DIRECT CONVERSION OF AGRICULTURAL OILS TO HYDROCARBONS

by

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A Thesis
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of
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in Partial Fulfillment of
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of
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Bachelor of Science
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DEDICATION

This is dedicated to my loving and supportive husband, Sultan Meshal, my sweet, precious daughter Manar, my encouraging and delightful parents, Abdullah and Sabha Alghamdi, and my well respected mother-in-law Sharifa Saad.

ACKNOWLEDGEMENTS

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ABSTRACT

DIRECT CONVERSION OF AGRICULTURAL OILS TO HYDROCARBONS

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George Mason University, 2015

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Biodiesel fuel is a far more advantageous energy source as compared to petrodiesel fuel because biodiesel is renewable, biodegradable, non-toxic, and does not contain significant amounts of sulfur and aromatics. Biodiesel is an environmentally safe fuel that can be used in any diesel engine without making any significant modifications. The production of hydrocarbons from agricultural oils is an essential area of study because it provides a safe, non-toxic, cost effective, and environmentally friendly alternative to petroleum derived fuels. The agricultural oils are directly converted to hydrocarbons through delayed coking, which is a process that mimics the petroleum refining process. The step by step conversion involves transesterification, removal of atmospheric oxygen by a freeze-pump-thaw cycle, thermal cracking (pyrolysis), and subsequent gas chromatography/mass spectrometry (GC/MS) analysis. The aim of this study was to synthesize hydrocarbons from wheat germ oil and black seed oil and then determine the hydrocarbon chain length generated and their percentage composition. This is significant

because the number of carbons in a hydrocarbon chain dictate which kind of fuel source would be synthesized from these agricultural oils. The results convey that the 30 minute pyrolysis at 675°C converted all the fatty acid methyl esters completely to alkenes for the wheat germ oil sample. The 60 minute pyrolysis at 675°C converted all of the fatty acid methyl esters to alkenes for the black seed oil sample. The highest percentage of hydrocarbons found in the wheat germ oil sample was a hydrocarbon chain length of 16 carbons, present at 26.3% for pyrolysis done at 675°C for 120 minutes. The highest percentage of hydrocarbons found in the black seed oil sample was a hydrocarbon chain length of 10 carbons, present at 51.7% for pyrolysis done at 675°C for 60 minutes. These findings are significant in that the conversion of wheat germ oil and black seed oil to hydrocarbons produces a robust amount of biodegradable, nontoxic, and environmentally safe biofuel, which would serve as an attractive alternative to the costly and harmful high emission profiles of petroleum based fuels.

CHAPTER ONE: INTRODUCTION

Petroleum-based fuels are a limited resource that is found only in certain geographic areas of the world, most notably in Russia and Saudi Arabia. Due to their limited availability, the fuel industry is under great pressure as these resources can soon reach their maximum production and as supplies of fossil fuel diminish day by day (Sheehan et al., 1998). There is a high demand for alternative renewable energy sources due to the scarcity of known petroleum reserves as well as releasing dependability on oil producing nations as the main source of fuel. Other disadvantages of utilizing fossil fuels are there high cost of production and also the release of toxic combustion-generated pollutants in the atmosphere (Sensoz et al., 2000). Therefore, there is a renewed interest for alternative fuels that will be environmental friendly and cost effective. Hydrocarbons are the main fuel source consumed by humans. Currently, the primary fuel source in the automobile industry is gasoline, despite the continuous change in resource availability and pricing. Hydrocarbons between 4 and 12 carbons per molecule are required to make gasoline and are derived from crude oils after a complex refining process (Werner et al., 2007). Jet fuel is another type of fuel that is derived from crude oil through the process of fractionated distillation. Jet fuel is a mixture of a great number of varying hydrocarbons. Kerosene-type jet fuel (including Jet A and Jet A-1) consists of a carbon range between approximately 8 and 16 carbons per molecule; naphtha-type jet fuel

(including Jet B) consists of a carbon range between about 5 and 15 carbons per molecule (Hemighaus et al., 2004). Diesel fuel is another type of liquid fuel that is composed of a great degree of compounds ranging from carbon atoms between 10 and 22, including hydrocarbons and aromatics (Bacha et al., 2007). Diesel fuel is specifically used for diesel engines and the most common type is derived from a fractional distillate of petroleum fuel oil. Unfortunately, diesel emissions release carcinogens, carbon dioxides, nitrous oxides, formaldehydes, acetaldehydes, and soot into the air. Therefore, the use of all three types of crude based oils, including gasoline, jet fuel, and diesel fuel produce many hazardous and carcinogenic pollutants into the atmosphere and exacerbate global warming through CO_2 emissions. Therefore, there is an urgent need to find safer, more cost effective, and environmental friendly fuels that would replace these limited and harmful petroleum fuels.

The synthesis of pure biodiesel fuel is a hot topic in the scientific arena for its capability to act as either a blending agent or a complete alternative for diesel fuel in engines. Biodiesel is an excellent lubricant, especially as compared to petrodiesel, with biodiesel exhibiting lubrication properties that are 66% better than petrodiesel. Specifically, the biodiesel methyl esters beneficially modify the diesel fuel blend by improving the lubrication properties of the diesel fuel blend. The lubrication properties of biodiesel fuels have been shown to be favorable with diesel engines in that they significantly reduce long term engine deterioration in diesel engines (Demirbas, 2008). Biodiesel is synthesized by reacting vegetables oils (such as canola and sunflower) with alcohol in the presence of either a strong acidic or strong basic catalyst. The advantages

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of biodiesel fuel over petroleum derived fuels include biodegradability, a renewable source, nontoxic, and releases less harmful pollutants. Not only are biodiesels environmentally friendly, but they are significantly lower in cost when compared to gasoline, even with partial-biodiesel fuel. Biodiesel is more stable in both extremes of temperature, has a higher flash point, and a decreased emission profile when compared to petroleum based fuels. The lack of sulfur for biodiesels is another benefit because petroleum based fuels contribute to acid rainfall due to sulfur emissions (Hill et al., 2006).

This study focuses on synthesizing agricultural derived biodiesel fuels based on a procedure that mimics refining petroleum in the fuel industry. This process is known as delayed coking and is used to produce hydrocarbons from the following agricultural oils. Delayed coking involves thermal cracking at very high temperatures (Ellis et al., 1998) and with a very minute sample size (approximately a tenth of a gram of oil). The same steel (316 stainless steel) utilized in the petroleum refinery process was also used in this current study. This study is unique for wheat germ oil and black seed oil (*Nigella sativa*) are being analyzed for biodiesel production and at high temperatures (675° C). Based on Knothe's study, chain length, degree of unsaturation, and branching of the chain are structural characteristics that dictate the physical and fuel properties of a fatty ester molecule (Knothe, 2005). These oils have been specifically chosen in order to compare how variability in total fatty acid composition (weight percent %) dictates the production of straight hydrocarbon chains. Table 1 displays total fatty acid composition (weight percent %) of wheat germ oil (Niu et al., 2013) and black seed oil (Gharby et al., 2013).

