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Effect of Heating on Heat Capacity of Vegetable Oils Used for Biofuel Production

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Effect of Heating on Heat Capacity of Vegetable Oils Used for Biofuel Production

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
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Department of Chemical and Biomedical Engineering
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ABSTRACT

Biodiesel has become a major renewable fuel for diesel engines particularly from various waste sources. New biodiesel production technologies are emerging with data demands for efficient process design. This project highlights the data requirements, gaps in the thermo-physical property data, and consolidation of experimental and estimation methods for effective process development. Knowing the thermodynamic properties of a substance is important in order to know what process or procedures it has to go under. The aim of this project is to assess the potential of vegetable oils to serve as feedstock for biofuel production by determining their heat capacity (C_p). Such oils are common ingredients in daily cooking in every kitchen all over the world, as a result of which there is a lot of leftover oil that is thrown away. To understand the property and alterations of waste oils as a cheaper source for biofuel feedstock, this study has been carried out.

A methodology for measuring C_p values was followed with the use of a calorimeter. The oils studied were: canola oil, corn oil and carinata oil. The experimental findings show that as each oil was heated repeatedly, its heat capacity changed and was found to be increasing. The heat capacities of canola, corn and carinata oils increased by 5.01%, 4.08% and 4.46% respectively for five times heated oils compared to virgin oils. This increase is due to compositional changes in the oils on subjecting to heating treatments. The GC-MS analysis show that the PuFAs decrease with every heating cycle while the SFA and one MFA increase. The total amount of PuFA decrease is equivalent to the total amount of SFA and MFA increase, which confirm that there is a conservation of mass and PuFA undergoes saturation on heating.

CHAPTER 1: INTRODUCTION

Limited sources of fuels and increasing pollution have called for alternative sources to be developed, and biodiesel is a promising alternative. Biodiesel is produced from various kinds of vegetable oils including soybean oil, sunflower oil, rapeseed oil, etc. and even animal fats or grease. Many countries are trying to turn to manufacturing and using biodiesel. One major highlight of using biodiesel is it does not require any modification to existing diesel based or other fuel engines. Biodiesel can be used on any existing motors and can be expected to work as efficiently as the existing motor oils. In fact, biodiesel is expected to create more balance in the environment in terms of gas emissions as a result of burning regular diesel and fuel. In addition to this benefit, biodiesel can also be stored and pumped just like any other fuel [66].

Commercial grade biodiesel production in the U.S has been going on for since early 2000 and the growth of the production and utilization has increased remarkably. While the annual production was about 25 million gallons in early 2000, it reached an annual production of 2.8 billion gallons in 2016. As biodiesel production increases, it is relieving the nation of its dependence on another countries for fuel sources. There are reported to be about 200 biodiesel plants across the country with a capacity of about 3 billion gallons of fuel per year [16]. Another aspect of biodiesel is that its steady and consistent production is creating a new branch of jobs, not only in the U.S but also across the world.

As per the data of the U.S. Energy Information Administration, annual production of biodiesel up till February 2018 was 126 million gallons, which is 2 million gallons more than that was produced in January 2018. Figure 1-1 shows the evolution of biodiesel production since 2016.

Sales of biodiesel, on the other hand were 48 million gallons of 100% biodiesel, whereas another 70 million gallons were sold as a blend with another diesel fuel. For the feedstock production and usage, a total of 953 million pounds of feedstock was used to produce biodiesel. Out of those 953 million pounds, Soybean oil continued to be the favorite choice of feedstock with a total usage of 496 million pounds alone [15].

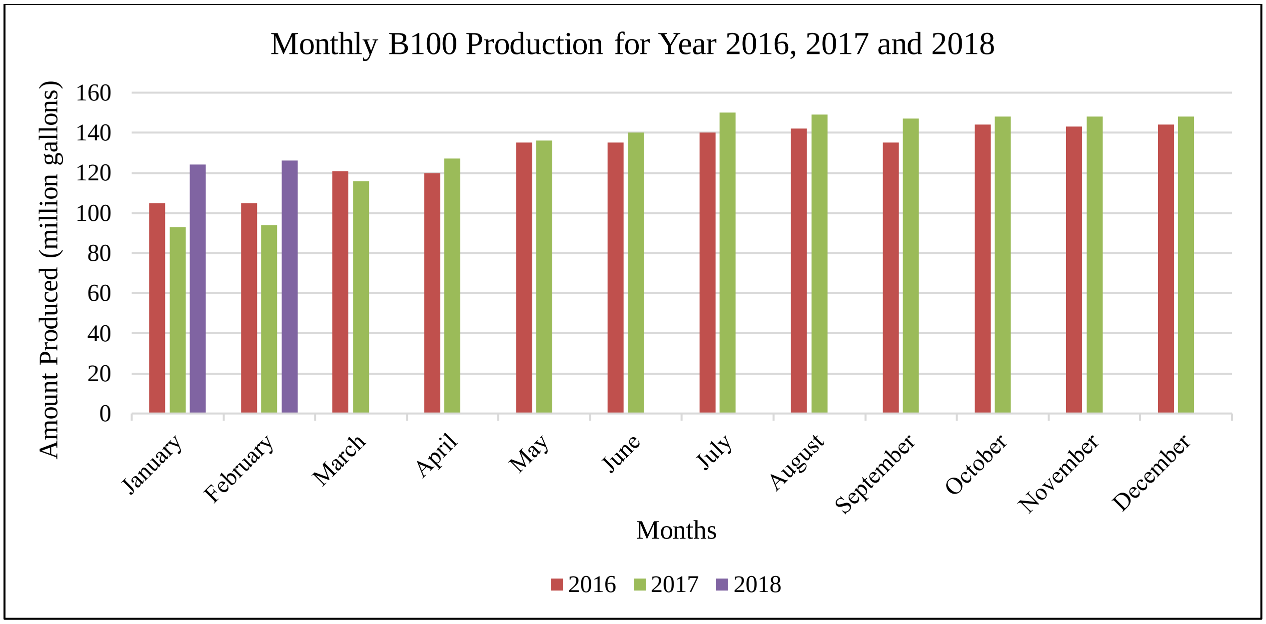


Figure 1-1 Comparison of monthly biodiesel production for the years 2016, 2017 and 2018 (from[15]; permission to use this figure is in Appendix D)

This project is related to heat capacity of feedstock which is both, easily available and the cheapest option: the cooking oils after kitchen use. We have chosen three non-soybean oils to study for this project. As per a report from U.S Energy Information Administration [14], in 2016 soybean oil was used as a feedstock for about 55% of the biodiesel produced that year in the U.S. Further, canola oil and corn oil consisted of 22% of all oils being used; usage includes other feedstocks like grease, animal fats etc. Since soybean oil is the current widely used feedstock, this project was targeted on other oils that can be used as raw materials. Heat capacity of fluids is one important parameter that needs to be taken into consideration in order to study a reaction to determine the overall heat of a substance or a reaction and to set up a plant [18]. This study has been carried out to determine the heat capacity of three oils namely, canola oil, corn oil and carinata oil in its commercially available form. Carinata oil is a member of the *brasiccaceae* [24, 25] plant group and is closely related to brassica canola and brassica camelina. These are grown as oilseed crops, but the higher content of undesirable erucic acid makes it less preferable for general cultivation as this oil does not find market for regular usage. Lately, carinata oil has found a huge market as a raw material in production of jet biofuels and hence is being grown exclusively over large fields. Canola oil and corn oil are also used widely in households and restaurants for cooking. Canola is a variant of the rapeseed plant without rapeseed's undesired traits and qualities, corn oil is made from corn bits and kernels [22]. As they have pleasant tastes, both canola and corn oils are used widely for culinary purposes [23] as a result of which the left-over oil is thrown away and wasted. The process of heating and using the oils for frying make alterations in their physical structures and properties. This study examines the heat capacities of waste oil from household kitchens to find how the heat capacity changes with usage.

This project focuses on biodiesel feedstock and starts with discussing general but important information regarding biodiesel. How biodiesel production is evolving over the years, the application and properties of this fuel, and various methods used to produce it are discussed in the next chapter. Chapter three discusses the feedstock under consideration, that is the vegetable oils and their fatty acid compositions, giving an insight on how composition vary for different oils despite the same fatty acids comprising them. The main focus of this project is to determine the property of the oils under consideration, and also to calculate the same using methods other than experimental values to assess how different are the values generated by different ways. Following, the next chapter, chapter four goes over the significance of calorimetry, importance to study heat energy for a substance or material *per se*, keeping process development in mind and physical property estimation methods. This section also gives some details about the equipment that is widely used to measure heat capacity. Following chapters go more into the experimental work of this project; chapter five shows results developed by two different estimation methods in order to verify and analyze the results achieved by the experiment, while chapters six and seven go into the details of the calorimetry and composition analysis. Towards the end, chapter eight reveals experimental results and discusses the results compared with the estimation model-based values. This project closes by theorizing the recommendations for future work.

CHAPTER 2: BIODIESEL

Biodiesel, as the name suggests, is the biodegradable and green alternative to petroleum diesel. The fuel is not a vegetable oil that can be used directly; the oils or animal fats are processed with small chain alcohols to make alkyl esters, which are in turn used as a fuel. Apart from the fact that biodiesel is an ecologically sound alternative fuel, another benefit of manufacturing more biodiesel is that it also gives an economic growth to farmers, who can then grow more oilseed crops and breed animals. As mentioned earlier, annual biodiesel production has increased considerably over the past decade [16], not only in the United States but many other countries. This chapter will give a small background of biodiesel followed by listing some properties of this biofuel and discussing different methods and conditions used to produce it.

2.1 Background

Biodiesel produced from vegetable oils or animal fats can be used in many types of engines. Considered to be a green fuel, biodiesel can be used for any regular diesel-based engine vehicles without any changes or modifications to the engine. Apart from vehicular fuel, biodiesel as a motor fuel can be used in various other applications such as, a heating oil in boilers or as a generator fuel [1, 66]. Biodiesel produced from certain oils is also good options for jet or aircraft fuels.

A major reason why biodiesel is being touted as the fuel of the era is because it is a green fuel as it produces very low to negligible harmful emissions and residue. What contributes to this nature of biodiesel are the raw materials that are used to produce it. Biodiesel is produced from some of the most natural materials such as vegetable oils, seed crop oils, animal fats and microalgae[1]. In some cases, grease is also used as a feedstock for biodiesel. Vegetable oils such as corn oil, or seed crop oils like soybean, sunflower, safflower, hazelnut, palm, olive, groundnut, rapeseed oils, are already being used as a feedstock. Animal fats, such as beef tallow, pork and chicken fat can also be used after they have been rendered to remove unwanted fats and solids. Grease is rarely used. There are two kinds of greases- ‘yellow grease’ which is used, wasted or recycled cooking/vegetable oil that is recovered from households, restaurants or any other kitchen and ‘brown grease’ is the oily-greasy materials that are trapped in kitchen drains before entering the sewer.

Figure 2-1 shows an overview of how University of South Florida is trying to make the process more environmentally efficient by reusing waste oils and alcohols as raw materials for biodiesel. This figure is adapted from the ‘Renew a Bull biodiesel project’, a project [19] funded by the Student Green Energy Funds at the USF.

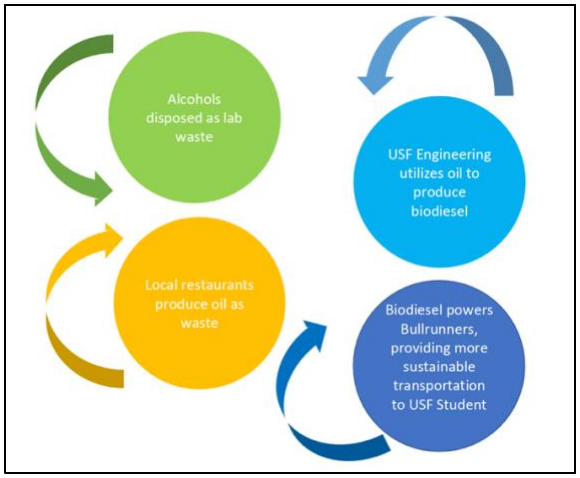


Figure 2-1 Recycled raw material integration (Adapted from [19])

2.2 Properties

Biodiesel is different from regular petroleum diesel in terms of its composition both physically and chemically; resulting in difference of properties between the two kinds of diesel. Some of the properties include that [7]: Biodiesel has a comparatively lesser viscosity which increases the lubricity; this means biodiesel slips and moves more readily compared to regular petroleum diesel. Lubricity is a positive aspect for biodiesel as it reduces the engine wear. As mentioned earlier, biodiesel is popularly known as a green energy fuel, meaning it causes significantly less or no pollution. Biodiesel has no sulfur content thus it does not further contribute to sulfur emissions in the atmosphere. Another positive point in terms of biodiesel's role in reducing emission is its higher content of oxygen as compared to petroleum diesel. Although higher oxygen content results in reducing peak engine power by 4%; this is not a huge number, so it can be considered in the acceptable range for daily use vehicles due to its environmental benefits. Biodiesel is also biodegradable due to the fact that is produced using oils and fats. Due to these positive aspects, biodiesel has lower toxicity level compared to petroleum diesel.

A few properties which are concerning and need more thoughtful attention are that [2]: Biodiesel is more prone to oxidation when left unattended or unused for a longer period of time. Biodiesel reacts with the oxygen from the air to form a semi-solid mass. When using biodiesel for engines or vehicles that are used less frequently, fuel should be stored in dry, tightly covered and semi cold container. Biodiesel is also more prone to thicken up at lower temperatures, making it a difficult or less preferred fuel of choice at extremely cold places or during colder climatic conditions. Chemically, biodiesel is more active as a solvent compared to petroleum diesel; it can more readily react with most of the materials used to store or carry it, contrasting with the relative safety of storing or carrying petroleum diesel.

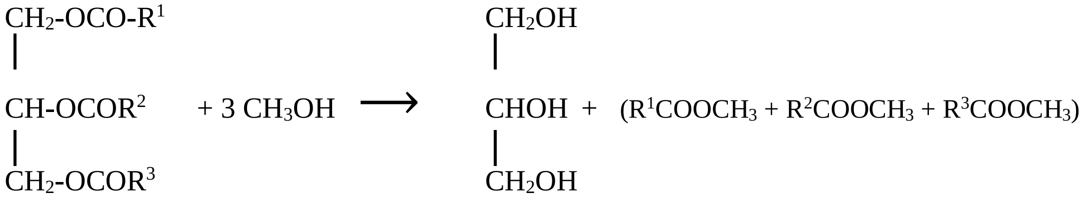
Even though these shortcomings exist, they are not major concerns since biodiesel as a 100% pure fuel source is used in very few cases. Mostly, a blend of biodiesel with petroleum diesel in ratios of 2%, 5% and 20% are used. These blends are termed B2, B5 and B20 respectively [14]. All the major concerns regarding storing, handling and using biodiesel are more likely to be resolved when used as a blend with petroleum diesel.

2.3 Methods to Produce Biodiesel

The biodiesel process requires triglycerides, alcohols and a catalyst and its favorable working conditions. Without the use of a catalyst, the process is noted to be extremely slow, with the eventual exhaustion of esters. Therefore, the process conditions are carried out in different ways leading to different methods of production. The types of catalysts, conditions under which a raw material is used, and the quality of the raw material make a difference in the categorizing of various production methods. Based on the condition and quality of raw materials, fats or oils are converted to biodiesel using various methods such as transesterification, thermal cracking and micro emulsions.

2.3.1 Transesterification

Transesterification is a widely used and economical method to make biodiesel from fats. Biodiesel is made from vegetable oils, animals fats, tallow and waste oil. In this process, the triglycerides (long chain esters, derived from free fatty acids and glycerol) react with small chain alcohols (mainly Methanol or Ethanol) to form methyl esters or ethyl esters, which are nothing but biodiesel. This reaction in itself is fairly slow or non-occurring. To make transesterification more efficient and faster, a catalyst is used. Transesterification is further classified in 3 different ways based on the catalyst used; two types are particularly, acidic medium and basic medium [5, 7] and the third is enzymatic catalysis. A general transesterification reaction for biodiesel production is as follows-



$$\begin{array}{l} CH_2\text{-}OCO\text{-}R^1 \\ | \\ CH\text{-}OCOR^2 \\ | \\ CH_2\text{-}OCOR^3 \end{array} \quad + 3\,CH_3OH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \quad (R^1COOCH_3 + R^2COOCH_3 + R^3COOCH_3)$$

Triglyceride *Methanol* *Glycerol* *Fatty Acid Methyl esters*

The *Acid Catalysed Transesterfication* method makes use of various acids such as HCl, H_3PO_4, BF_3, H_2SO_4 and sulfonic acid. Out of this list of acids, sulfuric acid and sulfonic acid are used more often since they require less reaction time. The yield by this method is almost 99%, but the reaction is slow compared to base catalyzed transesterification. The temperature requirement for this reaction is about 100 ^oC or higher, and reaction time can be anywhere between 3 hours to 48 hours. A Pryde et al. (1986) study found that the reaction between soybean oil and methanol takes about 50 hours [6] and a reaction temperature of about 65 ^oC to reach 99% oil conversion. The molar ratio of alcohol to oil required for this method ranges between 6:1 to 30:1 [6].

The *Base Catalyzed Transesterification* [1] is a more favorable method to make biodiesel because it is faster than acid catalyzed transesterification. Commonly used catalysts under this method are NaOH, KOH and Sodium Methoxide. The alkaline metal alkoxides are more active compared to metal hydroxides. Using a metal alkoxide can carry out this reaction in a shorter time period of about 30 minutes to 1 hour at maximum, with a conversion of 98% [7]. In addition to this benefit, the temperature requirement for this method is not too high, and most of the reactions can be carried out at 40^o - 60 ^oC. Another reason to prefer base catalyzed method over acid catalyzed transesterification is because bases are less corrosive than acids. For this method, the required molar ratio of the alcohol (usually methanol) to oil is in the range of 6:1- 18:1 [6].

2.3.2 Supercritical Process

In addition to acid or base catalyzed transesterification reaction methods, further progress was made to carry out this reaction in a more efficient manner and at a faster rate called supercritical transesterification. Compared to other transesterification methods, the reaction conditions for this particular method are higher than the two methods previously discussed. The temperature required to carry out this reaction is about 300^o - 340 ^oC and a pressure of about 1200 psi [6], while the other transesterification reactions are carried out at atmospheric pressures. This method is used because the reaction time to make biodiesel is less (10-15 minutes) with a conversion of above 90%. For this reaction to take place, methanol should be in a supercritical state and the molar ratio requirement should be about 42:1 for methanol to oil [6].

2.3.3 Thermal Cracking

Thermal cracking or pyrolysis is carried out at higher temperatures to break down the longer chain hydrocarbon biomasses in the absence of air. This reaction is carried out in a batch or continuous process. As it is a very long and time-consuming process, some catalysts, like zeolites, are used to make the process relatively faster. [66] The decomposition of biomass starts at around 350 ^{o}C and can go up to 800 ^{o}C. Further, depending on the biomass and gas residence time, range of temperature required, heating rates and reaction time, pyrolysis is categorized as conventional pyrolysis, fast pyrolysis and flash pyrolysis. Some drawbacks of this method are poor thermal stability and water content in the final product achieved. Other drawbacks include solids and char present in the finished biodiesel and the resulting biodiesel being corrosive in nature.

2.3.4 Micro Emulsions

Micro emulsion is defined as colloidal equilibrium dispersion of immiscible fluids with particle dimensions in the range of 1-150 nm. These two fluids can be used as two surfactants or a surfactant and a co-surfactant that are isotropic liquid mixtures. Biodiesel microemulsions may include diesel fuel, vegetable oils, alcohol and a surfactant along with a cetane improver [9]. Methanol and ethanol are the two alcohols of choice in any method to form biodiesel along with vegetable oil as they help improve viscosity by lowering the thickness. In addition, higher alcohols are used in microemulsions as surfactants while alkyl nitrates are used as cetane correctors. A downside of using this method to make biodiesel is that on continuous use of biodiesel, that is made by this method, may lead to injector needle sticking, carbon deposit formation and incomplete combustion [7]. Despite the negatives, some positive aspects to the biodiesel formed using this method is less viscosity and a better cetane number.

CHAPTER 3: VEGETABLE OIL AS FEEDSTOCK

There have been some misconceptions and misunderstandings that vegetable oils can directly be used as car fuel. While this is not true, vegetable oils are still used but as raw materials in the process to make biodiesel. Oils are made up of triglycerides and some typical triglyceride chains identified in the oils that are used for this project are shown in figure 3-1. These triglycerides are glycol esters of various long chain fatty acids composing the oils. The glycerides, when reacted with alcohols in presence of a catalyst or under other favorable conditions, produce methyl esters and glycol; the methyl ester thus produced is biodiesel.

