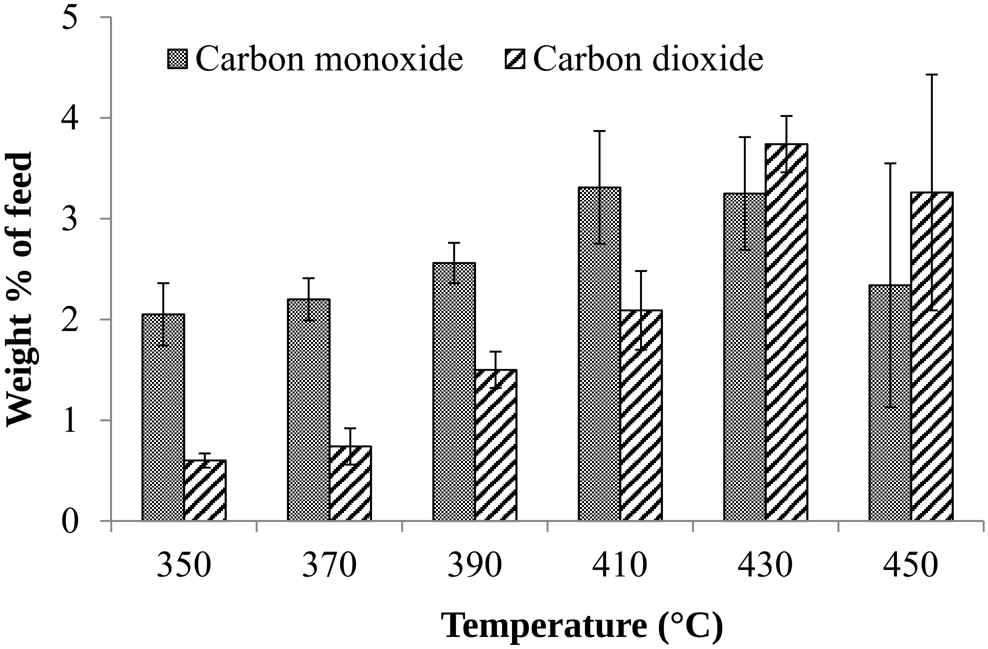

Figure 3.2. Percentages of CO and CO_2 in the gas fraction of oleic acid pyrolysis product at different temperatures for 4 h reaction time.

Kubatova et al. [37] measured both CO and CO_2 and observed that CO was relatively more abundant than CO_2 during the pyrolysis of canola and soybean oils during all their experimental runs. They also observed a relatively high amount of hydrogen in the gas product and attributed the high amount of CO to the reduction of CO_2 by hydrogen to form CO and H_2O. The results from our study do not support this explanation because only a small amount of hydrogen was produced at mild to medium reaction conditions, whereas a substantial amount of hydrogen is produced at higher temperature and reaction time (Table 3.1). Since the formation of CO from fatty acids also yields H_2O, the forward reaction of the water gas shift will be a more plausible explanation for the increase in CO_2 and H_2 at higher temperatures and reaction times. Another possible explanation for the observed differences could be the significant difference between the cracking mechanisms of free fatty acids as compared to TAGs [38].

3.3.3. Identification of products in the liquid fraction

The pyrolysis of oleic acid resulted in a series of products observed as periodic sets of peaks when analyzed by GC. Five distinct peaks were clearly identified through comparison to external standards and NIST mass spectral library. The series identified includes: a *n*-alkane series, 1-alkene series, a fatty acid series and two internal alkene series (series 1 before the *n*-alkane series and series 2 after the *n*-alkane series) as depicted in Figure 3.3. A notable difference between the pyrolysis of saturated (stearic acid) [23] and unsaturated (oleic acid) fatty acids is the observation of a series of unsaturated fatty acids in the pyrolysis of stearic acid which was not observed in this study, possibly as a result of saturation reactions.

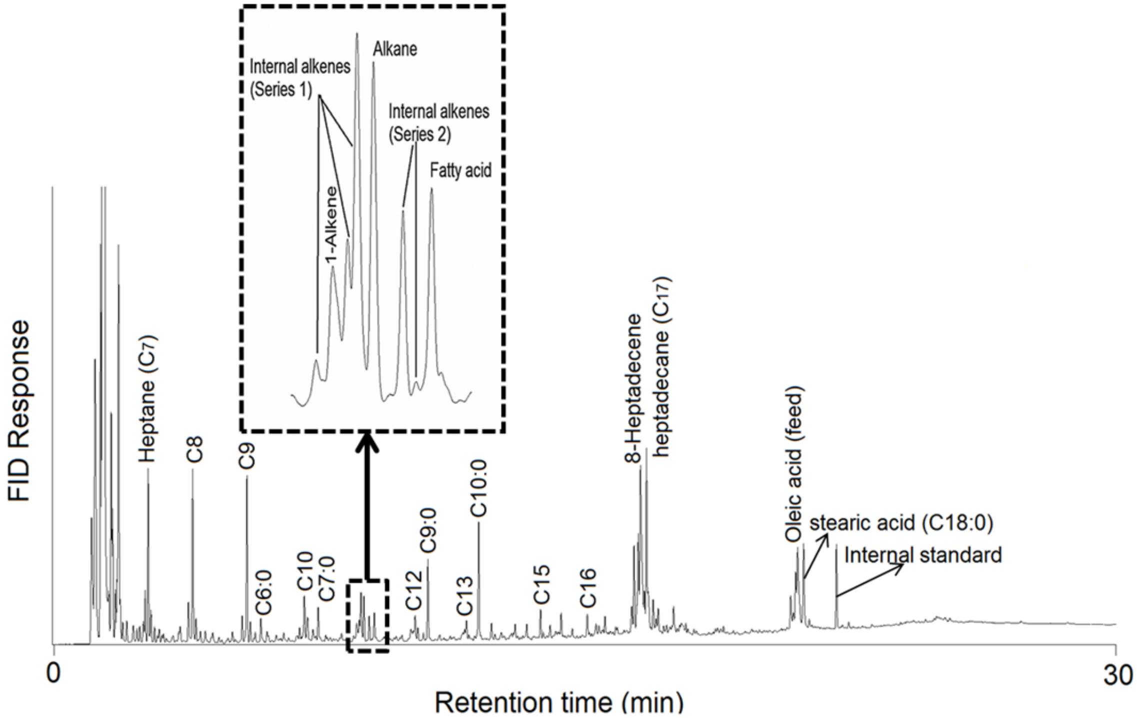

Figure 3.3. GC-FID chromatogram showing typical products in the liquid fraction of oleic acid pyrolysis product.

The product distribution was dependent on reaction temperature and time, with lower temperature and/or time resulting in lower conversion of feed into product and higher temperature and/or longer time increasing conversion and selectivity for lower molecular weight compounds. Chromatograms of reactions conducted at 390 and 450 °C are shown in Figure 3.4. Only products with molecular weight higher than pentane (C_5) were identified and quantified due to peak overlap between the solvent and low boiling compounds.

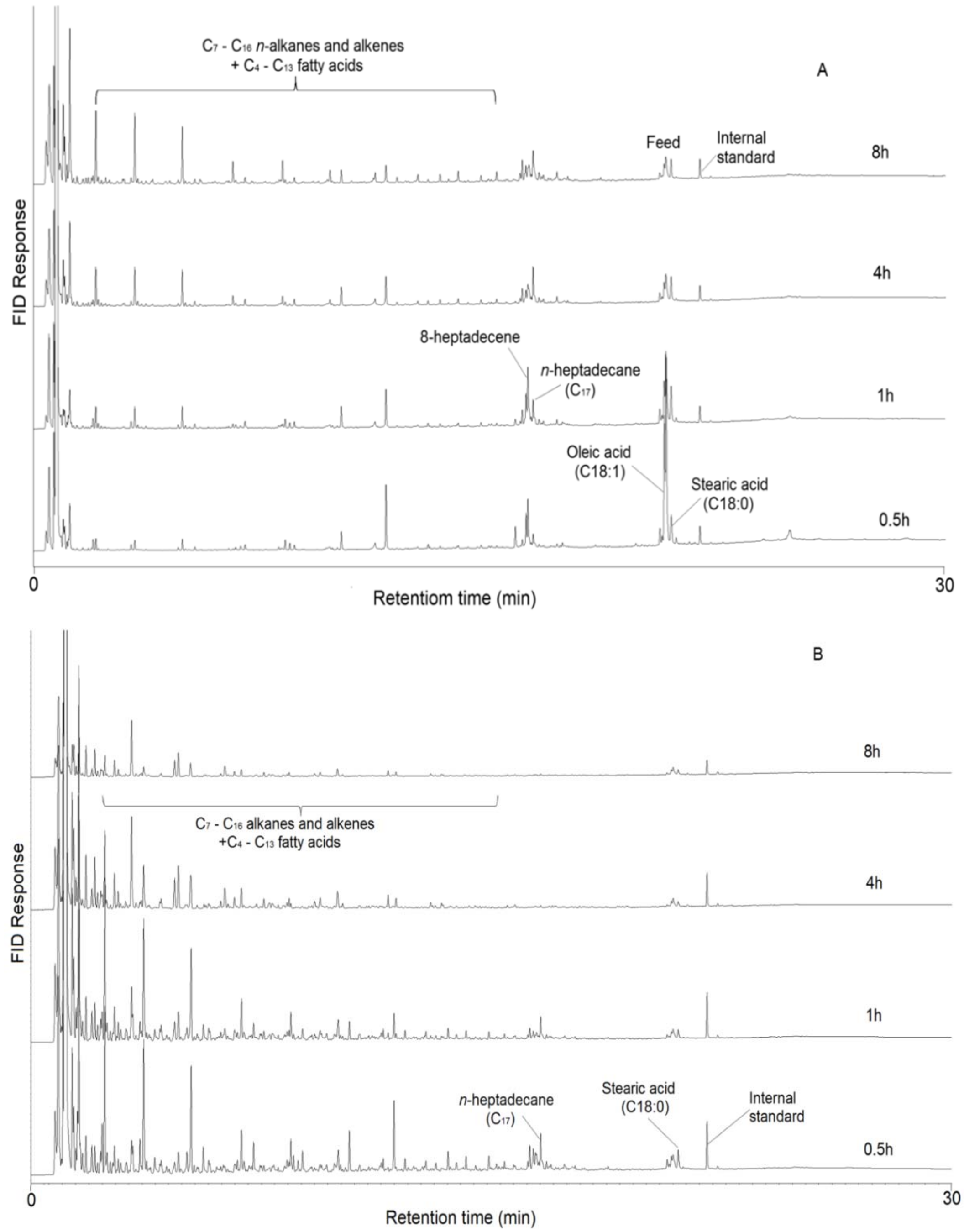

Figure 3.4. GC-FID chromatogram showing pentane-soluble oleic acid pyrolysis product at varying lengths of times at 390 °C (A) and 450 °C (B).

At low temperature and/or time the main products were decanoic acid (C10:0), nonanoic acid (C9:0), 8-heptadecenoic acid, and stearic acid (C18:0) as well as low molecular weight alkanes and alkenes (C_6 to C_{10}). Minor products included *n*-alkanes (C_{11} to C_{18}), 1-alkenes (C_6 to C_{11}) and internal alkenes (C_6 to C_{16}). As temperature and/or time increased, there was a marked decrease in the amount of fatty acids (C9:0 and C10:0) and a concurrent increase in C_6 to C_{10} alkanes. At higher temperature and longer times there was an almost complete depletion of fatty acids and internal alkenes and an increase in the low molecular weight hydrocarbons especially *n*-alkanes as well as the formation of cyclic hydrocarbons and aromatic compounds (Table 3.1). A similar observation was made in the stearic acid pyrolysis study [23].

Fabbri et al. [39] studied the pyrolysis of model triolein and reported alkadienes as the main reaction products whereas in this study the main products were *n*-alkanes and low molecular weight fatty acids. The observed difference could be explained in terms of the differences in the reaction conditions used and also the reported differences in the thermal cracking mechanism of free fatty acids compared to esterified fatty acids in TAGs [38].

The presence and position of the double bond influences the pyrolysis of unsaturated fatty acids as selectivity towards C_9 and C_{10} fatty acids and C_6 to C_{10} hydrocarbons is clearly demonstrated. Hartgers et al. [40] reported that, due to the lower bond dissociation energy of C-C bond compared to C-H and C-O, initiation of the pyrolysis reaction involves homolytic cleavage of the C-C bond rather than C-H or C-O bond. Additionally, the presence of oxygen (electron withdrawing atoms) in the carboxyl group weakens the C-C bond adjacent to the carboxyl group and therefore initiation was likely to involve homolytic cleavage of this C-C bond. This was clearly observed in the stearic acid pyrolysis with the formation of *n*-heptadecane before other compounds were formed in substantial amounts [23].

This mechanism was clearly observed also in the pyrolysis of oleic acid, as evidenced by the formation of 8-heptadecene and *n*-heptadecane. However, in the pyrolysis of oleic acid even at milder conditions, there was substantial formation of C_9 and C_{10} fatty acids as well as C_6 to C_9 alkanes. The formation of substantial amounts of C_9 and C_{10} fatty acids over 8-heptadecene (Figure 3.4) shows preferential homolytic cleavage of the allylic C-C bond compared to the C-C bond adjacent to the carboxyl group. This can be explained by the lower bond dissociation energy of the allylic C-C bond compared to the C-C bond adjacent the carboxyl group [40]. A similar observation was made when the sodium salt of oleic acid was pyrolyzed [40]. The propagation reaction was through β-scission, which results in the breaking of C-C bonds and the formation of unsaturated hydrocarbons and other radicals and hydrogen abstraction which results in substrate activation and formation of new radicals. The propagation mechanism is temperature dependent with β-scission being favoured at elevated temperatures [40].

The pyrolysis product had a higher amount of saturated products compared to unsaturated products at all the conditions tested (Figure 3.4 and 3.5, Table 3.1), possibly as a result of saturation reactions. A similar observation was made by Kubatova et al. [37] when canola oil and soybean oil which contain more than 90% and 80% unsaturated fatty acids, respectively, were pyrolyzed as well as by other researchers when different fats and oils were pyrolyzed with and without catalysts [1, 28, 32, 33, 41, 42].

3.3.4. Cyclic and aromatic compounds

Cyclic alkanes and alkenes with varying carbon numbers were produced during pyrolysis of oleic acid. The majority of these species were substituted cyclopentanes, cyclopentenes, cyclohexanes and cyclohexenes. As shown in Table 3.1, the amount of cyclic compounds increased as temperature increased. While cyclic compounds were always present in the liquid product at all conditions tested, none were observed in the gas product.

Idem et al. [28] reported the formation of C_5 cyclic compounds in the pyrolysis of canola oil, attributing this phenomenon to the addition of ethylene to propylene followed by dehydrocyclization and double bond conjugation. While this mechanism accounts for cyclopentane and cyclopentene, it does not explain the formation of substituted cyclic compounds such as those observed here.

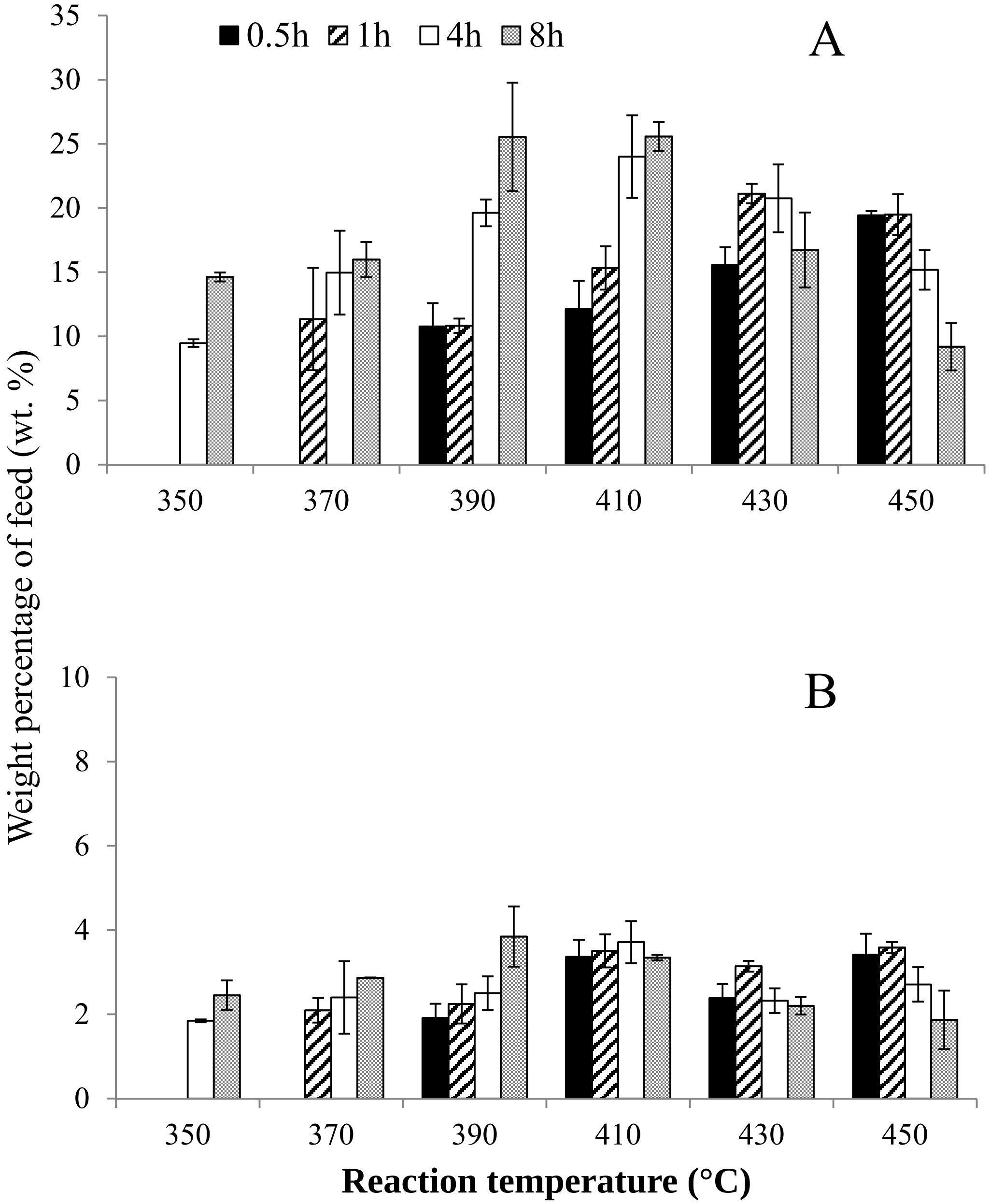

Figure 3.5. *n*-alkanes (A) and 1-alkenes (B) composition of pentane-soluble oleic acid pyrolysis product as a function of temperature and time.

Six carbon numbered rings are widely accepted to be formed predominantly by the Diel-Alder reaction involving a diene and a dienophile [28, 30, 34]. Kubatova et al. [43] recently proposed a new path to cyclic compound formation in pyrolysis of TAGs which involves the intramolecular cyclization of alkenyl radical with terminal double bond resulting in a product distribution consistent with our findings.

The total aromatic compounds in the liquid product are shown in Figure 3.6. Aromatic compounds were not observed at 350 °C for up to 8 h reaction time and at 370 °C and 390 °C for up to 1 h reaction time. As temperature and time increased the amount of aromatic compounds increased. The aromatic compounds ranged from 0.26 ± 0.06 wt % at 370 °C for 8 h to 9.47 ± 1.56 wt % at 450 °C for 8 h. At low temperature and short times, only mono-aromatic compounds such as toluene, ethylbenzene and xylenes were observed. As expected, the formation of polyaromatic compounds such as indanes, indenes, naphthalenes, fluorenes and pyrene was promoted at higher temperatures and reaction times.

The formation of mono aromatic compounds involves dehydrogenation of six carbon numbered cyclic alkanes and alkenes [28, 34, 43, 44]. Polyaromatic compounds are then formed through polymerization and dehydrogenation of the mono aromatic compounds [28, 45] and alternatively via an intramolecular radical cyclization mechanism [43]. Based on the data collected in this study, both mechanisms are possible. However, since the mechanism involving dehydrogenation of six carbon numbered cyclic alkanes and alkenes depends on the formation of cyclic alkanes and alkenes, it is plausible that intramolecular cyclization is the predominant mechanism of polyaromatic compound formation.

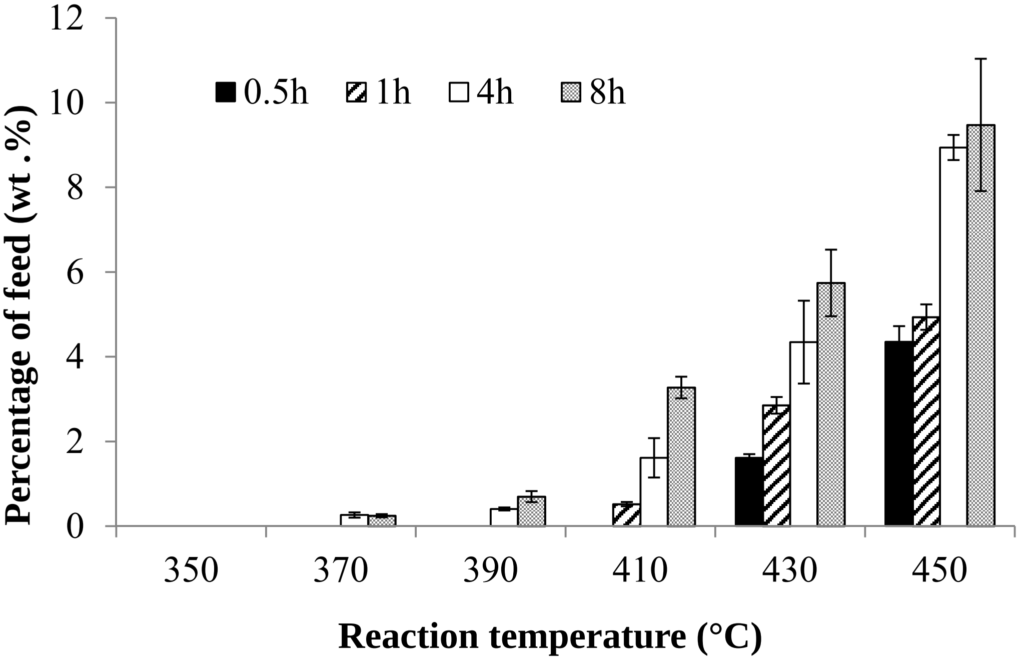

Figure 3.6. Percentage of aromatic compounds in the pentane-soluble oleic acid pyrolysis products as a function of temperature and time. Data represents mean ± SD with n=3.

3.3.5. Quantitative analysis

Conversion of oleic acid was calculated based on the difference in the amount of oleic acid and its positional isomers remaining in the product mixture after each reaction. The conversions calculated were all above 70 wt % for all the conditions tested. The lowest conversion was 75 ± 1% at 390 °C for 0.5 h with complete conversion at 410 °C for 8 h and 430 °C and 450 °C for 1, 4 and 8 h reaction. Maher et al. [23] studied stearic acid pyrolysis under similar conditions and reported conversions ranging from 32 to 97 wt % using the same method of calculation. Both reaction temperature and time influenced the gas product yield. Increasing both time and temperature resulted in increased gas yield. Increasing time from 0.5 to 8 h increased the gas yield from 6.9 ± 1.9 to 13 ± 3 wt % and 21 ± 1 to 45 ± 1 wt % at 390 °C and 450 °C, respectively. There is therefore a significant increase in conversion when oleic acid is pyrolyzed relative to stearic acid, possibly as a result of the presence of the double bond which decreases the bond dissociation energy at the allylic C-C bond and increases the positions where homolytic cleavage of C-C bond can occur.

Dupain et al. [38] carried out thermal and thermo-catalytic cracking of oleic acid and reported very low conversion (19%) of the feed in the case of thermal cracking. This result seems to contradict the results reported in this study where high conversions were achieved. The observed difference is due mainly to the reaction times used in the studies. Whereas in this study the minimum reaction time was 30 min, their study involved reaction times of 50 ms to 8 s which is generally referred to as flash pyrolysis. The observed conversion of 19% in their study implies the reaction is thermodynamically favourable. Therefore, the differences in conversion will be due to kinetic differences as a result of the different reaction times used.

The *n*-alkanes (C_6 to C_{19}) and 1-alkenes (C_6 to C_{17}) composition of the liquid product is shown in Figure 3.5. At 350, 370, 390 and 410 °C, the amount of *n*-alkanes increased with reactions time. At 430 °C the *n*-alkane increased initially up to 4 h and then decreased as the reaction time was increased to 8 h whereas at 450 °C the amount of *n*- alkanes remained constant up to 1 h and then decreased with increasing reaction time. Similarly, 1-alkenes amount increased with time at 350, 370 and 390 °C, but increased and then decreased as time increased at 410 and 410 °C and then at 450 °C the 1-alkenes amount decreased with time. The maximum combined amounts of *n*-alkanes and 1-alkenes were formed at 390 °C (29.4 wt %) and 410 °C (28.9 wt %) after 8 h of reactions.

The *n*-alkanes and 1-alkenes content at 390 °C as a function of carbon number is shown in Figure 3.7. The general trend observed is similar for the other temperatures studied. Increasing time resulted in an increase in the amount of *n*-alkanes of a particular carbon number. The most abundant *n*-alkanes formed were carbon numbers C_6 to C_9 and C_{17} at 4 and 8 h reaction times. Selectivity of C_6 to C_9 carbon numbers shows the influence of the double bond on the cracking of oleic acid. This was also observed in the relatively low amounts of C_{10} to C_{16} carbon numbers. The most abundant carbon numbers in the 1-alkenes were C_6 and $C_{10,}$ at 4 and 8 h reaction times. Another significant observation in the 1-alkenes composition is the absence of C_{12} to C_{15} carbon numbers. This also may be due to the presence of the double bond and the selectivity of cracking at the allylic C-C bond compared to the C-C bond next to the carboxyl group.