The table conveys that wheat germ oil is highly concentrated in unsaturated fatty acid (82.9%), especially in linoleic acid (64.8%) and oleic acid (13.2%). The percentage of total unsaturated fatty acids for black seed oil is 82.7% while the total unsaturated fatty acid percentage is 13.1%. The percentage of hydrocarbon content of the agricultural oils are then compared to reveal which oil would produces the most usable biodiesel fuel. Oleic acid is a monounsaturated oil that consists of 18 carbons and one double bond. The fatty acids that are present in the agricultural oils, which include oleic, linoleic, linolenic, palmitic, and stearic acid are predicted to decompose to hydrocarbons as the gas chromatogram runs. This research is beneficial because agricultural oil releases less harmful pollutants and yields more miles per gallon, which is environmentally friendly and cost effective for the consumer.

Table 1: Fatty acid composition of black seed and wheat germ oil (percent by weight of total fatty acids)**.**

Oil	Palmitic acid (C16:0)	Stearic acid (C18:0)	Oleic acid (C18:1)	Linoleic acid (mega-6) (C18:2)	Linolenic acid (omega-3) (C18:3)
Wheat germ	16.2	0.28	13.2	64.8	4.9
Black seed	13.1	2.3	23.8	58.5	0.4

CHAPTER TWO: METHODS AND MATERIALS

The synthesis of biodiesel fuel from the agricultural oils of wheat germ oil and black seed oil occurred through four main steps. Initially, the wheat germ oil and black seed oil were put through a transesterification process to produce wheat germ methyl ester and black seed methyl ester. Secondly, any atmospheric oxygen was removed from the fatty acid methyl esters (FAMEs) through vacuuming and a freeze-pump-thaw cycle. Then, the samples underwent pyrolysis by heating in a furnace set at 675°C (948.15K) for time durations of either 15, 30, 60, or 120 minutes. Finally, the samples were analyzed via gas chromatography/mass spectrometry (GC/MS) to detect hydrocarbons numbers and percent composition.

1. Fatty Acid Methyl Ester

Initially, the same process is utilized to convert the triglycerides in wheat germ and black seed oils to their fatty acid methyl-ester derivatives. Transesterification involves a triglyceride reacting with methanol and potassium hydroxide catalyst to produce glycerol and methyl ester, as shown by Equation 1.

Equation 1: Transesterification.

$$CH_2OOCR_1 \qquad\qquad R_1COOH_3 \qquad CH_2OH$$
$$|$$
$$CHOOCR_2 \quad + 3CH_3OH \xrightarrow{\ KOH\ } R_2COOH_3 \quad + \quad CHOH$$
$$|$$
$$CH_2OOCR_3 \qquad\qquad R_3COOH_3 \qquad CH_2OH$$

Triglyceride   Methanol   Methyl Ester   Glycerol
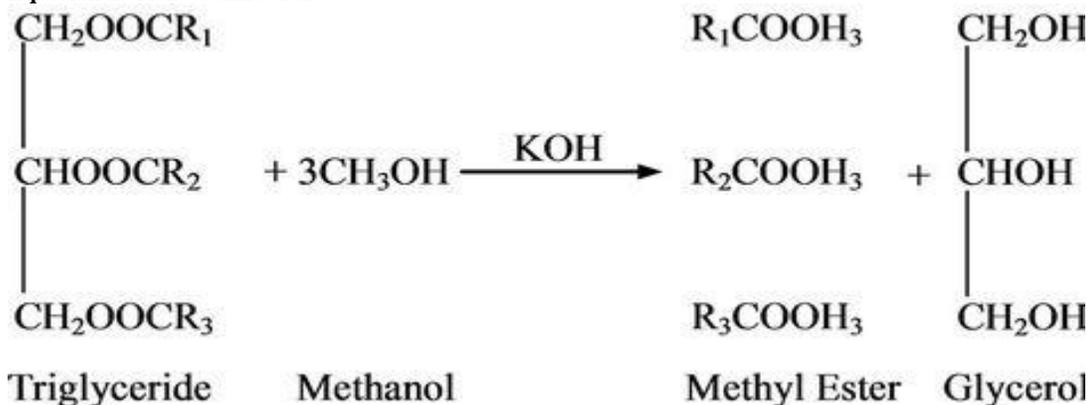
A sample size of 10 mL was pipetted into a dry 50 mL glass flask already containing a magnetic stirrer. The 50 mL flask and its contents were then nestled on top of an aluminum stand which was placed on a hot plate stirrer. The aluminum stand also contained a thermometer in order to accurately measure temperature. A water-jacket condenser was then attached to the 50 mL flask (see Figure 1). Dryness is absolutely essential as any moisture in the system will consume some of the catalyst and decrease the rate of the transesterification. In another 10 mL volumetric flask, 0.1 grams of KOH (acting as catalyst) was mixed with approximately 2 mL of methanol until all of the KOH dissolved. The methanol/KOH mixture was quickly added to the oil and stirred vigorously for 30 minutes at 55°C using the hot plate stirrer. All the liquid in the flask was then transferred to a 15 mL centrifuge tube, capped, and centrifuged for 20 minutes. The transesterification reaction produced two visible layers, with the bottom layer containing glycerin, and the top layer containing the methyl ester (biodiesel)

(See Figure 2). The top layer, which contained the biodiesel, was poured into another 50

mL flask and heated for 30 minutes at 70°C, followed by a 20 minute centrifugation. The

top layer was then separated again and placed in a vial to prepare for the freeze-pump-