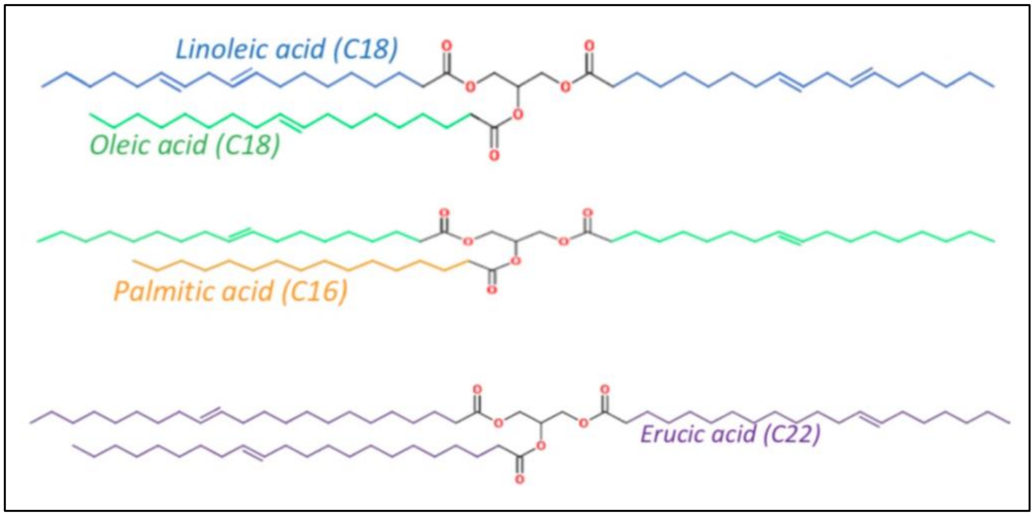


Figure 3-1 Typical triglyceride molecules of fatty acids on glycerol backbone

Even though all the oils consist of same ranges of fatty acids what makes them different is the proportion in which the fatty acids are contained. All the seed crop and vegetable oils are made up of five major fatty acids, namely stearic acid, palmitic acid, oleic acid, linoleic acid and alpha-linolenic acid. A few other fatty acids such as myristic, palmitoleic and arachidic acids may be present in traces. The fatty acids that comprise vegetable oils have a carbon chain of no longer than C18 while some oils such as carinata oil contains much heavier fatty acid with carbon chain C22, making the oil unfit for eating purpose. This oil and some other such oils with much heavier fatty acids have been identified to make biodiesel that is extensively used as a jet fuel. This chapter will give a composition indication of the oils used in this project.

3.1 Oil Composition

As explained earlier in this work, more or less any vegetable oil or seed crop oil is a potential feedstock for biodiesel. Each oil is composed of the same fatty acids yet are different than each other and what makes them different is the weight percentage composition of the comprising fatty acids. Each oil has triglyceride molecules that are three long chains of fatty acids attached to glycerol [67]. Furthermore, the lengths and bonds within the fatty acids are also different for different oils, making it another reason to draw a distinction between the oils. Fatty acids are long hydrocarbon chains and the number of carbons and double bonds vary amongst various oils. Therefore, based on the intermolecular bonds of fatty acids, they are categorized as: Saturated Fatty Acids (SFA), Monounsaturated Fatty Acids (MFA) and Polyunsaturated Fatty Acids (PuFA).

Saturated Fatty Acids (SFA) as the name suggests are long chain single bond hydrocarbons ending with a carboxylic acid group. The fatty acids that fall under this category and those commonly present in vegetable oils are stearic acid and palmitic acid. Other SFAs that may be present in few other oils are myristic acid, margaric acid, arachidic, palmitoleic acid, behenic acid and lignoceric acid. As the name goes, since there is no unsaturated or unstable double bond present, these fatty acids are less susceptible and comparatively not as easy for alternations under any process.

Monounsaturated Fatty Acids (MFA) are long chain carboxylic acids with one double bond in its chain. A fatty acid that comes under this category which is mainly present in oils is oleic acid. Apart from this, other MFAs are gondoic acid, nervonic acid and erucic acid to name a few. These fatty acids have one double bond in the chain making it relatively less stable as compared to SFAs.

Polyunsaturated Fatty Acids (PuFA) are the last category that have more than one double bond in the chain. These fatty acid chains have at least two double bonds and are the most vulnerable to any physical or chemical structural changes under any process. The most common PuFAs present in vegetable oils are linoleic acid and alpha-linolenic acid. Some more to add to the list of this category are eicosadienoic acid and docoadienoic acid.

3.2 Oils Used

The vegetable oils used for the experimental purpose in this research study were canola oil, corn oil and carinata oil. The canola and corn oils were purchased from a local grocery store while the carinata oil was supplied by Applied Research Associates (ARA) from their ongoing project. Out of these three, canola and corn oil are edible oils while carinata oil is harmful to be digested due to higher percentage of erucic acid, making carinata oil inedible.

Canola oil is a derivative of the rapeseed oil that has been eliminated of its unwanted traits. The unwanted trait of rapeseed crop is the presence of erucic acid in higher percentage which is harmful for human health if ingested. The origin of canola oil or the rapeseed oil happens from the family of seed crop called as Brassicaceae [21]. Oil makes up about 44% of the canola seeds [21] which makes it a popular crop to extract oil and being one of the oldest crops to be cultivated and used in day to day life, canola oil has a good market in food industry. Despite soybean oil is the favorite feedstock for biodiesel production in the United States of America, Europe is known to have invested highly in developing fields and improving infrastructure and other desired facilities to grow and use canola oil as a choice of raw material for biodiesel.

Corn oil is extracted from the maize bits and kernels which fall under the plant family termed as Gramineae [22] and is also one of the oldest cultivated plants in various parts of the world, as corn is known to be a staple food in some countries. Being comparatively less expensive than other vegetable oils, corn oil is also likely to be used widely all around the world for cooking purposes. As extracting oil for cooking is not the only use of corn or maize, as it is already in use as a feedstock for another type of bio fuel called ethanol fuel [22]. This makes corn oil as another potential feedstock option for producing biodiesel.

Carinata oil is yet another member of the plant family Brassicaceae just as the canola oil. Oilseeds in this plant family are identified to have higher content of erucic acid. Even though the presence of erucic acid was previously a reason for lesser cultivation of carinata making it unfit as a daily use oil, it is discovered that this oil is immensely useful in making bio jet fuel. Hence this oilseed crop has given farmers yet another opportunity of growing it in large quantities without hampering other crop cultivation [24]. Its resistance to drought, insects and diseases and its nature of being a high yielding seed crop, opened a whole new market for carinata oil in the biofuel industry.

Mentioned below in the Tables 3-1 and 3-2 are the literature [35] and container based [9] fatty acid weight percent composition for canola oil and corn oil respectively. The fatty acid composition content on the containers bought was not a cent percent match with the composition available in literature. The composition for carinata oil provided by the ARA is given in the Table 3-3.

Table 3-1 Canola oil composition

	Fatty acid	Literature composition	Container composition
SFA	Palmitic acid	4	4.76
	Stearic acid	2	2.38
MFA	Oleic acid	61	57.14
PuFA	Linoleic acid	22	19.64
	Alpha-Linolenic acid	10	8.93

Table 3-2 Corn oil composition

	Fatty acid	Literature composition	Container composition
SFA	Palmitic acid	11	12.08
	Stearic acid	2	2.20
MFA	Oleic acid	28	28.57
PuFA	Linoleic acid	58	56.17
	Alpha-Linolenic acid	1	0.97

Table 3-3 Carinata oil composition

	Fatty acid	ARA provided composition
SFA	Myristic acid	
	Palmitic acid	3.9
	Stearic acid	
	Margaric acid	
	Arachidic acid	
	Behenic acid	
	Lignoceric acid	
MFA	Oleic acid	
	Hexadecenoic acid	
	Gondoic acid	9.3
	Erucic acid	42.1
	Nervonic acid	2.4
PuFA	Linoleic acid	30.8
	Alpha-linolenic acid	
	Eicosadienoic acid	
	Docosadienoic acid	

CHAPTER 4: CALORIMETRY

Heat capacity of a material represents the heat energy (in joules) it can absorb or release. In a process design and scale-up, heat capacity is an essential parameter that is taken into consideration for process development, as heat capacity helps to determine any kind of heat involved in a reaction. In other words, heats of reaction, formation, absorption, mixing, etc. in turn can be used to design process reactors, other equipments and to determine of the operating conditions for a process. Thus, studying the heat capacities of vegetable oils can be used to determine the heats of the reaction of biodiesel production which can in turn be correlated to other parameters to develop a process. This chapter targets on the significance of calorimetry, calorimeters and modular estimation methods of heat capacity. The chapter additionally discusses a pre-published experiment that demonstrates how temperature rises in oil as compared to water, giving an understanding of the nature of an oil.

4.1 Significance of Calorimetry

Any chemical or physical changes causes some heat interactions and changes in a system. To determine such heat changes, a technique called calorimetry is used to quantify the heat flow, to or from the system under consideration. The study of calorimetry is done on a device called calorimeter. The principle behind a calorimeter is that the heat energy absorbed or released by a substance is the measurement of the change of temperature of the substance. On the other hand, heat flow in or out of a body also depends on the mass of the body. Hence, to equate the heat flow with mass and temperature change, a thermodynamic property of specific heat is used. In other words, calorimetry allows to measure the enthalpy and specific heat by studying the heat flow and temperature change for a given mass of a substance. A calorimeter consists of jacketed heating chambers and temperature controllers that are set to ambient temperature by default. The jackets, or the walls of the chambers, get heated up to the set temperature and in turn heat the samples under consideration by conduction. The temperature and heat flow controllers allow the temperature to reach a set value and then attain a thermal equilibrium for the heat flow between the jacket walls and sample. The heat required to increase the temperature is thus measured.

The enthalpy and heat capacity are important properties for any material as they allow for determination of various thermodynamic and kinetic parameters for a material or a reaction. Enthalpy is a variable that is used to describe various heat interactions of a system. For a thermodynamic system, enthalpy is given as: $H= U + PV$ where, U is the internal energy, P is the pressure and V is the volume of the system. Thermodynamically, heat capacity is the change in enthalpy with change in temperature at a constant pressure. The change in enthalpy is expressed as: $dH = dU + d(PV)$. From the equation above, dU indicates the change in internal energy which is caused either by adding heat, Q, to a system or when work, W, is done by the system. Hence, change in internal energy is written as: $dU = \delta Q + \delta W$. In other words, work done is expressed as change of volume of the system by maintaining constant pressure. Hence δW is written as $-PdV$ where negative indicates the work done by the system. Thus, by using these notations, [64] equation for change in enthalpy can be written as:

$$dH = dU + d(PV),$$

$$dH= \delta Q + \delta W + d(PV),$$

$$dH = \delta Q – PdV + PdV + VdP,$$

$$dH = \delta Q + VdP$$

This equation gives the change in enthalpy at constant pressure and is denoted as C_p. Therefore,

$(\partial H/ \partial T)_P = (\partial Q/ \partial T)_P = C_p$.

Further, enthalpy also allows for determination of the kinetics of a reaction. For example, the enthalpy is related to the equilibrium constant by the Van't Hoff equation: $d(\ln K_{eq})/dT = \Delta H/RT^2$.The equilibrium constant signifies the ratio of the equilibrium concentrations of the products to that of the reactants. Enthalpy is also related to the enthalpy of reaction, which allows to determine the extent of reaction, expressed as [64] $\Delta H_R = (\partial H/\partial \xi)_{P, T}$ where, H_R is the enthalpy or heat of reaction and ξ is the extent of reaction.

The definition of heat capacity is the amount of heat needed by a substance to increase its temperature by one-degree Celsius or Kelvin while specific heat is the amount of heat measured to raise the temperature of one-unit mass of a substance by one degree Celsius or Kelvin temperature. Therefore, specific heat is nothing but an intensive property where the heat capacity of a substance is mass based. Heat capacity determination, in a general sense, is a thermal analysis of a substance which relates to studying physical and chemical properties of a substance as function of temperature. Heat capacity (or specific heat) is a function of heat and temperature. If Q is quantity of heat released or absorbed (in joules), that is the heat present in a substance, is given by a formula $Q= m*C* \Delta T$ where m is mass in grams, C is specific heat in J/g K and ΔT is the change in temperature measured in Kelvin. This project uses a rearranged form of this formula to find heat capacity.

4.2 Equipments Used to Determine Heat Capacity

Since studying and gathering such data can be critical, the devices and instruments used for the purpose are sensitive to any changes in the atmosphere, system settings etc. Hence it is essential that all the trivial details are given importance and taken care of.

A calorimeter is the equipment that is used to measure heat capacity or rather heat flow in or out of a system and other heat related changes for a single substance, mix of substances or a reaction. The heat data obtained from the calorimeter, is used to calculate the heat capacity from a rearranged formula of heat energy. Based on what functions can be carried out and how they are operated, there are many kinds of calorimeters available. The ideal ones that are used for laboratory purpose of are more reliable, controllable, efficient and sensitive to data and sample, than the basic ones.

Differential Scanning Calorimeter (DSC), [8] is a thermal analysis method mostly used in bioscience studies. The calorimeter plots the specific heat vs temperature and curve generated that depicts the enthalpy change of a substance. This equipment is widely used to study the stability of proteins by determining their melting temperature, heat of melting and various such parameters. A DSC is widely used for various heat determination studies and is preferred for research work due to its speed, wide availability, efficiency and sensibility for even a small quantity of sample measured in milligrams. The limitation to using DSC is that, the instrument is fast to give results which means it is very dyanamic and hence it is imperative to keep collecting the data constantly and vigorously without a lag. The sample under study is heated either by a temperature ramp of small size or can be heated upto a desired higher temperature directly without breaking down into smaller ramps. It is followed by analyzing the change of heat over the course of temperature increment for the sample. The ramped up temperature rises linearly as a function of time. Furthermore, a definitive contact of the sample with the bottom or the base of the crucible or pan that is used to place the sample is a critical restricting factor as it makes it difficult to work with solids that have irregular shapes and sizes. In addition, failing to achieve a complete physical contact of the sample in crucible or pan may lead to poor thermal contact of the instrument with the sample. This loss of thermal contact of the sample results in inconsistent and unreliable data generated. As mentioned earlier, DSC is very sensitive to any changes within or outside the system and therefore the set-up cannot be disturbed while it is being operated.

The basic principle of an *isothermal calorimeter* and its mechanism are very similar to that of a DSC. In an isothermal reaction calorimeter, two vertical glass vials are used as opposed to a crucible or a pan, one as a reference and another one as a sample vial. Similar to a DSC, the heat flow in or out of the system is studied as a function of temperature since the temperature is ramped linearly over a period of time. A primary operational difference in an isothermal calorimeter is that it requires a significantly measurable amount of sample to generate reliable results. Another difference in this type of calorimeter compared to DSC is that it is more time consuming. In case of an isothermal calorimeter, it takes about an hour for the calorimeter to set itself to room temperature thermal stability at start, and to run a complete ramp cycle. For DSC, this entire cycle requires only a few minutes. Additionally, it is important that an isothermal calorimeter is maintained at consistent and undisturbed working conditions and surroundings since it is sensitive to any interference within the system or in the surrounding, including the quality and quantity of the sample.

The calorimeter used for the study of this project is the isothermal mixing and reaction calorimeter. The apparatus set-up requires two cylindrical vials, which can efficiently carry any irregularly shaped solid and liquid to a maximum volume of 15 mL. The requirements for an effective operation explained above holds true for this calorimeter as well. For operating this calorimeter, we can set up the parameters such as ramp rate, initial temperature and final temperature for the ramp and isothermal delay (isothermal hold) before starting a ramp in minutes. The only limitation for this instrument is that it is very time consuming. On the positive side, it is very stable and hence has lesser chance of error in displaying the values. Also, since the thermal or physical contact of the sample with the vial bottom or surface is not a problem in this case, there are least chances of anomalies in the data generated. A detailed procedure to use this calorimeter is discussed in Chapter 6.

4.3 Heat Capacity Estimation

The physical properties of every substance are dependent on the nature of molecules the substance is made up of. The reasoning behind the dependence of physical properties of a substance on molecules and their structure requires a complete understanding of molecular behavior [26]. Even though this molecular behavior is not entirely understood and available, a lot has been researched and developed in this aspect since the beginning of the nineteenth century. In the book ‘The properties of gases and liquids’ by Poling *et al*, the authors explain that one of the earliest and important correlations of properties developed was the gas law which is expressed as PV=nRT. Later, the deviations from this ideal gas law equation lead to van der waals equation, virial equation and so on for real gases, where constant terms in the modified equations were introduced. The introduction of these constant terms are some examples of inter-relating physical properties with molecular behavior to improve and modify a general equation. Gradually many physical, thermodynamic and transport properties were correlated using various equations which were quantitatively related to the molecular properties. In general, estimation of any property can either be done on the basis of theory or on the basis of some experimental correlations [28, 39], but the best results have been found when both the theory and empirical correlations are combined. For example, gas law states PV=NRT, but the modified form of this equation is given by van der waals equation of state which is expressed as $(P + a/V^2)(V-b) = RT$. Here the empirical correlation constants a and b help to bridge the gap between ideal and real gases that the incomplete theory fails to analyze. As explained by *Poling, Prausnitz and O’Connell,* an ideal approach to estimate a physical property provides reliable physical and thermodynamic data, designates the physical state of substance, requires minimum input details and takes the route with minimum errors [26]. Keeping these requirements in mind, some methods of physical property estimations used are detailed below.

Law of corresponding states [26, 36] generalizes that the properties which are dependent on intermolecular forces are also related to critical properties in the same way for all compounds. This means, relation of pressure to volume at constant temperature may vary for different substances, but when the pressure, volume and temperature are related to the corresponding critical properties to obtain resulting reduced pressure, volume and temperature; the interrelation between the reduced properties thus obtained are same for each substance. In other words, the functions inter-relating the reduced properties (expressed as fractions of critical properties) are same for each substance. The application of this method can be understood better in section 5.1 where the heat capacity is calculated as a function of reduced temperature.

Structure and bonding, this method of a thermophysical property estimation considers that all the properties are related to the molecular structure and gives major importance to intermolecular forces, atoms, atomic groups and bond type. Therefore, it suggests that magnitude of the intermolecular forces can be used to determine macroscopic properties from group contribution [36]. For example, knowing the storage capacity of a molecule and its energy is a good way to determine the heat capacity. A property that intimately uses the structural correlations is that of the ideal-gas heat capacities C_p^o that relates a polynomial equation of C_p^o as a function of temperature and constants in a polynomial equation. The constants involved in this equation are determined by atoms, atomic groups and types of bonds. The definite values or empirically weighed factors that are assigned to molecular groups are fixed in an algebraic function to calculate the desired polynomial constants. This method developed and modified by Rowlison-Bondi to determine heat capacities of oils is explained and used ahead in chapter 5.

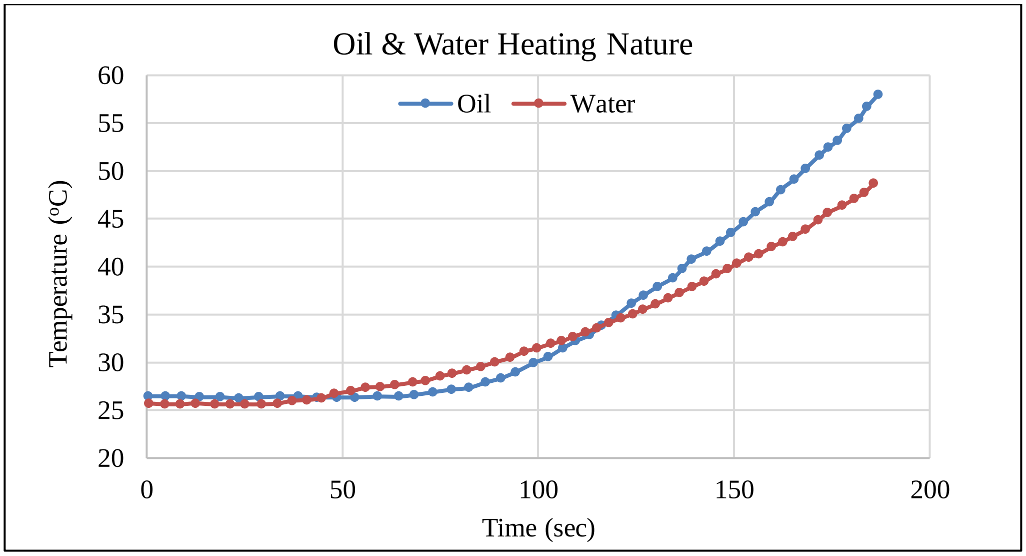


Figure 4-1 Study of nature of oil in respect to temperature vs time [13]

A literature experiment [13], compares the nature of oil to that of water by studying the change of temperature as a function of time. It states that "heat capacity of a substance is the willingness to change its temperature." From the results, it was found that temperature change for oil as compared to water over the course of the experiment was more pronounced, which meant that the heat necessary to change the temperature of oil is lower as compared to water. Thus, the heat capacity of an oil is less than that of the water. Figure 4-1 depicts the results for the experiment. An additional observation was made in the experiment with respect to inconsistency of rising oil temperature in contrast with water. Initially, the temperature rise for water is more than oil and then keeps increasing at a constant rate while the oil heats up more after a certain point. The conclusion to this was drawn by relating it to the physical parameter of viscosity; water being less viscous heats up quickly initially while the oil heats up gradually at first to become less viscous and it catches up with the temperature rise of water and crosses over to reach higher values.