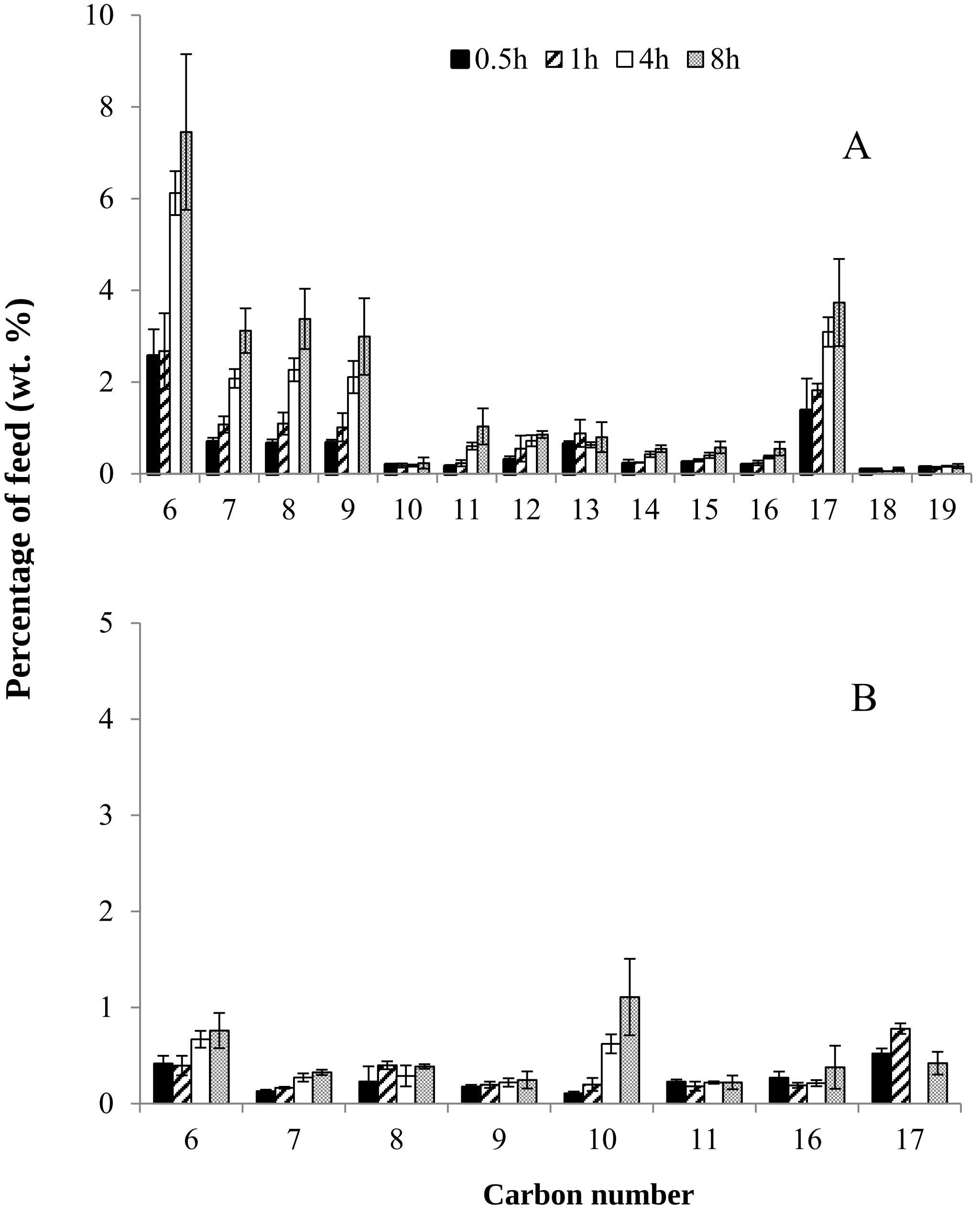

Figure 3.7. Percentage of *n*-alkanes (A) and 1-alkenes (B) at 390 °C as a function of carbon number and reaction time.

3.4. Conclusions

While decarboxylation was the first step in saturated fatty acid pyrolysis, during the pyrolysis of oleic acid both deoxygenation and cracking of the allylic C-C bonds occur simultaneously. Cracking of the allylic C-C bond is preferred due to lower bond dissociation energy as a result of the double bond compared to the C-C bond adjacent to the carboxyl group. Deoxygenation reaction proceeded through decarbonylation as well as decarboxylation, as exemplified by the presence of both CO and CO_2 in the gas phase product. Decarbonylation is favoured at lower reaction temperature conditions while decarboxylation is the dominant reaction at higher temperatures. Saturation reactions are also an important reaction occurring in the initial stages of the pyrolysis reaction resulting in the formation of saturated product of the feed. The optimal conditions for producing the highest yield of hydrocarbons are 390 and 410 °C for 4 to 8 h. This work demonstrates that the production of hydrocarbons through pyrolysis of unsaturated fatty acids from lipid hydrolysis is technically feasible.

3.5. References

[1] A.O. Adebanjo, A.K. Dalai, N.N. Bakhshi, Production of diesel-like fuel and other value-added chemicals from pyrolysis of animal fat, Energy & Fuels, 19 (2005) 1735-1741.

[2] S.P.R. Katikaneni, J.D. Adjaye, N.N. Bakhshi, Catalytic conversion of canola oil to fuels and chemicals over various cracking catalysts, Canadian Journal of Chemical Engineering, 73 (1995) 484-497.

[3] P.A. Jalil, Investigations on polyethylene degradation into fuel oil over tungstophosphoric acid supported on MCM-41 mesoporous silica, Journal of Analytical and Applied Pyrolysis, 65 (2002) 185-195.

[4] D.G. Lima, V.C.D. Soares, E.B. Ribeiro, D.A. Carvalho, E.C.V. Cardoso, F.C. Rassi, K.C. Mundim, J.C. Rubim, P.A.Z. Suarez, Diesel-like fuel obtained by pyrolysis of vegetable oils, Journal of Analytical and Applied Pyrolysis, 71 (2004) 987-996.

[5] F.R. Ma, M.A. Hanna, Biodiesel production: a review, Bioresource Technology, 70 (1999) 1-15.

[6] F.A. Twaiq, N.A.M. Zabidi, S. Bhatia, Catalytic conversion of palm oil to hydrocarbons: Performance of various zeolite catalysts, Industrial & Engineering Chemistry Research, 38 (1999) 3230-3237.

[7] E. DeOliveira, R.L. Quirino, P.A.Z. Suarez, A.G.S. Prado, Heats of combustion of biofuels obtained by pyrolysis and by transesterification and of biofuel/diesel blends, Thermochimica Acta, 450 (2006) 87-90.

[8] C.M.R. Prado, N.R. Antoniosi, Production and characterization of the biofuels obtained by thermal cracking and thermal catalytic cracking of vegetable oils, Journal of Analytical and Applied Pyrolysis, 86 (2009) 338-347.

[9] I.C.P. Fortes, P.J. Baugh, Pyrolysis-GC/MS studies of vegetable oils from Macauba fruit, Journal of Analytical and Applied Pyrolysis, 72 (2004) 103-111.

[10] H. Lappi, R. Alen, Production of vegetable oil-based biofuels-Thermochemical behavior of fatty acid sodium salts during pyrolysis, Journal of Analytical and Applied Pyrolysis, 86 (2009) 274-280.

[11] N.O.V. Sonntag, Structure and composition of fats and oils, 4th ed., John Wiley and Sons, New York, 1979.

[12] A. Demirbas, Fuel conversional aspects of palm oil and sunflower oil, Energy Sources, 25 (2003) 457-466.

[13] K.D. Maher, D.C. Bressler, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals, Bioresource Technology, 98 (2007) 2351-2368.

[14] N. Taufiqurrahmi, S. Bhatia, Catalytic cracking of edible and non-edible oils for the production of biofuels, Energy & Environmental Science, 4 (2011) 1087-1112.

[15] P. Maki-Arvela, I. Kubickova, M. Snare, K. Eranen, D.Y. Murzin, Catalytic deoxygenation of fatty acids and their derivatives, Energy & Fuels, 21 (2007) 30-41.

[16] P. Maki-Arvela, M. Snare, K. Eranen, J. Myllyoja, D.Y. Murzin, Continuous decarboxylation of lauric acid over Pd/C catalyst, Fuel, 87 (2008) 3543-3549.

[17] M. Snare, I. Kubickova, P. Maki-Arvela, K. Eranen, D.Y. Murzin, Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel, Industrial & Engineering Chemistry Research, 45 (2006) 5708-5715.

[18] J.G. Immer, M.J. Kelly, H.H. Lamb, Catalytic reaction pathways in liquid-phase deoxygenation of C18 free fatty acids, Applied Catalysis a-General, 375 (2010) 134-139.

[19] J.G. Immer, H.H. Lamb, Fed-Batch Catalytic Deoxygenation of Free Fatty Acids, Energy & Fuels, 24 (2010) 5291-5299.

[20] A.A. Peterson, F. Vogel, R.P. Lachance, M. Froling, M.J. Antal, J.W. Tester, Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies, Energy & Environmental Science, 1 (2008) 32-65.

[21] J. Fu, X.Y. Lu, P.E. Savage, Catalytic hydrothermal deoxygenation of palmitic acid (vol 3, pg 311, 2010), Energy & Environmental Science, 3 (2010) 2015-2015.

[22] J. Fu, X.Y. Lu, P.E. Savage, Hydrothermal Decarboxylation and Hydrogenation of Fatty Acids over Pt/C, Chemsuschem, 4 (2011) 481-486.

[23] K.D. Maher, K.M. Kirkwood, M.R. Gray, D.C. Bressler, Pyrolytic decarboxylation and cracking of stearic acid, Industrial & Engineering Chemistry Research, 47 (2008) 5328-5336.

[24] D.C. Bressler, M.R. Gray, Hydrotreating chemistry of model products from bioprocessing of carbazoles, Energy & Fuels, 16 (2002).

[25] W. Kanda, I. Siu, J. Adjaye, A.E. Nelson, M.R. Gray, Inhibition and deactivation of hydrodenitrogenation (HDN) catalysts by narrow-boiling fractions of Athabasca coker gas oil, Energy & Fuels, 18 (2004).

[26] S.M. Richardson, M.R. Gray, Enhancement of residue hydroprocessing catalysts by doping with alkali metals, Energy & Fuels, 11 (1997).

[27] K. Tanabe, M.R. Gray, Role of fine solids in the coking of vacuum residues, Energy & Fuels, 11 (1997).

[28] R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Thermal cracking of Canola oil: Reaction products in the presence and absence of steam, Energy & Fuels, 10 (1996) 1150-1162.

[29] S. T., N. D., K. T., Industrial and Laboratory pyrolysis, in: A. L.F., C. B.L. (Eds.) ACS symposium Series, American Chemical Society, Washington, 1976, pp. 32-60.

[30] C.C. Chang, S.W. Wan, Chinas motor fuels from tung oil, Industrial and Engineering Chemistry, 39 (1947) 1543-1548.

[31] E. Vonghia, D.G.B. Boocock, S.K. Konar, A. Leung, Pathways for the deoxygenation of triglycerides to aliphatic-hydrocarbons over activated alumina, Energy & Fuels, 9 (1995) 1090-1096.

[32] R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Catalytic conversion of canola oil to fuels and chemicals: Roles of catalyst acidity, basicity and shape selectivity on product distribution, Fuel Processing Technology, 51 (1997) 101-125.

[33] J.M. Encinar, J.F. Gonzalez, G. Martinez, S. Roman, Catalytic pyrolysis of exhausted olive oil waste, Journal of Analytical and Applied Pyrolysis, 85 (2009) 197-203.

[34] A.W. Schwab, G.J. Dykstra, E. Selke, S.C. Sorenson, E.H. Pryde, Diesel fuel from thermal-decomposition of soybean oil, Journal of the American Oil Chemists Society, 65 (1988) 1781-1786.

[35] S. Lestari, P. Maki-Arvela, I. Simakova, J. Beltramini, G.Q.M. Lu, D.Y. Murzin, Catalytic Deoxygenation of Stearic Acid and Palmitic Acid in Semibatch Mode, Catalysis Letters, 130 (2009) 48-51.

[36] M. Snare, P. Maki-Arvela, I.L. Simakova, J. Myllyoja, D.Y. Murzin, Overview of Catalytic Methods for Production of Next Generation Biodiesel from Natural Oils and Fats, Russian Journal of Physical Chemistry B, 3 (2009) 1035-1043.

[37] A. Kubatova, Y. Luo, J. Stavova, S.M. Sadrameli, T. Aulich, E. Kozliak, W. Seames, New path in the thermal cracking of triacylglycerols (canola and soybean oil), Fuel, 90 (2011) 2598-2608.

[38] X. Dupain, D.J. Costa, C.J. Schaverien, M. Makkee, J.A. Moulijn, Cracking of a rapeseed vegetable oil under realistic FCC conditions, Applied Catalysis B-Environmental, 72 (2007) 44-61.

[39] D. Fabbri, V. Bevoni, M. Notari, F. Rivetti, Properties of a potential biofuel obtained from soybean oil by transmethylation with dimethyl carbonate, Fuel, 86 (2007) 690-697.

[40] W.A. Hartgers, J.S.S. Damste, J.W. Deleeuw, Curie-point pyrolysis of sodium-salts of functionalized fatty-acids, Journal of Analytical and Applied Pyrolysis, 34 (1995) 191-217.

[41] L. Dandik, H.A. Aksoy, Effect of catalyst on the pyrolysis of used oil carried out in a fractionating pyrolysis reactor, Renewable Energy, 16 (1999) 1007-1010.

[42] J. Gornay, L. Coniglio, F. Billaud, G. Wild, Octanoic acid pyrolysis in a stainless-steel tube: What is the role of the coke formed on the wall?, Journal of Analytical and Applied Pyrolysis, 87 (2010) 78-84.

[43] A. Kubatova, J. St'avova, W.S. Seames, Y. Luo, S.M. Sadrameli, M.J. Linnen, G.V. Baglayeva, I.P. Smoliakova, E.I. Kozliak, Triacylglyceride Thermal Cracking: Pathways to Cyclic Hydrocarbons, Energy & Fuels, 26 (2012) 672-685.

[44] J.A. Melero, M.M. Clavero, G. Calleja, A. Garcia, R. Miravalles, T. Galindo, Production of Biofuels via the Catalytic Cracking of Mixtures of Crude Vegetable Oils and Nonedible Animal Fats with Vacuum Gas Oil, Energy & Fuels, 24 (2010) 707-717.

[45] J.A. Melero, G. Vicente, G. Morales, M. Paniagua, J. Bustamante, Oxygenated compounds derived from glycerol for biodiesel formulation: Influence on EN 14214 quality parameters, Fuel, 89 (2010) 2011-2018.

4. Pyrolysis of Polyunsaturated Fatty acids [1]

4.1. Introduction

The development of renewable fuels and chemicals has been the focus of many research programs. The motivations driving these efforts are the rising cost of petroleum and its dwindling reserves [1-3] as well as energy policy agenda of both advanced and emerging economies in response to both geopolitical and environmental concerns [4, 5]. To this end several techniques have been developed to convert renewable feedstock (biomass) into renewable fuels and platform chemicals. Conversion technologies such as fermentation, transesterification, gasification and pyrolysis are the most commonly used and studied [6-8]. Pyrolysis is a thermal conversion technology in the near absence of oxygen (air) [8]. Pyrolysis is especially attractive because it employs well-established methodologies and produces a range of compounds that may be integrated into existing petroleum infrastructure [4, 9, 10].

Fats and oils are composed primarily of triacylglycerols (TAGs) which are tri-esters of fatty acids and glycerol [11]. Product composition and distribution of fat and oil pyrolysis depends on the source of fat or oil [2, 4, 12-14]. The most common fatty acids in naturally occurring fats and oils are saturated, palmitic (hexadecanoic acid) and stearic (octadecanoic acid), monounsaturated oleic (9-octadecenoic acid) and diunsaturated linoleic (9,12-octadecadienoic acid) acids [11, 14].

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[1] A version of this chapter has been published. J. Asomaning, P. Mussone, D.C. Bressler, Pyrolysis of Poly Unsaturated Fatty acids, Fuel Processing Technology. 120 (2013): 89-95.

While the pyrolysis of TAGs has been extensively studied and information abounds in the literature, little work has been done on the thermal pyrolysis of free fatty acids recovered from hydrolysis of fats and oils. Our research group studied the pyrolysis of stearic acid and provided detailed fundamental information on the thermal decarboxylation and subsequent pyrolysis of the *n*-alkane resulting from the decarboxylation of stearic acid [15]. Information on the thermal pyrolysis of polyunsaturated fatty acids, key components of lipids is also very limited. While the presence of unsaturated carbon-carbon bonds is known to play an important role in the formation of cyclic and aromatic compounds through the Diels-Alder reaction in olefins [13, 16-18], little is known about these reactions in the presence of unsaturated fatty acids. Similarly, the role played by the unsaturation on the alkane and alkene distribution in the pyrolysates is virtually unknown in the literature.

This work seeks to address these existing knowledge gaps by investigating the dominant chemical pathways occurring during pyrolysis of linoleic acid and to characterize the chemical profile of the resulting pyrolysates.

4.2. Materials and methods

4.2.1. Materials

Linoleic acid (≥99%), nonadecanoic acid methyl ester (≥98 %), pentane (≥99%), diethyl ether (≥99%), CO (≥99%), gaseous alkanes and alkene standards (C1-C4) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Diazomethane for derivatization of fatty acids was prepared using a Diazald kit

(Sigma-Aldrich, St. Louis, MO, USA) following the manufacturer’s procedures. N_2, H_2, CO_2 and CH_4 standards were purchased from Praxair (Praxair Inc., Danbury, CT, USA). All chemicals were used as received.

4.2.2. Pyrolysis Reactions

Pyrolysis reactions were conducted in 15 mL batch microreactors constructed with stainless steel Swagelok fittings and tubing (0.75-inch) and heated in a fluidized bed sand bath (Techne, Burlington, NJ) as previously described for the pyrolysis of stearic acid [15]. Similar microreactors have also been used in previous studies [15-18].

Approximately 1g of linoleic acid was weighed into a clean and dry microreactor which was then closed, checked for leaks, purged with nitrogen (PP 4.8, Praxair), and sealed. The microreactor was heated at the desired temperature (350 – 450 °C) under constant agitation for the desired length of time (0.5 – 8 h) and then quenched in a bucket of water at room temperature. The microreactor was then cleaned and dried using compressed air to ensure it was clean of sand. All pyrolysis reactions were carried out in triplicates at each of the conditions studied.

4.2.3. Analytical methods

The analytical instruments, supplies and programming used in the product characterization were the same as those discussed in Chapter 3 (sections 3.2.3 – 3.2.5) without modifications.

4.3. Results and discussion

4.3.1. Identification of products in the liquid fraction

Pyrolysis of linoleic acid resulted in products structured as a periodic set of peaks on the chromatograms. Six distinct peaks were identified: an *n*-alkane peak, 1-alkene peak, two cyclic alkanes and alkenes peaks (series 1 before and series 2 after the *n*-alkane peak) and internal alkene peaks (Figure 4.1). It is important to note that while Figure 4.1 shows a general trend observed for most of the conditions tested, some deviations were observed especially as the carbon number increased. For example, the cyclic alkanes and alkenes were not observed after C13 at high reaction temperature conditions for longer periods of time. A similar observation was made in the pyrolysis of stearic acid [15]. However, the cyclic alkanes and alkenes series were not observed in the pyrolysis product of stearic acid.

The products formed in linoleic acid pyrolysis were clearly dependent on the reaction conditions, with higher reaction temperatures and longer reaction times resulting in the formation of a greater proportion of lower molecular weight compounds. Figure 4.2 shows the chromatograms of linoleic acid pyrolysis at 390 °C and 450 °C for various reaction times. Due to the method used in the extraction of the liquid product, only compounds which elute after pentane in the GC analysis were identified and quantified, enabling a direct comparison with the results from pyrolysis of stearic acid.

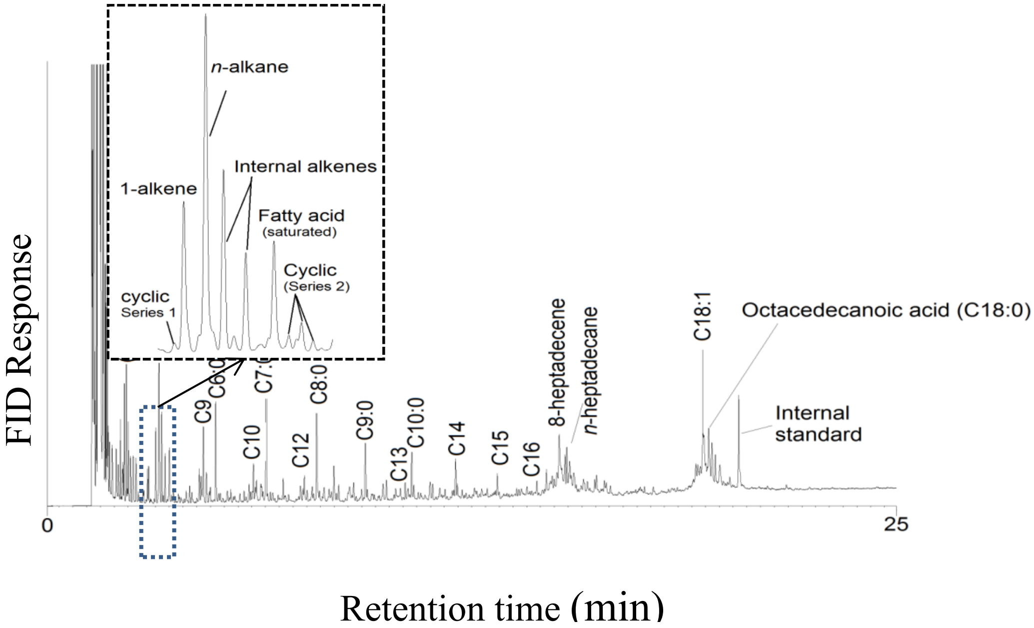

Figure 4.1. GC-FID chromatogram showing typical pentane soluble liquid pyrolysis product of linoleic acid.

The major products in the liquid fraction at low temperature and reaction time were hexane (C6) to decane (C10) alkanes, heptanoic acid (C7:0), octanoic acid (C8:0) and nonanoic acid (C9:0), 8-heptadecene and *n*-heptadecane as well as 8-octadecenoic acid and octadecanoic acid. Minor products included 1-alkenes (C6 to C10), cyclo alkanes and alkenes (C6 to C13), and aromatic compounds (C6 to C10). As temperature and time increased, a reduction in fatty acids, 1-alkenes and internal alkenes was observed concurrently with an increase in the amount of cyclic compounds as well as aromatic compounds (Figure 4.2 and Table 4.1). Also, as temperature and reaction time increased, the selectivity for lower molecular weight compounds became dominant, similar to previous observations in pyrolysis reactions of stearic acid [15].

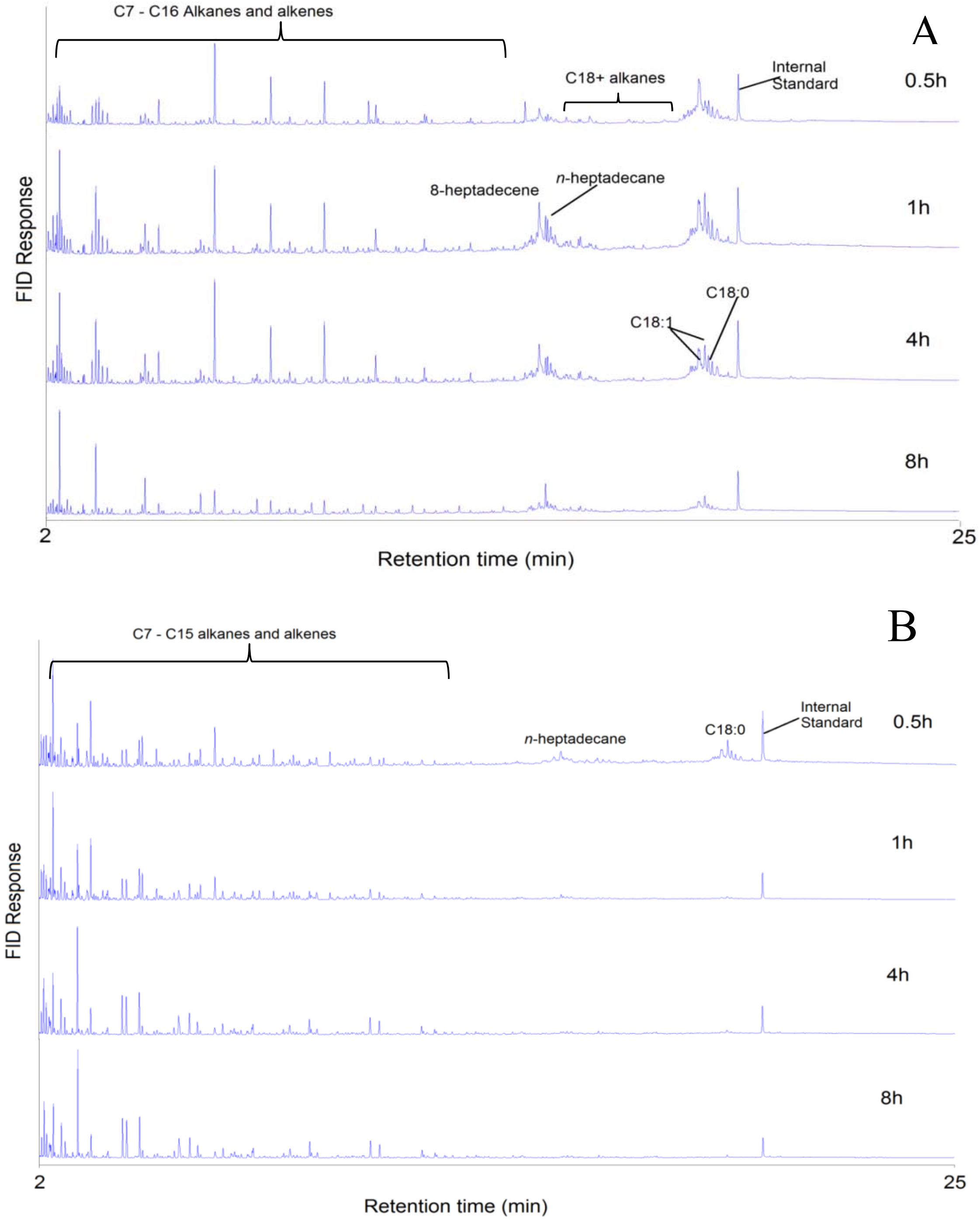

Figure 4.2. GC-FID chromatogram of pentane soluble linoleic acid pyrolysis product at 390°C (A) and 450°C (B) for various reaction times.