thaw cycle (Karaosmanoglu et al., 1996; Lang et al., 2001; Kondamudi et al., 2009).
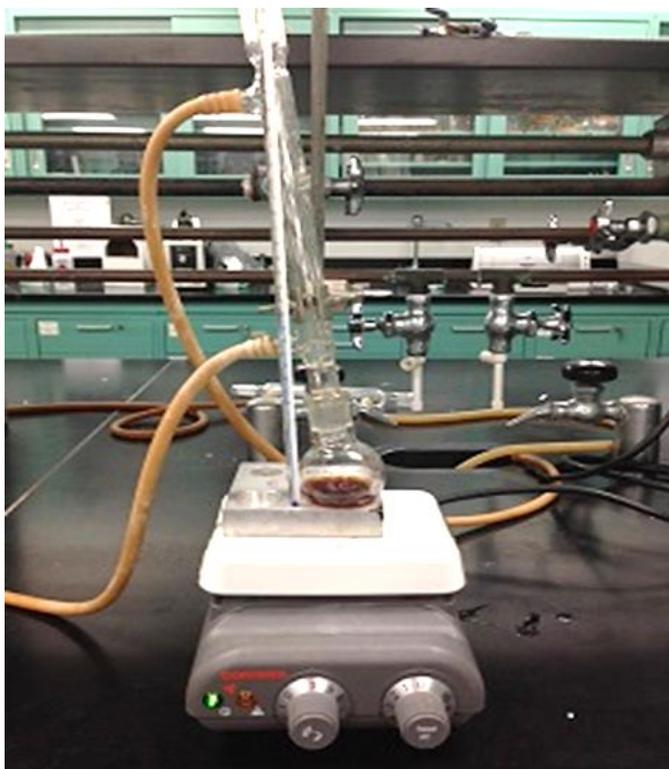
Figure 1: Transesterification for Black seed oil using flack attached to a water-jacket condenser.

Figure 2: Wheat germ oil shows two layers the top layer is wheat germ methyl ester (Biodiesel) and the bottom layer is glycerin.

2. Freeze- Pump-Thaw Cycle

A tenth of a gram was abstracted from the sample that had underwent transesterification and placed in a 15-cm-long, 6.4-mm-o.d. (¼- inch-o.d.) 316 stainless-steel tube. The tube was sealed at one end and fitted on the other end with a stainless steel valve utilizing a Swagelok fitting. The stainless steel tubes were utilized for many runs and were cleaned by filling the tubes with methanol, acetone, and then methylene chloride. They were then scrubbed with a stainless steel brush, rinsed twice with methylene chloride, and then air dried at 449.85°C (723 K) for 1 hour. The stainless steel

tube with the 0.1 grams was attached to a vacuum system (See Figure 3) and then placed in a dry ice/isopropyl mixture at -78.15°C (195 K). The sample was then subjected to three freeze-pump-thaw cycles (Mushrush et al., 1984). The freeze-pump portion of the cycle included vacuuming of the tube while being immersed in the dry ice/isopropyl mixture. The vacuum was turned on for a duration of three minutes. Immediately after the vacuum was turned off, the tube was immersed in warm water in order to thaw the sample. This process of freezing, vacuuming, and thawing was repeated 4-5 times. The valve was turned off and the tube was then removed from the vacuum system and sealed tightly to prevent the introduction of any atmospheric oxygen. The tube was equilibrated to room temperature before continuing on with pyrolysis.
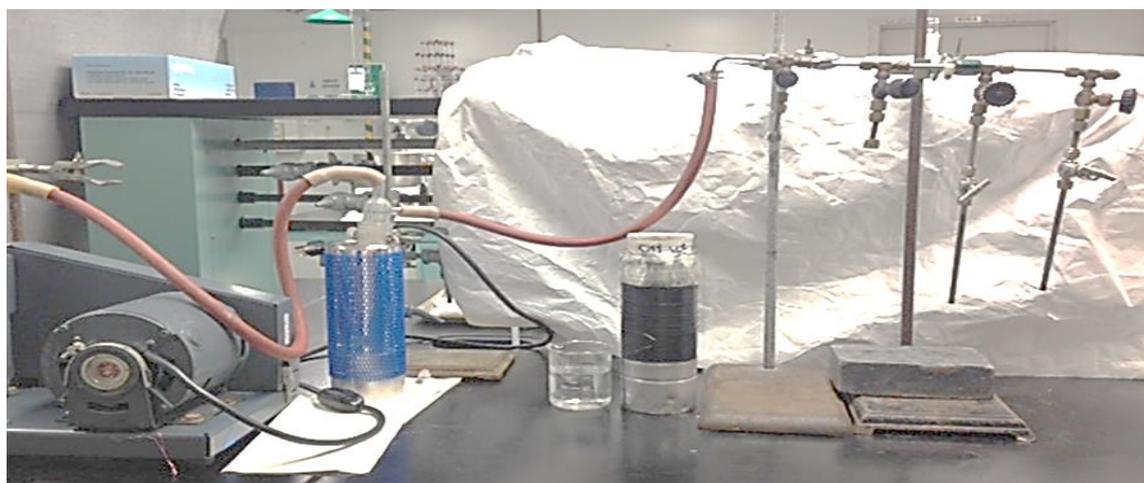
Figure 3: Freeze-pump-thaw process.

3. Pyrolysis

The next step involved the pyrolysis of the methyl ester oils obtained from the freeze-pump-thaw cycle. Pyrolysis was performed at 675°C (948.15 K) for time durations of either 15, 30, 60, or 120 minutes. The stainless steel tube walls showed no visible catalysis except for n-tridecyl cyclohexane. Kunzu et al. supports this finding for there was no observable catalytic behavior of stainless steel in the cracking of nonane at 923-1023 K (Kunzu, 1972). Pyrolysis was achieved by placing the tube inside a furnace (See Figure 4) that contained a temperature controller set at 675°C (948.15 K)(Furnace 47900). After 15 minutes, the reaction was immediately halted by placing the tube into dry ice for 5 minutes. The sample in the tube was rinsed with methylene chloride in 0.5 ml increments for a total of four rinses, which resulted in 1.5 mL of methylene chloride rinse. The tube was sealed and allowed to equilibrate to room temperature. The sample was then diluted with methylene chloride at 1:10 and immediately poured inside a screw-cap vial and analyzed by GC/MS. The same process was applied to both the wheat germ oil and the black seed oil for 30, 60, and 120 minutes.

Figure 4: Oven with control temperature.

4. Gas Chromatography/Mass Spectrometry (GC/MS)

The GC/MS instrument utilized was an Agilent Technologies Model 6890 connected to a 5975C mass spectrometer. The GC contained an all glass inlet system which housed a 0.32 mm x 30 m fused silica capillary column composed of cross-linked 5% phenyl methyl silicone (Agilent Technologies). The column performed at a flow rate of l mL/min and consisted of cross-linked 5% phenyl methyl silicone. The temperature setting consisted of a gradient temperature, with an initial temperature of 50°C for a time duration of 7 minutes, followed by a gradual rate of increase of 9°C/mm, until a final

temperature of 300°C was attained. Although the allowed maximum temperature of the

column was 325°C, this study set the maximum temperature to 300°C. The mass

spectrometer was set in the electron impact ionization mode (70 eV). The following

parameters utilized included: continuous scan acquisition from 50 to 300 amu at a cycling

rate of 1 scan/sec, electron multiplier was 1050 V, source temperature was 200°C. The

data obtained from mass spectrometry was analyzed by using the database from the

National Institute of Standards and Technology (NIST).