CHAPTER 5: MODEL BASED HEAT CAPACITY ESTIMATION

The ways of estimating physical properties is discussed previously in chapter four. One method described was structure. For determining heat capacity by group contribution, Poling *et al* made an assumption that various groups in a molecular compound contribute a significant and a definite value to the total molecular heat capacity [26]. This assumption also means that the contribution of one particular group is definite and independent of the other contributing groups in a molecule. The liquid heat capacity estimation methods are categorized as theoretical, group contribution method, corresponding state and Watson's thermodynamic cycle [36]. The theoretical method of estimation is done by considering each mode of energy storage at constant volume. This method is considered as less reliable as compared to other estimation methods. Watson's thermodynamic cycle method of liquid heat capacity estimation functions for four listed thermodynamic conditions: 1) when a saturated liquid is heated by maintaining saturation conditions, 2) a liquid at higher temperature is vaporized and expanded in isothermal condition to a low pressure ideal gas, 3) the material is cooled from higher temperature to lower as an ideal gas and 4) when a fluid is compressed in isothermal condition to a saturated vapor and condensed [36]. This method is noted to be difficult to implement, especially with liquids like oils due to their relatively higher boiling point and higher viscosity. This method has also been tested to give inconsistent and irregular results [36]. The method of group contribution takes into account all the atomic groups and tabulates a definite value that a corresponding group is accounted to contribute to the total heat capacity of a compound molecule, for example, $-CH_3$, $-CH_2-$, $=CH_2$, -OH, $-ONO_2$ and -Cl to list a few. These values are used in a specified expression and added together based on how many different groups are present and number of groups present of the same type in a compound. Thus, using a group contribution method on the basis of the structure of an oil molecule is a reliable approach to determine heat capacity.

For instance, Ruzicka and Domalski implement group contribution to calculate liquid heat capacity by using an expression:

C_p= R [A + B * (T/100) + C* $(T/100)^2$] ;

where, R is gas constant and T is temperature.

A, B and C are the constants. They are calculated as A= $\sum n_i a_i$; B = $\sum n_i b_i$; C= $\sum n_i c_i$; a, b and c are values listed in the table for group contribution parameters of Ruzicka and Domalski’s method [26], n_i is number of times a group repeats itself in a compound.

Although this method is the simplest way to calculate heat capacity of a compound based on its molecular structure, it is not as efficient as the method of corresponding states. The method of corresponding states relates the heat capacity of a liquid to the ideal heat capacity as a function of reduced temperature. As explained in the last chapter, it is assumed that the functions relating reduced properties are the same for all the substances.

Two different approaches, called the Rowlison-Bondi mathematical model (RB model) and the Peng Robinson equation of state (PREOS) method on Aspen tool, were used to calculate heat capacities of the oils numerically in order to verify and analyze the experimentally obtained values. Although both of these methods give a close enough estimation, it is observed that the values generated do not match-up exactly and have some deviation from the experimental values. The reason for this can be attributed to the fact that these models are constructed for ideal mixtures in ideal conditions. On the contrary, vegetable oils used in real life may vary depending on how much time and temperature they were used at. It also depends on the level of refining treatment used after being used in kitchen and before using it for biodiesel process.

5.1 Rowlison-Bondi Model

The Rowlison-Bondi method takes into consideration every individual group of a compound. The bond strength, molecular structure and hence the molecular behavior of different organic groups are different. The baseline postulation for the group contribution method of ideal heat capacity is the estimation that bonds in a particular group possesses characteristic frequencies of bending and stretching and hence these vibrations contribute to thermodynamic properties. Thus, the constants contributing to calculate the heat capacity vary as well for every atomic group. C_p^o is an ideal gas heat capacity that is calculated by Rihany and Doraiswamy's group contribution method for fatty acids. The designated values of a, b, c and d for every aliphatic, aromatic, oxygen containing, nitrogen containing and sulfur containing groups are tabulated by Rihany and Doraisamy [10], are used to calculate the overall ideal gas heat capacity constants a, b, c and d of fatty acids. The ideal gas heat capacity C_p^o, for each fatty acid is calculated by the equation:

$$C_p^o = a + bT + cT^2 + dT^3$$

The ideal heat capacities of fatty acids are then used to calculate liquid fatty acid heat capacity by the expression mentioned below. Here, the heat capacity is expressed as a function of reduced temperature and acentric factors and thus the law of corresponding states is applied [11].

$$(C_{p\ F.A} - C_p^o)/R = 1.45 + 0.45(1-T_r)^{-1} + 0.25\ \omega\ [17.11 + 25.2(1-T_r)^{1/3}T_r^{-1} + 1.742(1-T_r)^{-1}],$$

$$C_{p\ F.A} = \{1.45 + 0.45(1-T_r)^{-1} + 0.25\ \omega\ [17.11 + 25.2(1-T_r)^{1/3}T_r^{-1} + 1.742(1-T_r)^{-1}]\}*R + C_p^o$$

where, R is gas constant,

T_r is the reduced temperature,

ω is acentric factor, and

these individual fatty acid heat capacities thus calculated were further used to calculate the oil heat capacity based on the weight percent composition for an oil [11].

$$C_{p\ oil} = \sum X_{F.A}\, C_{p\ F.A};$$

where, $X_{F.A}$ is mass fraction of a fatty acid (from the oil composition) and $C_{p\ F.A}$ is the heat capacity for the fatty acid. Thus, this model incorporates the group contribution method along with the method of corresponding states. The heat capacities calculated by this method are listed in the Tables 5-1 to 5-3 below.

Table 5-1 RB model based heat capacities of canola, canola 2H and canola 5H oils

	Canola	Canola 2H	Canola 5H
Temp (^oC)	C_p (J/g ^oC)	C_p (J/g ^oC)	C_p (J/g ^oC)
30	2.2367	2.2492	2.2602
40	2.2624	2.2625	2.2895
50	2.3028	2.3096	2.3669
60	2.3417	2.3542	2.4039
70	2.3932	2.3903	2.4376
80	2.4214	2.4415	2.4647
90	2.4428	2.4993	2.5129
100	2.4974	2.5365	2.5789
110	2.5348	2.6083	2.6364
120	2.5914	2.6511	2.6993

Table 5-2 RB model based heat capacities of corn, corn 2H and corn 5H oils

	Corn	Corn 2H	Corn 5H
Temp (^oC)	C_p (J/g ^oC)	C_p (J/g ^oC)	C_p (J/g ^oC)
30	2.2448	2.2575	2.2939
40	2.2762	2.3224	2.3179
50	2.3071	2.3491	2.3508
60	2.3348	2.3778	2.4071
70	2.3765	2.4158	2.4357
80	2.4345	2.4728	2.5082
90	2.4914	2.5190	2.5609
100	2.5305	2.5730	2.6214
110	2.6094	2.6162	2.6849
120	2.6545	2.6801	2.7423

Table 5-3 RB model based heat capacities of carinata, carinata 2H and carinata 5H oils

	Carinata	Carinata 2H	Carinata 5H
Temp (°C)	C_p (J/g °C)	C_p (J/g °C)	C_p (J/g °C)
30	1.9869	1.9932	2.0207
40	2.0158	2.0854	2.0804
50	2.0339	2.1327	2.1270
60	2.1443	2.1845	2.2068
70	2.1895	2.2399	2.2804
80	2.2136	2.2985	2.3636
90	2.2639	2.3491	2.4162
100	2.3216	2.4041	2.4834
110	2.4007	2.4807	2.5446
120	2.4956	2.5463	2.6167

5.2 Peng-Robinson Method

For further verification, the heat capacities were also plotted using Aspen tool for the same temperature range. All the composing fatty acids were added to the component list and a property set for the heat capacity mix on mass basis was created. The PENG-ROB method, which is the Peng Robinson equation of state was selected as the base method. The PREOS method was chosen because it is most suitable for non-polar liquids and hydrocarbons [27].

The heat capacity, C_p of a fluid can be determined from the enthalpy of the fluid. Thermodynamically, the enthalpy of a real system is determined as change of the enthalpy with respect to the ideal or reference enthalpy since an absolute enthalpy of a system is insubstantial. Therefore, the enthalpy of real fluid is calculated as [65]-

$$H= (H- H^o) + (H^o – H^o_R) + H^o_R \qquad (i)$$

where, H is the real state enthalpy (kJ/mol),

H^o is the ideal gas enthalpy (kJ/mol),

H^o_R is the ideal gas enthalpy at reference state (kJ/mol).

$(H^o – H^o_R) = a (T - T_r) + (1/2)b^*(T^2 - T_r^2) + (1/3)c^*(T^3 - T_r^3) + (1/4)d^* (T^4 - T_r^4)$, and (ii)

$(H - H^o) = RT [(Z - 1) – 2.078 (1 + k) \alpha 1/2 \ln (Z + 2.414B)/(Z - 0.414B)]$ (iii)

where, R= gas constant,

T_r =reduced temperature = T/T_c,

T_c = critical temperature,

a, b, c and d = heat capacity constants,

$\alpha = (1 + k(1 - T_r^{1/2}))^2$,

$k = 0.37464 + 1.54226\ \omega - 0.26992\ \omega^2$, and

ω = acentric factor,

The compressibility factor, Z is derived by using an equation of state. An appropriate equation of state is selected based on the substance or mixture under consideration. In this case, the oils are non-polar hydrocarbons, for which Peng-Robinson equation of state (a cubic equation of state) is suitable [27]. The Peng-Robinson equation of state also enables C_p to be expressed as a function of critical temperature (or reduced temperature) and acentric factors. An added advantage of using a PREOS is that it has authentic, precise and error-free representation of temperature, pressure and binary or multi-component systems phase composition relations [68]. Therefore, compressibility factor, Z for the Peng- Robinson equation of state is given by:

$Z = (V/V-B) - (AV/RT (V^2 + 2BV - B^2))$,

where, $A = 0.45724\ P_r\ \alpha/T_r^2$,

$B = 0.0778\ P_r/T_r$, (A and B are equation of state constants)

V = molar volume,

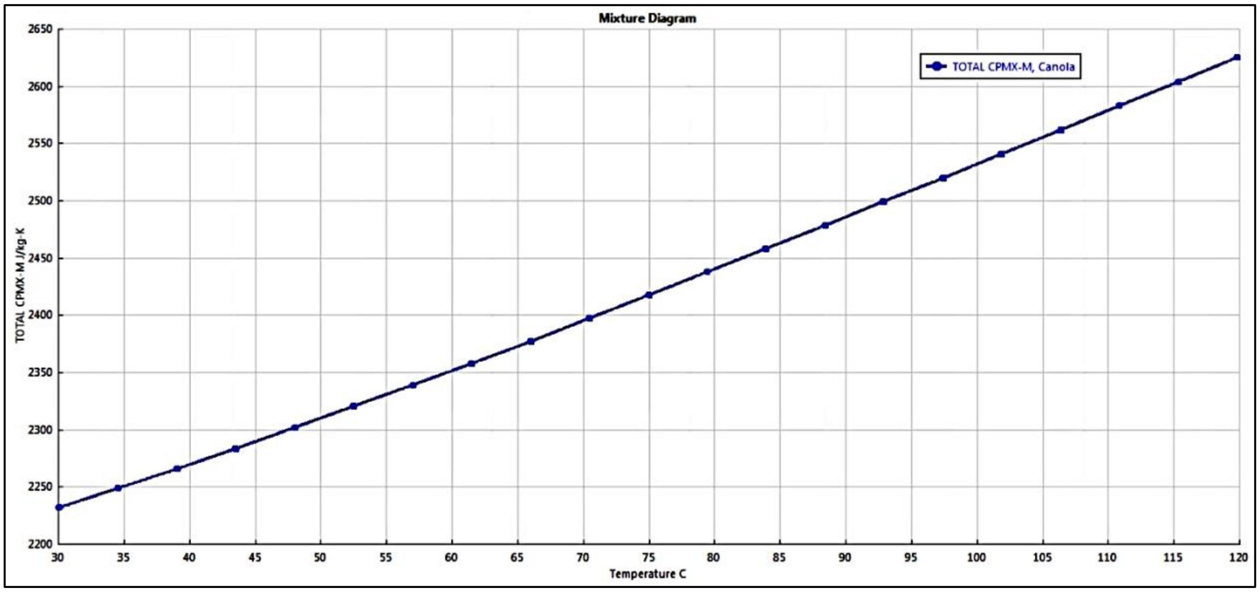
P_r = reduced pressure = P/P_c, and

P_c = critical pressure.

By substituting (ii) and (iii) in (i), enthalpy H for real state can be determine by using Peng-Robinson equation of state. Finally heat capacity, C_p is change in enthalpy with respect to temperature, at a constant pressure. This is expressed as:

$$C_p = (dH/dT)_P$$

The plots generated using Aspen are shown below.



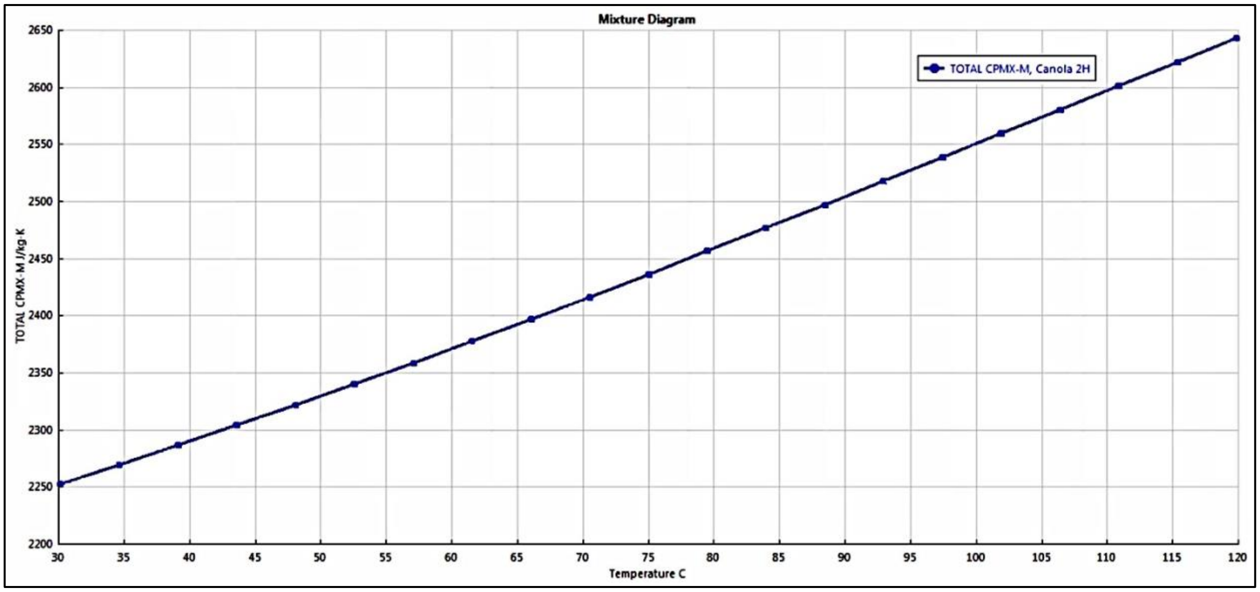


Figure 5-1 PREOS method based heat capacity plots for canola, canola 2H and canola 5H oils

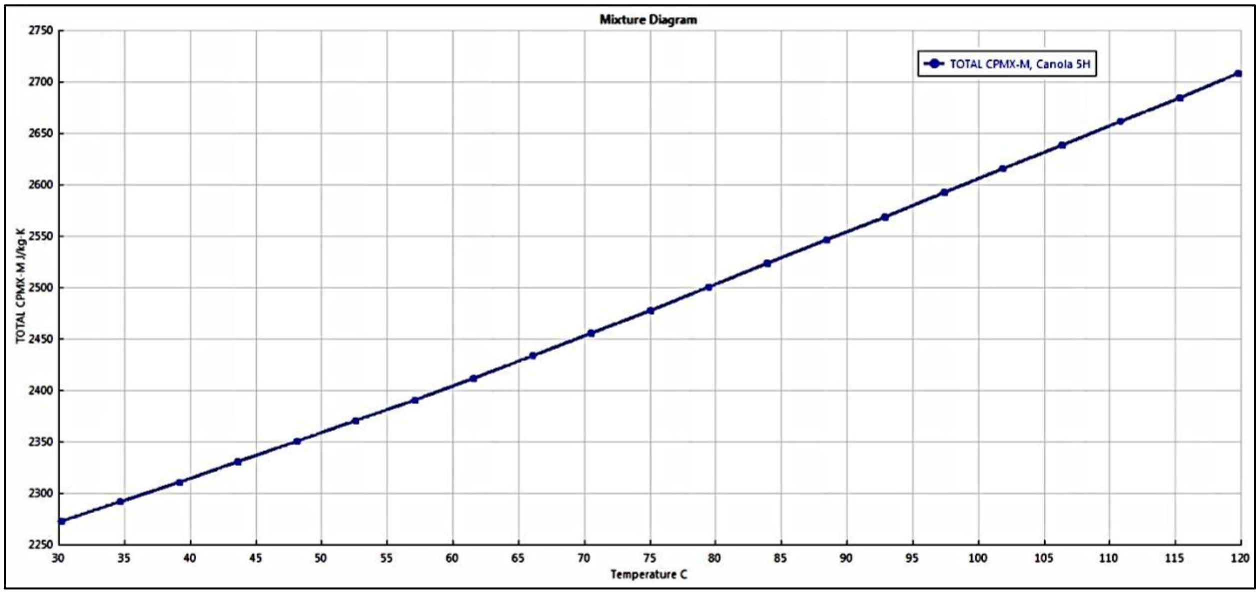


Figure 5-1 (continued)

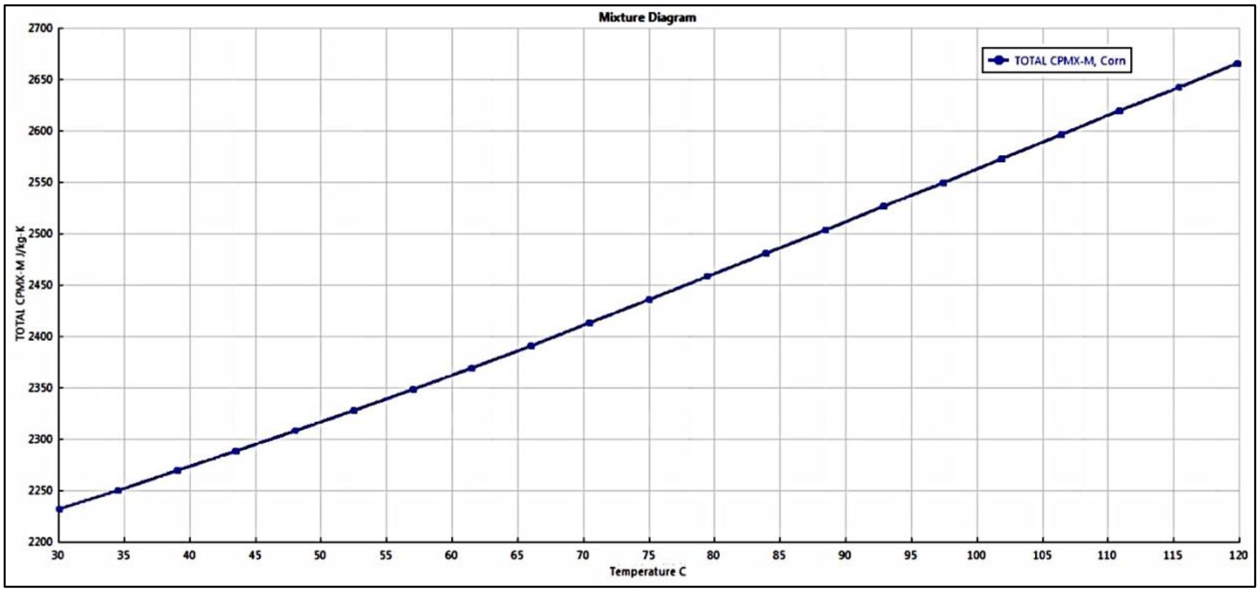


Figure 5-2 PREOS method based heat capacity plots for corn, corn 2H and corn 5H oils