4.3.2. Cracking behaviour

The presence of products with carbon numbers less than ten and greater than sixteen may be explained by the presence of the double bonds. The pyrolysis of fatty acids proceeds through the breaking of C-C and C-O bonds through β-scission reactions [4, 16, 17]. In the reaction temperature regimes studied here, the breaking of these bonds has been postulated to follow two competing routes: on the one hand there is deoxygenation followed by C-C bond cleavage to produce hydrocarbon radicals and on the other hand is C-C bond cleavage of the hydrocarbon chain followed by deoxygenation of the short chain molecule [4, 17, 18].

The presence of double bonds (unsaturation) determines which of the two routes is favored. Whereas in saturated fatty acids deoxygenation precedes C-C bond breaking, in the case of unsaturated fatty acids C-C bond breaking is favored [4] due to the lower bond dissociation energy of the allylic C-C bond compared to C-C bond next to the carboxyl group [16, 17, 19, 20]. In the pyrolysis of stearic acid there was formation of *n*-heptadecane (a deoxygenation product) before the formation of other low molecular weight compounds was observed [15]. However, in this study even at a low to mild reaction condition a substantial amount of low molecular weight compounds (the product of C-C bond breaking) was observed (Figure 4.2 and Table 4.1).

Table 4.1. Mass balance of select linoleic acid pyrolysis

	weight % of feed	
Gas fraction	390°C, 4h	450°C, 4h
C_1 to C_4 alkanes	4.32 ± 0.68	19.63 ± 0.76
C_2 to C_4 alkenes	1.54 ± 0.42	1.68 ± 0.23
C5+ alkanes and alkenes	1.04 ± 0.20	1.06 ± 0.08
CO_2	1.92 ± 0.10	3.16 ± 0.18
CO	4.09 ± 0.31	3.19 ± 0.07
Balance (Unidentified)	2.63 ± 0.53	2.21 ± 0.43
Hydrogen **(% volume of gas)**[a]	2.72 ± 0.30	4.53 ± 0.26
Liquid fraction		
C_6 to C_{20} *n*-alkanes	18.67 ± 0.32	15.04 ± 1.36
C_6 to C_{10} 1-alkenes	1.69 ± 0.28	0.96 ± 0.02
C_6 to C_{17} internal alkenes	6.84 ± 0.472	1.75 ± 0.21
Cyclic		
Alkanes	3.05 ± 0.66	4.07 ± 0.44
Alkenes	2.09 ± 0.23	2.47 ± 0.28
Branched alkanes and alkenes	1.66 ± 0.58	3.47 ± 1.35
C_3 to C_{18} fatty acids		
Saturated	7.94 ± 1.02	3.38 ± 0.13
Unsaturated	0.92 ± 0.13	0.38 ± 0.20
Aromatic		
Mono	3.50 ± 0.38	14.92 ± 0.91
Poly	2.23 ± 0.15	2.75 ± 0.36
Pentane insoluble residue	ND	8.26 ± 2.10
Balance (Unidentified)	37.71 ± 1.32	13.67 ± 1.95

a – unit is % volume of gas as the amount was too low when calculated in wt % of feed.

ND – not detected.

The predominance of saturated compounds at the condition tested (Figures 4.2 and 4.3 and Table 4.1) may be due to saturation reactions. Evidence to support this explanation can be found in the presence of hydrogen measured in the gas fraction. Our findings confirm previous observations by other researchers who reported hydrogen in the pyrolysis product of different lipid feedstock [13, 18, 21-24]. Further evidence of saturation reactions was the formation of octadecenoic and octadecanoic acids which are the partial and complete saturation products respectively, of the feed at low temperatures and reaction times (Figure 4.2).

4.3.3. Cyclic and Aromatic Compounds

Cyclic alkanes and alkenes were produced under all conditions tested at higher reaction temperatures resulting in comparatively larger amounts of cyclic compounds (Table 4.1). The cyclic compounds consisted of both C5 (cyclopentanes and cyclopentenes) and C6 (cyclohexanes and cyclohexenes) structures. The results also showed that the formation of cycloalkanes were favored over that of cycloalkenes further supporting the occurrence of saturation reactions as part of the pyrolysis of linoleic acid. The most widely accepted mechanism for the formation of cyclic compounds in literature is the Diel-Alder reaction of dienes with an alkene [18, 21, 25]. However, this mechanism only accounts for the formation of cyclohexenes and upon hydrogenation formation of cyclohexanes. To better account for the formation monocyclic compounds, Kubatova et al [26] proposed a second mechanism of cyclic hydrocarbon formation involving intramolecular radical cyclization. The proposed mechanism fits better with the current data as both C5 and C6 cycloalkanes and cycloalkenes were formed at all the conditions studied.

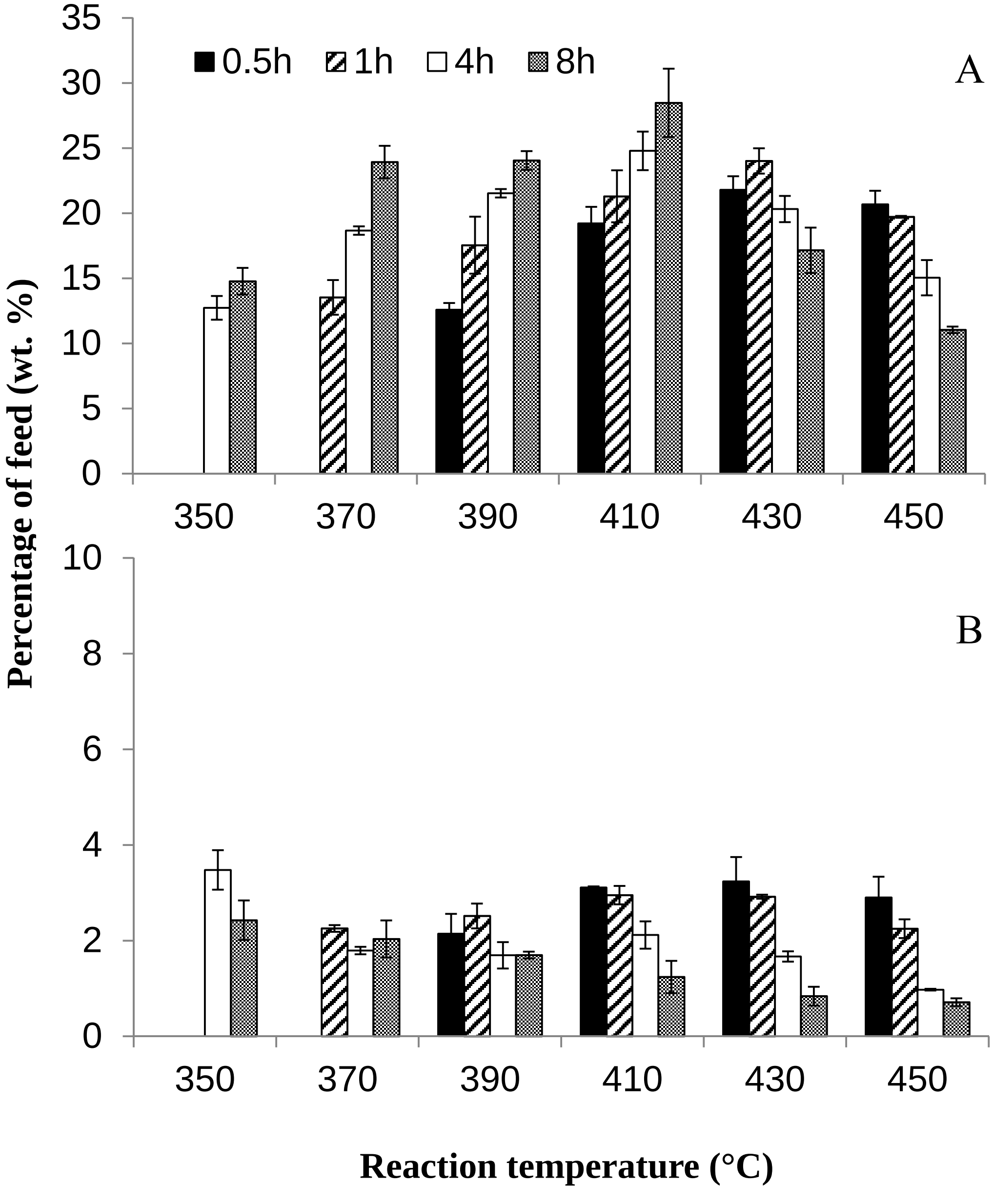

Figure 4.3. *n*-alkane (A) and 1-alkene (B) composition of pentane soluble linoleic acid pyrolysis product at various temperatures and reaction times.

Another important class of cyclic compounds formed was the aromatic compounds. Figure 4.4 shows the total aromatic compounds formed at each temperature and time combination. The results show that there was formation of aromatic compounds under all the conditions tested. In general, higher reaction temperatures and reaction times resulted in larger amounts of aromatic compounds in the pyrolysates. Table 4.1 shows that majority of the aromatic compounds were mono aromatic and increasing temperature increased significantly the mono aromatic compounds but only slightly increased the poly aromatics in the liquid product. This could be due to the poly aromatic compounds being converted to insoluble polymerization products (coke) at the higher temperature [4, 18]. The main aromatic compounds formed were benzene, toluene, ethylbenzene and xylenes. Other aromatic compounds such as indanes and indenes, naphthalenes, fluorenes, anthracenes and pyrenes were identified in the pyrolysis product. The formation of aromatic compounds is widely accepted to be through dehydrogenation of cyclohexenes to form mono aromatic compounds [4, 25, 26]. The mono aromatic compounds then undergo polymerization to produce polyaromatics, which upon further polymerization result in coke formation.

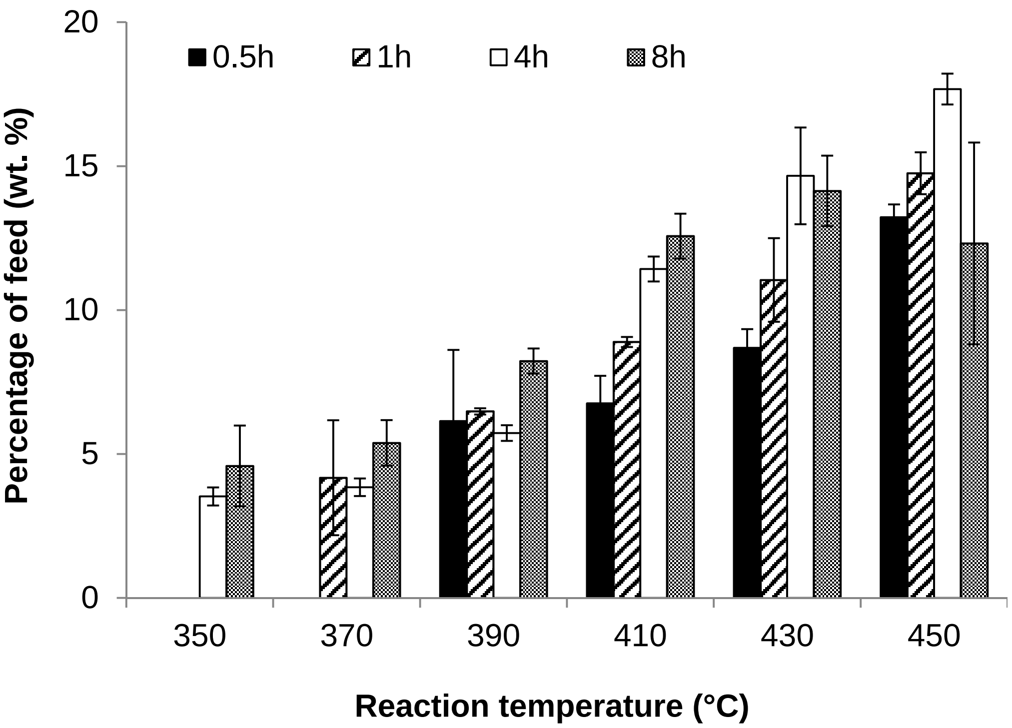

Figure 4.4. Aromatic compound content of pentane soluble linoleic acid pyrolysis product at various temperatures and reaction times

4.3.4. Hydrocarbons in the gas fraction

Analysis of the gas fraction of the pyrolysis product of linoleic acid indicated that gaseous hydrocarbons were present under all conditions tested and that saturated hydrocarbons were formed preferentially over the unsaturated hydrocarbons. As shown in Figure 4.5 and Table 4.1, at low reaction temperature and short time the most abundant hydrocarbon products in the gas fraction were propane and ethane. As the reaction time increased, ethylene decreased while ethane increased possibly as a result of saturation reaction of ethylene to ethane. Similarly, the amount of propene decreased as reaction time increased with a concurrent increase in the amount of propane. The formation of the bulk of the hydrocarbons in the gas phase can be explained through the well-described C-C bond cleavage through β-scission and ethylene elimination [4, 18].

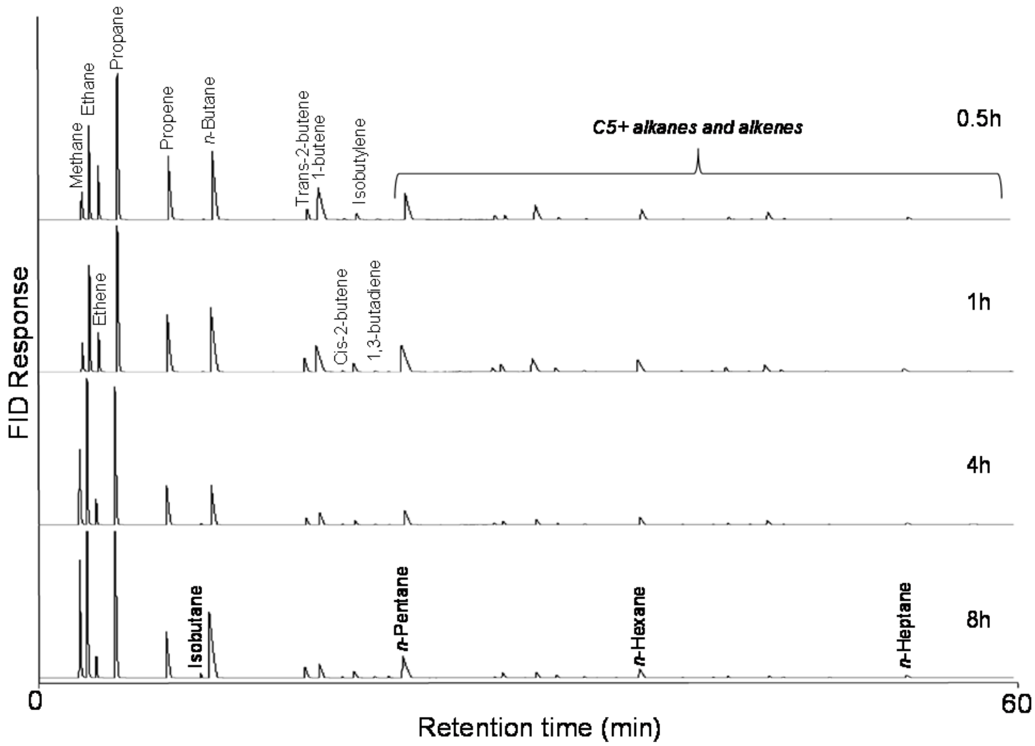

Figure 4.5. GC-FID chromatogram of hydrocarbons in the gas fraction of linoleic acid pyrolysis product at 390°C for various reaction times

In contrast with the pattern observed in this study, Idem et al [18] reported the formation of higher amounts of unsaturated hydrocarbons (ethylene and propene) in the gas fraction during the pyrolysis of canola oil between 300 °C and 500 °C. This discrepancy may be attributed to the different feedstock used. While canola oil is composed primarily of TAGs, the feed in this study eas fatty acid used in this study is linoleic acid (a fatty acid). According to Melero et al [4] the consumption of hydrogen produced in the thermal cracking of fats and oils to yield saturated hydrocarbons is an important reaction step and as a result hydrogen left at the end of the reaction is negligible.

The formation of more saturated over unsaturated hydrocarbons in the gas fraction may be due to saturation of the feed to yield saturated compounds is a more plausible explanation for the observation made.

4.3.5. Deoxygenation and hydrogen formation

Figure 4.6 shows the carbon dioxide (CO_2) and carbon monoxide (CO) composition of the gas fractions obtained at selected reaction conditions. The general trend observed in Figure 4.6 is representative of the other conditions tested. Further evidence of deoxygenation is the formation at most reaction conditions tested of 8-heptadecene and *n*-heptadecane which are deoxygenation products of 8-octadecenoic acid and octadecanoic acid, respectively. It should be noted that heptadecadiene which would be a direct deoxygenation product of the feed was not observed in the pyrolysis product at all conditions tested. CO and CO_2 are formed through decarbonylation and decarboxylation respectively [27-30].

The formation of CO and CO_2 in the thermal and pyrolityc cracking of various fats and oils has been reported by several researchers. A detailed composition of CO and CO_2 at various temperature-time combinations has however until now not been reported in the literature.

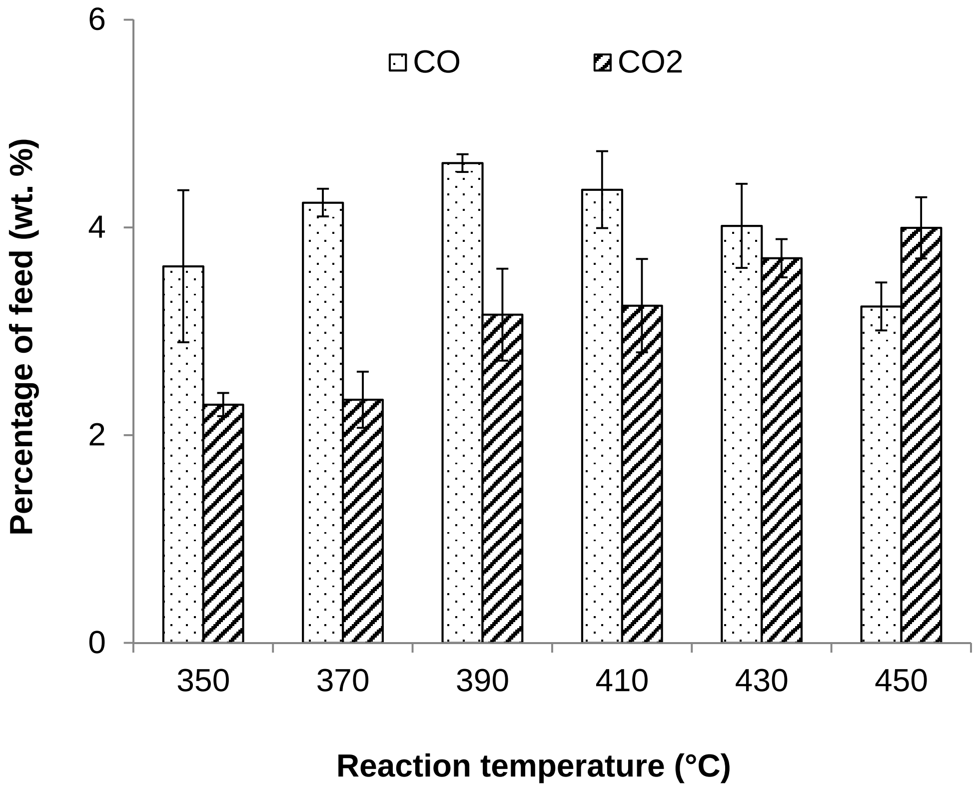

Figure 4.6. Carbon monoxide and carbon dioxide content of the gas fraction of linoleic acid pyrolysis product at 4 h for various reaction temperatures

As shown in Figure 4.6 and Table 4.1, at mild reaction conditions there was substantially more CO than CO_2, indicating that decarbonylation reactions are favored over decarboxylation reactions in this regime. As temperature increased from 350 °C to 410 °C an increase in both CO and CO_2 was observed and decarbonylation remained the dominant deoxygenation pathway. At more severe temperatures (430 °C and higher) and for long reaction times, decarboxylation was the prevailing deoxygenation mechanism.

Table 4.1 shows that the amount of hydrogen in the gas fraction increased as a function of reaction temperature. Hydrogen formation is attributed to dehydrogenation reactions in the formation of cyclic alkenes and aromatic compounds as well as polymerization reactions involving these compounds [4, 18]. Another possible mechanism for the formation of hydrogen is the water gas shift reaction involving CO and water to produce hydrogen and CO_2. The same mechanism can be the process by which the observed decrease in the amount of CO with a concurrent increase in CO_2 observed under severe reaction conditions occurred.

4.3.6. Quantitative analysis

Fatty acid feedstock conversion was calculated as the difference in mass between the amount of linoleic acid and any positional isomers of linoleic acid remaining in the product mixture at the end of the reaction and the amount of feed used. Complete conversion of the feed was measured at all the reaction conditions tested. This is in contrast to the pyrolysis of stearic acid where a conversion of between 32 and 97 wt % were achieved under similar conditions [15]. The difference in conversion between the stearic acid and the linoleic acid can be explained by the presence of the double bonds in the linoleic acid. This results in lower bond dissociation energy of the allylic C-C bond and consequently in an increase in the positions at which C-C bond cleavage can occur, thereby transforming the feed into reaction products [4, 16, 17, 19, 20].

Figure 4.7 shows the *n*-alkane and 1-alkene content as a function of carbon number at 4 h reaction time for the various temperatures studied. The most abundant *n*-alkane at all the reaction temperatures studies was hexane (C6).

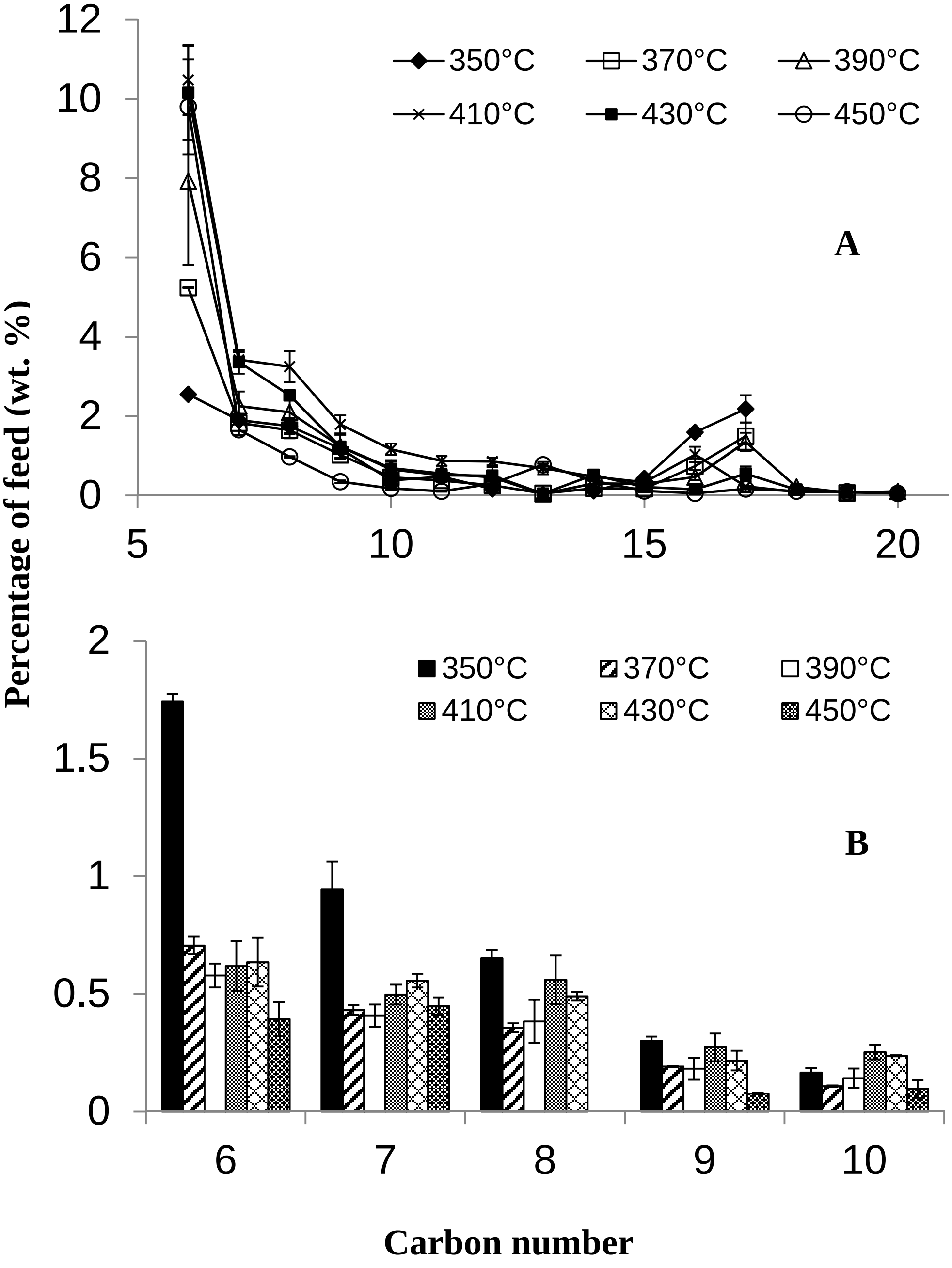

Figure 4.7. *n*-alkane (A) and 1-alkene (B) composition as a function of carbon number at various temperatures for 4 h reaction time.

In general the product distribution was such that as the carbon number increased from C6 the relative amount decreased until pentadecane (C15) and then increased as carbon number grew to heptadecane (C17). Finally the weight percentage of the product decreased with carbon number up to C20 except at 450 °C. At this temperature, the amount of product deceased from C6 to C11 and then increased up to C15 and from there on decreased to C20. With respect to 1-alkenes, only carbon number C6 to C10 were present in the liquid fraction. The general trend was such that the relative amount decreased as carbon number increased from C6 to C10 at the different temperatures studied with the exception of 410 °C when there was a slight increase from C7 to C8 and then a reduction from there on to C10. The maximum amounts of combined *n*-alkane and 1-alkene were formed at 410 °C at 8 h (29.72 wt %) and 430 °C for 1 h (26.93 wt %) of reactions.

4.4. Conclusion

This study demonstrates the viability of fatty acid pyrolysis to produce liquid hydrocarbons. Unlike pyrolysis of saturated fatty acids where decarboxylation was the initial reactions and predominant step before the formation of appreciable amounts of cracking products, in the pyrolysis of linoleic acid (a di unsaturated fatty acid) both deoxygenation and cracking of allylic C-C bonds proceed concurrently. Results indicated that deoxygenation reaction occurred through both decarboxylation and decarbonylation confirmed from the presence of CO and CO_2 in the gas fraction. Decarboxylation was favored at higher reaction temperatures whereas decarbonylation was favored at milder reaction conditions. Saturation reactions were another important step in the pyrolysis of linoleic acid. The optimal conditions for producing the highest amount of hydrocarbon compounds were 390 and 410 °C for reaction times ranging from 4 to 8 h and 430 to 450 °C for reaction times of 0.5 to 1 h.