CHAPTER THREE: RESULTS AND DISCUSSION

1. Wheat Germ Methyl Ester

The hydrocarbon chain length and percentage of composition were examined for all three oils at different times of pyrolysis (15 minutes, 30 minutes, 60 minutes, and 120 minutes at 675°C). The GC chromatograph for wheat germ methyl ester at a time duration of 15 minute pyrolysis at 675° C (Figure 5) displays the peaks for the main fatty acid methyl esters in the oil. The 15 minutes duration for pyrolysis proves to be insufficient as the chromatograph reveals that the main fatty acid methyl esters have still not been converted to hydrocarbons. Figure 6 displays the MS data for palmitic acid but the formula from the output displays $C_{17}H_{34}O_2$. Initially, this might seem a discrepancy because palmitic acid contains 16 carbons, and not 17 carbons. However, since this study incorporated methyl ester, each fatty acid contained an additional carbon with two additional hydrogens resulting in the $C_{17}H_{34}O_2$. Table 2 displays the total fatty acid percentage for wheat germ methyl ester for the same conditions (15 minute pyrolysis at 675° C) with palmitic acid comprising 34.1%, oleic acid comprising 25.7%, linoleic acid comprising 13.8%, and stearic acid being present in the lowest composition of 6.3%. The remaining composition of the wheat germ oil included short chain fatty acids that ranged from C12-C14 and other alkene compounds, such as 1-tetradecene (Figure 7). The fatty acids with the shorter chains are expected to have resulted from the cleavage of longer

chain fatty acids. Wheat germ oil is known to contain linolenic acid but the GC

chromatogram did not reveal a peak for linolenic acid. This is easily explained by the

fact that linolenic acid was never vaporized because the boiling point of linolenic acid is

443°C (MSDS, 2015), while the maximum temperature of the column was only 325°C.
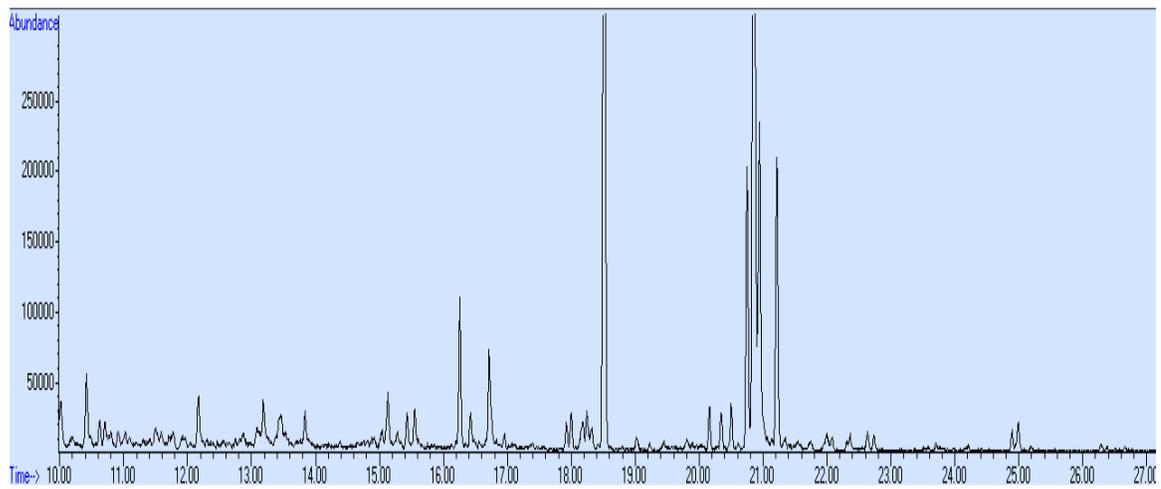
Figure 5: GC chromatograph for wheat germ methyl ester for 15 minute pyrolysis.
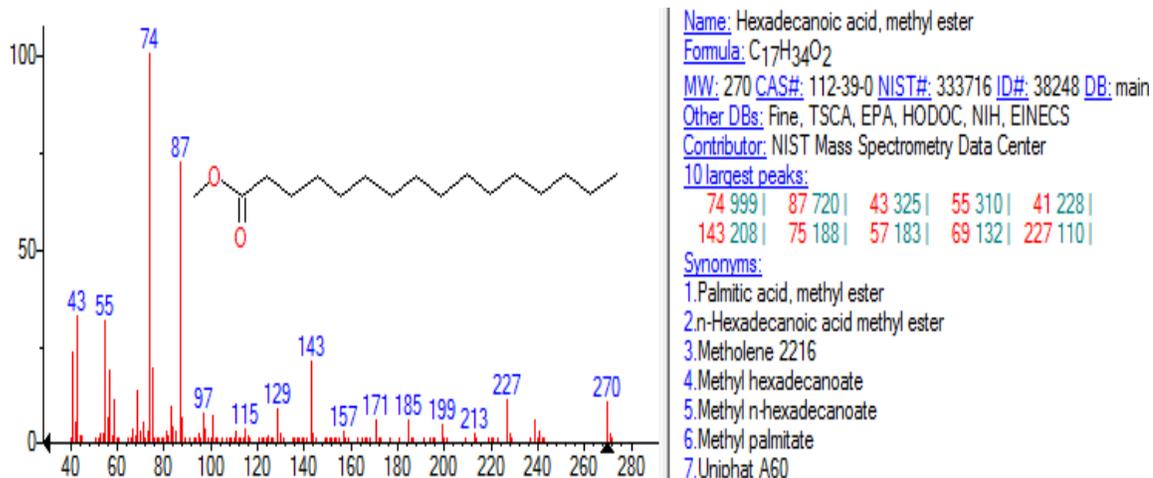
Figure 6: Palmitic acid, methyl ester showed by NIST library as hexadecanoic acid, methyl ester.

Table 2: Total fatty acid percentage by the peaks for wheat germ methyl ester 15 minutes.