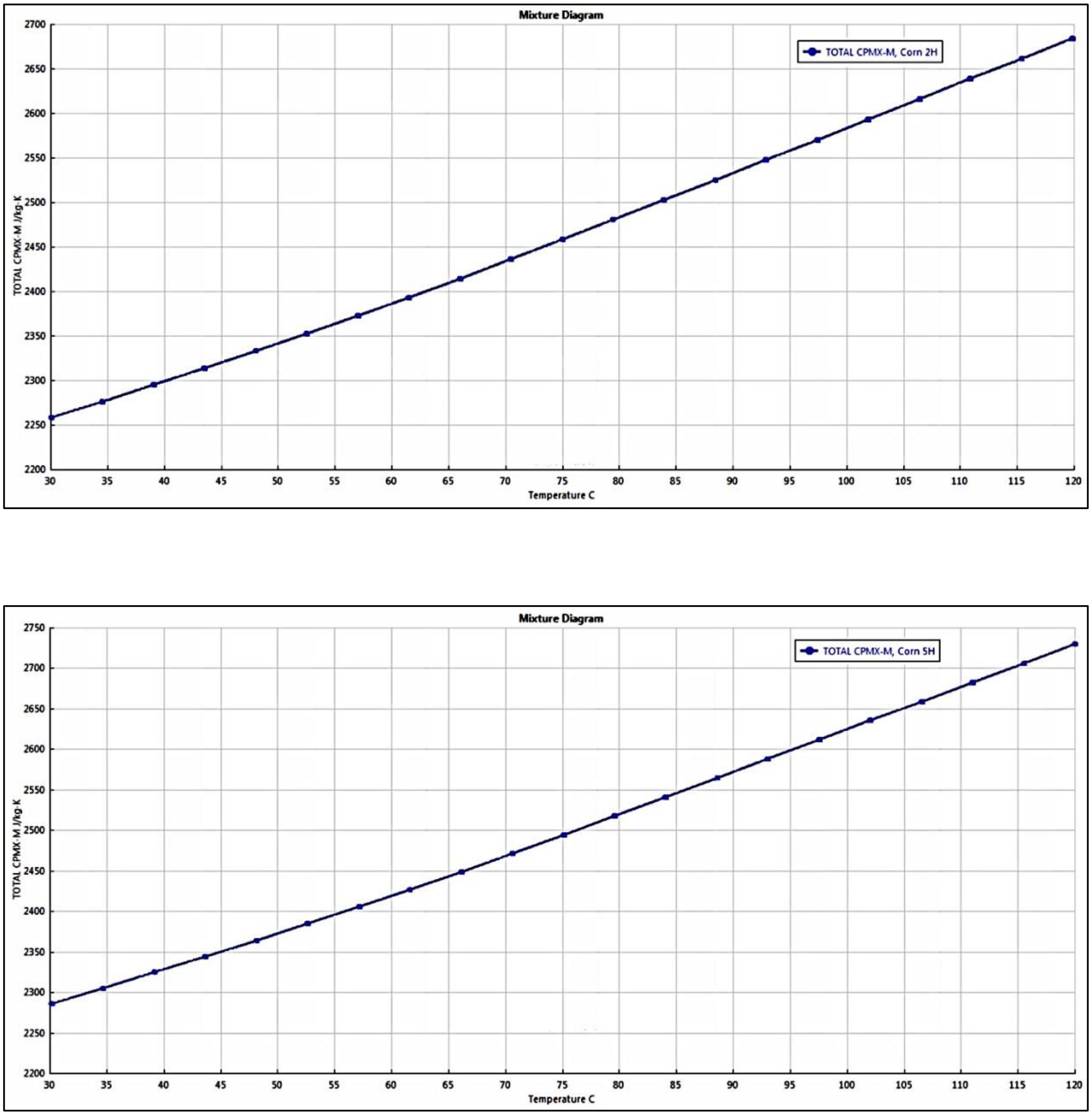


Figure 5-2 (continued)

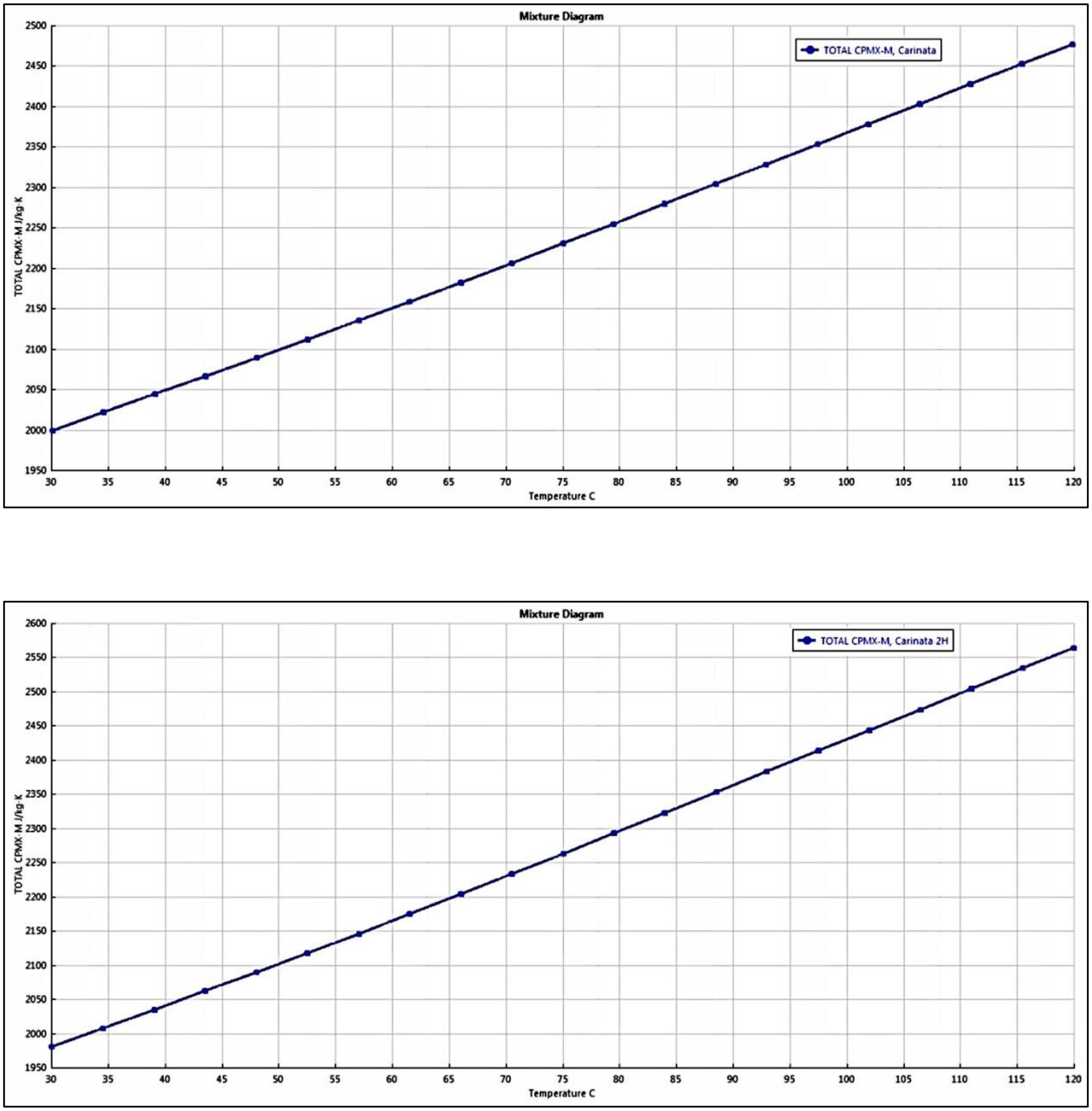


Figure 5-3 PREOS method based heat capacity plots for carinata, carinata 2H and carinata 5H oils

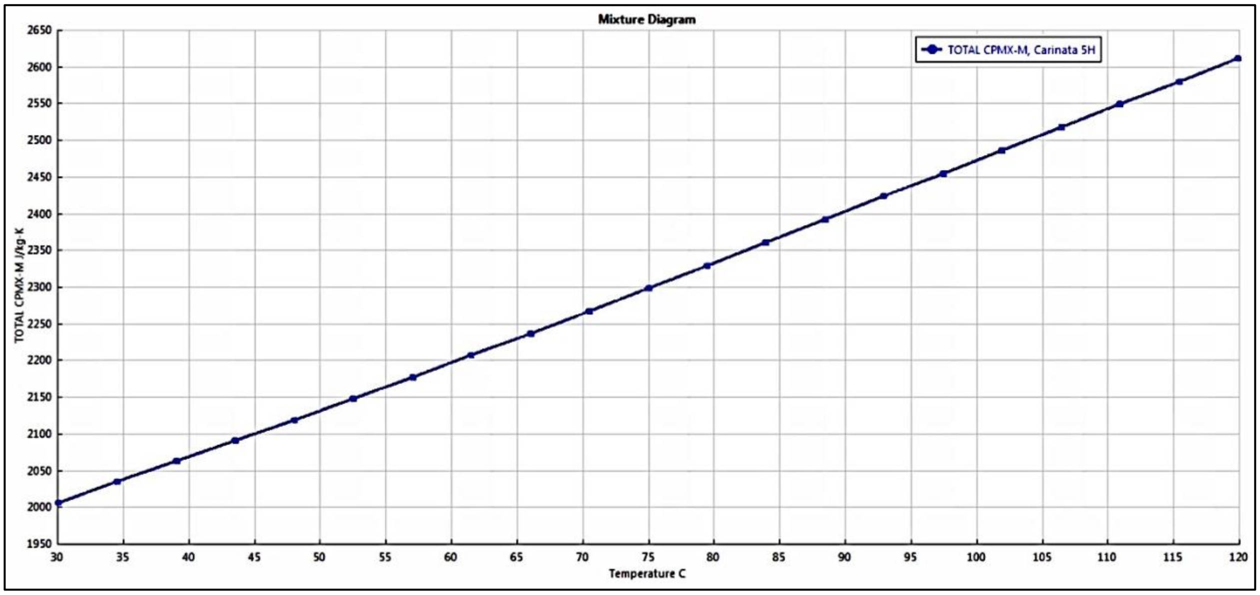


Figure 5-3 (continued)

CHAPTER 6: HEAT CAPACITY

The study of sustainability intends to find out additional ways in which an existing process can be made environmentally friendly. Utilizing raw materials that are recycles and reused can lessen the environmental impact of making biodiesel. This chapter reports the apparatus set-up, materials and experimental procedure followed to study unused oils and waste oils.

6.1 Apparatus

The instrument used to study the oils is an isothermal mixing and reaction calorimeter, model number SuperCRC 20-305-2.4 from Omnical Technologies, shown in Figure 6-1 below. The calorimeter is a heat conduction type, which needs an input power source of 115 VAC, 60 Hz and 10 A max and operates within a temperature range of -50 to 200 ^{o}C. The calorimeter has two slots for the vials to be placed on top portion of the calorimeter, which is covered with a transparent box that prevents the system from being disturbed by any surrounding changes or interference. Shown below is the image of the calorimeter in use. The calorimeter is equipped with a WinCRC software that helps to remotely control the functions through a desktop.

Figure 6-1 The calorimeter apparatus

6.2 Materials

The vegetable oils used for these experiments, canola oil and corn oil were purchased from the local grocery store Publix while the carinata oil was supplied by ARA from an ongoing project at the University of Florida. The calorimeter was operated in small runs initially to determine the operating conditions required to yield the most consistent results. Based on this sample mass calibration, the sample weight was chosen and restricted to 4g with a tolerance of 0.05g. The oils were used in their original form for one set of experiments to study unused oil. Later the edible oils were used twice for frying french fries and snacks, then they were resused five times to replicate the used oils from restaurants. The carinata oil being an inedible oil has a strong smell and hence was heated in same fashion without using it to fry any snack items.

When the oils were used to make french fries, they were filtered completely to remove any solids or leftover small particles from the fries and other sediments. They were then transferred to sealed storage bottles and kept away from any further exposure from light and air.

6.3 Procedure

The procedure followed for all three oils: canola oil, corn oil and carinata oil was exactly the same. For the experiments, two vials of similar or relatively closer weights were chosen. The cleaning steps for vials followed a soap water rinse, followed by an isopropanol and DI water rinse to get rid of any dust. After rinsing the vials, they were placed in vacuum oven at 7.2 psi which was maintained at 40 ^{o}C, until dry. It was necessary to do proper rinses and drying after every calorimeter run so as to remove any sort of particulates, dust or oil traces from the vials.

The parameters set on the calorimeter were:

- Starting Temperature (^{o}C): 20 (for example)
- Final Temperature (^{o}C): 30 (for example)
- Ramp Rate (^{o}C/min): 2
- Isothermal delay before ramp (min): 2

For a *blank run,* two vials of closer weights were selected. For example, weight of reference vial used was 13.639 g and weight of sample vial used was 13.642 g. Blank run was done with both empty vials to determine the heat absorbed by blank/empty vials. The heat of the blank vial was deducted from the heat of the vial containing oils samples in order to get the heat of oil. The mathematical expression to determine heat capacity is shown below. Both vials were securely placed in the two slots in the calorimeter and power was switched on. As the power was turned on, the calorimeter gradually set itself to thermal equilibrium and stabilized at initial temperature, atmospheric pressure and set parameters (mentioned above). All the desired working conditions were set up remotely on the software. The initial or starting temperature for the first ramp, for instance started at around 20 °C and final temperature was set to 30 °C to maintain a ramp size of 10 °C. The temperature recorded on the instrument were within a tolerance of ±0.3 °C. The isothermal delay enabled to the calorimeter to hold at initial temperature for two minutes before starting the ramp. Each ramp, with a ramp size of 10 °C, took 40-45 minutes to complete and reach the set final temperature followed by attaining the thermal equilibrium at that temperature. These ramping steps were followed for an oil run, from 20 °C to 120 °C. At the end of each ramp, the heat curve that had developed as a plot of heat flow as a function of temperature, was integrated to determine the heat at that temperature. A note was made at the end of every ramp for the integrated heat (in joules) at that temperature along with the read initial and final temperatures.

For a *sample run*, the same vials from the blank run were used after following the cleaning and drying procedure. The empty sample vial was placed on the weighing scale and tared to zero. Gradually, the desired oil sample was added with the help of a pipette to weigh the oil sample to approximately 4 g. The tolerance for the sample weight, as mentioned earlier, was up to +0.05g. The vials were securely placed in slots. On switching on the calorimeter, the exact same procedure was followed as the blank runs. The operating conditions were set on the software. When the calorimeter reached initial thermal equilibrium, the ramps were started with an isothermal hold of 2 mins at the starting temperature followed by 10 °C ramp size until it reached the set final temperature and thermal equilibrium. Similarly, ramping steps were followed from 20 °C to 120 °C for oil samples and the heat curves at the end of every ramp were integrated to determine the heat of vials containing the samples.

The heat capacity for oil samples were studied in triplicates for reliability. To calculate the heat capacities of the oil samples, the following formula was used:

$C_p = ((H_t/\Delta T) - (H_r/ \Delta T)) /W$; (J/g K or J/g °C)

or, $C_p = (Q_t - Q_r) / W$

where, H_r= Integrated heat for a blank run, in joules (at a particular temperature),

H_t= Integrated heat for a sample run, in joules (at the same temperature),

ΔT= Temperature ramp size (°C), and

W=Weight of the sample (g).

CHAPTER 7: COMPOSITION ANALYSIS

An oil is composed of fatty acids which are categorized depending on the number of double bonds in it. These categories of fatty acids are saturated, monounsaturated and polyunsaturated as mentioned earlier. The composition of an oil is likely to change upon heating; hence the composition of a waste oil may vary as compared to the unused oil. To study the degree of change in fatty acid profile, composition analysis was carried out for all three oils in each of their three variants: unused, after two heating cycles and after five heating cycles. The instrument used for this purpose was a gas chromatograph with a mass spectrometer detector (GC-MS). A GC combined with MS has the ability to separate complex mixtures, detect and quantify them. This chapter discusses in detail about the procedure and findings of the analysis.

7.1 Apparatus and Materials

The instrument used to analyze all nine oil samples was a Perkin Elmer 580 Clarus GC attached with a Perkin Elmer 560 D Clarus MS detector. The instrument was connected to a Turbomass software that acts as the user interface to operate the instrument. The column used was the Agilent J&W HP-88 column with dimensions 60m x 0.25mm x 0.25µm and temperature limits within 0-260 ^{o}C. The image below shows the gas chromatograph instrument and the table following lists the inlet and flow settings.

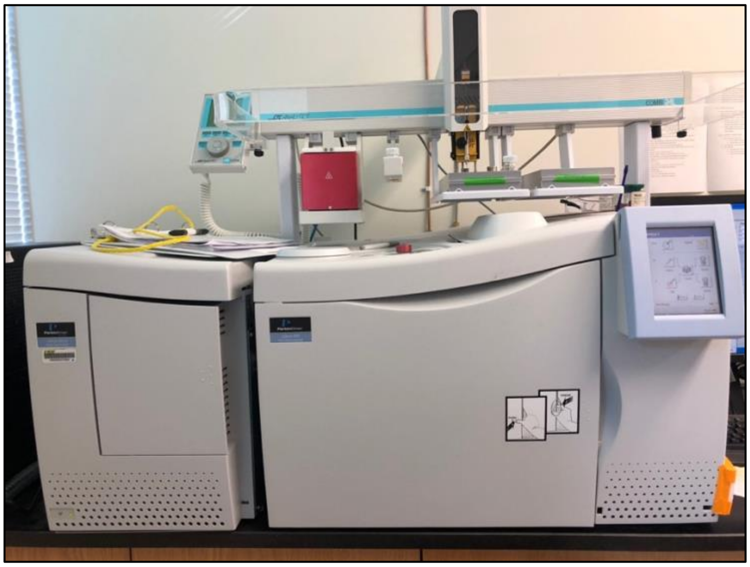


Figure 7-1 Gas chromatograph with mass spectrometer

Table 7-1 Inlet and flow settings on gas chromatograph

Column	Agilent J&W HP-88 column with dimensions 60 m x 0.25 mm x 0.25 µm
Carrier gas	Helium, constant flow mode
Carrier gas flow rate	1 ml/min
Acquisition mode	40-400 amu
Solvent delay	4 min
GC inlet	Manual injection, 1 µl
Inlet Temperature	260 ^oC
Split Ratio	30:1
Oven Temperature Program	140 ^oC (5 min), 5 ^oC/min to 240 ^oC (10 min)

The materials used as standards to obtain calibration curves were methyl palmitate (MP), methyl stearate (MS), methyl oleate (MO), methyl linoleate (ML1), methyl linolenate (ML3) and methyl erucate (ME). Margaric acid was used as an internal standard, 10% BF_3 in methanol was used as the derivatizing agent and analytical grade n-hexane was used as the solvent. All the chemicals were bought from Fisher Scientific. Oils used for analysis were unused canola oil (Canola), canola oil after two heating cycles (Canola 2H), canola oil after five heating cycles (Canola 5H), corn oil (Corn), corn oil after two heating cycles (Corn 2H), corn oil after five heating cycles (Corn 5H), carinata oil (Carinata), carinata oil after two heating cycles (Carinata 2H) and carinata oil after five heating cycles (Carinata 5H). Canola and corn oils were used to cook french fries for two and five heating cycles.

7.2 Procedure and Sample Preparation

An oil cannot be analyzed in its original form as its fatty acid chains are heavy and long to be carried in the column and are tough to be detected. Therefore, the fatty acids in the oils are derivatized to their corresponding fatty acid methyl esters. Initially, calibration was performed for all standard methyl esters for the range of 30-500 ppm. For each methyl ester standard, 5 samples of concentration 500 ppm, 250 ppm, 125 ppm and 62.5 ppm and 31.25 ppm were prepared by serial dilution of factor 2 and ran to develop calibration curves. The image below shows the calibration curves for every standard and the following table shows the trendline equation, retention time and coefficient of determination (R^2). The value of R^2 indicates the definiteness of the correlation between peak area and concentration, where R^2 ~1 indicates a good fit.