4.5. References

[1] N. Taufiqurrahmi, S. Bhatia, Catalytic cracking of edible and non-edible oils for the production of biofuels, Energy & Environmental Science, 4 (2011) 1087-1112.

[2] D.G. Lima, V.C.D. Soares, E.B. Ribeiro, D.A. Carvalho, E.C.V. Cardoso, F.C. Rassi, K.C. Mundim, J.C. Rubim, P.A.Z. Suarez, Diesel-like fuel obtained by pyrolysis of vegetable oils, Journal of Analytical and Applied Pyrolysis, 71 (2004) 987-996.

[3] W.C. Wang, N. Thapaliya, A. Campos, L.F. Stikeleather, W.L. Roberts, Hydrocarbon fuels from vegetable oils via hydrolysis and thermo-catalytic decarboxylation, Fuel, 95 (2012) 622-629.

[4] J.A. Melero, M.M. Clavero, G. Calleja, A. Garcia, R. Miravalles, T. Galindo, Production of Biofuels via the Catalytic Cracking of Mixtures of Crude Vegetable Oils and Nonedible Animal Fats with Vacuum Gas Oil, Energy & Fuels, 24 (2010) 707-717.

[5] http://www.ec.gc.ca/default.asp?lang=En&n=714D9AAE-1&news=2D84D5D6-F152-4F5F-A4B9-BE973BE6821B. Last accessed on July 23, 2013.

[6] E. DeOliveira, R.L. Quirino, P.A.Z. Suarez, A.G.S. Prado, Heats of combustion of biofuels obtained by pyrolysis and by transesterification and of biofuel/diesel blends, Thermochimica Acta, 450 (2006) 87-90.

[7] I.C.P. Fortes, P.J. Baugh, Pyrolysis-GC/MS studies of vegetable oils from Macauba fruit, Journal of Analytical and Applied Pyrolysis, 72 (2004) 103-111.

[8] H. Lappi, R. Alen, Production of vegetable oil-based biofuels-Thermochemical behavior of fatty acid sodium salts during pyrolysis, Journal of Analytical and Applied Pyrolysis, 86 (2009) 274-280.

[9] A.A. Lappas, S. Bezergianni, I.A. Vasalos, Production of biofuels via co-processing in conventional refining processes, Catalysis Today, 145 (2009) 55-62.

[10] G.W. Huber, A. Corma, Synergies between bio- and oil refineries for the production of fuels from biomass, Angewandte Chemie-International Edition, 46 (2007) 7184-7201.

[11] N.O.V. Sonntag, Structure and composition of fats and oils, 4th ed., John Wiley and Sons, New York, 1979.

[12] Y. Luo, I. Ahmed, A. Kubatova, J. St'avova, T. Aulich, S.M. Sadrameli, W.S. Seames, The thermal cracking of soybean/canola oils and their methyl esters, Fuel Processing Technology, 91 (2010) 613-617.

[13] A. Kubatova, Y. Luo, J. Stavova, S.M. Sadrameli, T. Aulich, E. Kozliak, W. Seames, New path in the thermal cracking of Triglycerides (canola and soybean oil), Fuel, 90 (2011) 2598-2608.

[14] H. Lappi, R. Alen, Pyrolysis of vegetable oil soaps-Palm, olive, rapeseed and castor oils, Journal of Analytical and Applied Pyrolysis, 91 (2011) 154-158.

[15] K.D. Maher, K.M. Kirkwood, M.R. Gray, D.C. Bressler, Pyrolytic decarboxylation and cracking of stearic acid, Industrial & Engineering Chemistry Research, 47 (2008) 5328-5336.

[16] A. Osmont, L. Catoire, I. Gokalp, M.T. Swihart, Thermochemistry of C-C and C-H bond breaking in fatty acid methyl esters, Energy & Fuels, 21 (2007) 2027-2032.

[17] A. Osmont, L. Catoire, I. Gokalp, Thermochemistry of methyl and ethyl esters from vegetable oils, International Journal of Chemical Kinetics, 39 (2007) 481-491.

[18] R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Thermal cracking of Canola oil: Reaction products in the presence and absence of steam, Energy & Fuels, 10 (1996) 1150-1162.

[19] W.W. Nawar, thermal degradation of lipids . A Review, Journal of Agricultural and Food Chemistry, 17 (1969) 18-&.

[20] W.A. Hartgers, J.S.S. Damste, J.W. Deleeuw, Curie-point pyrolysis of sodium-salts of functionalized fatty-acids, Journal of Analytical and Applied Pyrolysis, 34 (1995) 191-217.

[21] R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Catalytic conversion of canola oil to fuels and chemicals: Roles of catalyst acidity, basicity and shape selectivity on product distribution, Fuel Processing Technology, 51 (1997) 101-125.

[22] L. Dandik, H.A. Aksoy, Effect of catalyst on the pyrolysis of used oil carried out in a fractionating pyrolysis reactor, Renewable Energy, 16 (1999) 1007-1010.

[23] J.M. Encinar, J.F. Gonzalez, G. Martinez, S. Roman, Catalytic pyrolysis of exhausted olive oil waste, Journal of Analytical and Applied Pyrolysis, 85 (2009) 197-203.

[24] J. Gornay, L. Coniglio, F. Billaud, G. Wild, Octanoic acid pyrolysis in a stainless-steel tube: What is the role of the coke formed on the wall?, Journal of Analytical and Applied Pyrolysis, 87 (2010) 78-84.

[25] A.O. Adebanjo, A.K. Dalai, N.N. Bakhshi, Production of diesel-like fuel and other value-added chemicals from pyrolysis of animal fat, Energy & Fuels, 19 (2005) 1735-1741.

[26] A. Kubatova, J. St'avova, W.S. Seames, Y. Luo, S.M. Sadrameli, M.J. Linnen, G.V. Baglayeva, I.P. Smoliakova, E.I. Kozliak, Triacylglyceride Thermal Cracking: Pathways to Cyclic Hydrocarbons, Energy & Fuels, 26 (2012) 672-685.

[27] J.G. Immer, H.H. Lamb, Fed-Batch Catalytic Deoxygenation of Free Fatty Acids, Energy & Fuels, 24 (2010) 5291-5299.

[28] J.G. Immer, M.J. Kelly, H.H. Lamb, Catalytic reaction pathways in liquid-phase deoxygenation of C18 free fatty acids, Applied Catalysis a-General, 375 (2010) 134-139.

[29] C.C. Chang, S.W. Wan, Chinas motor fuels from tung oil, Industrial and Engineering Chemistry, 39 (1947) 1543-1548.

[30] C.M.R. Prado, N.R. Antoniosi, Production and characterization of the biofuels obtained by thermal cracking and thermal catalytic cracking of vegetable oils, Journal of Analytical and Applied Pyrolysis, 86 (2009) 338-347.

5. Thermal cracking of free fatty acids in inert and light hydrocarbon gas atmospheres [1]

5.1. Introduction

The development of renewable alternatives to petroleum derived fuels and chemicals have become imperative due to socio-economic, geopolitical and environmental concerns. This has led to the development of several technologies to convert lipids and lignocellulosic biomass into renewable chemicals and fuels. One of the most promising technologies being developed for converting biomass is pyrolysis [1-4]. Lipids in the form of triacylglycerols (TAGs) are a particularly important feedstock because of their high energy density and widespread availability compared to other biomass sources [5].

Pyrolysis of TAGs has been the focus of intense research and development as well as commercialization efforts. Typical feedstocks include canola oil, soybean oil, sunflower oil, jatropha oil, lard and tallows as well as vegetable oil soaps and waste cooking oils. Pyrolysis products at room temperature and atmospheric pressure may be liquid, gas and/or solid depending on the feedstock used and on the process reaction conditions such as temperature, time, pressure, atmosphere, catalyst etc.[6-9].

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[1] A version of this chapter has been accepted for publication in the Journal Fuel. J. Asomaning, P. Mussone, D.C. Bressler, Thermal cracking of free fatty acids in inert and light hydrocarbon gases atmosphere. (2014). http://dx.doi.org/10.1016/j.fuel.2014.02.069

An analysis of the main products reported from the pyrolysis of these fats and oils revealed the presence of compounds such as linear, branched and cyclic hydrocarbons, aromatics, carbonyls, alcohols, carboxylic acids, carbonic gases and hydrogen. The distribution of the classes of compounds is also dependent on the feedstock and reaction conditions employed [10-12]. The thermal and thermo-catalytic deoxygenation and pyrolysis of free fatty acids have also been reported in the literature with product composition and distribution being influenced by the aforementioned feedstock and reaction conditions employed [13-17].

Pyrolysis of biomass has generally been conducted under inert atmosphere with gases such as nitrogen, helium or argon although some studies involving the use of reactive atmosphere have been reported in the literature. Both thermal and thermo-catalytic biomass pyrolysis under steam atmosphere at various temperatures have been studied and compared to inert atmospheres [10, 18-20]. In these cases, an increase in organic liquid product yields was measured compared to inert atmospheres. The thermo-catalytic deoxygenation and pyrolysis of fatty acids under hydrogen atmosphere has been reported to increase both reactions rate and product yields over those obtained under inert atmosphere [15, 21-23]. However, Kubatova et al [12] and Luo et al [24] found that at reaction temperatures above 400 °C the thermal cracking of canola oil, soybean oil and their methyl esters under hydrogen did not positively impact the liquid product yields.

Recycling of the product gas stream has been suggested as an economical way of operating large scale pyrolysis plants [9, 25]. The gas product stream is typically composed of CO, CO_2, light hydrocarbons and H_2 depending on the feedstock composition and reactions conditions [26,27]. Literature on biomass pyrolysis under CO, CO_2 and hydrocarbon atmosphere to study the effect of recycling the gas product is scarce. Mante et al. [28] and Zhang et al. [26] studied the effect of lignocellulosic biomass pyrolysis under the non-condensable gases CO, CO_2, CH_4 and compared it with reactions done under inert atmospheres. Both studies reported an increase in liquid product yield. In the case of Mante et al. [28], a decrease in char/coke yield was also observed. There are no studies reported in the literature on the pyrolysis of lipids, particularly fatty acids under reactive non-condensable hydrocarbon gases.

The purpose of this work is to address these knowledge gaps by studying the effect of short-chain non-condensable alkane and alkene gases on the pyrolysis of free fatty acids by uncovering the dominant chemical pathways. In particular, this work seeks to study the effect of such gases on the product portfolio and the overall product yield.

5.2. Materials and methods

5.2.1. Materials

Oleic acid (≥99%), internal standard for GC analysis of liquid product, nonadecanoic acid methyl ester (≥99 %), pentane (≥99%), diethyl ether (≥99%), CO standard (≥99%), gaseous alkanes and alkene standards (C1-C4) were purchased from Sigma-Aldrich (St. Louis, MO, USA). N_2 (99.998%), CO_2 standard (99.9%), methane (99%), ethane (99%), ethylene (99%), propane (99%)

and propylene (99%) were obtained from Praxair (Mississauga, ON, Canada). Diazomethane for derivatization of fatty acids was prepared using a Diazald kit (Sigma-Aldrich, St. Louis, MO, USA) following the manufacturer's procedures. All chemicals were used as received.

5.2.2. Pyrolysis Reactions

Pyrolysis reactions were conducted in 15 mL batch microreactors constructed with stainless steel Swagelok fittings and tubing (0.75-inch) and heated in a fluidized bed sand bath (Techne, Burlington, NJ) as previously described [13]. Approximately 1g of oleic acid was weighed into a clean and dry microreactor which was then closed, checked for leaks and purged with the desired gas (N_2, methane, ethane, ethylene, propane or propylene). The reactor was then pressurized to between 130 and 500 psi (896.3 and 3447.4 kPa) with the desired gas and the microreactor was sealed. The microreactor was heated at 410 °C under constant agitation for 2 h and then immediately quenched in a bucket of water at room temperature. The reaction temperature and time used were selected based on work conducted by our group on the thermal cracking of oleic acids discussed in Chapter 3. The reaction conditions selected for this study maximizes fatty acid feed conversion and liquid product yield while minimizing gas, aromatic compounds and solids formation. The outside surface of the microreactor was then cleaned and dried using compressed air to ensure the microreactor was clean of sand from the sand bath. All pyrolysis reactions were carried out in triplicates at each of the conditions studied.

5.2.3. Analytical methods- Gas product analysis

The weight of the gas fraction produced was determined by weighing the microreactors before and after venting the gas product in the microreactor. A 0.25inch stainless steel Swagelok tube fitting with a septum was screwed onto the microreactor in order to sample the gas product for gas chromatography (GC) analysis according to the method described by Maher et al [13]. Gas samples were then analyzed on a GC-FID and GC-TCD using instruments, supplies and methods described in Chapter 3 (section 3.2.3).

5.2.4. Analytical methods - Liquid product analysis

After venting, the microreactors were opened and the weight of liquid product was determined. The liquid and gas products were then analyzed on GC-FID and GC-MS using instruments, supplies and methods described in in Chapter 3 (section 3.2.4).

5.2.5. Products identification and quantification

Compounds in the gas and liquid fraction were quantified according to the procedures described in Chapter 3 (section 3.2.5). Data in all tables and figures represent mean ± standard deviation of triplicate experiments, unless otherwise indicated. Statistic tests were performed using ANOVA or T-test to determine significant differences in data at the 95% confidence level.

5.3. Results and Discussion

5.3.1. Liquid product yield

Pyrolysis of oleic acid under nitrogen and light hydrocarbons resulted in the formation of liquid and gas products under all the conditions tested. Solid products were not observed in any of the experiments. The liquid product yields at 130 psi initial headspace pressure are shown in Table 5.1. While oleic acid pyrolysis in presence of methane, ethane and propane did not result in higher liquid product yields, significant increases were measured under ethylene (17%) and propylene (26%) compared to reaction conducted under nitrogen atmosphere.

Table 5.1. Headspace gas and recovered liquid from the pyrolysis of oleic acid product at 410 °C for 2 h.

Headspace gas/pressure (psi)	Mole ratio (feed : gas)[1]	% weight of liquid product recovered
Nitrogen (130)	1 : 1.8	81.4 ± 2.6 [a]
Ethylene (130)	1 : 1.9	98.2 ± 0.9 [b]
Ethane (130)	1 : 1.9	83.0 ± 1.4 [a,c]
Propylene (130)	1 : 2.0	107.4 ± 2.6 [d]
Propane (130)	1 : 2.0	83.8 ± 1.1 [a,c]
Methane (130)	1 : 1.8	76.7 ± 1.1[e]

[1] Moles of gas calculated using the Peng-Robinson equation of state

[a] values with the same superscript letters are not significantly different at 95% confidence level.

This phenomenon may be explained in terms of increased reactivity of the pi bond electrons in these compounds compared to the saturated light hydrocarbon gases' sigma bonds [29]. The increased reactivity implies the unsaturated hydrocarbon gases could act as reactants compared to the saturated hydrocarbon, resulting in the observed increase in the liquid product yield. A possible explanation for this increase may be found in the formation of branched alkanes and alkenes (described in detail in section 5.3.4). Additionally, the increased liquid product yield could be due to ethylene-ethylene or propylene-propylene radical addition reactions [30].

5.3.2. Liquid product composition

The classes of compounds in the liquid pyrolysis product under inert and light hydrocarbon headspace at 130 psi are shown in Table 5.2. The "unidentified" represents GC eluted peaks that could not be unambiguously identified. The "unaccounted" fraction represents the difference between the GC eluted peaks percentage and 100%. This fraction represents compounds which have molecular weights lower than or equal to C5 that could not be integrated due to solvent peak overlap and possibly, high molecular weight compounds which could not be eluted on the GC.

The liquid product was composed primarily of linear, cyclic and branched hydrocarbon, fatty acids and aromatics with carbon numbers between C6 and C19. Irrespective of the headspace gas used, *n*-alkanes (C6 to C19) were the most abundant class of compounds and they constituted on average about 23% of the liquid product with the exception of propylene headspace which had 19%. A similar observation was made with the linear alkenes where there was only limited difference between the inert headspace and the hydrocarbon headspace.

Linear alkanes and alkenes are well-known products of the direct deoxygenation of the fatty acid feed or cracking product of feed and the cracking of deoxygenated hydrocarbon product through free radical mechanism [10, 12, 13]. Evidence of deoxygenation was found in the gas product analysis where CO and CO_2 which are decarbonylation and decarboxylation [30, 31] products, respectively, of free fatty acids were found (discussed in section 5.3.5).

Cyclic alkanes and alkenes ranging in carbon number from 6 to 13, which were mostly substituted, are shown in Table 5.2. There were no significant differences in the total cyclic hydrocarbons with the different headspaces gases. The cyclic hydrocarbons were predominantly C5 (cyclopentanes and cyclopentenes) and C6 (cyclohexanes and cyclohexenes) cyclic structures. The cyclic hydrocarbons accounted for 9.2 to 11.2% of the liquid product. Under N_2 atmosphere, cyclopentanes and cyclopentenes accounted for 34% and cyclohexanes and cyclohexenes were 51% of the cyclic hydrocarbon composition. Similar results were observed when ethylene atmosphere was used resulting in 39% of 5-carbon and 49% of 6-carbon rings.

Table 5.2. Liquid product composition at an initial pressure of 130 psi under inert and light hydrocarbon gas atmosphere

Class of compounds	Weight % of liquid product					
	Headspace gas					
	Nitrogen	Methane	Ethane	Propane	Ethylene	Propylene
C_6 to C_{12} 1-Alkenes	3.5 ± 0.2	4.1 ± 0.4	3.4 ± 0.2	3.3 ± 0.4	3.8 ± 0.4	4.9 ± 1.5
C_6 to C_{18} Internal alkenes	11.3 ± 0.7	11.7 ± 0.9	12.5 ± 0.5	12.6 ± 1.3	11.2 ± 0.2	10.6 ± 1.4
C_6 to C_{19} *n*-Alkanes	23.6 ± 1.9[a]	23.3 ± 2.5[a]	22.4 ± 2.6[a]	23.5 ± 1.1[a]	23.9 ± 0.9[a]	19.5 ± 0.9[a]
Aromatics	4.7 ± 0.3[a]	4.4 ± 0.4[a]	4.6 ± 0.5[a]	4.7 ± 0.1[a]	5.5 ± 0.2[a]	6.1 ± 0.3[b]
Branched hydrocarbons	3.5 ± 0.4[a]	3.4 ± 0.4[a]	3.0 ± 0.7[a]	2.8 ± 0.6[a]	7.8 ± 1.5[b]	6.9 ± 0.9[b]
Cyclic hydrocarbons	9.8 ± 0.7[a]	9.2 ± 0.4[a]	10.2 ± 0.5[a]	10.9 ± 0.7[a]	10.8 ± 0.3[a]	11.2 ± 0.4[a]
C4 to C18 Fatty acids	15.5 ± 0.8[a]	12.6 ± 2.4[a]	11.7 ± 1.7[a]	13.8 ± 1.3[a]	10.9 ± 1.9[b]	9.0 ± 0.2[b]
Unreacted feed + Isomers	2.1 ± 0.6	2.5 ± 0.8	2.8 ± 1.9	2.5 ± 0.8	1.0 ± 0.3	1.0 ± 0.5
Unidentified	18.5 ± 2.8	17.2 ± 1.8	15.9 ± 0.2	16.0 ± 1.9	18.1 ± 2.9	19.9 ± 1.8
Unaccounted	8.8 ± 3.4	11.5 ± 4.3	13.6 ± 1.1	9.9 ± 1.9	6.9 ± 2.0	10.6 ± 3.1

[a] values in the same row are not significantly different at the 95% confidence level from N_2 atmosphere if they have the same letters.

It is accepted widely that six carbon numbered rings are formed predominantly by the Diel-Alder reaction involving a diene and a dienophile [10, 31, 32]. However, Kubatova et al [34] recently proposed a new path to cyclic compound formation in pyrolysis of TAGs which involves the intramolecular cyclization of alkenyl radical with terminal double bond. The data from this study do not support the predominance of the Diels-Alder reaction in the formation of 6-carbon rings since the presence of the excess dienophile (ethylene or propylene) did not result in an increase in the C6 cyclic compounds compared to inert (N_2) atmosphere.

Total aromatic compounds are also presented in Table 5.2. Under inert N_2 atmosphere, total aromatics accounted for 4.7% of the liquid product. The results showed that products from reactions with methane, ethane, ethylene and propane headspaces had total aromatic compounds which were not significantly different from N_2 atmosphere. On the other hand pyrolysis in presence of propylene resulted in increased total aromatics content to 6.1%. The majority of the aromatic compounds produced under the conditions used in this study were predominantly mono-aromatic (65-75% of the aromatic compounds) compounds with BTEX (benzene, toluene, ethylbenzene and xylenes) accounting for nearly 40% of the total aromatic compounds. Mono-aromatic compounds are formed through dehydrogenation of six carbon numbered cyclic alkanes and alkenes [10, 32-34]. Polyaromatic compounds are then formed through polymerization and dehydrogenation of the mono-aromatic compounds [10, 35] and alternatively via an intramolecular radical cyclization mechanism [33].

The total branched hydrocarbon compounds in the liquid product are reported in Table 5.2. Similar to the total aromatic compounds the saturated light hydrocarbon gas atmosphere resulted in total branched hydrocarbon compounds that were not significantly different from the inert atmosphere accounting for about 3.5% of the liquid product. The unsaturated hydrocarbon atmosphere resulted in a significantly higher total branched hydrocarbon yield representing 7.8 and 6.9% of the liquid product under ethylene and propylene atmosphere, respectively. The results indicated that the unsaturated hydrocarbon atmosphere promoted branching reaction possibly through radical addition reactions discussed in detail in section 5.3.4.

Fatty acid deoxygenation was promoted during pyrolysis in the presence of unsaturated short-chain hydrocarbon gases compared to inert atmosphere (Table 5.2). The total fatty acids weight percentage in the pyrolysates decreased significantly from 15.5 under inert N_2 atmosphere to 10.9 and 9.0, respectively, when ethylene and propylene were used. Short-chain alkenes also increased conversion of the feed when compared to inert atmosphere (Table 5.2). The increased rate of fatty acid deoxygenation is discussed in detail in section 5.3.5.

The weight percentage of alkanes and alkenes (linear, branched and cyclics) in the pyrolysates is reported in Figures 5.1a and 5.1b, respectively. Between carbon numbers 6 and 13 there was generally higher total alkanes and alkenes when unsaturated hydrocarbon atmosphere was used compared to inert atmosphere. The trend is generally reversed between carbon numbers 14 and 17 where the inert atmosphere resulted in relatively higher total alkanes and alkenes.

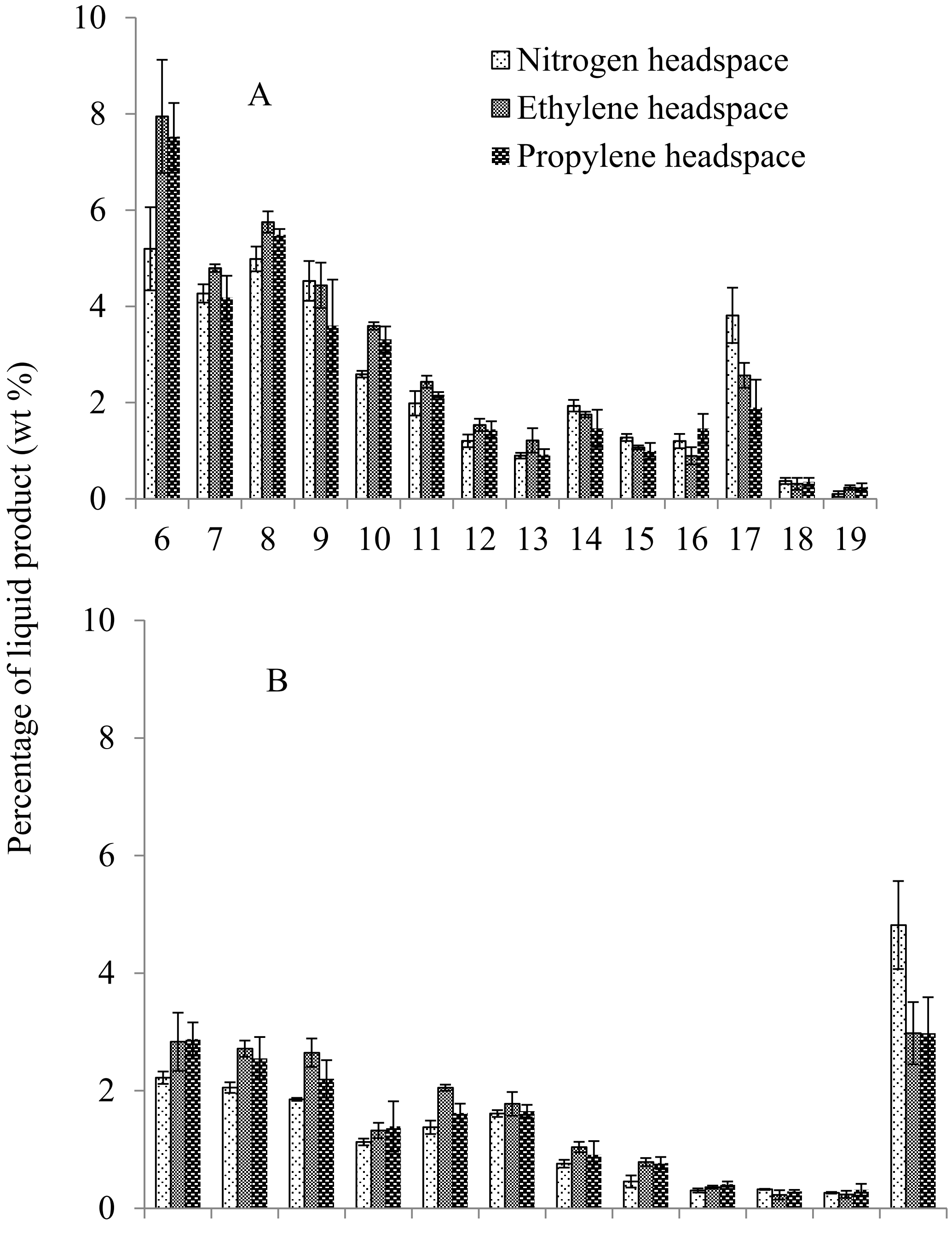

Figure 5.1. Total alkanes (linear, branched, cyclic) (A) and total alkenes (linear, branched, cyclic) (B) composition by carbon number in oleic acid liquid pyrolysis product at 410 °C, 2 h and 130 psi initial pressure.