Fatty Acids	Peak Number	Retention Time	% of Total
Palmitic acid (C16:0)	13	18.517	34.1
Stearic acid (C18:0)	17	21.218	6.3
Oleic acid (C18:1)	15	20.857	25.7
Linoleic acid (C18:2)	14 and 16	20.747 and 20.946	13.8

15
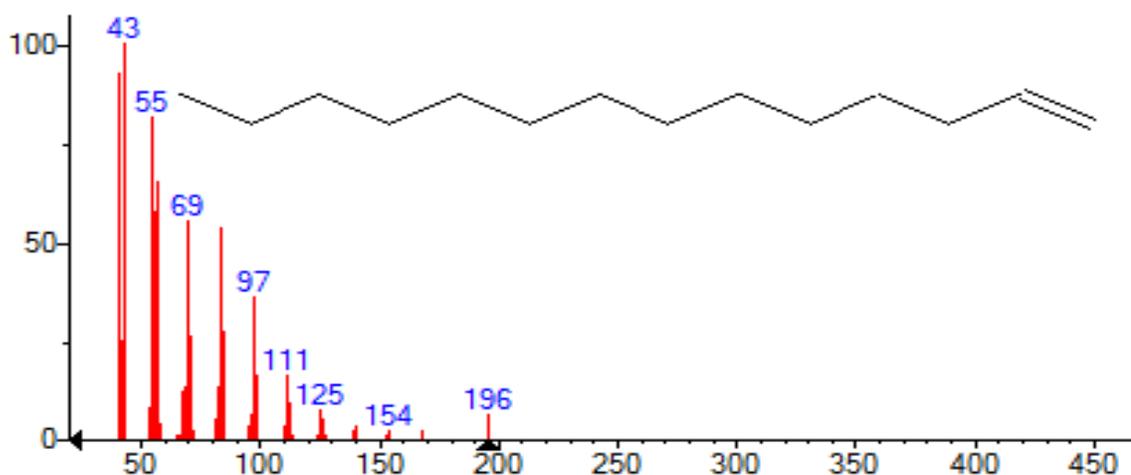
Figure 7: 1-Tetradecene is a long chain hydrocarbon alkene.

Table 3 displays the range of carbons between C10 to C19 for wheat germ methyl ester at a time duration of 15 minutes for pyrolysis. The highest percent composition of carbon chains found in wheat germ was the C19 (45.9%), which was derived from the fatty acid methyl ester. The second highest percent composition of carbon chains was the C17 (34.1%).

Table 3: The percent composition of hydrocarbon in wheat germ methyl ester for 15 minute pyrolysis.

hydrocarbon chain length	% of hydrocarbon in the sample
C10	2.0%
C11	4.0%
C12	1.7%
C13	5.0%
C14	6.8%
C17	34.1%
C19	45.9%

The 30 minute pyrolysis at 675°C for wheat germ methyl ester produced more peaks on the GC chromatograph, as shown in Figure 8. The results reveal that the 30 minute pyrolysis produced approximately 97.5% alkene and the mass spectrometry data confirmed 0% of fatty acid methyl ester. This data indicates that the 30 minute pyrolysis at 675°C was sufficient for converting all of the fatty acids to alkenes.
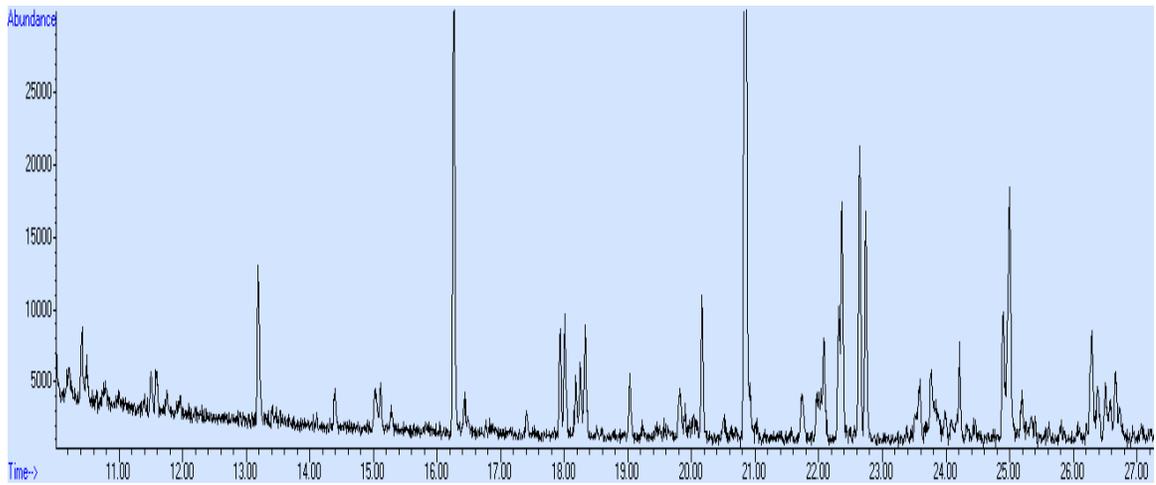
Figure 8: GC chromatograph for wheat germ methyl ester for 30 minute pyrolysis.

The range of carbon numbers produced (Table 4) were between C10 to C24, and the highest carbon percent composition belonged to C16, at a percent of 17.8% for 30 minute pyrolysis.

Table 4: The percent composition of hydrocarbon in wheat germ methyl ester for 30 minute pyrolysis.

hydrocarbon chain length	% of hydrocarbon in the sample
C10	14.7%
C11	9.3%
C12	1.9%
C13	1.4%
C14	4.5%
C15	4.1%
C16	17.8%
C17	9.2%
C18	6.3%
C19	2.8%
C20	9.0%
C21	2.7%
C22	7.1%
C23	1.5%
C24	4.6%

The GC chromatograph for the 60 minute pyrolysis of wheat germ methyl ester at 675°C is (Figure 9) similar to the 30 minute pyrolysis chromatograph, as the peak numbers are approximately identical. The fatty acid and alkane percentage present for the 60 minute pyrolysis for the wheat germ methyl ester resulted in 0%. The percent composition of alkene was 90.8% and the percent composition for the solvent was 9.2%.