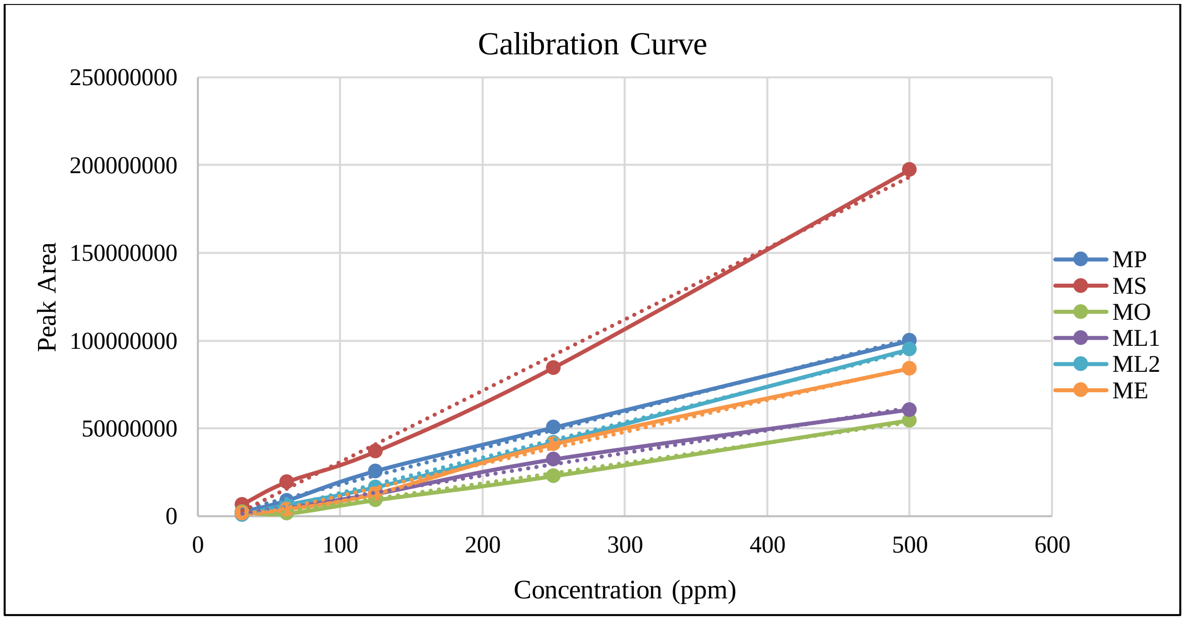


Figure 7-2 Standard methyl esters calibration curves

Table 7-2 Methyl ester standards trendline equations, retention times and R^2 values

Standard	Retention Time (min)	Trendline Equation	R^2 Value
Methyl Palmitate	13.86	y = 205748x - 4E+06	0.9979
Methyl Stearate	16.68	y = 406441x - 6E+06	0.9953
Methyl Oleate	17.31	y = 119186x - 6E+06	0.9916
Methyl Linoleate	18.37	y = 125374x - 3E+06	0.9959
Methyl Linolenate	19.58	y = 187961x - 5E+06	0.9984
Methyl Erucate	22.14	y = 174235x - 7E+06	0.9953

Before derivatizing the main oil samples, a series of six samples were derivatized using varying amounts (0.5 ml, 1 ml, 1.5 ml, 2 ml, 2.5 ml and 3 ml) of 10% BF_3 in methanol to ensure complete conversion of fatty acids. The peaks for 0.5 ml, 1 ml and 1.5 ml were seen to be increasing with the amount of reagent while peaks were seen to be leveling off for 2 ml, 2.5 ml and 3 ml indicating complete conversion. Figures 7-3 and 7-4 below compares the chromatograms for the six samples.

For oil analysis, [41] 100 mg of oil was weighed in a glass vial, 2 ml n-hexane, 2.5 ml 10% BF_3 in methanol and 20 mg of margaric acid were added. Margaric acid was added to determine the internal standard response factor for quantifying targeted fatty acid esters. The solution was heated to 55 ^{o}C for 30 minutes and was then cooled to room temperature. On cooling, 2 ml of distilled water was added, and the vial was left for phase separation. The supernatant layer formed is the hexane layer carrying targeted analytes, which is used for GC analysis. The derivatized oil is diluted with more solvent in order to bring the concentration within the calibration range. All nine oil samples (Canola, Canola 2H, Canola 5H, Corn, Corn 2H, Corn 5H, Carinata, Carinata 2H and Carinata 5H) were prepared using this method. The samples were manually injected using a Thermo Fisher precision syringe. The samples were subjected to the oven temperature program

[43] to develop respective chromatograms. The images below are the chromatograms for all nine oils.

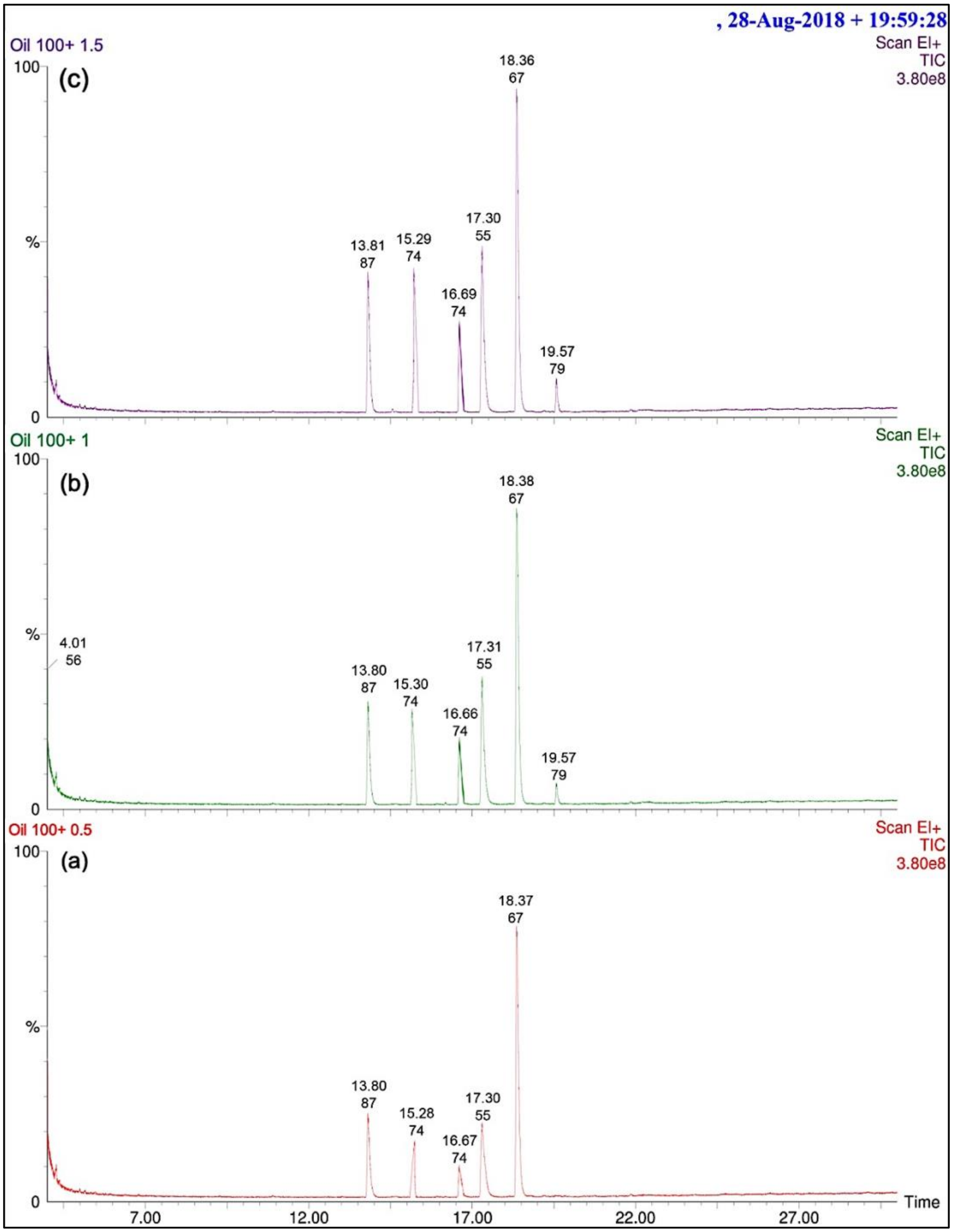


Figure 7-3 Derivatization comparison chromatograms with varying amounts of derivatizing agent. (a) with 0.5ml (b) with 1 ml (c) with 1.5 ml (d) with 2 ml (e) with 2.5 ml (f) with 3 ml

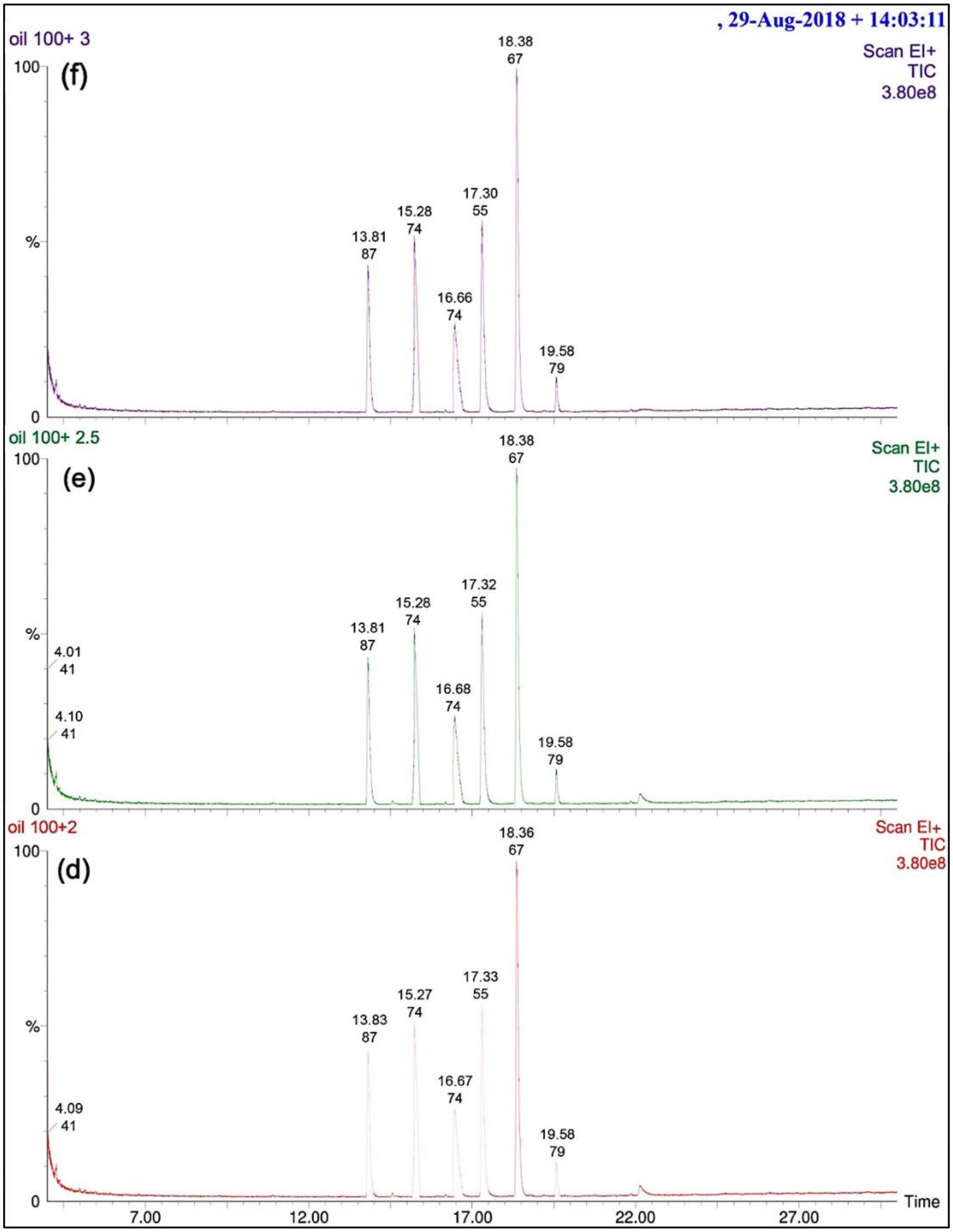


Figure 7-3 (continued)

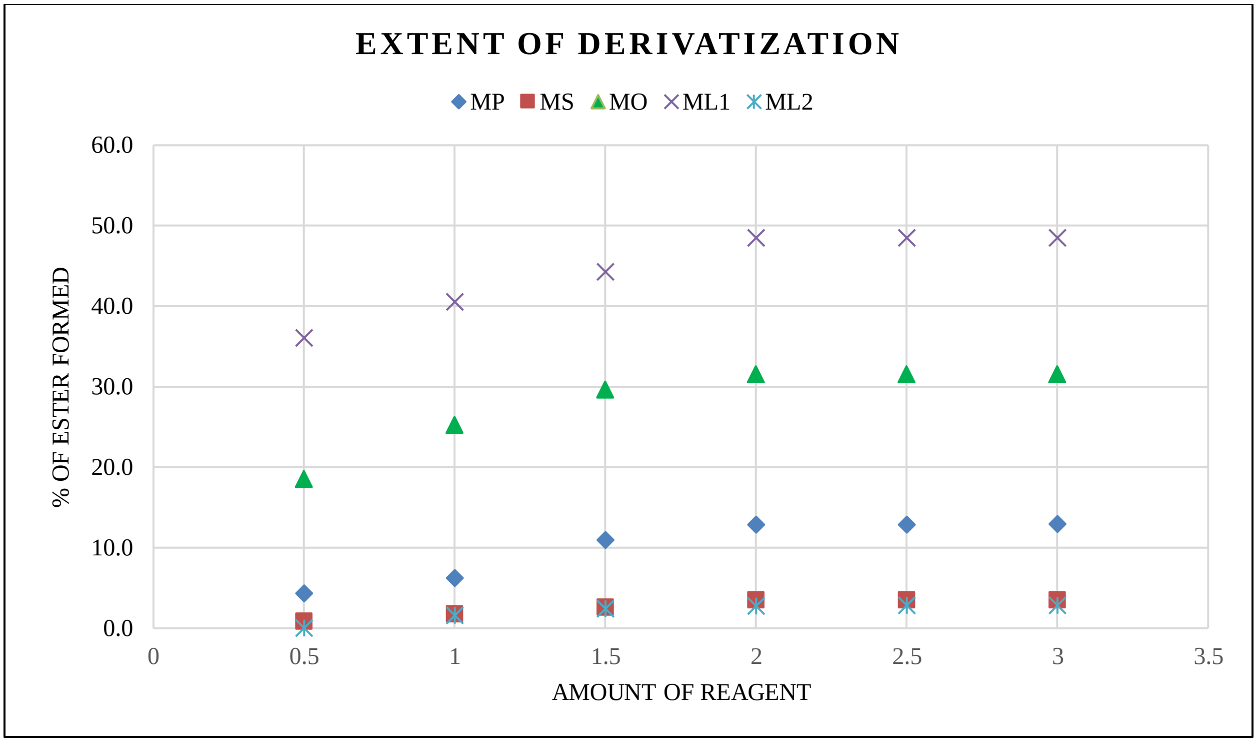


Figure 7-4 Comparison of extent of derivatization

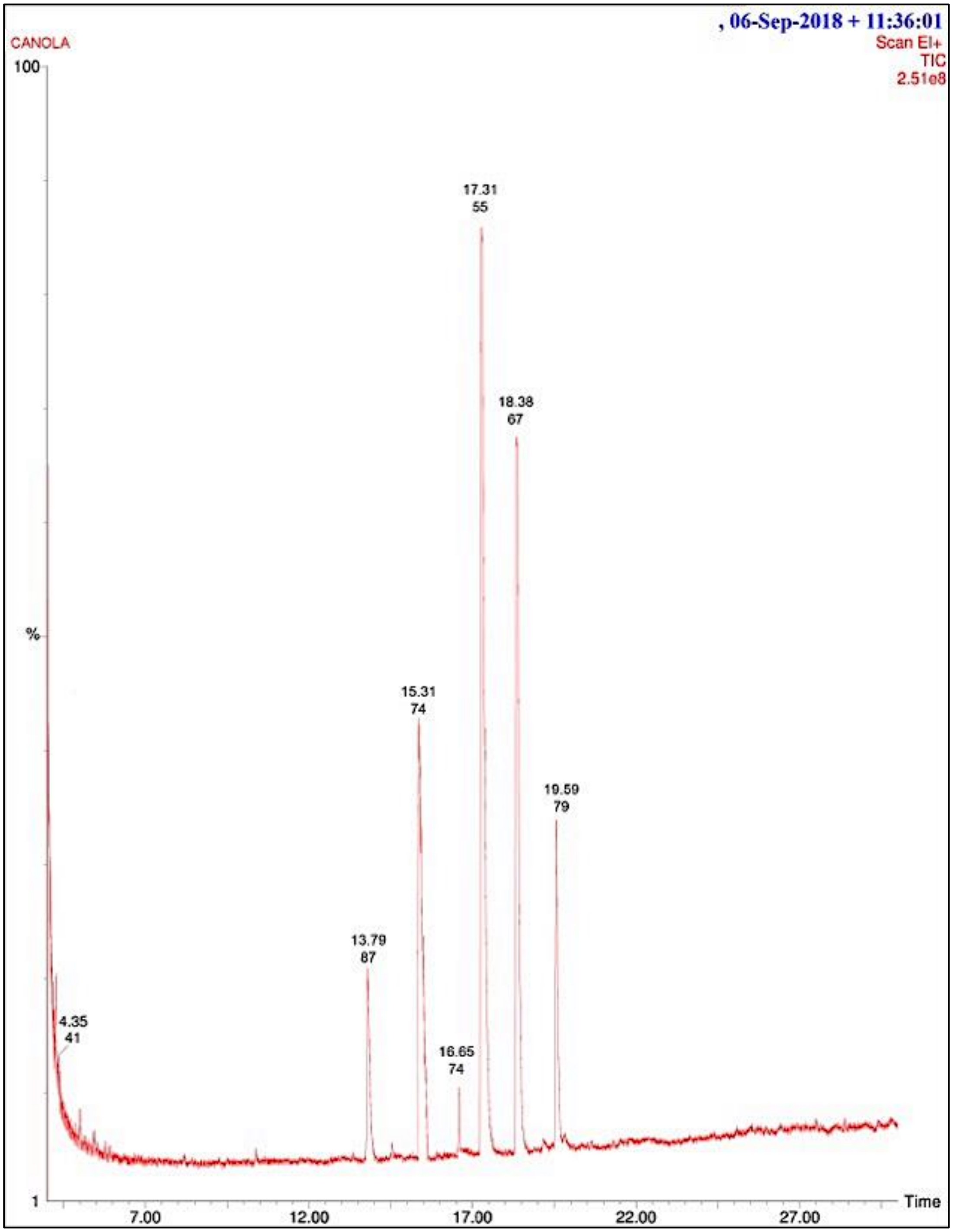
On generating the chromatograms, the peaks for every fatty acid were quantified and the oil composition was determined by using the method of single point internal standard. First the response factor for the internal standard (that is the margaric acid) was determined using the formula [45]:

Internal Response factor (IRF) = [area_{is} X amount_{s}]/ [$\text{amount}_{\text{is}}$ X area_{s}]

where, area_{is} and area_{s} are the areas of internal standard peak and sample peaks, $\text{amount}_{\text{is}}$ and amount_{s} are the amounts of internal standard and sample respectively.