Irrespective of the atmosphere, there is marked selectivity towards C6 to C12 total alkanes and alkenes (Figure 5.1). This observation may be attributed to the influence of the carbon double bond on the fatty acid feed on the pyrolysis reaction. The details of the influence of the fatty acid double bond on the pyrolysis reaction was discussed in Chapter 3 (section 3.3.3 – 3.3.5). The observed higher C17 alkenes (Figure 5.1b) maybe explained in terms of the direct deoxygenation of the fatty acid feed resulting in the formation of heptadecene isomers.

5.3.3. Effect of headspace initial pressure

The effect of the initial headspace pressure on the pyrolysates distribution was studied by conducting pyrolysis reactions in the presence of ethylene at 200 and 500 psi. The liquid product yields are presented in Figure 5.2. Increasing initial pressure did not positively influence the liquid product yield under N_2 atmosphere, but rather there was a slight decrease in the liquid product yield from 81% at 130 psi to 74% at 500 psi. However, under ethylene atmosphere, increasing the initial pressure positively influenced the liquid product yield, increasing from 98% to 152% when compared to the starting fatty acid mass at 130 psi and 500 psi, respectively.

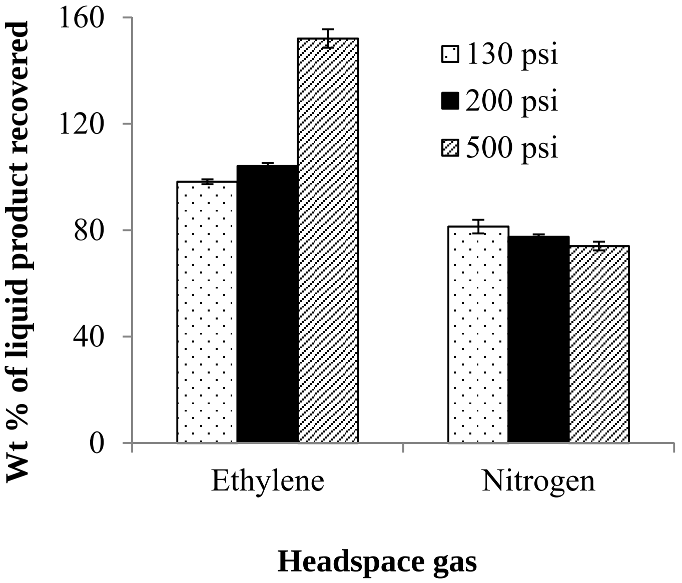

Figure 5.2. Oleic acid pyrolysis liquid product yields at 410 °C for 2 h at different initial headspace pressure under nitrogen and ethylene atmosphere.

5.3.4. Increased branching reactions and products

Figure 5.3 shows a section of GC-FID chromatogram of liquid oleic acid pyrolysis products. The increase in branched hydrocarbons under unsaturated light hydrocarbon gas (ethylene) atmosphere compared to inert atmosphere as previously mentioned in section 5.3.2 can be clearly observed. The effect is enhanced when the initial headspace pressure is increased as shown in Figure 5.4. The total branched hydrocarbon in the liquid fraction remained mostly unchanged with increasing initial pressure under inert atmosphere whereas under ethylene it increased from 7.8% to more than double the amount when the initial headspace pressure was increased from 130 psi to 500 psi.

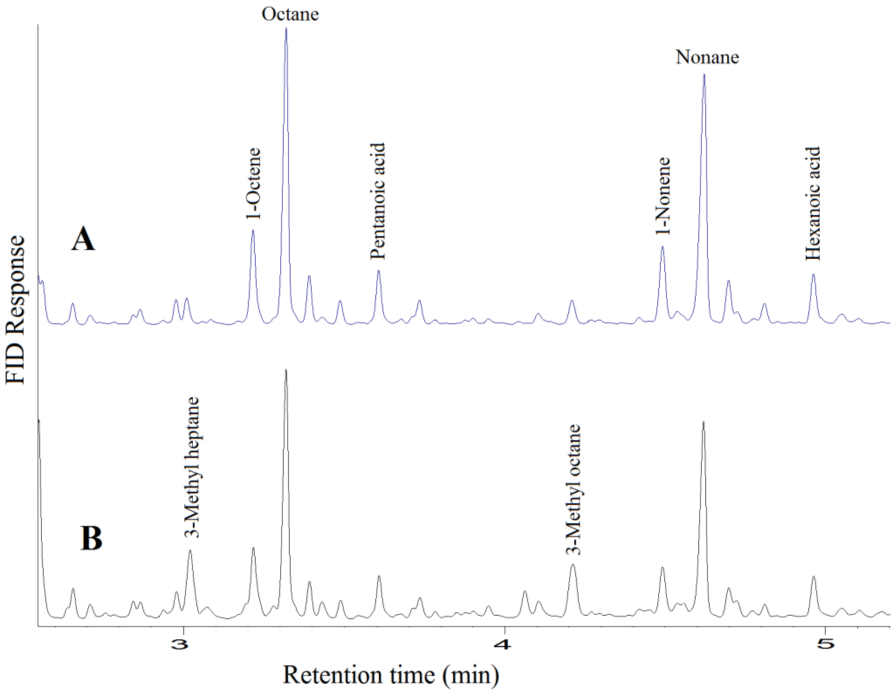

Figure 5.3. Sections of GC-FID chromatograms showing liquid pyrolysis products under initial pressure of 130 psi using nitrogen (A) and ethylene (B)

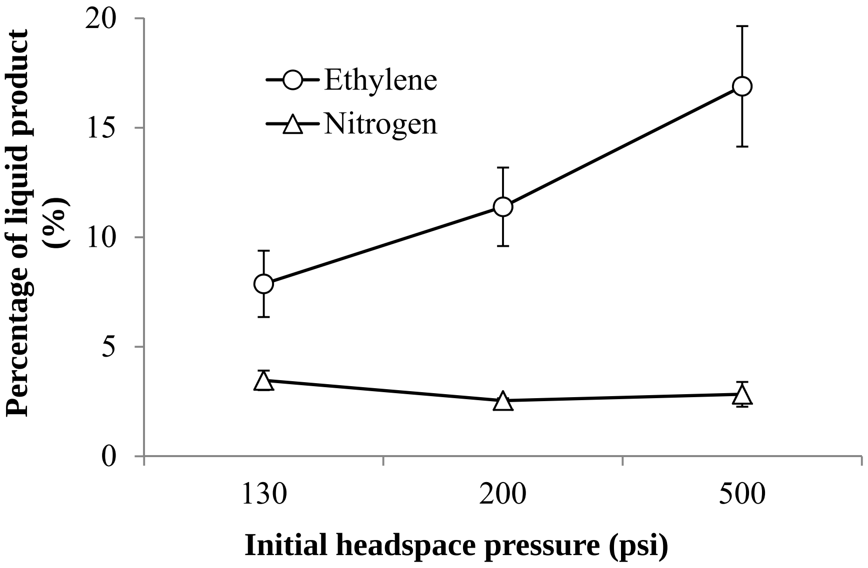

Figure 5.4. Total branched alkanes and alkenes in the liquid product under nitrogen and ethylene atmospheres at different initial headspace pressures.

A possible explanation for the increase in total branched hydrocarbons under unsaturated light hydrocarbon gases could be the direct addition of the unsaturated light hydrocarbon gas to free radicals resulting from the cracking of the oleic acid feed. Also, the formation of ethyl and ethenyl radicals from the disproportionation of two ethylene molecules has been suggested as one of the most important radical initiation steps in ethylene pyrolysis [36-39]. Therefore, another possible explanation of the increase in total branched hydrocarbons under ethylene is the addition of ethyl and ethenyl radicals formed from the disproportionation of ethylene to cracking products of the fatty acid feed.

5.3.5. Deoxygenation

Figure 5.5 shows typical GC-FID chromatograms of the liquid product recovered from oleic acid pyrolysis conducted at 410 °C for 2 h under inert atmosphere and in the presence of ethylene with an initial pressure of 500 psi. In both reactions, the deoxygenation product of the feed (C17 alkenes) as well as the deoxygenation product of C18:0 (*n*-heptadecane) were clearly visible. It must be noted that the *n*-heptadecane could also be the product of C17 alkenes (heptadecenes) saturation reactions. A greater degree of deoxygenation was observed for the reactions conducted in the presence of ethylene. The total fatty acids remaining under inert atmosphere were 15.5% at 130 psi and 9.4% at 500 psi, whereas when processed under an ethylene headspace the total fatty acid decreased to 10.9% and 5.3% at the same pressures.

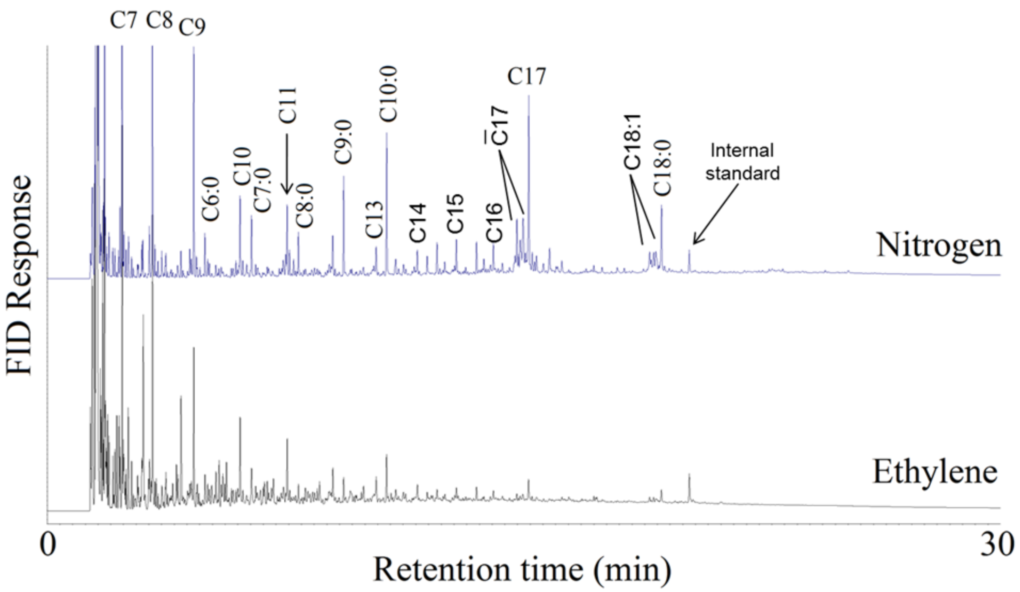

Figure 5.5. GC-FID chromatograms of liquid oleic acid pyrolysis products from reactions conducted under initial pressure of 500 psi using nitrogen and ethylene

In order to understand the influence of ethylene on the deoxygenation, CO and CO_2 were analyzed and quantified in the gas product after pyrolysis reaction. Figure 5.6 shows the presence of both CO and CO_2, indicating deoxygenation proceeded through both decarbonylation and decarboxylation. Whereas the decarbonylation reaction was minimally influenced by the use of ethylene, a significant increase in CO_2 was observed at all of the pressures studied. The results indicated that the positive influence on enhanced deoxygenation observed under ethylene atmosphere was due to increased decarboxylation.

The mole ratio of unsaturation (moles of double bonds in feed to moles of double bonds in ethylene) at the different initial pressures calculated using the Peng-Robinson equation of state are 1:1.9 at 130 psi, 1:2.9 at 200 psi and 1: 8.9 at 500 psi. The increase in deoxygenation could be due to the higher amount of double bonds in reactions conducted under ethylene atmosphere compared with N_2 atmosphere. Additionally, the observed increase in deoxygenation could be result of differences in reactivity of internal olefins (in the case of the double bonds present in the feed) and α-olefins (in the case of double bonds present in ethylene).

5.4. Conclusion

The pyrolysis of a model free fatty acid in the presence of short-chain alkanes and alkenes was studied at different initial pressures to determine the dominant reaction pathways and effect on liquid product yield. While saturated short-chain alkane gases (methane, ethane and propane) did not influence the liquid product yields and composition, unsaturated short-chain alkenes (ethylene and propylene) resulted in increased liquid product yield and greater feed conversion. For the latter reactions, chromatographic analysis of the products portfolio revealed the presence of desirable branched compounds and increased conversion of the fatty acid feedstock. The observed influence of the unsaturated light hydrocarbon gases could be attributed to the presence of the relatively electron rich reactive pi bonds. The results of this study show liquid product yield and feed conversion of fatty acid pyrolysis can be improved through recycling of gaseous product.

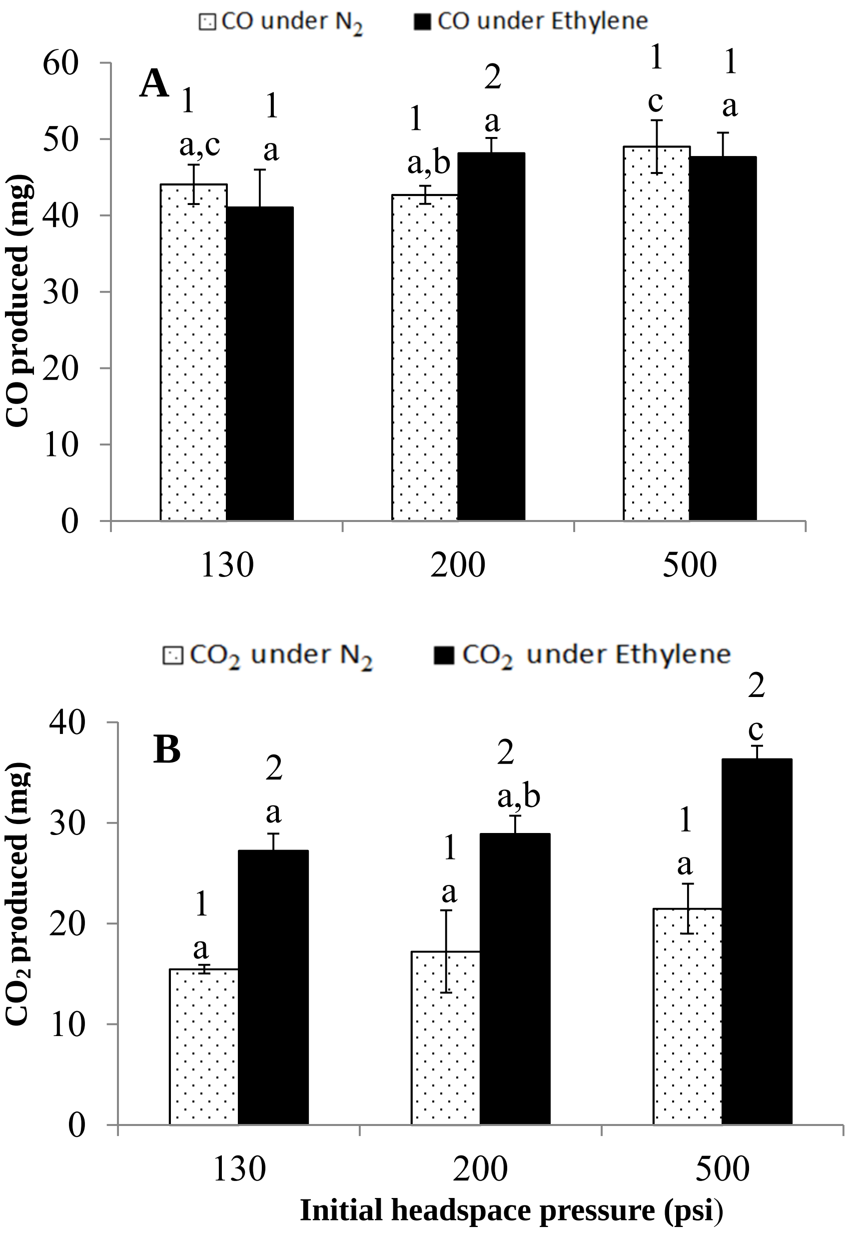

Figure 5.6. Carbon monoxide (A) and carbon dioxide (B) contents in the gas products of nitrogen and ethylene headspace at different initial pressures.

[1] Values with the same numbers are not significantly different at the 95% confidence level between the headspace gases at the same pressure.

[a] Values with the same letters are not significantly different at the 95% confidence level for the same headspace gas at different initial headspace pressures.

5.5. References

[1] H. Lappi, R. Alen, Production of vegetable oil-based biofuels-Thermochemical behavior of fatty acid sodium salts during pyrolysis, Journal of Analytical and Applied Pyrolysis, 86 (2009) 274-280.

[2] K.D. Maher, D.C. Bressler, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals, Bioresource Technology, 98 (2007) 2351-2368.

[3] H. Tian, C.Y. Li, C.H. Yang, H.H. Shan, Alternative processing technology for converting vegetable oils and animal fats to clean fuels and light olefins, Chinese Journal of Chemical Engineering, 16 (2008) 394-400.

[4] G.W. Huber, A. Corma, Synergies between bio- and oil refineries for the production of fuels from biomass, Angewandte Chemie-International Edition, 46 (2007) 7184-7201.

[5] Sonntag, N.O.V., Structure and composition of fats and oils, 4th ed., John Wiley and Sons, New York, 1979.

[6] E. Buzetzki, K. Sidorova, Z. Cvengrosova, J. Cvengros, Effects of oil type on products obtained by cracking of oils and fats, Fuel Processing Technology, 92 (2011) 2041-2047.

[7] T. Ito, Y. Sakurai, Y. Kakuta, M. Sugano, K. Hirano, Biodiesel production from waste animal fats using pyrolysis method, Fuel Processing Technology, 94 (2012) 47-52.

[8] T.G. Smagala, E. Christensen, K.M. Christison, R.E. Mohler, E. Gjersing, R.L. McCormick, Hydrocarbon Renewable and Synthetic Diesel Fuel Blendstocks: Composition and Properties, Energy & Fuels, 27 (2013) 237-246.

[9] C. Jindarom, V. Meeyoo, T. Rirksomboon, P. Rangsunvigit, Thermochemical decomposition of sewage sludge CO2 and N-2 atmosphere, Chemosphere, 67 (2007) 1477-1484.

[10] R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Thermal cracking of Canola oil: Reaction products in the presence and absence of steam, Energy & Fuels, 10 (1996) 1150-1162.

[11] M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer, C. Roy, Characterization of bio-oils in chemical families, Biomass & Bioenergy, 31 (2007) 222-242.

[12] A. Kubatova, Y. Luo, J. Stavova, S.M. Sadrameli, T. Aulich, E. Kozliak, W. Seames, New path in the thermal cracking of triacylglycerols (canola and soybean oil), Fuel, 90 (2011) 2598-2608.

[13] K.D. Maher, K.M. Kirkwood, M.R. Gray, D.C. Bressler, Pyrolytic decarboxylation and cracking of stearic acid, Industrial & Engineering Chemistry Research, 47 (2008) 5328-5336.

[14] P. Maki-Arvela, I. Kubickova, M. Snare, K. Eranen, D.Y. Murzin, Catalytic deoxygenation of fatty acids and their derivatives, Energy & Fuels, 21 (2007) 30-41.

[15] P. Maki-Arvela, M. Snare, K. Eranen, J. Myllyoja, D.Y. Murzin, Continuous decarboxylation of lauric acid over Pd/C catalyst, Fuel, 87 (2008) 3543-3549.

[16] J.W. Jurg, E. Eisma, Petroleum hydrocarbons - generation from fatty acid, Science, 144 (1964) 1451-&.

[17] S. Lestari, P. Maki-Arvela, I. Simakova, J. Beltramini, G.Q.M. Lu, D.Y. Murzin, Catalytic Deoxygenation of Stearic Acid and Palmitic Acid in Semibatch Mode, Catalysis Letters, 130 (2009) 48-51.

[18] F. Ates, A.E. Putun, E. Putun, Catalytic pyrolysis of perennial shrub, Euphorbia rigida in the water vapour atmosphere, Journal of Analytical and Applied Pyrolysis, 73 (2005) 299-304.

[19] E. Putun, F. Ates, A.E. Putun, Catalytic pyrolysis of biomass in inert and steam atmospheres, Fuel, 87 (2008) 815-824.

[20] E. Putun, B.B. Uzun, A.E. Putun, Production of bio-fuels from cottonseed cake by catalytic pyrolysis under steam atmosphere, Biomass & Bioenergy, 30 (2006) 592-598.

[21] J.G. Immer, M.J. Kelly, H.H. Lamb, Catalytic reaction pathways in liquid-phase deoxygenation of C18 free fatty acids, Applied Catalysis a-General, 375 (2010) 134-139.

[22] W.F. Maier, W. Roth, I. Thies, P.V. Schleyer, Hydrogenolysis .4. Gas-phase decarboxylation of carboxylic-acids, Chemische Berichte-Recueil, 115 (1982) 808-812.

[23] M. Arend, T. Nonnen, W.F. Hoelderich, J. Fischer, J. Groos, Catalytic deoxygenation of oleic acid in continuous gas flow for the production of diesel-like hydrocarbons, Applied Catalysis a-General, 399 (2011) 198-204.

[24] Y. Luo, I. Ahmed, A. Kubatova, J. St'avova, T. Aulich, S.M. Sadrameli, W.S. Seames, The thermal cracking of soybean/canola oils and their methyl esters, Fuel Processing Technology, 91 (2010) 613-617.

[25] I. Fonts, G. Gea, M. Azuara, J. Abrego, J. Arauzo, Sewage sludge pyrolysis for liquid production: A review, Renewable & Sustainable Energy Reviews, 16 (2012) 2781-2805.

[26] H.Y. Zhang, R. Xiao, D.H. Wang, G.Y. He, S.S. Shao, J.B. Zhang, Z.P. Zhong, Biomass fast pyrolysis in a fluidized bed reactor under N-2, CO2, CO, CH4 and H-2 atmospheres, Bioresource Technology, 102 (2011) 4258-4264.

[27] M. Asadullah, M.A. Rahman, M.M. Ali, M.A. Motin, M.B. Sultan, M.R. Alam, M.S. Rahman, Jute stick pyrolysis for bio-oil production in fluidized bed reactor, Bioresource Technology, 99 (2008) 44-50.

[28] O.D. Mante, F.A. Agblevor, S.T. Oyama, R. McClung, The influence of recycling non-condensable gases in the fractional catalytic pyrolysis of biomass, Bioresource Technology, 111 (2012) 482-490.

[29] K.P.C. Vollhardt, N. Schore, E., Organic Chemistry: structure and Function, 5th ed., W.H. Freeman and Company, New York, 2007.

[30] J.G. Immer, H.H. Lamb, Fed-Batch Catalytic Deoxygenation of Free Fatty Acids, Energy & Fuels, 24 (2010) 5291-5299.

[31] C.C. Chang, S.W. Wan, Chinas motor fuels from tung oil, Industrial and Engineering Chemistry, 39 (1947) 1543-1548.

[32] A.W. Schwab, G.J. Dykstra, E. Selke, S.C. Sorenson, E.H. Pryde, Diesel fuel from thermal-decomposition of soybean oil, Journal of the American Oil Chemists Society, 65 (1988) 1781-1786.

[33] A. Kubatova, J. St'avova, W.S. Seames, Y. Luo, S.M. Sadrameli, M.J. Linnen, G.V. Baglayeva, I.P. Smoliakova, E.I. Kozliak, Triacylglyceride Thermal Cracking: Pathways to Cyclic Hydrocarbons, Energy & Fuels, 26 (2012) 672-685.

[34] J.A. Melero, M.M. Clavero, G. Calleja, A. Garcia, R. Miravalles, T. Galindo, Production of Biofuels via the Catalytic Cracking of Mixtures of Crude Vegetable Oils and Nonedible Animal Fats with Vacuum Gas Oil, Energy & Fuels, 24 (2010) 707-717.

[35] J.A. Melero, G. Vicente, G. Morales, M. Paniagua, J. Bustamante, Oxygenated compounds derived from glycerol for biodiesel formulation: Influence on EN 14214 quality parameters, Fuel, 89 (2010) 2011-2018.

[36] J.M. Roscoe, I.S. Jayaweera, A.L. Mackenzie, P.D. Pacey, The mechanism of ethylene pyrolysis at small conversions, International Journal of Chemical Kinetics, 28 (1996) 181-193.

[37] J.M. Roscoe, A.R. Bossard, M.H. Back, A kinetic modeling study of ethylene pyrolysis, Canadian Journal of Chemistry-Revue Canadienne De Chimie, 78 (2000) 16-25.

[38] T. Kunugi, T. Sakai, K. Soma, Y. Sasaki, Kinetics and mechanism of thermal reaction of ethylene, Industrial & Engineering Chemistry Fundamentals, 8 (1969).

[39] G. Dahlgren, J.E. Douglas, Kinetics of the thermal reactions of ethylene, Journal of the American Chemical Society, 80 (1958).

6. Two-stage thermal conversion of inedible lipid feedstocks to renewable chemicals and fuels [1]

6.1. Introduction

The global energy demand mostly in the form of transportation fuel is projected to increase by 56% by the year 2040 [1]. While the majority of this growth is currently met by fossil reserves [1-4], increasing societal concerns over long term environmental sustainability are driving considerable research efforts to develop fuel technology platforms based on renewable feedstock. The economic proposition and large scale industrial deployment of renewable fuel technologies is inextricably tied to the feedstock pricing and availability. For example, it has been estimated that up to 88% of the cost of current commercial base-catalyzed biodiesel production plants in the U.S. is from the feedstock [5-7]. Similarly, Bridgwater [8] estimated that for a biomass fast pyrolysis plant operating at one million t y^{-1} and a feedstock cost of €80 t^{-1}, the feedstock cost will represent approximately 40% of the production cost.

The utilization of widely available, low cost, inedible feedstocks such as waste oils and fats has been identified as a possible game-changer in the production of renewable fuels [9, 10]. A potential low cost feedstock is beef tallow, a by-product from the rendering industry. This material lost

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[1] A version of this chapter has been published. J. Asomaning, P. Mussone, D.C. Bressler, Two-stage thermal conversion of inedible lipid feedstocks to renewable chemicals and fuels. Bioresource Technology 158 (2014): 55-62. DOI:http://dx.doi.org/10.1016/j.biortech.2014.01.136.

considerable market value in most advanced economies as a result of legislation implemented to limit its use in the food and feed industries in response to bovine spongiform encephalopathy [9, 11, 12]. Additional important low cost feedstocks are yellow and brown grease which are mixtures of used cooking vegetable oils and animal fats from domestic, commercial and industrial operations with free fatty acid contents lower than 15% and higher than 15%, respectively [7, 10, 13-16]. These feedstocks are typically available at industrial scales in industrialized, urban centres where collection and modern waste management is implemented.