The C16 was present at greatest composition with a percentage of 23.9% for 60 minute pyrolysis (Table 5). The biggest variation between the 30 and 60 minutes pyrolysis time for wheat germ methyl ester is that the 60 minute pyrolysis time contained no C12, C23, or C24.
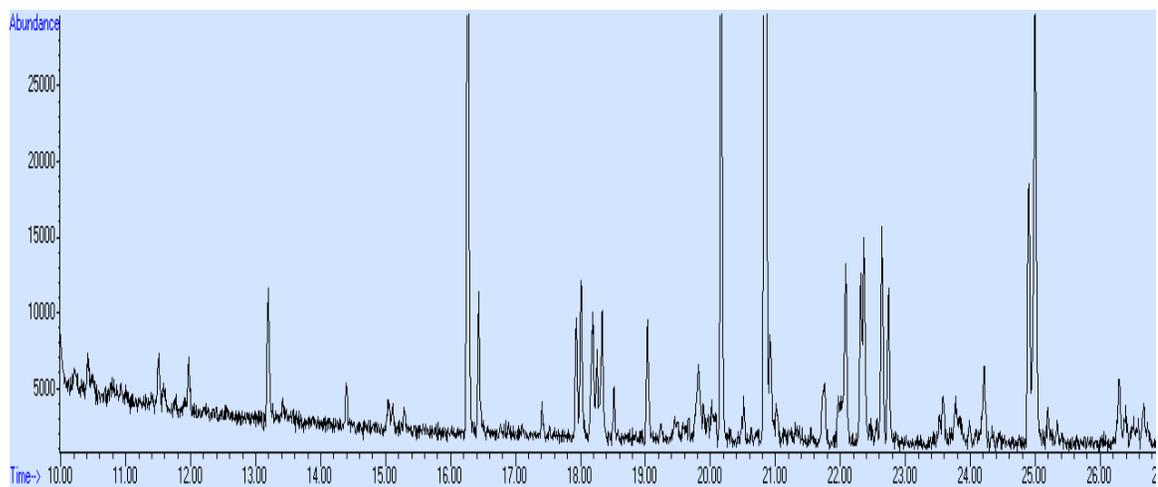
Figure 9: GC chromatograph for wheat germ methyl ester for 60 minute pyrolysis.

Table 5: The percent composition of hydrocarbon in wheat germ methyl ester for 60 minute pyrolysis.

hydrocarbon chain length	% of hydrocarbon in the sample
C10	13.7%
C11	3.3%
C13	1.5%
C14	8.1%
C15	6.6%
C16	23.9%
C17	10.5%
C18	10.0%
C19	0.8%
C20	9.4%
C21	0.5%
C22	2.0%

The GC chromatograph for the 120 minute pyrolysis at 675°C for the wheat germ oil (Figure 10) revealed the highest percentage of alkene. The 120 minute pyrolysis caused the composition to contain 100% of alkenes. The chromatogram did not show peaks for C21, C23, and C24, but the C16 percent composition has increased to 26.3% as compared to shorter pyrolysis times (Table 6).
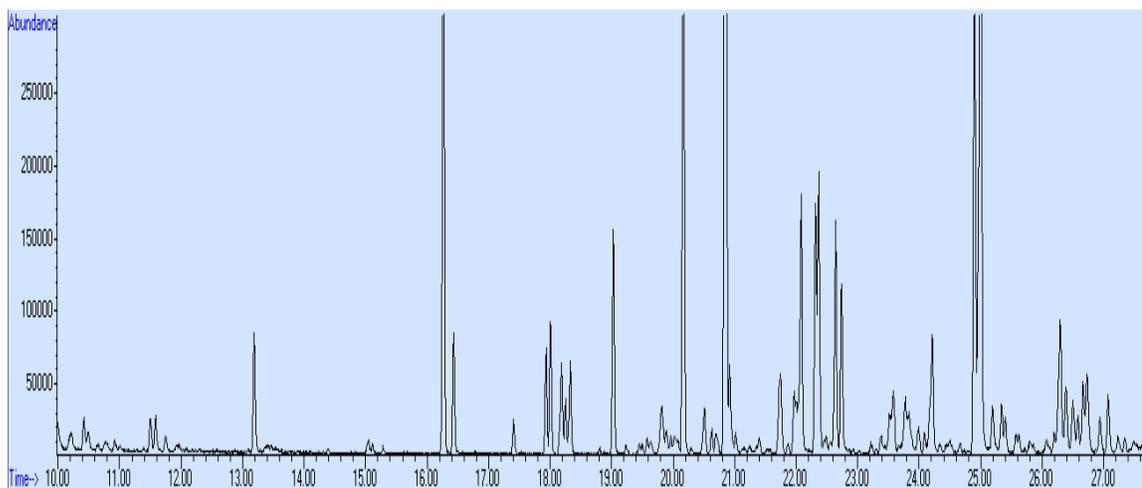
Figure 10: GC chromatograph for wheat germ methyl ester for 120 minute pyrolysis.

Table 6: The percent composition of hydrocarbon in wheat germ methyl ester for 120 minute pyrolysis.

hydrocarbon chain length	% of hydrocarbon in the sample
C10	10.3%
C11	4.1%
C12	0.9%
C13	5.2%
C14	2.7%
C15	0.9%
C16	26.3%
C17	11.1%
C18	13.8%
C19	1.4%
C20	17.0%
C22	6.5%

Table 7 summarizes the findings for the percent composition of alkane, alkene, and FAMEs in wheat germ methyl ester for pyrolysis at 675°C for 15 minutes, 30 minutes, 60 minutes, and 120 minutes. The table clearly demonstrates that all of the FAMEs present during the 15 minute pyrolysis run was completely converted to alkenes for pyrolysis of 30 minutes or greater.

Table 7: The percentage of FAMEs, alkane, and alkene in wheat germ methyl ester at varying times.

Time	Alkane	Alkene	FAME
15 minutes	0	10.2%	89.7%
30 minutes	0	97.5%	0
60 minutes	0	90.8%	0
120 minutes	0	100%	0

2. Black Seed Methyl Ester

Figure 11 displays the chromatograph for black seed oil sample with conditions of 15 minute pyrolysis at 675°C. The most relevant peaks are for the fatty acids of palmitic acid, linoleic acid, and oleic acid, with palmitic acid being present with 3.3%, linoleic acid being present 9.3%, and oleic acid being present with 7.1% (Table 8). According to Gharby et al. (2013), black seed oil is also known to contain stearic acid (2.3%) and linoleic acid (58.5%). However, the chromatograph does not reveal a peak for stearic

acid and there is only 9.3% composition of linoleic acid. The peak absence of stearic

acid is easily explained by the fact that stearic acid was not vaporized because its boiling

point of 350°C (Lide, 2005) was never attained since the maximum temperature of the

column was set at 300°C (and maximum possible temperature of the column is only

325°C). The reason why there is such a small percent composition of 9.3% for linoleic

acid as compared to Gharby's previously reported 58.5% linoleic acid, is because most of

the linoleic acid was most likely converted to other hydrocarbons.