Using this internal response factor, the amount of each fatty acid methyl ester was determined using the formula:

Amount of fatty acid methyl ester = [$\text{amount}_{\text{is}}$ X area_{s} X IRF]/ area_{is}



Note: The order of the peaks from left to right is: palmitic acid, internal standard, stearic acid, oleic acid, trans-linoleic acid (in 5H only), linoleic acid and α-linolenic acid

Figure 7-5 Canola, canola 2H and canola 5H chromatograms

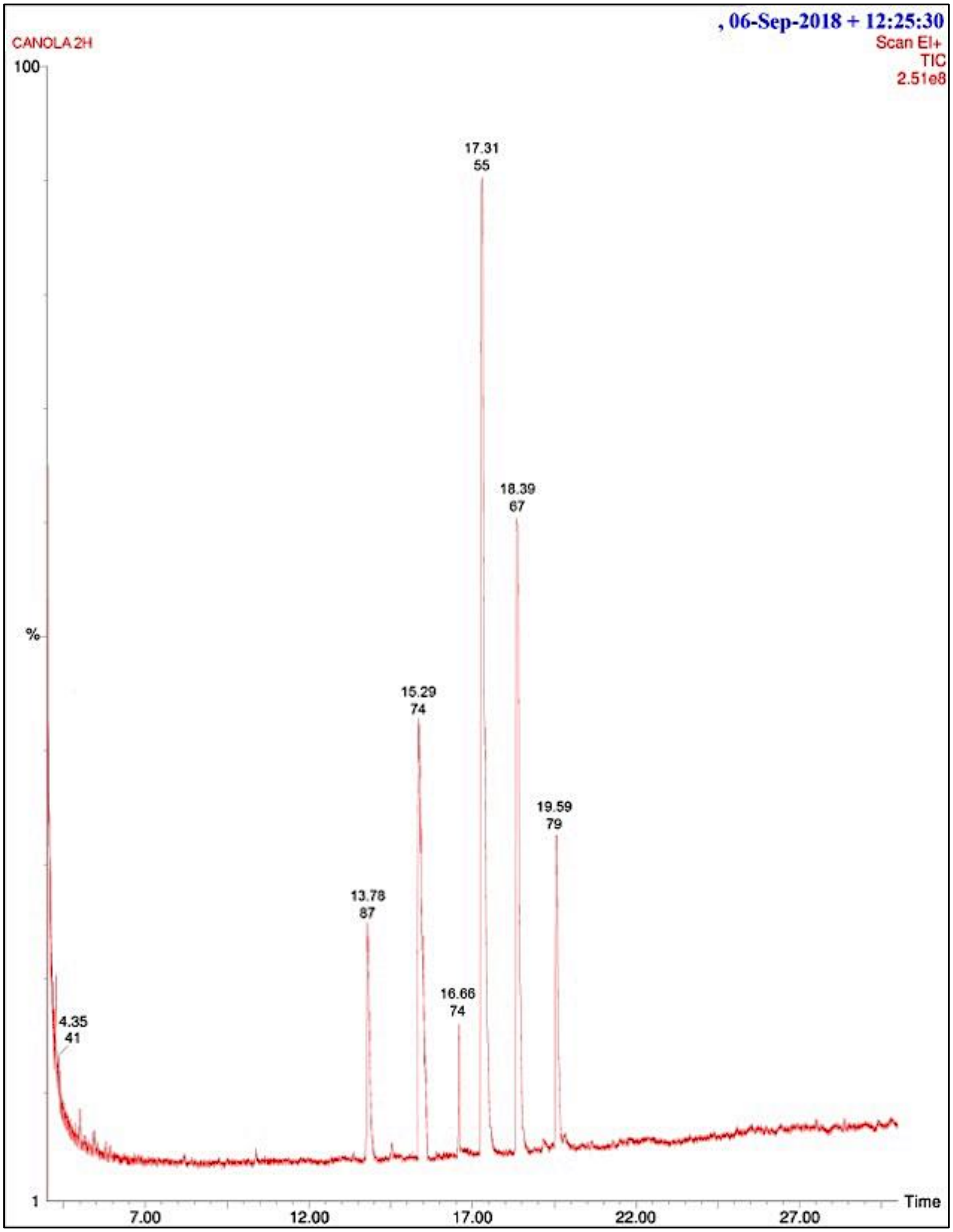


Figure 7-5 (continued)

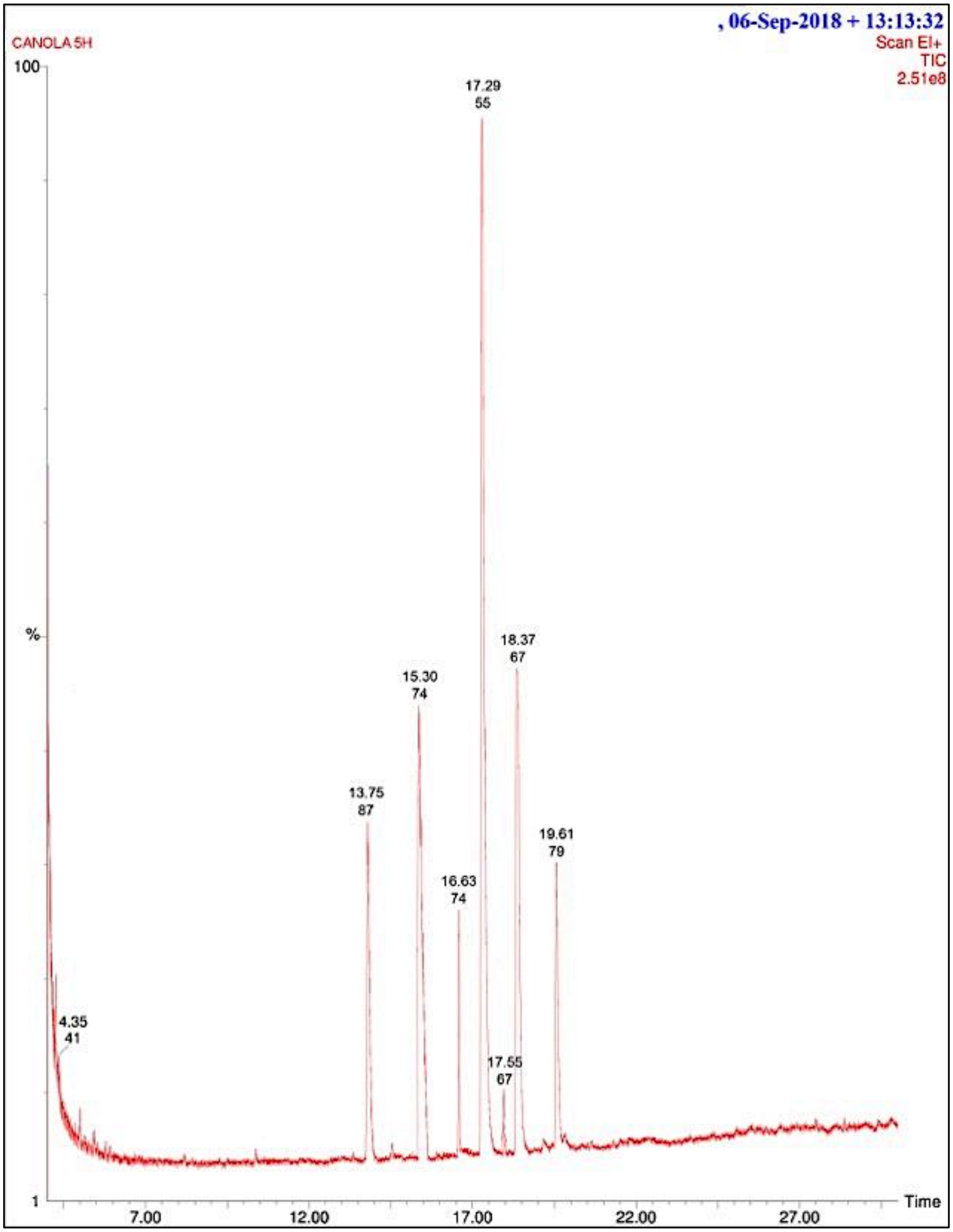
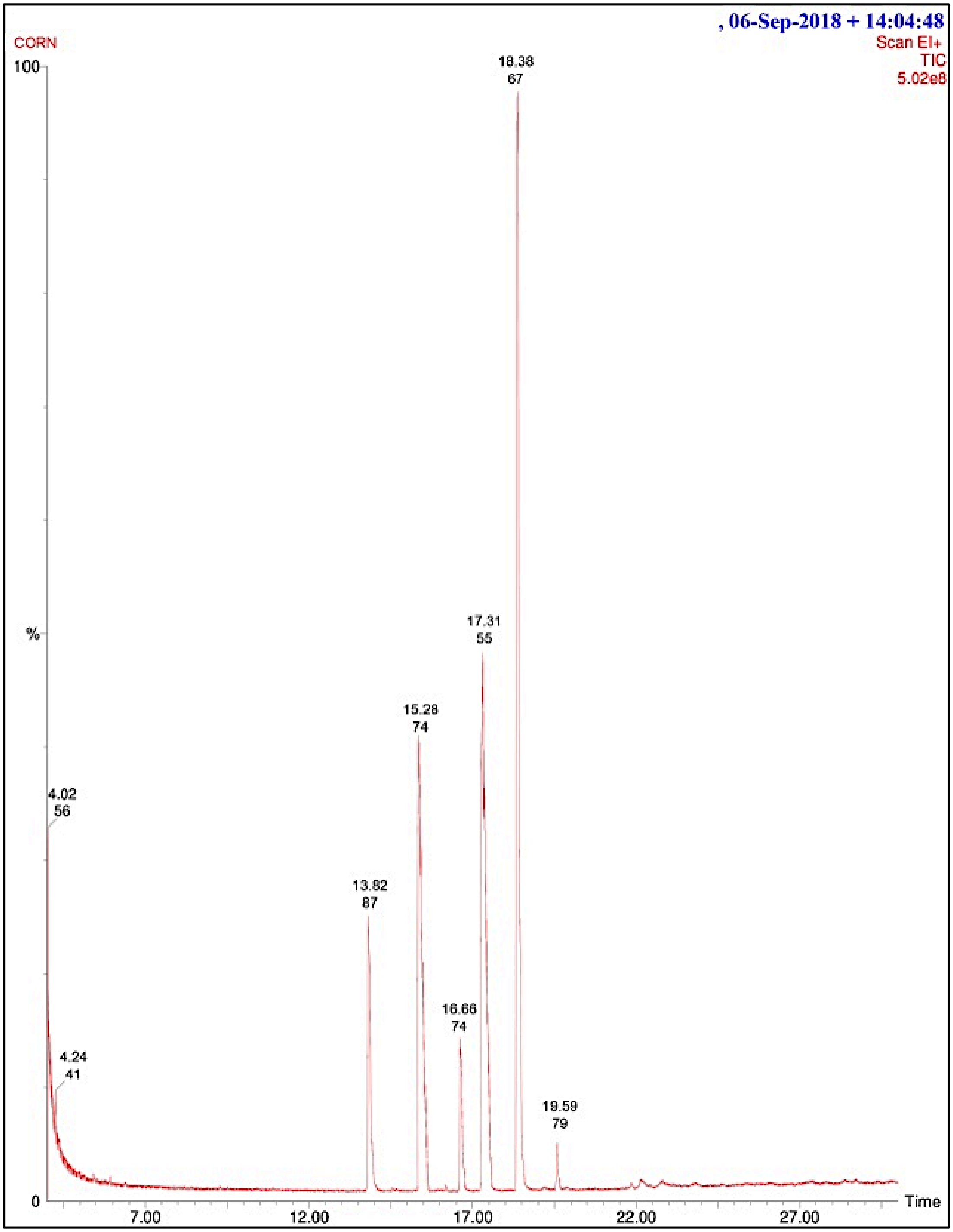


Figure 7-5 (continued)



Note: The order of the peaks from left to right is: palmitic acid, internal standard, stearic acid, oleic acid, trans-linoleic acid (in 5H only), linoleic acid and α-linolenic acid

Figure 7-6 Corn, corn 2H and corn 5H chromatograms

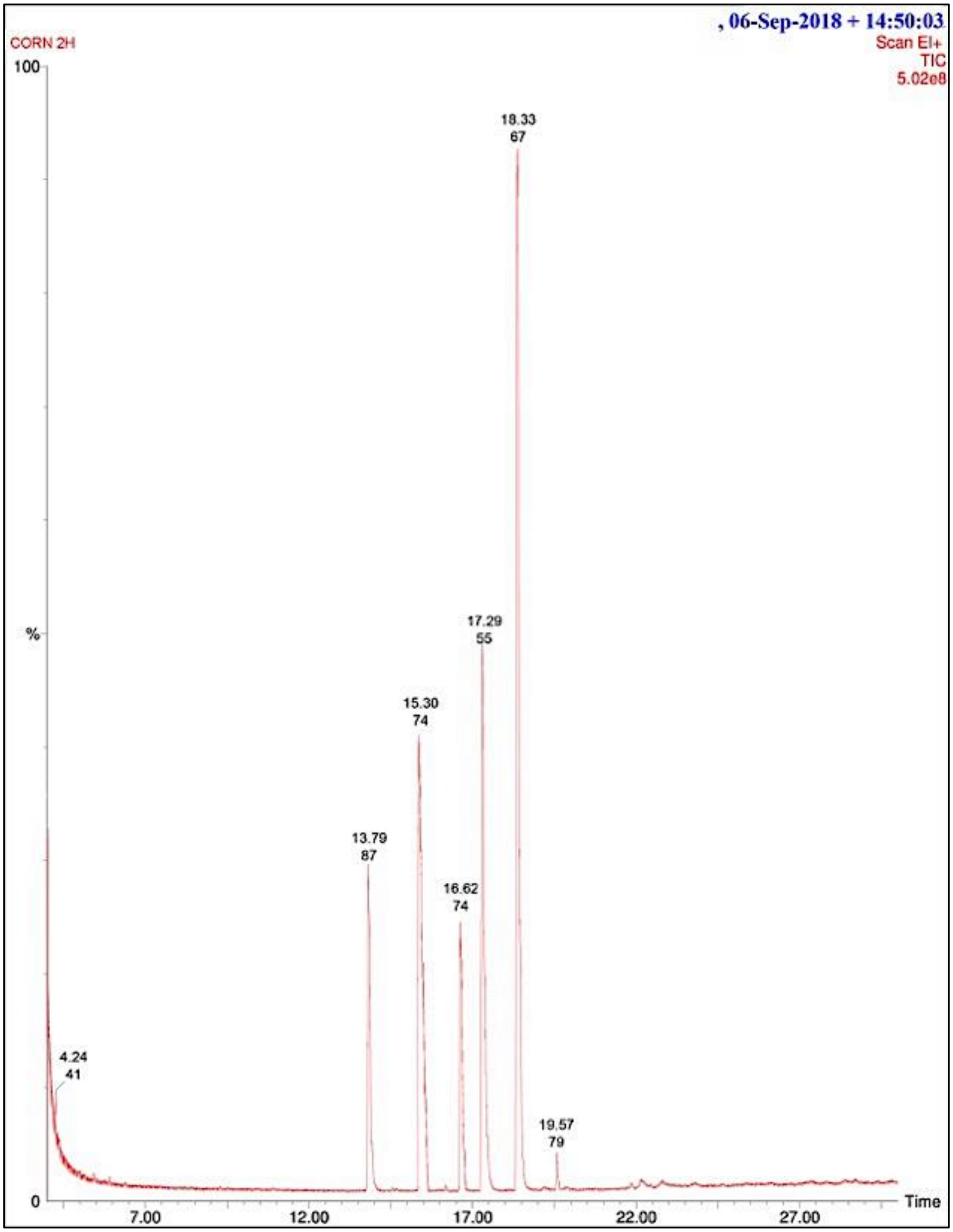


Figure 7-6 (continued)

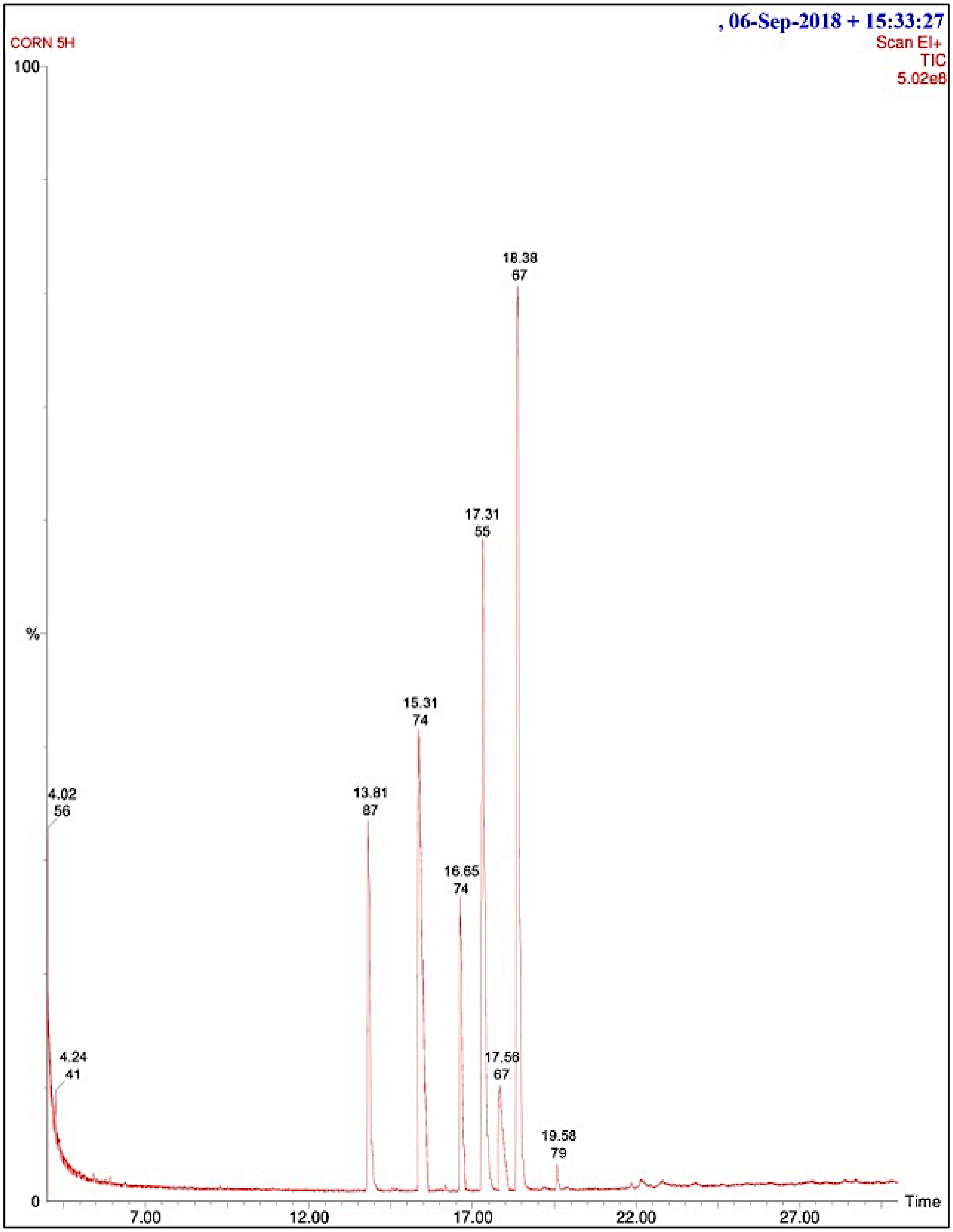
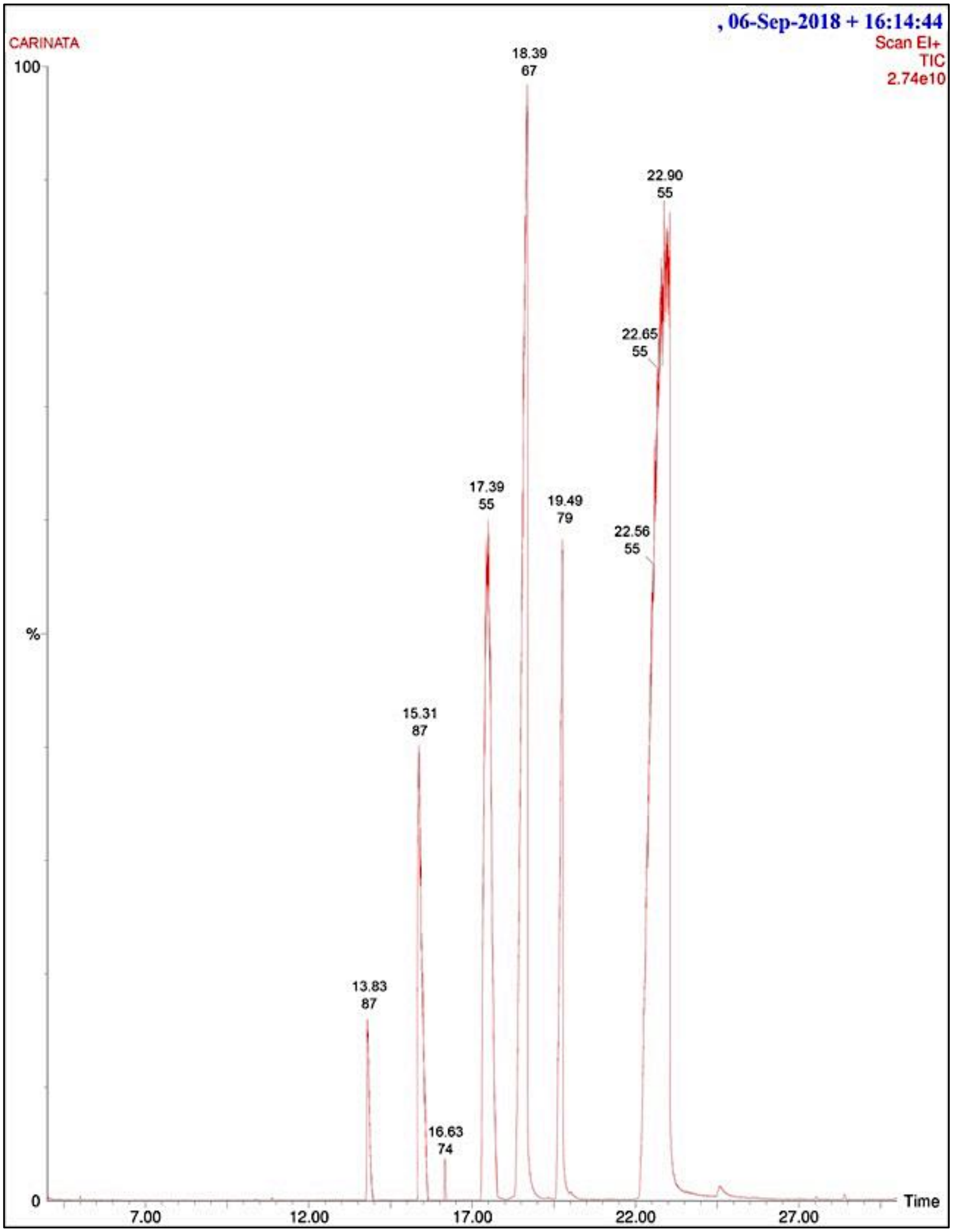