The production of methyl esters through triacylglycerol (TAG) transesterification represents the first industrial generation of technologies for the production of renewable fuels that can be blended with commercial diesel. While several transesterification processes have been scaled up to full industrial facilities using clean plant and animal lipids, the economic implementation of non-edible low grade oils remains elusive.

One of the most promising alternative lipid conversion technologies is thermochemical liquefaction or pyrolysis [12, 17, 18], a high temperature reaction in the absence of oxygen (air). Pyrolysis is particularly attractive because it employs an array of technological approaches that are similar to those used in the oil and gas industry [12] and therefore can be integrated within the existing processing infrastructure. The thermal and thermo-catalytic conversion of lipids in the form of TAGs, fatty acids and fatty acid soaps have been studied extensively [12, 18-36]. The product distribution, composition as well as properties reported were dependent on the feed and the operational conditions employed. The feasibility of producing renewable liquid hydrocarbons through the pyrolysis of free fatty acids has been demonstrated using model saturated [12] and unsaturated free fatty acids (Chapters 3 and 4). They reported the formation of mostly alkanes and alkenes as the main products with minor products being carboxylic acids and aromatic compounds. The model work provided insight into fundamental reaction chemistry and mechanism.

The goal of the present work was to demonstrate the viability of non-food lipid feedstock using a two-step hydrolysis-pyrolysis conversion technology. Batch, laboratory-scale experiments were conducted using four types of lipids representative of inedible plant, animal, and waste systems. Chemical characterization of the pyrolysis products were conducted using a combination of analytical techniques. These properties were correlated with the fuel properties of the liquid pyrolysis product and compared with commercial gasoline and diesel fuels.

6.2. Materials and Methods

6.2.1. Materials

Bleached fancy beef tallow (BFBT) and yellow grease (YG) were obtained from Sanimax (Montreal, QC, CA). Brown grease (BG) was supplied by Great Lakes Biosystems Inc. (Sturtevant, WI, USA) and cold pressed camelina oil (CPCO) was purchased from Prairie Gold-Oil (Picture Butte, AB, Canada). Fatty acid methyl ester (FAME) standards 15A and 463 were purchased from Nu-Chek Prep Inc. (Elysian, MN, USA). Nitrogen (99.998%) was purchased from Praxair

(Mississauga, ON, Canada). Diazomethane for derivatization of fatty acids was prepared using a Diazald kit (Sigma-Aldrich, St. Louis, MO, USA) following the manufacturer's procedures. All other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA). Samples and chemicals were used as received.

6.2.2. Hydrolysis Reactions

Hydrolysis reactions were conducted in a batch 5 L reactor (Model 4580, Parr Instrument Company, Moline, IL, USA) at 280 °C for 60 min with an initial pressure of 500 psi (3447.4 kPa) and a lipid to water mass ratio of 1:1 (this gave a mole ratio of approximately 1:49 fat to water). The time of reaction was started when the set temperature was reached. The heater was turned off at the end of the reaction and the reactor was cooled with an external heating bath set to -10 °C. The hydrolysis products were separated in a separatory funnel. The fatty acids (organic fraction) was dried in a convection oven at 110 °C for 4 h and then stored at 4 °C.

6.2.3. Pyrolysis reaction

Pyrolysis reactions were conducted in a stirred 1 L reactor (Parr Instrument Co., Moline IL, USA) heated by an electric heating element located outside of the reactor vessel. Thermocouples enabled the real time measurements of the reactor internal temperature and pressure transducers allowed measurement of the reactor internal pressure. Each reaction was conducted by loading approximately 100 g of fatty acid from the hydrolysis reaction into reactor vessel.

The reactor was checked for leaks and purged with nitrogen at 500 psi. The heater and stirrer at 300 rpm were then turned on. Reactions were carried out at 410 °C for 1.5 h after the set temperature was reached. The pyrolysis conditions were selected based on initial work conducted on the thermal cracking of model saturated fatty acid [12] and unsaturated fatty acids (Chapters 3 and 4). This was to maximize conversion and liquid product yields whiles at the same time minimizing gas, aromatic and solids formation. The reactor pressure increased throughout the reaction. A typical reactor internal temperature and pressure profile is presented in Figure 6.1. At the end of the reaction, the heater was stopped and the heating mantle removed from the reactor vessel to cool. All the pyrolysis reactions were carried out in triplicate for each of the different fatty acids from the hydrolysis.

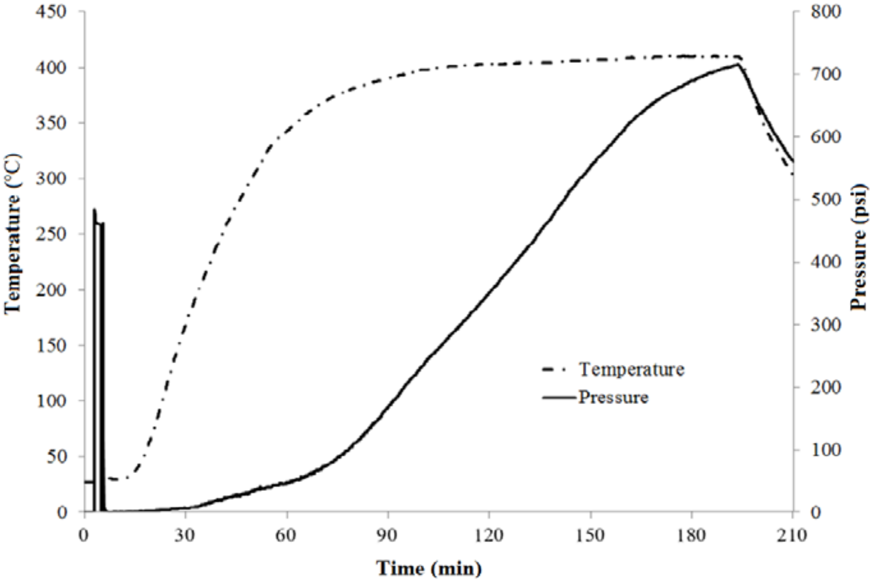

Figure 6.1. Typical reactor temperature and pressure profiles during pyrolysis reaction

At ambient conditions, the reaction products were separated into solid, liquid and gas fractions. The liquid fraction consisted of two phases which were separated into organic liquid fraction (OLF) and aqueous liquid fraction (ALF) and weighed. Solid product was also weighed and by difference the weight of the gas product was calculated.

6.2.4. Analytical methods

6.2.4.1. Feed characterization

Acyl glycerol (triacylglycerol (TAG), diacylglycerol (DAG), monoacylglycerol (MAG)) and free fatty acid (FFA) composition of the feeds were analyzed on an Agilent LC 1200 HPLC system equipped with evaporative light scattering detector (Agilent Technologies, Santa Clara, CA, USA) using a Phenogel column (300mm x 7.8mm ID x 5μm) (Phenomenex, Terrence, CA, USA) following the method described elsewhere [37]. The moisture and volatile matter were determined following ASTM method D5556-2011 and the ash content was determined following ASTM method D5347-2012.

6.2.4.2. Fatty acid product from hydrolysis

Fatty acid composition analysis of the hydrolysis products were conducted on an Agilent 7890A GC system (Agilent Technologies, Santa Clara, CA, USA) coupled to a flame ionization detector (FID) and a BP 20 column (30 m x 0.25 mm, film thickness 0.25 μm). The injector and detector temperature were kept constant at 230 °C and 250 °C, respectively, and the GC oven temperature program was initially at 5 °C for 0.5 min, 20 °C min^{-1} to 170 °C and held for 5 minutes, then 10 °C min^{-1} to 230 and held for an additional 13 min for a total run time of 30.5 min. The carrier gas was helium at a constant flow rate of 1 mL min^{-1} and injection volume was 1 µL. Product identification was performed by comparing retentions times to those of the FAME standards and confirmed by GC-MS and quantification was done by comparing peak areas to the area of the internal standard.

6.2.4.3. Pyrolysis gas product analysis

N_2, CO and CO_2 in the gas pyrolysis product were analyzed on an Agilent 7890A GC system (Agilent Technologies, Santa Clara, CA, USA) coupled to a thermal conductivity detector (TCD) with a 60/80 Carboxen-1000 packed column (4.6 m x 0.32 mm x 2.1 mm) (Sigma-Aldrich, St. Louis, MN, USA). The injector and detector temperatures were kept constant at 170 °C and 200 °C, respectively, and the GC oven temperature program was 40 °C for 5 min and then increased at 20 °C min^{-1} to 200 °C and held for an additional 17 min to achieve a total rum time of 30 min. Helium was used as carrier gas with a constant pressure of 20 psi (137.9 kPa). Injection was done manually with an injection volume of 100 µL using a Hamilton gas tight micro syringe and syringe guide (Hamilton Co., Reno, NV, USA). H_2 analysis was conducted using the same equipment and parameters but the carrier gas was changed from helium to argon.

Alkanes and alkenes in the gas product were analyzed on an Agilent 7890A GC system coupled with FID using column, supplies and instrument parameters as described in Chapter 3 (section 3.2.3).

6.2.4.4. Pyrolysis liquid product analysis

Approximately 100 μg of OLF was weighed into a GC vial and 0.5 mL of internal standard solution (C19 FAME in pentane) was added. Excess diazomethane was then added to convert fatty acids into their methyl ester derivatives allowing greater GC resolution. Analysis was carried out on an Agilent 6890N GC-FID with Agilent 7683 series autosampler and injector with an Agilent HP-5ms column (30 m x 0.32 mm, film thickness 0.25 μm) (Agilent Technologies, Santa Clara, CA, USA). The injector and detector temperatures were kept constant at 300 °C and 350 °C, respectively, and the GC oven temperature program was initially at 35 °C for 0.1 min and then increased at 10 °C min^{-1} to 280 °C and held for an additional 5.4 min for a total run time of 30 min. The carrier gas was helium at a constant flow rate of 1 mL min^{-1} and injection volume was 1 μL.

Mass spectrometry (MS) analysis was performed using instruments, supplies and conditions as described in Chapter 3 (section 3.2.4).

6.2.4.5. Products identification and quantification

Compounds in the gas and liquid fraction were quantified according to the procedures described in Chapter 3 (section 3.2.5). Data in all tables and figures represent mean ± standard deviation of triplicate experiments, unless otherwise indicated. Statistic tests were performed using ANOVA or T-test to determine significant differences in data at the 95% confidence level.

6.2.5. OLF property testing

Samples of OLF were analyzed by Maxxam Analytics (Edmonton, AB) using ASTM standard methods D86, D93, D97, and D7042. Other property testing were carried out using infrastructure available in our laboratory using the appropriate ASTM methods D1298, D240, D1796, D974, and D976. CHNS analyses were performed at the analytical suite of the Department of Chemistry at the University of Alberta. The same tests were performed on regular gasoline and diesel samples purchased from a local commercial gasoline and diesel station.

6.3. Results and discussion

6.3.1. Feedstock and hydrolysates composition

The lipid samples received were analyzed for moisture and volatiles and ash contents. The total lipids were calculated by difference. The lipid fractions were then analyzed for acylglycerol composition using HPLC. Feed composition is shown in Table 6.1. All the feeds had relatively low moisture and volatiles contents ranging from 0.94% for beef tallow to 3.2% for brown grease. Brown grease also had the highest ash content at 0.24% which was approximately two times the ash content of the other feedstocks. The total lipid contents of all feeds were higher than 95% with beef tallow containing approximately 99% lipids. The lipid fraction of beef tallow, yellow grease and camelina consisted predominantly of TAG accounting for over 90% and low FFA content (less than 1% of beef tallow and camelina and about 4% in yellow grease). Brown grease on the other hand had relatively high FFA content of 41% as well as partial glyceride content compared to the other feedstocks. Irrespective of the feedstock composition, there was complete hydrolysis of the acylglycerols to free fatty acids under the hydrolysis condition employed, confirmed using thin layer chromatography and HPLC.

Table 6.1. Feed characterization and composition

Composition	**Wt % of feed**			
	Beef tallow	**Yellow grease**	**Brown grease**	**Camelina**
Moisture and volatiles	0.94 ± 0.02	2.24 ± 0.10	3.16 ± 0.11	1.41 ± 0.04
Ash	0.10 ± 0.00	0.13 ± 0.01	0.24 ± 0.01	0.12 ± 0.00
Lipids	98.9 ± 0.1	97.6 ± 0.1	96.6 ± 0.2	98.5 ± 0.1
Lipid class	Wt % of lipid fraction			
TAG	98.5	90.7	50.7	99.8
DAG	0.94	4.96	6.16	ND
MAG	ND	0.06	2.35	ND
FFA	0.59	4.24	40.8	0.15

ND- not detected

The fatty acids composition of the hyrolysates of the different feedstocks is shown in Table 6.2. The fatty acids ranged in carbon number from 12 to 22 with different levels of unsaturation. The fatty acid composition of yellow grease and brown grease were very similar and was predominantly monounsaturated (approximately 50% of the fatty acids) with C18:1 being the most abundant fatty acid. Beef tallow was constituted mostly of saturated fatty acids such as C16:0 (hexadecanoic acid) and C18:0 (octadecanoic acid) which collectively accounted for approximately 72%. Camelina on the other hand was predominantly characterized by polyunsaturated fatty acids with C18:3 (51%) being the most abundant. Another important characteristic of the fatty acid composition of camelina is the presence of long chain fatty acid C20:1 which accounted for 17% of the fatty acids. The feed composition is an important factor influencing the pyrolysis product composition [12, 21].

6.3.2. Pyrolysis product distribution

A typical reactor internal temperature and development during the course of the reaction pressure is shown in Figure 6.1. It must be noted that the initial spike in pressure was the result of reactor purging with nitrogen in order to attain an inert atmosphere. The data show that the reactor pressure increased throughout the reaction. However, up to about 350 °C the increase in pressure was relatively slower when compared to that observed at temperature higher than 350 °C with a steeper slope. This may be due to the fatty acids moving into the gas phase and/or reflect production of significant amounts of volatile components as a result of cracking of the fatty acids into low molecular weight products at those temperatures [12, 27]. Reactor pressure decreased immediately after heating was interrupted.

Table 6.2. Fatty acid composition of hydrolysates

Fatty acid	**Hydrolysate fatty acid composition (wt %)**			
	Beef tallow	**Yellow Grease**	**Brown Grease**	**Camelina**
C12:0	-	-	1.27	-
C14:0	2.34	1.13	1.1	-
C16:0	38.5	19.6	18.8	5.51
C16:1	1.23	2.47	0.85	0.27
C17:0	1.27	0.36	0.15	-
C18:0	29.8	8.11	7.25	2.69
C18:1	24.3	50.8	47.2	2.89
C18:2	0.07	14.7	19.4	16.2
C18:3	0.20	2.35	2.10	50.8
C20:0	0.28	0.32	0.89	1.60
C20:1	2.00	-	0.79	16.6
C20:2	-	-	0.20	1.12
C22:0	-	0.18	0.20	-
C22:1	-	-	-	2.64
Saturates	**72.2**	**29.7**	**29.7**	**9.8**
Monounsaturates	**27.6**	**53.3**	**48.8**	**22.4**
Polyunsaturates	**0.27**	**17.0**	**21.7**	**68.1**

The pyrolysis product distribution at ambient temperature and pressure is shown in Table 6.3. The pyrolysis products were distributed between solid, liquid and gas with the liquid having two fractions; an organic liquid fraction and an aqueous liquid fraction. The organic liquid fraction was the most abundant ranging from 76% of the beef tallow to 79% of yellow grease, brown grease and camelina.

The aqueous liquid product accounted for 2.6 to 4% of the product yield depending on the feedstock. Gas product yield varied from 15 to 17% with beef tallow giving the highest gas product yield. The gas product yield was 16% for yellow grease and camelina and 17% for beef tallow and brown grease. Solid products were 1.2 to 3.2% of the product yield with brown and yellow grease having lower solids yield than beef tallow and camelina. Though the fatty acid compositions were different for the different feedstocks the product distribution especially the organic liquid fraction was not significantly different between the different feedstocks. This is an important observation for process flexibility, as the change in feedstock did not significantly impact the liquid product yield; allowing the use of different sources of feedstock depending on availability.

Table 6.3. Pyrolysis product distribution

Sample	Weight % of feed			
	Liquid product		Solid	Gas
	Organic Liquid Fraction	Aqueous Liquid Fraction		
Beef tallow	75.5 ± 0.8	3.9 ± 0.2	3.2 ± 0.3	17.4 ± 0.8
Yellow Grease	79.1 ± 1.2	3.5 ± 0.1	1.4 ± 0.1	15.5 ± 1.1
Brown Grease	78.7 ± 0.6	3.4 ± 0.1	1.2 ± 0.2	16.7 ± 0.7
Camelina	78.5 ± 2.1	2.6 ± 0.2	3.2 ± 0.5	15.5 ± 0.8

6.3.3. Organic liquid fraction composition

Figure 6.2 shows the weight % distribution of classes of compounds in the organic liquid fraction. The unidentified fraction represents GC eluted peaks which could not be unambiguously identified. The unaccounted fraction represents the difference between the GC eluted peaks percentage and 100%. This fraction represents compounds which have molecular weights lower than or equal to C5 that could not be integrated due to solvent peak overlap and possibly high molecular weight compounds which could not be eluted on the GC.

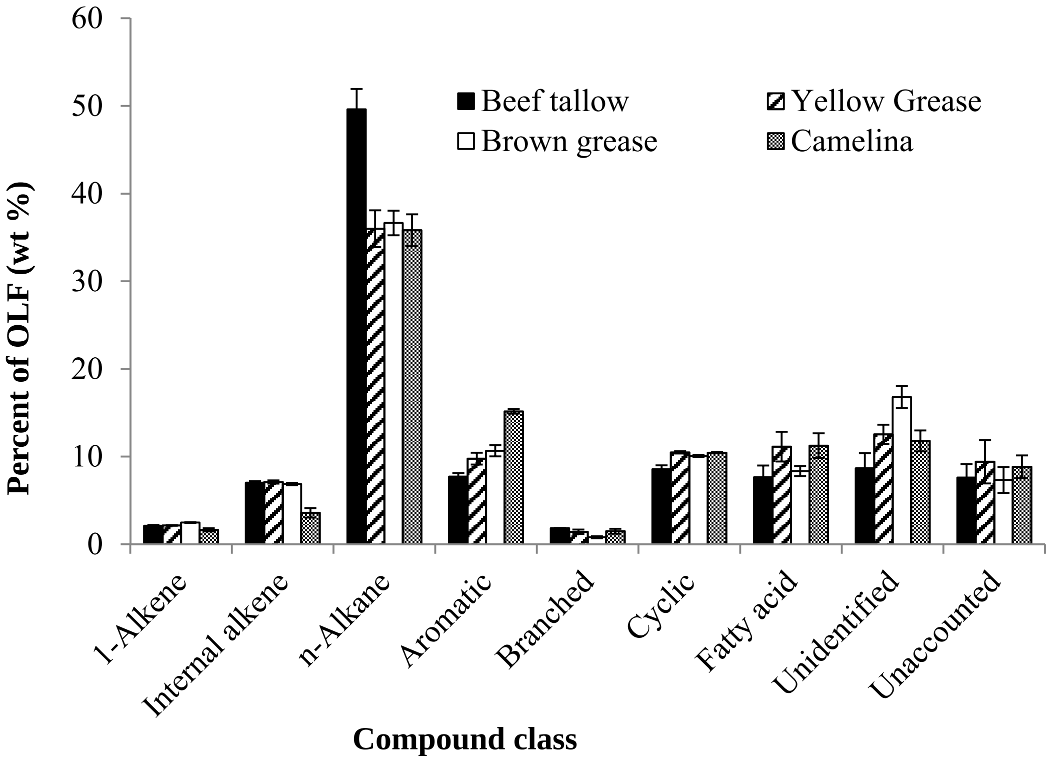

Figure 6.2. Classes of compounds in OLF

For all the feedstock used, the organic liquid fraction was composed primarily of *n*-alkanes. The total *n*-alkanes content in the OLF of yellow grease, brown grease and camelina was about 38%. Beef tallow had significantly higher *n*-alkanes at approximately 50% of the OLF compared to the other feedstocks. The distribution of *n*-alkanes in relation to carbon number is shown in Figure 6.3. The *n*-alkanes ranged in carbon number between 6 and 23 for all the feedstocks. There was a general decrease in *n*-alkanes as carbon number increased from 6 to 12, then relatively constant with the exception of beef tallow to C14. The observed spike at carbon number 15 is the result of direct deoxygenation of C16:0 fatty acid and carbon number 17 the deoxygenation of C18:0. Their relative abundance reflects that of the corresponding fatty acids.

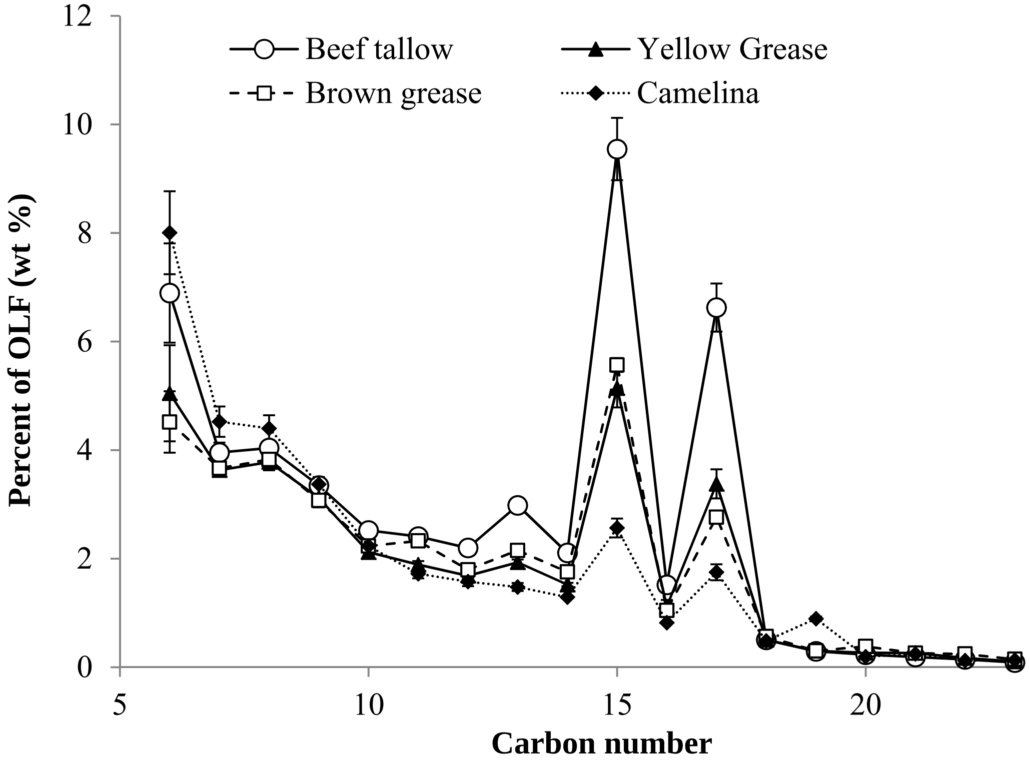

Figure 6.3. *n*-Alkanes as a function of carbon number of OLF

The range of carbon number in the *n*-alkanes demonstrates both the well-known cracking reactions (evidenced by compounds with carbon number much lower than that in the feedstocks) and well-documented addition reactions (evidenced by compounds with carbon number higher than that in the feedstocks) occurring during pyrolysis [12, 38, 39].

No significant difference at the 95% confidence level was observed in the 1-alkene content, which accounted for about 2% of the OLF, between the different feedstocks. Internal alkenes content was not significantly different between beef tallow, yellow grease and brown grease (about 7% of the OLF) whereas camelina had significantly lower internal alkene content (about 3.5%). The presence of linear alkanes and alkenes has been reported in both pyrolysis products of the direct deoxygenation of the fatty acid feed or cracking product of feed and the cracking of deoxygenated hydrocarbon product through free radical mechanism [12, 21, 27]. Evidence of deoxygenation was found in the gas product analysis where CO and CO_2 (data not shown) which are decarbonylation and decarboxylation [19, 40, 41] products, respectively, of free fatty acids were found.

Similar to the *n*-alkanes content, the cyclic compounds were not significantly different between yellow grease, brown grease and camelina accounting for approximately 10% of the OLF. However, beef tallow had a significantly lower (95% confidence level) cyclic compounds compared to the other feedstocks constituting about 8% of the OLF. The cyclic compounds were predominantly C5 (cyclopentanes and cyclopentenes) and C6 (cyclohexanes and cyclohexenes) ring structures that were mostly substituted. Formation of cyclic compounds is thought to proceed through the Diels-Alder reaction as well as through intramolecular cyclization of free radicals with terminal double bonds [21, 42, 43].

Aromatic compounds in the OLF were not significantly different between yellow grease and brown grease accounting for approximately 10% of the OLF. Beef tallow had a significantly lower aromatic content (about 8%) when compared to the other feedstocks and camelina had significantly higher aromatics content (about 15%) compared to the other feedstocks. The relatively higher aromatic content of camelina can be explained in terms of the fatty acid composition which was mostly polyunsaturated (C18:3) accounting for over 50%

of the fatty acid feed. The presence of the triple unsaturation promotes intramolecular cyclization leading to the formation of aromatic compounds [44]. The aromatic compounds consisted of monoaromatic as well as polyaromatic structures. Monoaromatic compounds are formed through dehydrogenation of six carbon numbered cyclic alkanes and alkenes [21, 27, 43, 45]. Polyaromatic compounds are then formed through polymerization and dehydrogenation of the mono-aromatic compounds [21, 45] and alternatively via an intramolecular radical cyclization mechanism [43].

Fatty acids ranging from carbon number 3 to 18 for beef tallow, yellow grease and brown grease and 3 to 20 for camelina in the OLF are shown in Figure 6.2. Beef tallow and brown grease had significantly lower fatty acids content (about 8%) compared to yellow grease and camelina oil (about 11%). The fatty acids represent both products of the fatty acid pyrolysis as well as unreacted fatty acid feed.

6.3.4. Organic liquid fraction properties

6.3.4.1. Elemental composition

The elemental composition of the organic liquid fraction together with the elemental composition of the hydrolysates and regular gasoline and diesel are shown in Table 6.4. The nitrogen and sulphur content of the hydrolysates were all below the detection limit of the instrument which was 10 ppm. As a consequence, the nitrogen and sulphur contents of the OLP of all the feedstocks were also below the detection limit.