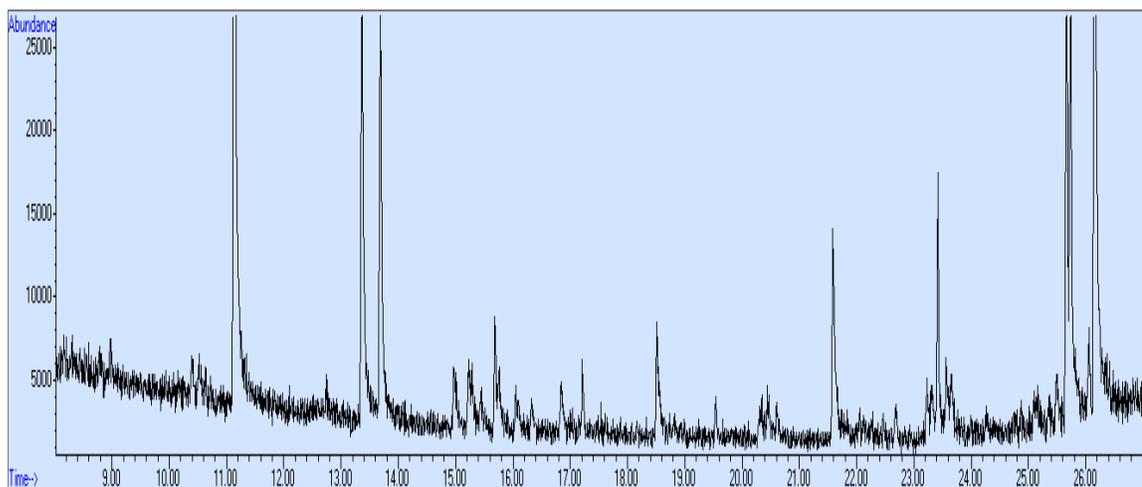

Figure 11: GC chromatograph for black seed methyl ester for 15 minute pyrolysis.

Table 8: Total fatty acid percentage by the peaks for black seed methyl ester 15 minutes.

Fatty Acids	Peak Number	Retention Time	% of Total
Palmitic acid (C16:0)	9	23.418	3.3%
Oleic acid (C18:1)	12	25.731	7.1%
Linoleic acid (C18:2)	11	25.663	9.3%

Table 9 displays the range of carbons between C10 to C19 for black seed methyl ester at a time duration of 15 minutes for pyrolysis. The highest percent composition of carbon chains found in black seed methyl ester was the C10 and C16 (22.2%).

Table 9: The percent composition of hydrocarbon in black seed methyl ester for 15 minute pyrolysis.

hydrocarbon chain length	% of hydrocarbon in the sample
C10	22.2%
C11	18.1%
C12	2.8%
C13	1.8%
C14	4.2%
C15	0.8%
C16	22.2%
C17	10.1%
C19	16.5%

Figure 12 displays the GC chromatograph for black seed oil with conditions of 30 minute pyrolysis at 675°C. There are more peaks visible as compared to the 15 minute pyrolysis, and this is due to the fact that the increased duration of pyrolysis caused conversion of fatty acid to hydrocarbons (alkenes). These additional peaks are due to the presence of hydrocarbons. The MS data reveals that only one peak belongs to a fatty

acid, and that is palmitic acid showing up with a composition of 4.4%. The hydrocarbon

present in greatest composition (See Table 10) was found to be C10 (23.7%). There were

no alkanes identified by the NIST library.

Figure 12: GC chromatograph for black seed methyl ester for 30 minute pyrolysis.

Table 10: The percent composition of hydrocarbon in black seed methyl ester for 30 minute pyrolysis.

hydrocarbon chain length	% of hydrocarbon in the sample
C10	23.7%
C11	15.8%
C12	16.3%
C13	8.1%
C14	8.8%
C15	2.8%
C16	2.0%

Figure 13 displays the GC chromatograph for black seed oil at conditions of 60 minute pyrolysis at 675°C. The chromatography is noticeably different than the 30 minute run, in that there is a significant reduction in peaks, with only 7 peaks being identified. All the peaks identified were alkenes and the hydrocarbon present in greatest composition was identified as Peak 1, a C10 chain comprising 51.7% (Table 11).
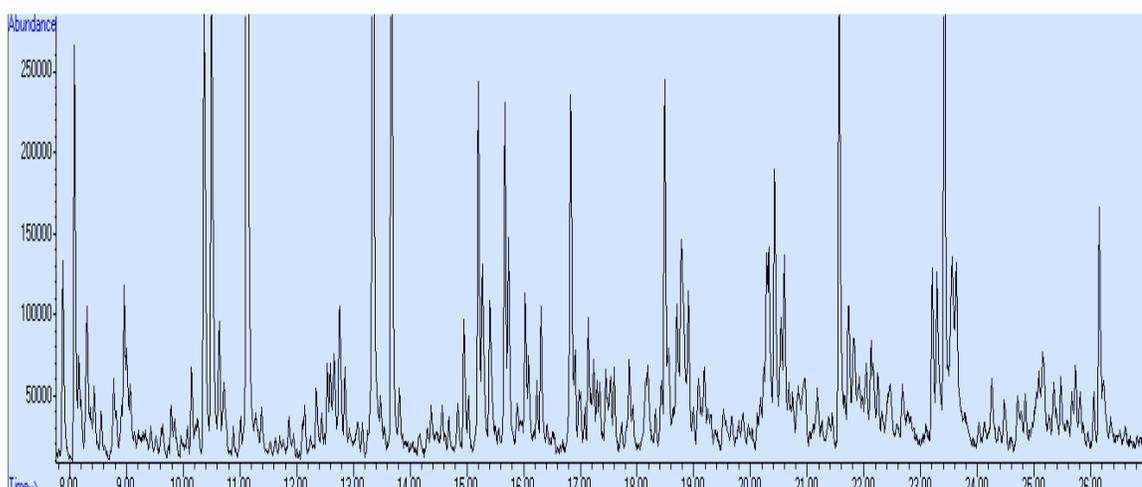
Figure 13: GC chromatograph for black seed methyl ester for 60 minute pyrolysis.

Table 11: The percent composition of hydrocarbon in black seed methyl ester for 60 minute pyrolysis.

hydrocarbon chain length	% of hydrocarbon in the sample
C10	51.7%
C11	27.0%
C12	7.5%
C13	1.2%
C16	1.8%