Figure 7-6 (continued)



Note: The order of the peaks from left to right is: palmitic acid, internal standard, stearic acid, oleic acid, trans-linoleic acid (in 5H only), linoleic acid, α-linolenic acid and erucic acid

Figure 7-7 Carinata, carinata 2H and carinata 5H chromatograms

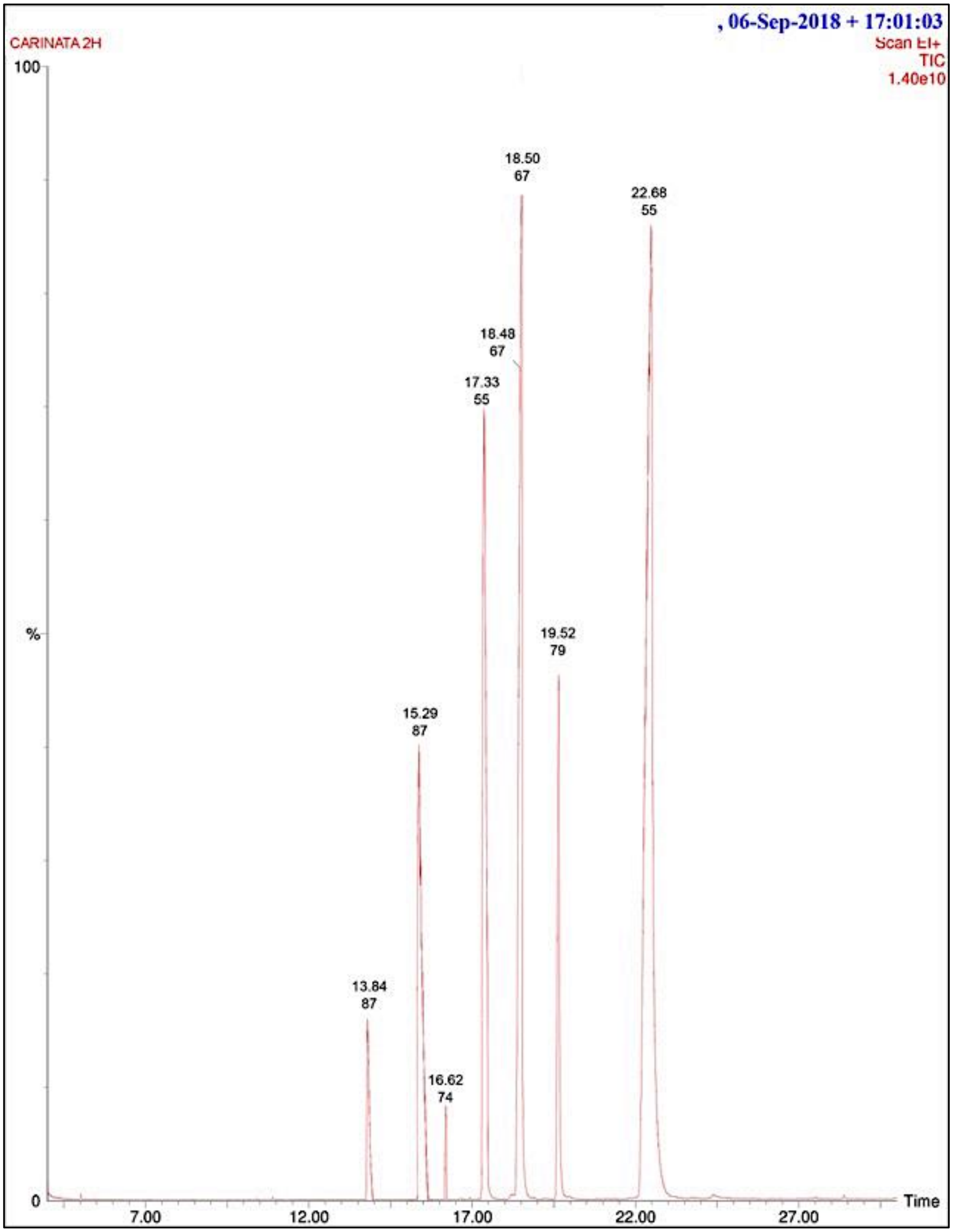


Figure 7-7 (continued)

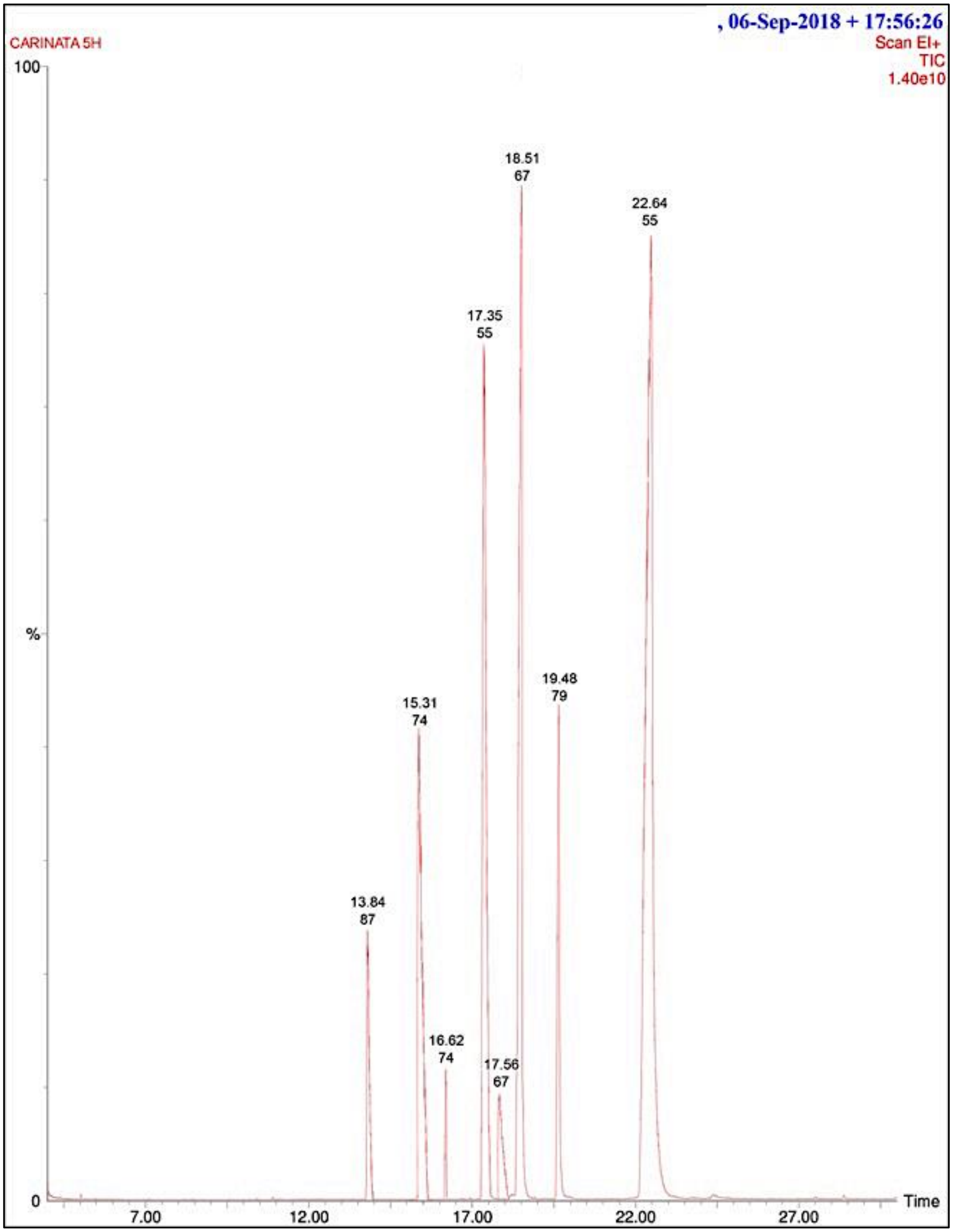


Figure 7-7 (continued)

Further, literature states that 1 mole of fatty acid methyl ester corresponds to 1 mole fatty acid in the original oil sample. Sample calculation is shown in appendix C. For all nine oil samples, a triplicate was run to verify the repeatability. The tables below show the composition of each oil sample as an average of three runs. A sample quantification calculation is shown in appendix C.

Table 7-3 Canola, canola 2H and canola 5H compositions

	Canola		Canola 2H		Canola 5H	
	Mass %	Mole %	Mass %	Mole %	Mass %	Mole %
Palmitic acid	5.11	5.56	6.05	6.60	6.93	7.55
Stearic acid	2.52	2.48	3.62	3.58	5.53	5.46
Oleic acid	63.79	63.26	66.39	66.03	71.17	70.73
Linoleic acid	20.91	20.87	16.34	16.36	10.17	10.18
Linolenic acid	7.79	7.83	7.37	7.43	5.18	5.22
Trans-Linoleic acid					1.05	0.87
Total	100.12	100	99.77	100	100.03	100

Table 7-4 Corn, corn 2H and corn 5H compositions

	Corn		Corn 2H		Corn 5H	
	Mass %	Mole %	Mass %	Mole %	Mass %	Mole %
Palmitic acid	12.86	13.87	14.48	15.63	16.25	17.56
Stearic acid	3.75	3.66	5.01	4.90	6.14	6.01
Oleic acid	28.56	28.11	32.17	31.67	34.48	33.99
Linoleic acid	51.85	51.38	47.01	46.60	40.05	39.74
Linolenic acid	2.99	2.98	1.2	1.20	1.02	1.02
Trans-Linoleic acid					2.03	1.68
Total	100	100	99.87	100	99.97	100

Table 7-5 Carinata, carinata 2H and carinata 5H compositions

	Carinata		Carinata 2H		Carinata 5H	
	Mass %	Mole %	Mass %	Mole %	Mass %	Mole %
Palmitic acid	3.24	3.76	4.79	5.58	5.60	6.47
Stearic acid	2.37	2.49	3.64	3.84	4.54	4.76
Oleic acid	15.00	15.89	18.01	19.16	20.52	21.63
Linoleic acid	23.29	24.84	19.88	21.30	17.15	18.21
Linolenic acid	17.32	18.59	15.09	16.28	12.37	13.22

Table 7-5 (continued)

Erucic acid	38.77	34.43	37.90	33.83	36.89	32.61
Trans-Linoleic acid					2.93	3.11
Total	100	100	99.30	100	100	100

CHAPTER 8: RESULTS AND DISCUSSION

This chapter discusses the results achieved from the experimental work on the unused and used oils, and further discusses what are the results obtained and deduces the nature of the oils. Waste oils/ used oils were used for either frying snacks in case of corn and canola oils and was heated without cooking for carinata oil. Waste oils were reused two times (2H) and five times (5H) individually.

8.1 Calorimetry Results

The integrated heat values generated from analyzing the curves on the calorimeter were put in the C_p formula to calculate heat capacity over the given temperature range. Both kinds of waste oils, 2H and 5H were studied separately and plotted alongside the unused oil values for comparison. The oils were observed to increase heat capacity with the increase in number of times the oils were heated.

Below are the values generated for canola oil, corn oil and carinata oil using the isothermal calorimeter in Table 8-1, 8-2 and 8-3. Sample calculations for the experimental heat capacity calculations are shown in Appendix B.3.

Table 8-1 Experimental heat capacities of canola oil

	Unused oil	Twice used oil (2H)	Five times used oil (5H)
Temp (°C)	C_p (J/g °C)	C_p (J/g °C)	C_p (J/g °C)
30	2.3015	2.3179	2.3313
40	2.3575	2.3464	2.3722
50	2.3949	2.3970	2.4390
60	2.4391	2.4488	2.4850
70	2.4929	2.4978	2.5357
80	2.5497	2.5653	2.5893

Table 8-1 (continued)

90	2.5927	2.6152	2.6381
100	2.6570	2.6606	2.7112
110	2.7003	2.7363	2.7709
120	2.7618	2.7867	2.8357

Table 8-2 Experimental heat capacities of corn oil

	Unused oil	Twice used oil (2H)	Five times used oil (5H)
Temp (^{o}C)	C_p (J/g ^{o}C)	C_p (J/g ^{o}C)	C_p (J/g ^{o}C)
30	2.2937	2.3221	2.3366
40	2.3688	2.3586	2.3893
50	2.4092	2.3889	2.4234
60	2.4512	2.4622	2.4866
70	2.4977	2.5250	2.5490
80	2.5595	2.5674	2.6154
90	2.6119	2.6411	2.6802
100	2.6406	2.6938	2.7520
110	2.7351	2.7512	2.8107
120	2.7681	2.8089	2.8812

Table 8-3 Experimental heat capacities of carinata oil

	Unused oil	Twice heated (2H)	Five times heated (5H)
Temp (^{o}C)	C_p (J/g ^{o}C)	C_p (J/g ^{o}C)	C_p (J/g ^{o}C)
30	2.0530	2.0758	2.0977
40	2.1058	2.1282	2.1633
50	2.1283	2.1927	2.2176
60	2.2411	2.2634	2.3053
70	2.2943	2.3395	2.3808
80	2.3212	2.4096	2.4610
90	2.3818	2.4680	2.5303
100	2.4203	2.5271	2.6064
110	2.5112	2.6009	2.6408
120	2.5927	2.6616	2.7084

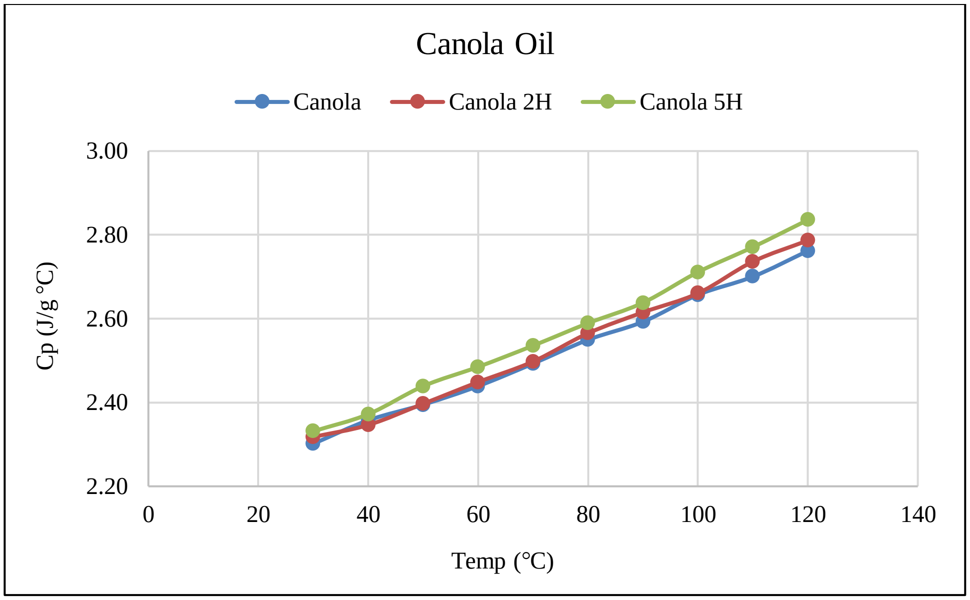


Figure 8-1 Heat capacities of canola oil

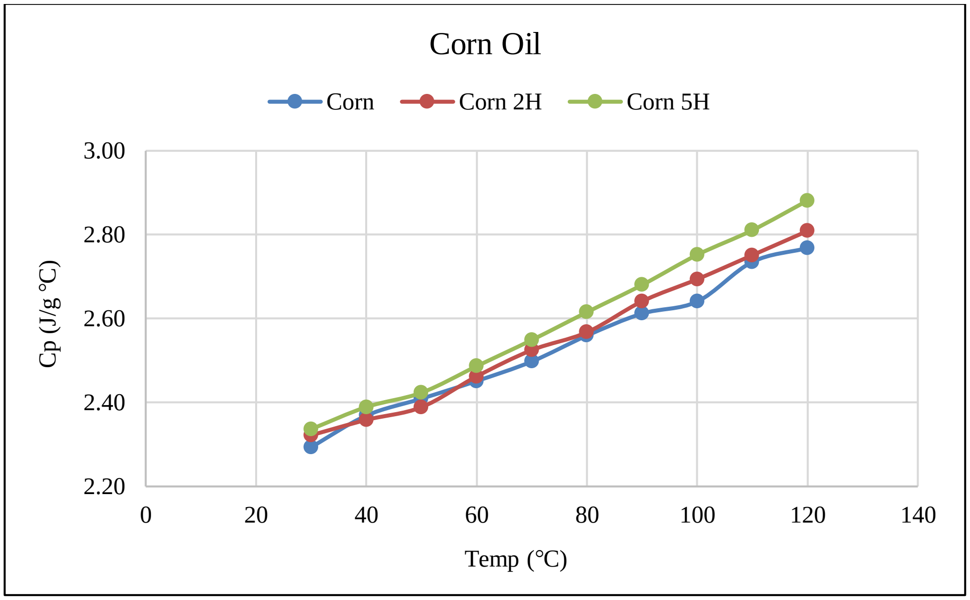


Figure 8-2 Heat capacities of corn oil

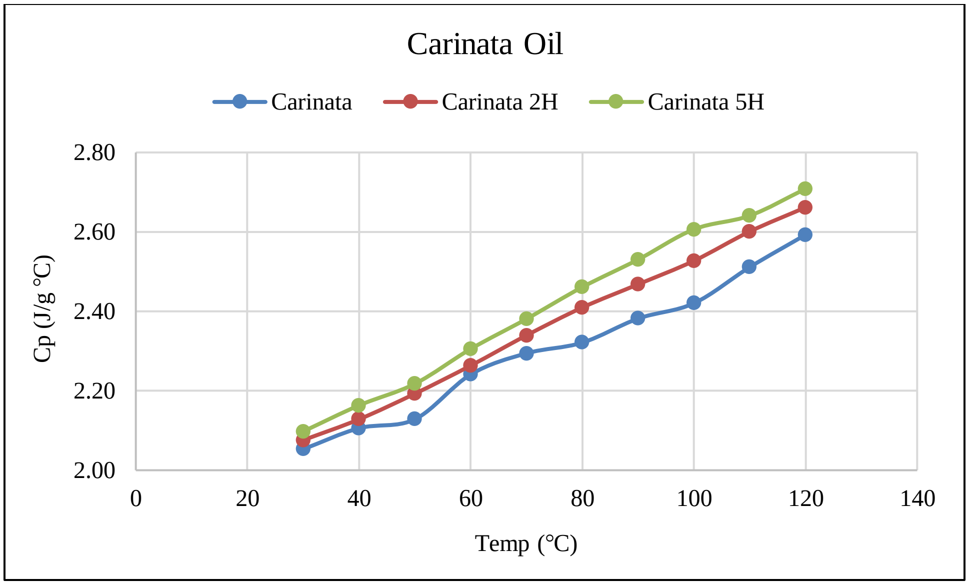
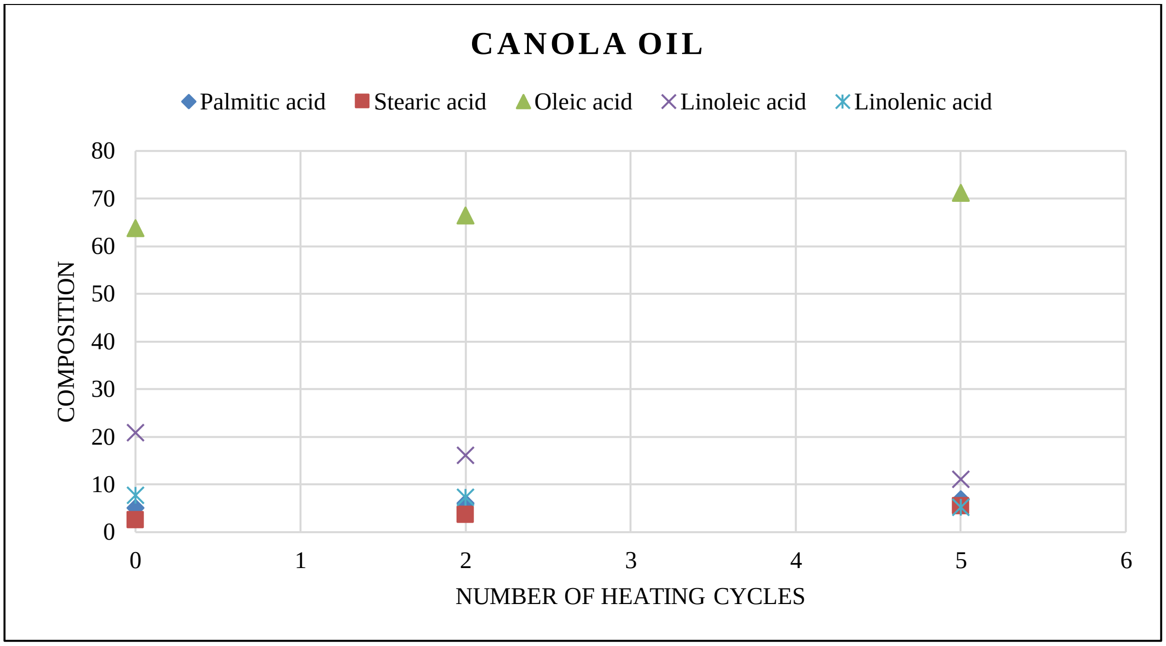


Figure 8-3 Heat capacities of carinata oil

8.2 Analysis Results

From the GC composition analysis for all oils, it was found that the fatty acid compositions in the oils changed with the heating cycles. The polyunsaturated fatty acids (PuFA) were seen to be decreasing with every cycle of heating, while the saturated (SFA) and monounsaturated fatty acids (MFA) were seen to be increasing. The change in composition of fatty acids at every heating stage is shown in Figure 8-4 below. The figures indicate the increment of palmitic, stearic and oleic acid with every heating cycle, while there is a significant decrement in linoleic, α-linolenic acid and also erucic acid in carinata oil. A formation of small amount of trans-isomer of linoleic acid was observed for 5H oil samples.