The sulphur content was well below the maximum specification set out by the Canadian General Standards Board (CGSB) for automotive gasoline (CSGB-3.5-2011) of 80 ppm, diesel (CSGB-3.517-2013) of 15 ppm and Jet turbine fuel (CGSB 3.23-2012) of 0.30% by mass. There was significant decrease in the oxygen content of all the feedstocks in the OLF and concurrent increase in carbon. The oxygen in the OLF can be attributed to the fatty acids in the OLF (Figure 6.2). The regular gasoline sample had an oxygen content of 2.7% and the regular diesel had an oxygen content of 0.8%. The gasoline oxygen content could be due to blending with ethanol as the pump had a notice that the fuel may contain up to 10% ethanol. Diesel blending with renewable fuel is mandated in Canada with at least 2% by volume [46]. Thus the observed oxygen in the diesel may be from blending of biodiesel into the diesel fuel.

6.3.4.2. Distillation

The distillation curve of the OLF of the different feedstocks together with samples of regular gasoline and regular diesel for comparison are presented in Figure 6.4. The distillation curves of the OLF obtained from different feedstock were remarkably similar although feedstock fatty acid compositions were different. This further demonstrates the flexibility of the process used to accommodate different feedstocks. The distillation range from the initial boiling point (IBP) to the 80% evaporated were 262 °C for beef tallow and 295 °C for brown grease and camelina oil. Whereas the distillation range was 125 °C for the regular gasoline sample and 141 °C for the regular diesel sample.

Table 6.4. Elemental composition of hydrolysates and OLF together with regular gasoline and diesel

Hydrolysates	**Elements (wt %)**				
	C	**H**	**N**	**S**	**O***
Beef tallow	74.5 ± 0.2	11.9 ± 0.1	BDL	BDL	13.6 ± 0.2
Brown grease	73.6 ± 0.6	11.5 ± 0.2	BDL	BDL	14.9 ± 0.8
Yellow grease	75.8 ± 0.2	11.9 ± 0.0	BDL	BDL	12.3 ± 0.2
Camelina	76.3 ± 0.1	11.4 ± 0.1	BDL	BDL	12.3 ± 0.2
OLF					
Beef tallow	83.0 ± 0.5	12.9 ± 0.1	BDL	BDL	4.0 ± 0.6
Brown grease	83.2 ± 0.3	12.2 ± 0.1	BDL	BDL	4.6 ± 0.4
Yellow grease	82.3 ± 0.3	12.1 ± 0.0	BDL	BDL	5.6 ± 0.3
Camelina	82.8 ± 0.5	11.5 ± 0.2	BDL	BDL	5.7 ± 0.7
Regular Gasoline	84.1 ± 0.3	13.2 ± 0.0	BDL	BDL	2.7 ± 0.3
Regular Diesel	85.9 ± 0.1	13.2 ± 0.0	BDL	BDL	0.8 ± 0.1

* - calculated by difference, BDL- Below detection limit (10 ppm)

The data in Figure 6.4 also shows that approximately 30% of the OLF is in the gasoline range and 50% is in the diesel range. Thus, if all other properties were brought to acceptability, the OLF potentially can be fractionated to serve either as renewable gasoline or diesel fuel alternative or used in blending with fossil derived fractions of gasoline or diesel.

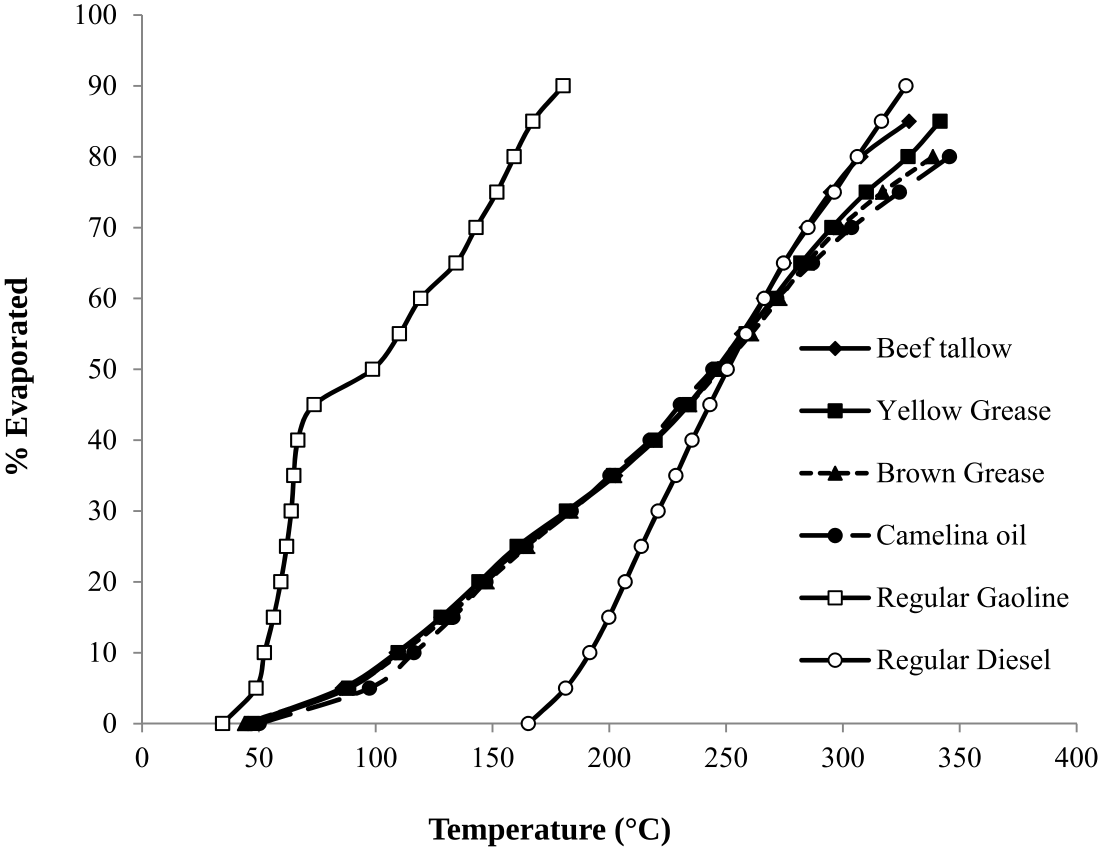

Figure 6.4. Distillation curves (ASTM D86) of OLF together with regular gasoline and diesel.

6.3.4.3. Other fuel properties

The values of some fuel properties of the OLF together with values for samples of regular gasoline and regular diesel are shown in Table 6.5. The fuel properties of the OLF fractions were more comparable to diesel fuel with a few exceptions. This was expected as the majority of the OLF was in the diesel distillation range (Figure 6.4). The acid number was particularly high compared to the gasoline and diesel samples and all the OLF from the different feedstocks had acid number values which were much higher than the maximum values of 0.10 mg KOH/g specified by the CGSB for fuels. Beef tallow and brown grease had relatively lower acid number compared to yellow grease and camelina which can be explained in terms of the significantly lower fatty acid content of the former (Figure 6.2). It must be noted that the analysis was done on the crude pyrolysis product and the acid number can be reduced to acceptable level through process optimization and/or further processing. Also, fatty acid extraction from pyrolysis products of TAG using water and aqueous NaOH [47] or aqueous amines [48] have been reported in the literature and can be used to extract the fatty acids thereby reducing the acid number to acceptable levels.

The flash points of the OLF were comparable to that of gasoline at <-35 °C and significantly lower than that of the diesel fuel. The flash point is important for safe handling purposes and too low flash point increases the potential for fire hazard [17]. The presence of the low boiling fraction in the OLF is responsible for the lower flash point as they can vaporize relatively easily compared to the high

Table 6.5. Fuel properties of OLF together with regular gasoline and diesel

Property	ASTM Method	Product properties					
		Beef tallow	Brown Grease	Yellow grease	Camelina	Regular gasoline	Regular diesel
Acid number (mg KOH/g)	D974	38	41	57	65	<0.02	0.02
Flash point (°C)	D93	<-35	<-35	<-35	<-35	<-35	51
Density (kg/m^3)	D1298	802	819	822	838	754	858
Kinematic viscosity at 40°C (mm^2/s)	D7042	1.66	1.90	1.84	1.68	0.5631	2.354
Water and sediments (% vol)	D1796	0.08	0.08	0.07	0.06	0.00	0.00
Pour point (°C)	D97	-21	-39	-27	-36	<-65	-27
Heat of combustion (MJ/kg)	D240	42.9	42.1	42.4	42.1	40.5	45.3
Cetane index	D613	59	53	52	45	-	41

boiling fraction. The pour points of all the OLF were below -20 °C which implies they will have good cold flow properties.

The calculated cetane indices of the OLF were all higher than the cetane index of the diesel fuel. The calculated cetane index is a good approximation of the cetane number where a test engine is not available or sample quantities are limited as in this study. The higher cetane indices of the OLF especially from beef tallow, yellow grease and brown grease compared to the diesel fuel implies there is potential for the OLF to be used as cetane enhancers of fossil derived fuels.

6.4. Conclusion

Thermal hydrolysis was used to successfully convert low cost non-food lipid feedstocks to free fatty acids which were then pyrolyzed. The pyrolysis product consisted of solid, liquid and gas fractions with comparable product yields between the different feedstock used. The organic liquid fraction constituted the majority of the pyrolysis accounting for nearly 80% of the product. Distillation properties of the organic liquid fraction showed it account for approximately 30% in the gasoline boiling range and 50% in the diesel boiling range. Other fuel property tests showed that the OLF mostly met the limits set out by the CGSB for diesel fuel with the exception of acid number which was higher than specified and flash point which was lower than specified. The results showed the flexibility of using the thermal hydrolysis-pyrolysis conversion method for producing OLF with relatively consistent yields and properties from different low cost feeds.

6.5. References

[1] U.S. Eenergy Iinformation Administration, International Energy Outlook 2013. Available online at http://www.eia.gov/forecasts/ieo/pdf/0484(2013).pdf last accessed October, 2013.

[2] A. Demirbas, K. Dincer, Sustainable green diesel: A futuristic view, Energy Sources Part a-Recovery Utilization and Environmental Effects, 30 (2008) 1233-1241.

[3] A. Demirbas, Progress and recent trends in biofuels, Progress in Energy and Combustion Science, 33 (2007) 1-18.

[4] M. Calonaci, R. Grana, E.B. Hemings, G. Bozzano, M. Dente, E. Ranzi, Comprehensive Kinetic Modeling Study of Bio-oil Formation from Fast Pyrolysis of Biomass, Energy & Fuels, 24 (2010) 5727-5734.

[5] C.V. McNeff, L.C. McNeff, B. Yan, D.T. Nowlan, M. Rasmussen, A.E. Gyberg, B.J. Krohn, R.L. Fedie, T.R. Hoye, A continuous catalytic system for biodiesel production, Applied Catalysis a-General, 343 (2008) 39-48.

[6] M.J. Haas, A.J. McAloon, W.C. Yee, T.A. Foglia, A process model to estimate biodiesel production costs, Bioresource Technology, 97 (2006) 671-678.

[7] M. Kim, C. DiMaggio, S.L. Yan, H.L. Wang, S.O. Salley, K.Y.S. Ng, Performance of heterogeneous ZrO_2 supported metaloxide catalysts for brown grease esterification and sulfur removal, Bioresource Technology, 102 (2011) 2380-2386.

[8] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass & Bioenergy, 38 (2012) 68-94.

[9] J. Iglesias, G. Morales, Biodiesel from waste oils and fats, Advances in Biodiesel Production: Processes and Technologies, (2012) 154-178.

[10] H.J. Kim, H. Hilger, S. Bae, $NiSO_4/SiO_2$ Catalyst for Biodiesel Production from Free Fatty Acids in Brown Grease, Journal of Energy Engineering-Asce, 139 (2013) 35-40.

[11] A.O. Adebanjo, A.K. Dalai, N.N. Bakhshi, Production of diesel-like fuel and other value-added chemicals from pyrolysis of animal fat, Energy & Fuels, 19 (2005) 1735-1741.

[12] K.D. Maher, K.M. Kirkwood, M.R. Gray, D.C. Bressler, Pyrolytic decarboxylation and cracking of stearic acid, Industrial & Engineering Chemistry Research, 47 (2008) 5328-5336.

[13] J.L. Qiul, X.H. Fan, H.Y. Zou, Development of biodiesel from inedible feedstock through various production processes. Review, Chemistry and Technology of Fuels and Oils, 47 (2011) 102-111.

[14] M. Canakci, H. Sanli, Biodiesel production from various feedstocks and their effects on the fuel properties, Journal of Industrial Microbiology & Biotechnology, 35 (2008) 431-441.

[15] W. Diaz-Felix, M.R. Riley, W. Zimmt, M. Kazz, Pretreatment of yellow grease for efficient production of fatty acid methyl esters, Biomass & Bioenergy, 33 (2009) 558-563.

[16] D.E. Lopez, J.G. Goodwin, D.A. Bruce, E. Lotero, Transesterification of triacetin with methanol on solid acid and base catalysts, Applied Catalysis a-General, 295 (2005) 97-105.

[17] N.P. Bahadur, D.G.B. Boocock, S.K. Konar, Liquid hydrocarbons from catalytic pyrolysis of sewage-sludge lipid and canola oil - evaluation of fuel properties, Energy & Fuels, 9 (1995) 248-256.

[18] H. Lappi, R. Alen, Production of vegetable oil-based biofuels-Thermochemical behavior of fatty acid sodium salts during pyrolysis, Journal of Analytical and Applied Pyrolysis, 86 (2009) 274-280.

[19] C.C. Chang, S.W. Wan, Chinas motor fuels from tung oil, Industrial and Engineering Chemistry, 39 (1947) 1543-1548.

[20] J.W. Alencar, P.B. Alves, A.A. Craveiro, Pyrolysis of tropical vegetable-oils, Journal of Agricultural and Food Chemistry, 31 (1983) 1268-1270.

[21] R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Thermal cracking of Canola oil: Reaction products in the presence and absence of steam, Energy & Fuels, 10 (1996) 1150-1162.

[22] R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Catalytic conversion of canola oil to fuels and chemicals: Roles of catalyst acidity, basicity and shape selectivity on product distribution, Fuel Processing Technology, 51 (1997) 101-125.

[23] S.P.R. Katikaneni, R.O. Idem, N.N. Bakhshi, Catalytic conversion of a biomass-derived oil using various catalysts, 1997.

[24] S.P.R. Katikaneni, R.O. Idem, N.N. Bakhshi, E. Amer Inst Chem, Potential of producing high octane additives and hydrogen from biomass-derived oils, 1997.

[25] H. Lappi, R. Alen, Pyrolysis of vegetable oil soaps-Palm, olive, rapeseed and castor oils, Journal of Analytical and Applied Pyrolysis, 91 (2011) 154-158.

[26] E. Kozliak, R. Mota, D. Rodriguez, P. Overby, A. Kubatova, D. Stahl, V. Niri, G. Ogden, W. Seames, Non-catalytic cracking of jojoba oil to produce fuel and chemical by-products, Industrial Crops and Products, 43 (2013) 386-392.

[27] A. Kubatova, Y. Luo, J. Stavova, S.M. Sadrameli, T. Aulich, E. Kozliak, W. Seames, New path in the thermal cracking of triacylglycerols (canola and soybean oil), Fuel, 90 (2011) 2598-2608.

[28] S.N. Naik, V.V. Goud, P.K. Rout, A.K. Dalai, Production of first and second generation biofuels: A comprehensive review, Renewable & Sustainable Energy Reviews, 14 (2010) 578-597.

[29] E. Buzetzki, K. Sidorova, Z. Cvengrosova, J. Cvengros, Effects of oil type on products obtained by cracking of oils and fats, Fuel Processing Technology, 92 (2011) 2041-2047.

[30] J.M. Xu, J.C. Jiang, T.J. Zhang, W.D. Dai, Biofuel Production from Catalytic Cracking of Triglyceride Materials Followed by an Esterification Reaction in a Scale-up Reactor, Energy & Fuels, 27 (2013) 255-261.

[31] D.G. Lima, V.C.D. Soares, E.B. Ribeiro, D.A. Carvalho, E.C.V. Cardoso, F.C. Rassi, K.C. Mundim, J.C. Rubim, P.A.Z. Suarez, Diesel-like fuel obtained by pyrolysis of vegetable oils, Journal of Analytical and Applied Pyrolysis, 71 (2004) 987-996.

[32] S. Wang, Z. Guo, Q. Cai, L. Guo, Catalytic conversion of carboxylic acids in bio-oil for liquid hydrocarbons production, Biomass & Bioenergy, 45 (2012) 138-143.

[33] W.C. Wang, N. Thapaliya, A. Campos, L.F. Stikeleather, W.L. Roberts, Hydrocarbon fuels from vegetable oils via hydrolysis and thermo-catalytic decarboxylation, Fuel, 95 (2012) 622-629.

[34] V. Botton, D. Riva, E.L. Simionatto, V.R. Wiggers, L. Ender, H.F. Meier, A.A. Chivanga Barros, Thermo-catalytic cracking of the mixture of used frying oil - textile stamping sludge for the production of oil with low acidity index, Quimica Nova, 35 (2012) 677-682.

[35] V.R. Wiggers, G.R. Zonta, A.P. França, D.R. Scharf, E.L. Simionatto, L. Ender, H.F. Meier, Challenges associated with choosing operational conditions for triglyceride thermal cracking aiming to improve biofuel quality, Fuel, 107 (2013) 601-608.

[36] A. Wisniewski, Jr., V.R. Wiggers, E.L. Simionatto, H.F. Meier, A.A.C. Barros, L.A.S. Madureira, Biofuels from waste fish oil pyrolysis: Chemical composition, Fuel, 89 (2010) 563-568.

[37] K. Kittirattanapiboon, K. Krisnangkura, Separation of acylglycerols, FAME and FFA in biodiesel by size exclusion chromatography, European Journal of Lipid Science and Technology, 110 (2008) 422-427.

[38] G.Z. Wu, Y. Katsumura, C. Matsuura, K. Ishigure, J. Kubo, Comparison of liquid-phase and gas-phase pure thermal cracking of n-hexadecane, Industrial & Engineering Chemistry Research, 35 (1996) 4747-4754.

[39] F. Khorasheh, M.R. Gray, High-pressure thermal-cracking of n-hexadecane, Industrial & Engineering Chemistry Research, 32 (1993).

[40] J.G. Immer, H.H. Lamb, Fed-Batch Catalytic Deoxygenation of Free Fatty Acids, Energy & Fuels, 24 (2010) 5291-5299.

[41] M. Arend, T. Nonnen, W.F. Hoelderich, J. Fischer, J. Groos, Catalytic deoxygenation of oleic acid in continuous gas flow for the production of diesel-like hydrocarbons, Applied Catalysis a-General, 399 (2011) 198-204.

[42] A. Kubatova, J. St'avova, W.S. Seames, Y. Luo, S.M. Sadrameli, M.J. Linnen, G.V. Baglayeva, I.P. Smoliakova, E.I. Kozliak, Triacylglyceride Thermal Cracking: Pathways to Cyclic Hydrocarbons, Energy & Fuels, 26 (2012) 672-685.

[43] A.W. Schwab, G.J. Dykstra, E. Selke, S.C. Sorenson, E.H. Pryde, Diesel fuel from thermal-decomposition of soybean oil, Journal of the American Oil Chemists Society, 65 (1988) 1781-1786.

[44] F. Destaillats, P. Angers, On the mechanisms of cyclic and bicyclic fatty acid monomer formation in heated edible oils, European Journal of Lipid Science and Technology, 107 (2005) 767-772.

[45] J.A. Melero, M.M. Clavero, G. Calleja, A. Garcia, R. Miravalles, T. Galindo, Production of Biofuels via the Catalytic Cracking of Mixtures of Crude Vegetable Oils and Nonedible Animal Fats with Vacuum Gas Oil, Energy & Fuels, 24 (2010) 707-717.

[46] Federal Renewable fuel regulation, Canada. Available online at http://www.ec.gc.ca/energie-energy/default.asp?lang=En&n=828C9342-1. Last acccessed October, 2013.

[47] S. Gandhi, J. Kadrmas, J. St'avova, A. Kubatova, D. Muggli, W.S. Seames, S.M. Sadrameli, B.M. Tande, Extraction of Fatty Acids from Noncatalytically Cracked Triacylglycerides with Water and Aqueous Sodium Hydroxide, Separation Science and Technology, 47 (2012) 66-72.

[48] M.P. Braegelmann, A.D. Azure, D.C. Stahl, A. Kubatova, W.S. Seames, B.M. Tande, Extraction of Fatty Acids from Noncatalytically Cracked

Triacylglycerides Using Aqueous Amines, Separation Science and Technology, 46 (2011) 2167-2173.

7. General discussion and conclusions

Triacylglycerols (TAGs) are present in naturally occurring oils and fats produced by a number of crops, microorganisms (bacteria, algae), and animals. They are produced as energy storage compounds in the tissues of plants and animals, making it the most energy-dense biomass resource available [1, 2]. Chemically, TAGs are composed of three fatty acid molecules esterified to glycerol. Fatty acids vary in carbon chain length and the level of unsaturation (the number of carbon-carbon double bonds present in the molecule). The source of the TAG influences the nature and composition of the fatty acids present in the oil or fat. The diversity and prevalence of sources for TAG compounds suggests that they could serve as an attractive renewable resource. Thus, TAGs may be used as feedstock for the production of chemicals utilized in transportation fuel formulations and industrial applications. In fact, TAGs are currently used in the transesterification processes that produce most of the biodiesel products commercially available today.

Thermal cracking or pyrolysis is one of the most promising TAG conversion technologies being researched for alternative fuel development. The thermal cracking of vegetable oil and animal fat TAGs has been extensively studied and literature is readily available. TAG thermal cracking results in oxygenated compounds that are not directly compatible with existing petroleum infrastructure [3-5]. The thermal cracking of free fatty acids, which can be released from TAGs through hydrolysis reaction, on the other hand, has received limited attention in the available literature. The feasibility of producing liquid hydrocarbons from free fatty acids was demonstrated using stearic acid as a model saturated compound [6]. An understanding of the thermal cracking of unsaturated free fatty acids will not only help elucidate the reaction mechanism and fundamental reaction chemistry but also help understand and optimize the thermal cracking of fatty acids hydrolyzed from TAG based feedstocks. In this thesis research, the thermal cracking of monounsaturated fatty acids (oleic acid as model compound) and polyunsaturated fatty acid (linoleic acid as model compound) was studied to understand the fundamental reaction chemistry and mechanism and to carry out detailed product yield determination and gas product analysis (Chapters 3 and 4) as well as study the effect of using hydrocarbon gas atmosphere instead of inert atmosphere on product yield and distribution (Chapter 5). Finally, the conversion of inedible TAG based lipid feedstocks to renewable hydrocarbons were studied employing a thermal hydrolysis step followed by pyrolysis of the resulting fatty acids and determining some product characteristics and comparing them to those of petroleum derived gasoline and diesel (Chapter 6).

In Chapter 3 the thermal cracking of oleic acid at temperatures of 350 – 450 °C and reaction times of 0.5 – 8 h were conducted in batch microreactors. Conversion of the feed ranged from 75% to complete conversion. The conversion was dependent on reaction temperature and time with increasing temperature and time resulting in increased conversion. Complete conversion was achieved at 430 and 450 °C for reaction times of 1 – 8 h as well as 410 °C for 8 h. Similarly, liquid product yields were dependent on the reaction temperature and time with increasing temperature decreasing liquid product yield. These findings support earlier work which found that product yields were heavily dependent on product composition and reaction conditions [7-9]. Whereas in the thermal cracking of stearic acid [6] deoxygenation preceded cracking of the alkyl chain, in the thermal cracking of oleic acid deoxygenation and thermal cracking of the alkyl chain occurred simultaneously. This demonstrated the importance of the presence of the carbon double bond in the thermal cracking and product selectivity. Deoxygenation proceeded through both decarbonylation and decarboxylation, evidenced by the presence of both CO and CO_2, respectively, in the gas product. This observation confirms results reported on the thermal cracking of vegetable oils and animal fats [10-12].

Lower reaction temperatures favoured decarbonylation whereas higher reaction temperatures favoured decarboxylation. The effect of temperature on the deoxygenation mechanism of fatty acids reported in this study represents an important contribution and adds to the available knowledge of the thermal deoxygenation of free fatty acids. This observation is important because the formation of CO results in the formation of H_2O which is undesirable and therefore its formation should be minimized. The formation of stearic acid (a saturation product of the oleic acid feed) as well as the predominance of saturated compounds in the reaction product suggested that saturation reactions are important reactions occurring in the initial stages of the thermal cracking of monounsaturated fatty acids. Aromatic compounds were not detected at reaction temperatures of 350 °C at all reaction times and 370 °C and 390 °C for up to 1 h reaction time. The amount of aromatic compounds increased with increasing reaction temperature and reaction time once they were detected. The significance of this observation is related to the minimization of H_2O formation which would require utilizing high temperatures to promote decarboxylation over decarbonylation. However, higher reaction temperature also promotes the formation of aromatic compounds which are precursors for coke (solids) formation (another undesirable reaction). An optimization of reaction conditions to balance the minimization of aromatics and H_2O formation will be required.

The oleic acid study provided important information on reaction mechanism and fundamental reaction chemistry of thermal cracking of a monounsaturated fatty acid. In Chapter 4, the thermal cracking of polyunsaturated fatty acids with linoleic acid as model compound was carried out in batch microreactors and product distribution and characterization conducted to further elucidate the influence of unsaturation on the thermal cracking of fatty acids. Complete conversion of linoleic acid was achieved under all the reaction conditions employed. This is in contrast to the monounsaturated fatty acid thermal cracking where incomplete conversion occurred under certain reaction conditions. The observed complete conversion in linoleic acid can be explained in terms of the lower bond dissociation energy of the allylic C-C bond [13]. The polyunsaturation means higher number of allylic C-C bonds compared to monounsaturated fatty acids thereby increasing the number of positions at which cracking of these bonds can occur. Similar to the observation made in the deoxygenation of monounsaturated fatty acids, linoleic acid deoxygenation occurred through decarbonylation and decarboxylation and increasing temperature also promoted decarboxylation.