Figure 14 displays the chromatograph for black seed oil at conditions of pyrolysis for 120 minutes at 675°C. The results for the 120 minute pyrolysis are similar to the 60 minute pyrolysis in that approximately same amount of peaks are present. The

hydrocarbon present (Table 12) in greatest composition was still found to be the C10 (34.91%).
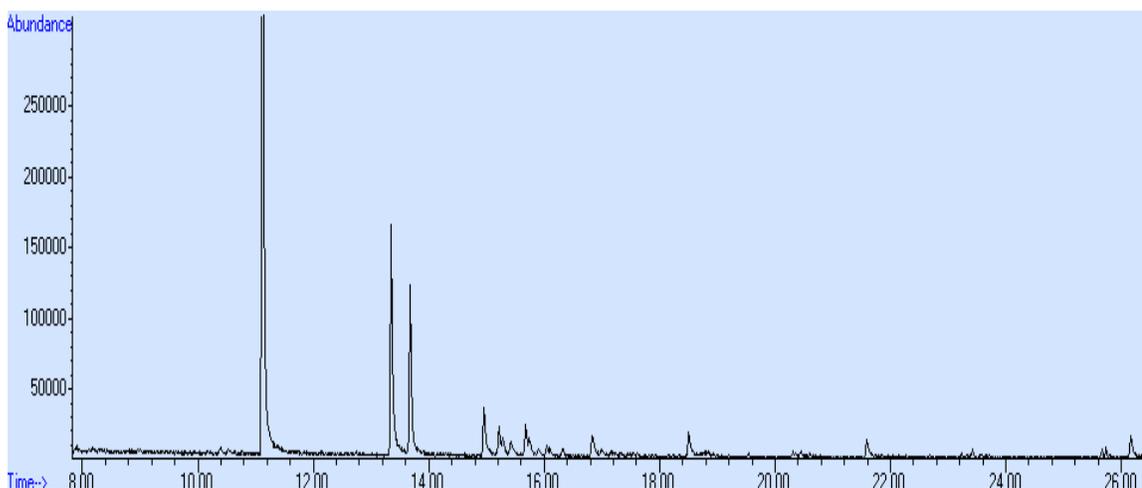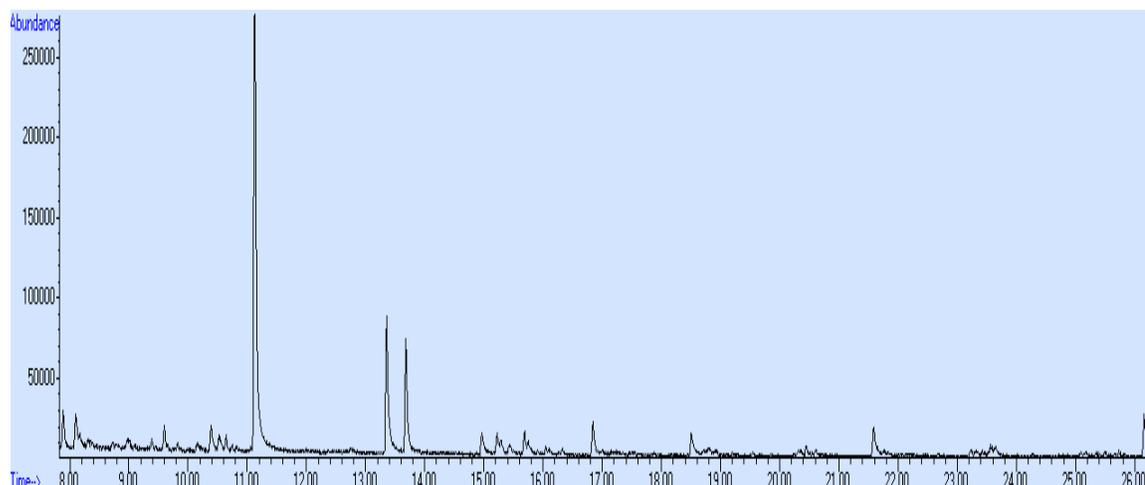

Figure 14: GC chromatograph for black seed methyl ester for 120 minute pyrolysis.

Table 12: The percent composition of hydrocarbon in black seed methyl ester for 120 minute pyrolysis.

hydrocarbon chain length	% of hydrocarbon in the sample
C10	34.9%
C11	13.9%
C12	5.3%
C13	1.4%
C14	1.8%
C16	2.2%

Table 13 summarizes all the results by comparing the percentage of alkanes, alkenes, and fatty acid methyl esters present at 15 minute pyrolysis, 30 minute pyrolysis, 60 minute pyrolysis, and 120 minute pyrolysis for black seed methyl ester. The most relevant information is that all of the fatty acid methyl esters were completely converted to alkenes at 60 minute pyrolysis and beyond. No alkanes were found to be present for any of the pyrolysis times.

Table 13: The percentage of FAMEs, alkane, and alkene in black seed methyl ester at varying times.

Time	Alkane	Alkene	FAME
15 minutes	0	87.5%	12.4%
30 minutes	0	95.5%	4.4%
60 minutes	0	100%	0
120 minutes	0	100%	0

When comparing wheat germ oil and black seed oil, the wheat germ oil converted all of the fatty acid methyl esters to alkenes at 30 minute pyrolysis while the black seed oil had complete conversion to alkenes at 60 minute pyrolysis. The C16 generated from wheat germ oil is the hydrocarbon that could potentially be used for jet fuel since kerosene and diesel fuels both utilize C16 (as shown in Table 14). The reason being is

that the C16 hydrocarbon chain was continuously present in highest percent composition for wheat germ oil at all durations of pyrolysis. Additionally, the percent composition of C16 spiked at 30 minute pyrolysis, and increased in percent composition as pyrolysis time increased. The highest percentage of C16 found in wheat germ oil was 26% at 120 minute pyrolysis (675°C).

The C10 generated from black seed oil is the hydrocarbon that would be a great energy source for kerosene and gasoline fuel (as shown in Table 14). The highest percentage of C10 found in black seed oil was 51.7% at 60 minute pyrolysis (675°C).

Table 14: Fuel fraction.

Fraction	C atoms
Gas	1-4
Gasoline	5-12
Kerosene	10-16
Diesel	15-22

The amount of peaks were substantially lower for the GC chromatographs of both wheat germ oil and black seed oil after 30 minute pyrolysis because the longer chain hydrocarbons had degraded to smaller hydrocarbons as pyrolysis time increased. This

resulted in the formation of such gaseous compounds (very short hydrocarbon chain) as

methane, which has a mass of 16 amu, and is not detected by the GC/MS. The primary

focus of this study was to determine the amount of useful hydrocarbon obtain from wheat

germ oil and black seed oil.

CHAPTER FOUR: CONCLUSION

Although there are many ways to produce fatty acid methyl esters,
transesterification was chosen because it is an efficient process that is achieved simply by
using a strong base and an alcohol. In order to yield a pure and concentrated amount of
hydrocarbon from the agricultural oils, it was necessary to remove any atmospheric
oxygen and carboxylic acid. The freeze-pump-thaw cycle ensured removal of any
oxygen while the pyrolysis lysed the fatty acid in order to create hydrocarbon chains.
Analysis by GC/MS provided a means of determining hydrocarbon chain length and
percent composition derived from each agricultural oil. This was necessary in order to
investigate the most useful hydrocarbon generated for fuel from wheat germ oil and black
seed oil. This study was unique in that although delayed coking had been previously
employed, this is the first study that incorporates such a high temperature of 675°C for
the pyrolysis of both wheat germ oil and black seed oil.

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