Another distinction between the thermal cracking of monounsaturated and polyunsaturated fatty acids is the formation of aromatic compounds at all reaction conditions tested in the polyunsaturated fatty acid whereas aromatic compounds were not formed below 370 °C for 1 h when monounsaturated fatty acid was pyrolyzed. The observed higher aromatic compounds in the thermal cracking of polyunsaturated fatty acid compared to monounsaturated fatty acid confirms results from previous studies [13, 14] where pyrolysis of the sodium salt of polyunsaturated fatty acids resulted in higher aromatic compounds formation when compared to monounsaturated fatty acids salts. This observation is important for process optimization and maximizing liquid product yield since aromatic compounds are important precursors of coke/solids formation. Similar to monounsaturated fatty acid thermal cracking, saturation reactions were also important initial reactions in the thermal cracking of polyunsaturated fatty acids. This observation is evidenced by the presence of oleic acid and stearic acid in the liquid product of linoleic acid thermal cracking as well as the predominance of saturated products in both the liquid and gas products.

The studies in Chapters 3 and 4 provided valuable information on the thermal cracking of unsaturated fatty acids under inert reaction atmosphere. However, the reaction atmosphere is an important factor, which can influence product distribution and reaction pathways. Therefore, in Chapter 5 the influence of reaction atmosphere particularly under light hydrocarbon gases on thermal cracking of fatty acids was studied in batch microreactors and product distribution as well as characterization performed. This study is unique in a sense that, it is the first study involving the thermal cracking of fatty acids under light hydrocarbon gases with the aim of studying the potential for recycling of the gas product during pyrolysis. Under saturated hydrocarbon gases (methane, ethane and propane), liquid product yield was not significantly different ($p > 0.05$) when compared to inert (N_2) atmosphere. This observation contrasts the results reported by Zhang et al. [15] who reported an increase in liquid product yield when corncob was pyrolyzed under methane. However, the observed differences can be explained in terms of differences in the feedstock composition used. Whereas in this study fatty acids were used as feedstock, in their study corncob, which has a relatively low carbon to oxygen ratio was used.

In contrast to the saturated light hydrocarbon gas atmosphere, the use of unsaturated hydrocarbon gas (ethylene and propylene) atmosphere resulted in liquid product yield being significantly increased from 81% under N_2 to 98% under ethylene and 107% under propylene at 130 psi initial pressure. Increasing the initial pressure to 200 psi and 500 psi (increasing mole ratio of headspace gas to feed) resulted in a further increase in the liquid product yield. The observed increase under unsaturated light hydrocarbon gases was attributed to the presence of the relatively reactive pi bonds in these compounds compared to the sigma bonds in the saturated light hydrocarbon gases. The unsaturated light hydrocarbon gas atmosphere also promoted deoxygenation and increased conversion compared to inert atmosphere. Analysis of the gas product showed the observed promotion of deoxygenation was the result of increased decarboxylation evidenced by the significantly higher CO_2 produced when unsaturated hydrocarbon gas atmosphere is used. Also the use of unsaturated light hydrocarbon gas atmosphere resulted in increased branched hydrocarbons that are desirable in applications such as jet fuel. The results of this study demonstrated the possibility of recycling the pyrolysis gas product to increase liquid product yield and promote desirable reactions such as decarboxylation and branching.

The studies using model fatty acids were useful in providing fundamental data on reaction chemistry and mechanism. However, natural vegetable oils and animal fats are complex mixtures of fatty acids with varying chain lengths and degrees of saturation. Therefore, in Chapter 6 thermal hydrolysis followed by pyrolysis was used to convert low cost inedible TAG based feedstocks to hydrocarbons. The feedstocks were beef tallow (primarily saturated fatty acids 72 %), brown grease and yellow grease (mostly monounsaturated fatty acids up to 53 %) and cold pressed camelina oil (mostly polyunsaturated fatty acid 68 %). The organic liquid product yield was not significantly influenced by the feedstock under the conditions used in this study. This was an important result demonstrating the feedstock flexibility of the thermal hydrolysis followed by the pyrolysis conversion technique employed. Fuel property testing of the crude organic liquid fractions showed about 30% in the gasoline boiling range and 50% in the diesel boing range. Other fuel properties tested indicated the crude organic liquid fractions mostly met the diesel specification set forth by the Canadian General Standards Board.

Overall, the objectives of this research have been largely achieved. The model fatty acid compounds helped elucidate important fundamental fatty acids thermal cracking mechanism and chemistry, which are important in process design and optimization as well as scale-up for large scale deployment. The inedible low cost triacylglycerol feedstocks study demonstrated the possibility of utilizing these readily available feedstocks that do not directly compete with food and feed applications in the production of renewable hydrocarbons. Additionally, it demonstrated the feedstock flexibility of the two-stage thermal conversion approach which is important for process economics as different feedstock sources can be utilized without significant modification to infrastructure.

7.1. Recommendation for future research

Although this study has elucidated fundamental reaction chemistry and demonstrated the feasibility of producing renewable hydrocarbons from the thermal hydrolysis and pyrolysis of lipid based feedstocks, further studies could be performed to compliment current work and to explore in detail the mechanisms involved in some of the findings of this work. A list of suggested studies for future research is presented below.

i. Scale-up to continuous system

Small scale batch reactors were used in this study due to their ease of use and manufacturing, relative low cost, etc. The batch reactor work in this research provided valuable information on mechanism and fundamental reaction chemistry. However, batch processes can be impractical in larger scale operations as they require clean-up and charging of the feed after each run and often experience low throughput and frequent interruptions [7,8]. Thus, the next logical step will be to scale up the reaction in a continuous reactor system. The findings presented in this study could be used to develop a continuous flow type reactor system. The continuous reactor system can also be used to assess potential of recycling and heat efficiency improvement by the use of heat exchangers.

ii. In-depth studies on fatty acid thermal cracking under unsaturated light hydrocarbon gas atmosphere

The results from the light hydrocarbon gas atmosphere thermal cracking of oleic acid provided valuable initial data on improved liquid product yield, higher conversion, increased decarboxylation and branching reactions. However, the mechanism and reaction chemistry are currently unknown and more research needs to be done in this regard to better understand the mechanisms and fundamental reactions occurring to account for the observations made. This can help optimize the process and help with scale up of the process. Studies could include varying reaction temperature and time as well as using other model fatty acids and fatty acids from hydrolyzed vegetable oils and animal fats.

iii. Studies on real-time recycling of gas product

The improvements gained in the use of unsaturated light hydrocarbon gases give an initial indication of the possibility of recycling the gas product during thermal cracking as an economical way of running the reaction. However, it will be important to conduct experiments to test this assumption by recycling in real-time the gas product and determining the impact of this operation mode on the liquid product yield as well as composition. This work could be tied into the work suggested in point one above regarding the scale up of the process to a continuous reactor system.

iv. Characterization of the aqueous liquid fraction

An aqueous liquid fraction was obtained during the experiments involving the thermal hydrolysis and pyrolysis of inedible TAG based feedstock. In future studies, characterization of the aqueous liquid fraction, particularly experiments in a continuous reactor system will be essential. Characterization will help identify important reaction products, which could be recovered as well as ensure the development of proper treatment before disposal should the need arise.

v. Development of downstream separation

The thermal cracking of fatty acids results in the formation of a wide range of compounds with varying chain lengths and functional groups. In the future, identification of products or fractions of interest from crude product as well as the development of appropriate separation methods for their extraction will be necessary. Options may include column distillation or fractionation, liquid-liquid extraction, solid phase extraction etc.

7.2. References

[1] E. Kozliak, R. Mota, D. Rodriguez, P. Overby, A. Kubatova, D. Stahl, V. Niri, G. Ogden, W. Seames, Non-catalytic cracking of jojoba oil to produce fuel and chemical by-products, Industrial Crops and Products, 43 (2013) 386-392.

[2] A. Demirbas, Progress and recent trends in biofuels, Progress in Energy and Combustion Science, 33 (2007) 1-18.

[3] Y. Ali, M.A. Hanna, Alternative diesel fuels from vegetable-oils, Bioresource Technology, 50 (1994) 153-163.

[4] F.R. Ma, M.A. Hanna, Biodiesel production: a review, Bioresource Technology, 70 (1999) 1-15.

[5] K.D. Maher, D.C. Bressler, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals, Bioresource Technology, 98 (2007) 2351-2368.

[6] K.D. Maher, K.M. Kirkwood, M.R. Gray, D.C. Bressler, Pyrolytic decarboxylation and cracking of stearic acid, Industrial & Engineering Chemistry Research, 47 (2008) 5328-5336.

[7] C. Jindarom, V. Meeyoo, T. Rirksomboon, P. Rangsunvigit, Thermochemical decomposition of sewage sludge CO2 and N-2 atmosphere, Chemosphere, 67 (2007) 1477-1484.

[8] R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Thermal cracking of Canola oil: Reaction products in the presence and absence of steam, Energy & Fuels, 10 (1996) 1150-1162.

[9] M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer, C. Roy, Characterization of bio-oils in chemical families, Biomass & Bioenergy, 31 (2007) 222-242.

[10] E. Vonghia, D.G.B. Boocock, S.K. Konar, A. Leung, Pathways for the deoxygenation of triglycerides to aliphatic-hydrocarbons over activated alumina, Energy & Fuels, 9 (1995) 1090-1096.

[11] C.M.R. Prado, N.R. Antoniosi, Production and characterization of the biofuels obtained by thermal cracking and thermal catalytic cracking of vegetable oils, Journal of Analytical and Applied Pyrolysis, 86 (2009) 338-347.

[12] J.G. Immer, M.J. Kelly, H.H. Lamb, Catalytic reaction pathways in liquid-phase deoxygenation of C18 free fatty acids, Applied Catalysis a-General, 375 (2010) 134-139.

[13] W.A. Hartgers, J.S.S. Damste, J.W. Deleeuw, Curie-point pyrolysis of sodium-salts of functionalized fatty-acids, Journal of Analytical and Applied Pyrolysis, 34 (1995) 191-217.

[14] H. Lappi, R. Alen, Production of vegetable oil-based biofuels-Thermochemical behavior of fatty acid sodium salts during pyrolysis, Journal of Analytical and Applied Pyrolysis, 86 (2009) 274-280.

[15] H.Y. Zhang, R. Xiao, D.H. Wang, G.Y. He, S.S. Shao, J.B. Zhang, Z.P. Zhong, Biomass fast pyrolysis in a fluidized bed reactor under N-2, CO2, CO, CH4 and H-2 atmospheres, Bioresource Technology, 102 (2011) 4258-4264.

Appendix: Picture and schematic diagrams of sand bath system, purging unit and microreactor.

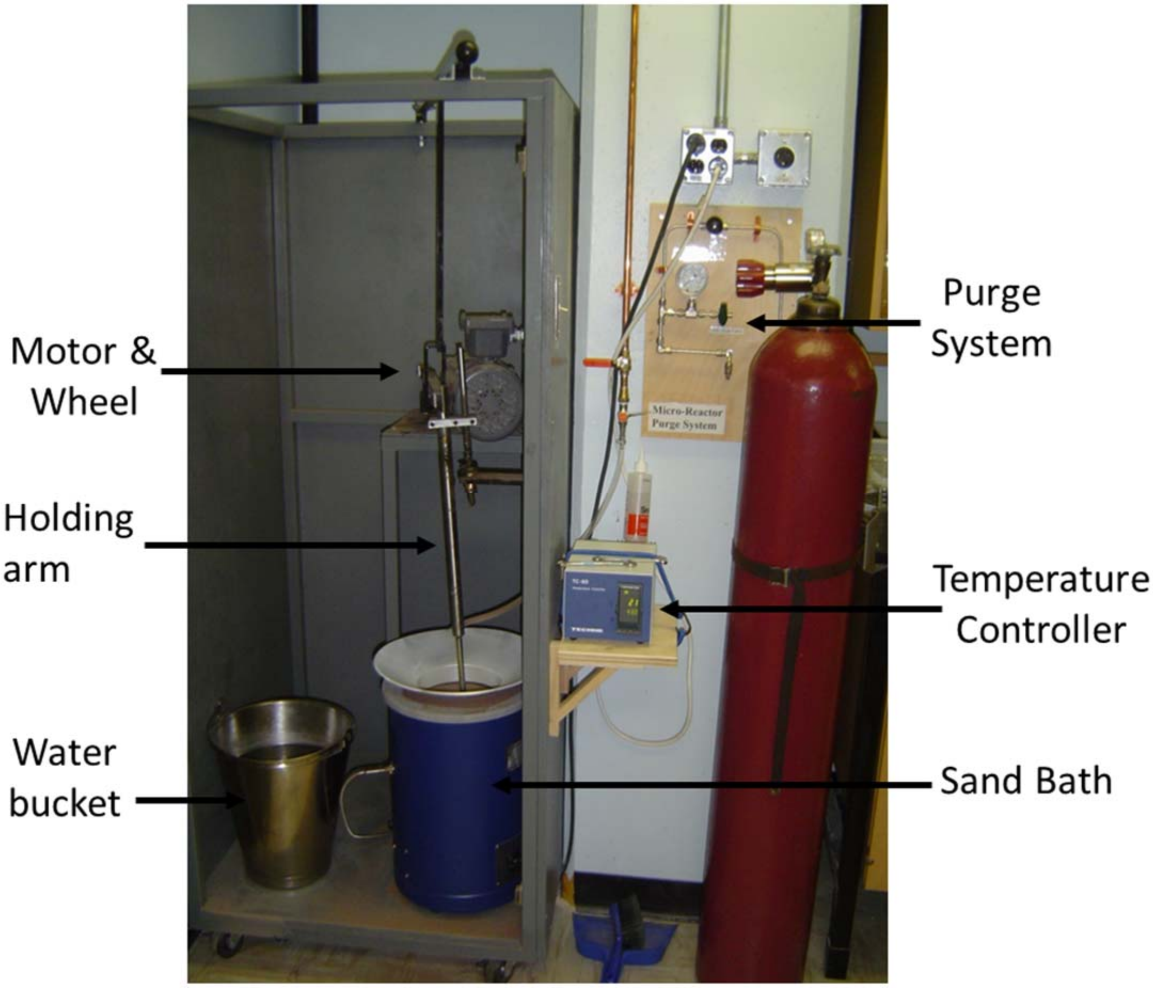

Figure A1. Picture of sand bath and purge system

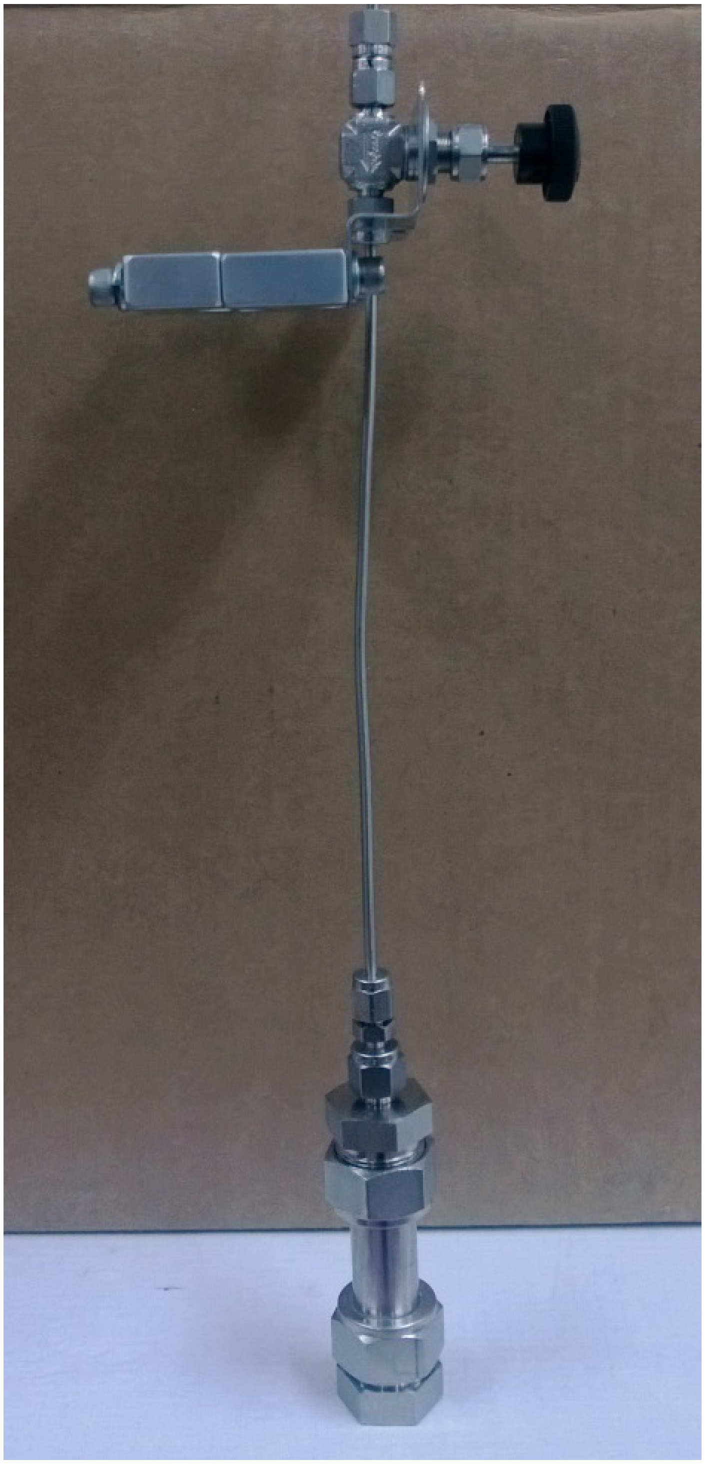

Figure A2. Picture of microreactor unit

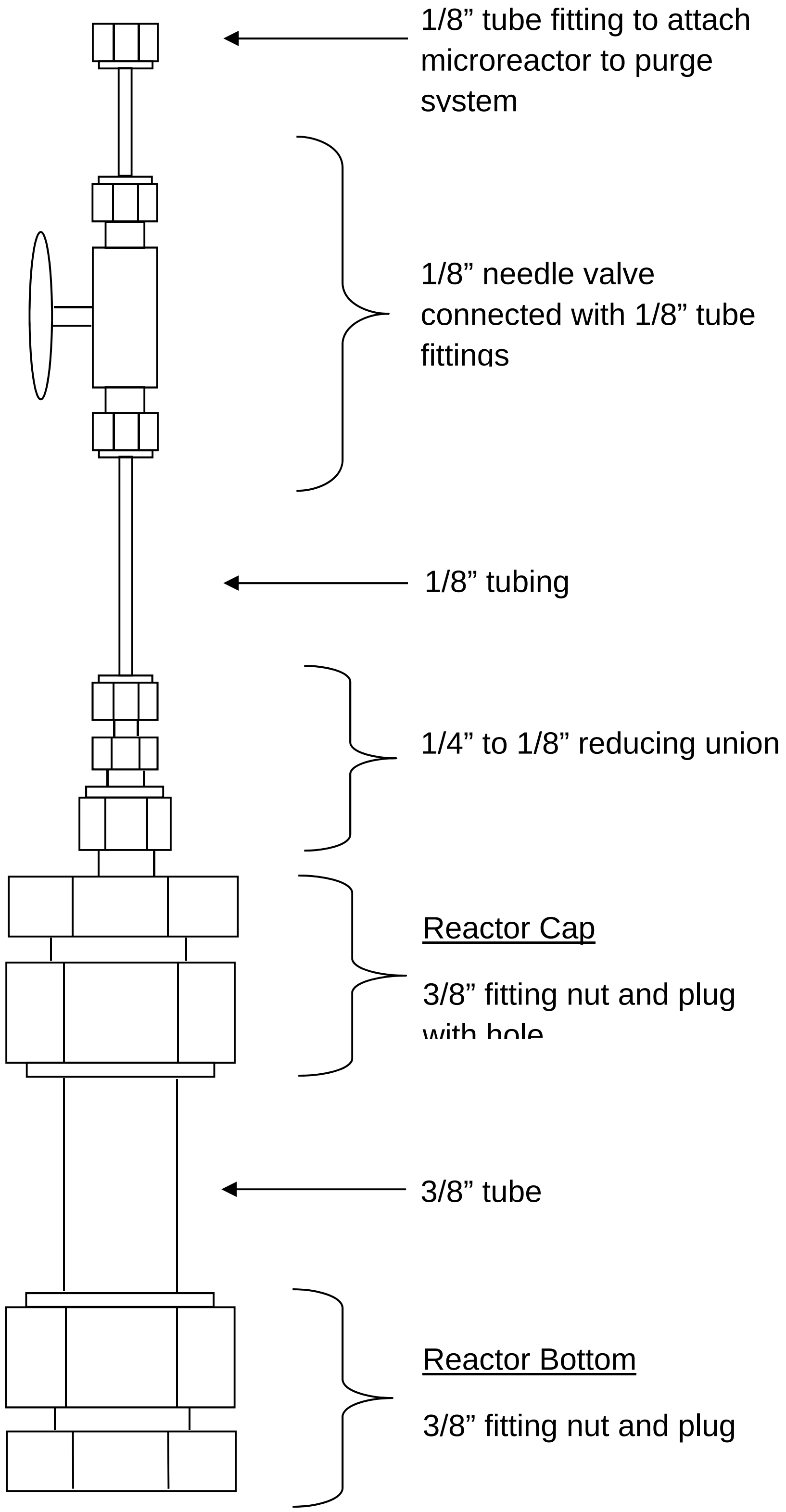

Figure A3. Schematic of microreactor unit (reprinted with permission [1])

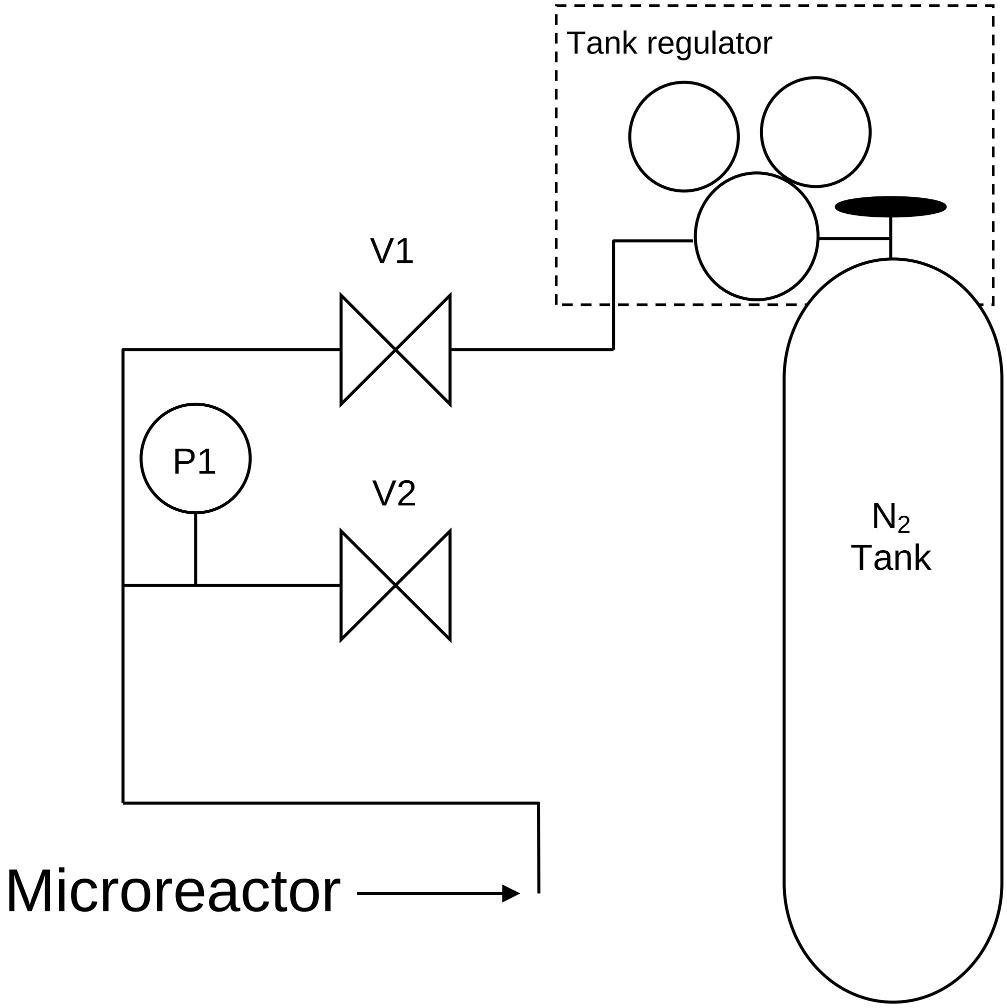

Figure A4. Schematic of purge system (reprinted with permission [1])

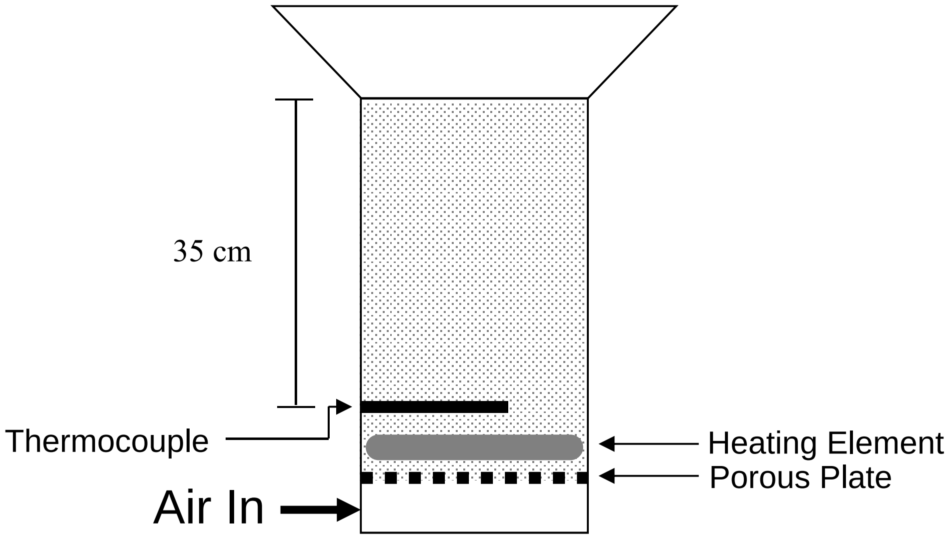

Figure A5. Schematic of Sand bath (reprinted with permission [1])

Reference

K.D. Maher. Pyrolysis of lipids for the production of renewable fuels and chemicals. Thesis submitted to the University of Alberta, Edmonton, AB. 2007.