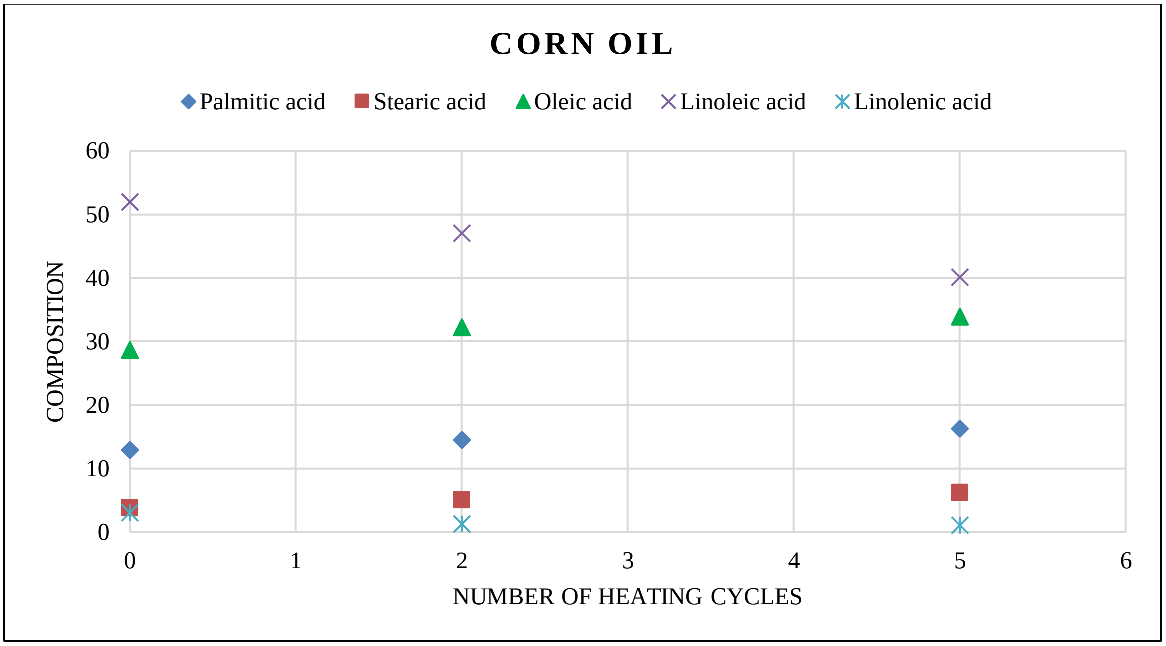


Figure 8-4 Composition changes for waste oils

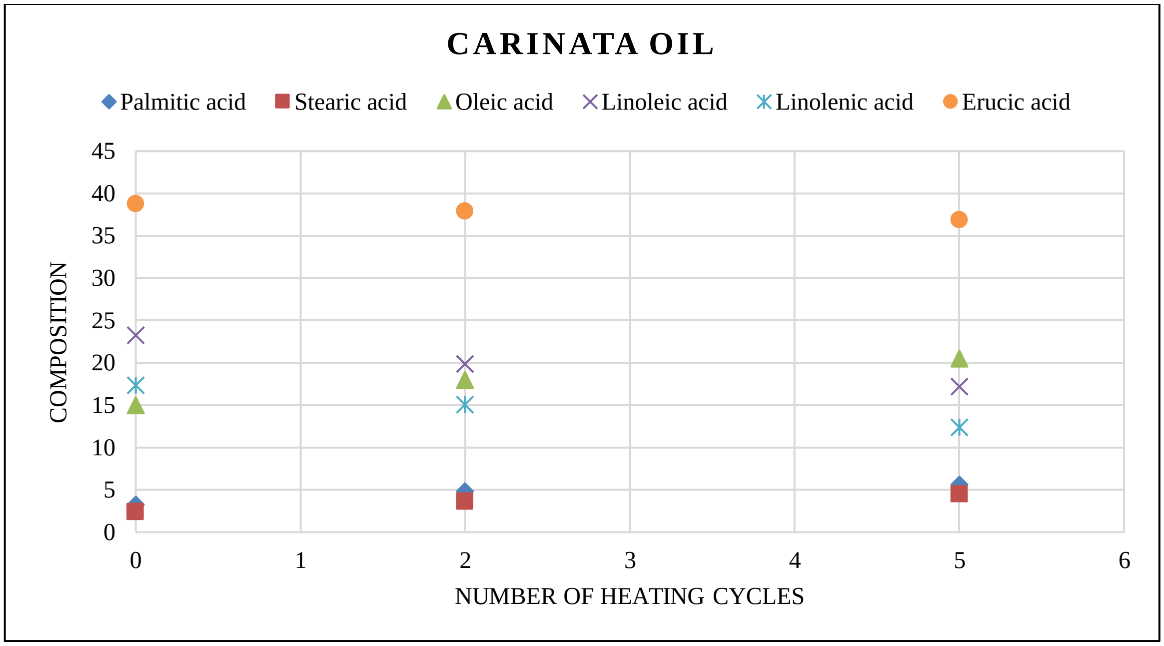


Figure 8-4 (continued)

8.3 Discussion

The oils used, canola, corn and carinata oils were observed to have increased heat capacities with every heating cycle. Further, the oil compositions were analyzed because heat capacity or any thermophysical property is a function of the compound structure and its composition. It was found that with every heating cycle, the composition of PuFA decreased, while that of SFA and MFA increased. From the observed pattern for change of composition, and also from some previously published literature [17, 48], the PuFA were expected to undergo saturation with every heating cycle, thus increasing the composition of MFA and SFA. From studying the pattern of change, it was found that the quantity of decreased PuFA was very close to the quantity of increased SFA and MFA after the heating cycle. This observation indicates a conservation of amount and can be attributed to conversion or breaking down of PuFAs to MFA and SFAs. Tables 8-4, 8-5 and 8-6 show the changing amount of FAs for all three oils. The decreased PuFA values include the quantities of linoleic and linolenic acids that decreased after every heating cycle. The increased

S.F.A values include the quantities of palmitic, stearic and oleic acids that increased along with the trans-linoleic acid that formed for the 5H stage only.

Table 8-4 Fatty acid change pattern in canola oil

Heating Stage	SFA increased (g)	PuFA decreased (g)
2H	4.64	4.99
5H	9.28	9.87

Table 8-5 Fatty acid change pattern in corn oil

Heating Stage	SFA increased (g)	PuFA decreased (g)
2H	6.48	6.63
5H	7.06	7.14

Table 8-6 Fatty acid change pattern in carinata oil

Heating Stage	SFA increased (g)	PuFA decreased (g)
2H	5.82	6.51
5H	6.37	6.46

Experimental calorimetry values show that heat capacities increased over successive heating cycles. It is postulated that the heat capacity alters with the physical structure of a molecular or the composition of the compound. To verify if the composition change was causing the heat capacity to increase and to verify the experimental values, the Rowlison- Bondi (RB) model and the Peng Robinson equation of state (PREOS) method on Aspen was used for the compositions obtained by GC analysis. Thus, as we see from the results, the heat capacities were increased by some degrees for the altering composition of used oils. The heat capacity of the oils used twice were more than that of the unused oils while, the values for the oils used five times were more than that for twice used oils. The calorimetry experiments were carried out at atmospheric pressure and over the range of temperature of 30 °C to 120 °C to study the behavior of an oil. For this work, the error percent or deviation of the RB model (group contribution method) and the PREOS method with respect to experimental values are listed for all three oils in the tables 8-4, 8-5 and 8-6 below. Canola oil's deviation or error percentages for the RB model and PREOS were up to 4.50% and 4.99% respectively. Corn oil's error percentages were up to 4.90% and 4.92% respectively. Lastly, carinata oil's error percentages were 4.95% and 4.92% respectively. The values calculated for RB model are shown in appendix B.3. Figures 8-5 through 8-13 show the deviations in a graphical format.

Table 8-7 Error percent of RB model and PREOS heat capacity values with respect to experimental values for canola oil

Temp (^oC)	Experimental	RB model	PREOS	Error[1]	Error[2]
30	2.3015	2.2367	2.2307	2.81	3.08
40	2.3575	2.2624	2.2701	4.03	3.71
50	2.3949	2.3028	2.3095	3.84	3.56
60	2.4391	2.3417	2.3522	3.99	3.56
70	2.4929	2.3932	2.3960	4.00	3.89
80	2.5497	2.4214	2.4409	4.66	4.27
90	2.5927	2.4428	2.4858	4.57	4.12
100	2.6570	2.4974	2.5328	4.93	4.67
110	2.7003	2.5348	2.5799	4.86	4.46
120	2.7618	2.5914	2.6248	4.44	4.96

Note: Error[1] is the error percentage or deviation of RB model C_p values w.r.t experimental values while Error[2] is the error percentage or deviation of PREOS C_p values w.r.t. experimental values.

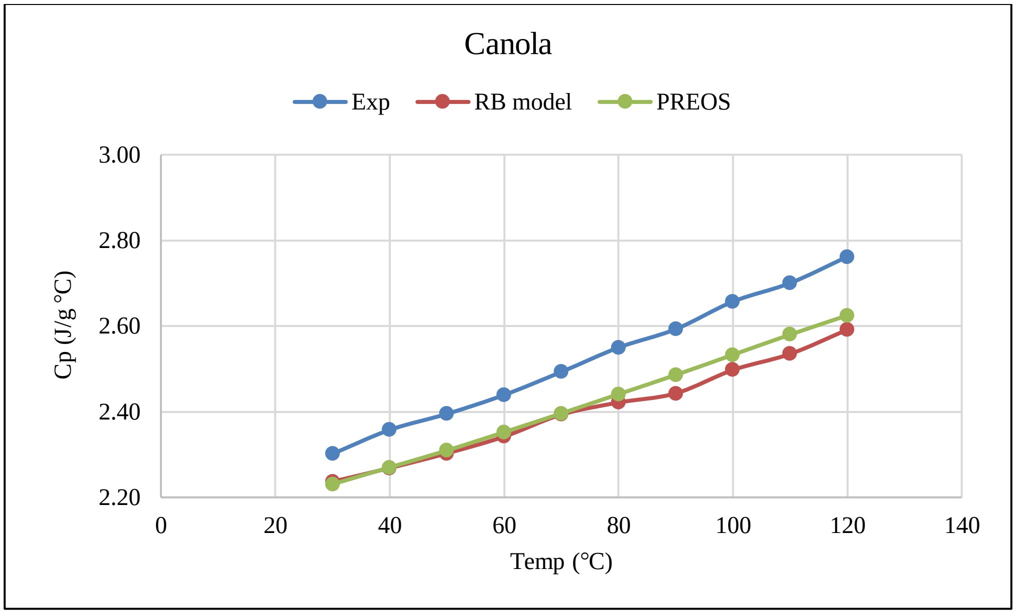


Figure 8-5 Deviation of experimental heat capacity values with respect to RB model and PREOS for canola oil

Table 8-8 Error percent of RB model and PREOS heat capacity values with respect to experimental values for canola 2H oil

Temp (°C)	Experimental	RB model	PREOS	Error[1]	Error[2]
30	2.3179	2.2492	2.2546	2.96	2.73
40	2.3464	2.2625	2.2916	3.58	2.33
50	2.3970	2.3096	2.3297	3.65	2.80
60	2.4488	2.3542	2.3700	3.86	3.21
70	2.4978	2.3903	2.4147	4.30	3.33
80	2.5653	2.4415	2.4615	4.82	4.04
90	2.6152	2.4993	2.5051	4.43	4.21
100	2.6606	2.5365	2.5508	4.67	4.13
110	2.7363	2.6085	2.5997	4.68	4.99
120	2.7867	2.6511	2.6634	4.87	4.42

Note: Error[1] is the error percentage or deviation of RB model C_p values w.r.t experimental values while Error[2] is the error percentage or deviation of PREOS C_p values w.r.t. experimental values.

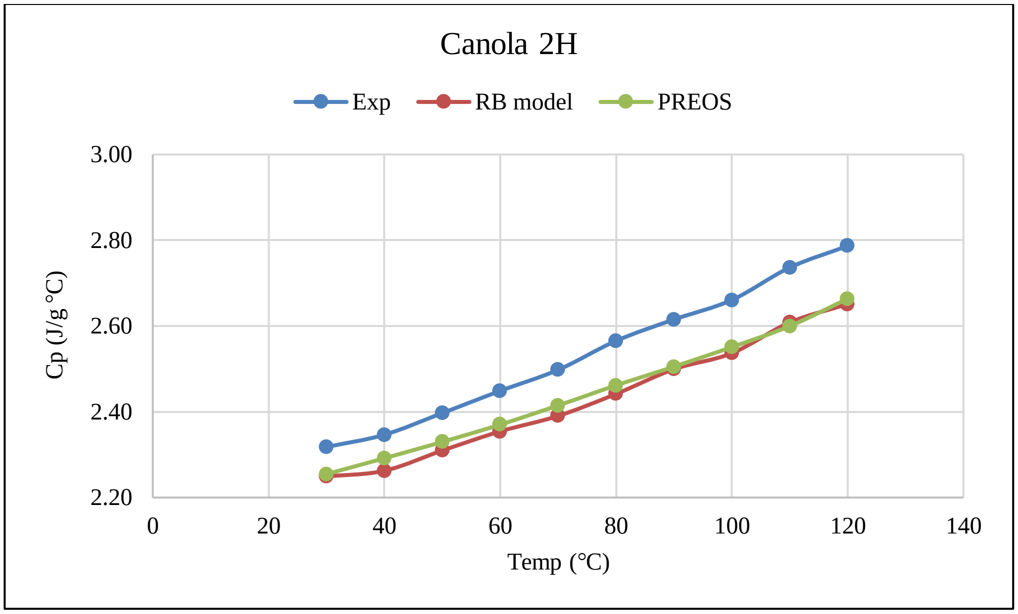


Figure 8-6 Deviation of experimental heat capacity values with respect to RB model and PREOS for canola 2H oil

Table 8-9 Error percent of RB model and PREOS heat capacity values with respect to experimental values for canola 5H oil

Temp (ºC)	Experimental	RB model	PREOS	Error[1]	Error[2]
30	2.3313	2.2602	2.2732	3.05	2.49
40	2.3722	2.2895	2.3156	3.48	2.38
50	2.4390	2.3669	2.3580	2.95	3.32
60	2.4850	2.4039	2.4053	3.26	3.21
70	2.5357	2.4376	2.4514	3.87	3.32
80	2.5893	2.4647	2.5035	4.81	3.31
90	2.6381	2.5129	2.5545	4.74	3.17
100	2.7112	2.5789	2.6042	4.88	3.94
110	2.7709	2.6364	2.6564	4.85	4.13
120	2.8357	2.6993	2.7061	4.81	4.57

Note: Error[1] is the error percentage or deviation of RB model C_p values w.r.t experimental values while Error[2] is the error percentage or deviation of PREOS C_p values w.r.t. experimental values.

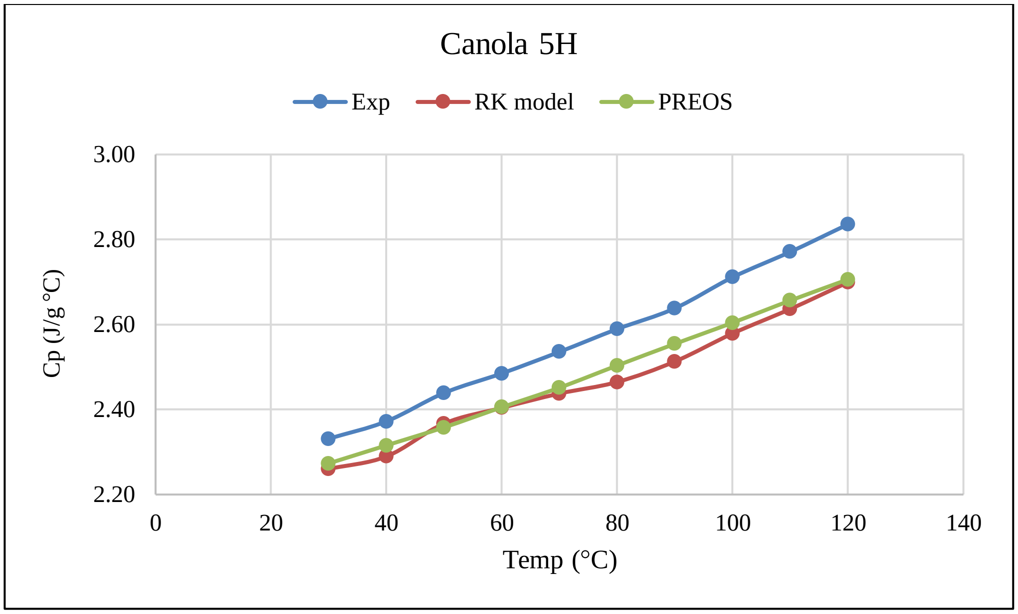


Figure 8-7 Deviation of experimental heat capacity values with respect to RB model and PREOS for canola 5H oil

Table 8-10 Error percent of RB model and PREOS heat capacity values with respect to experimental values for corn oil

Temp (°C)	Experimental	RB model	PREOS	Error[1]	Error[2]
30	2.2937	2.2448	2.2293	2.13	2.81
40	2.3688	2.2762	2.2723	3.91	4.07
50	2.4092	2.3071	2.3164	4.24	3.85
60	2.4512	2.3348	2.3606	4.75	3.70
70	2.4977	2.3765	2.4096	4.85	3.53
80	2.5595	2.4345	2.4623	4.88	3.80
90	2.6119	2.4914	2.5077	4.62	3.99
100	2.6406	2.5305	2.5628	4.17	2.95
110	2.7351	2.6094	2.6155	4.60	4.37
120	2.7681	2.6545	2.6658	4.10	3.70

Note: Error[1] is the error percentage or deviation of RB model C_p values w.r.t experimental values while Error[2] is the error percentage or deviation of PREOS C_p values w.r.t. experimental values.

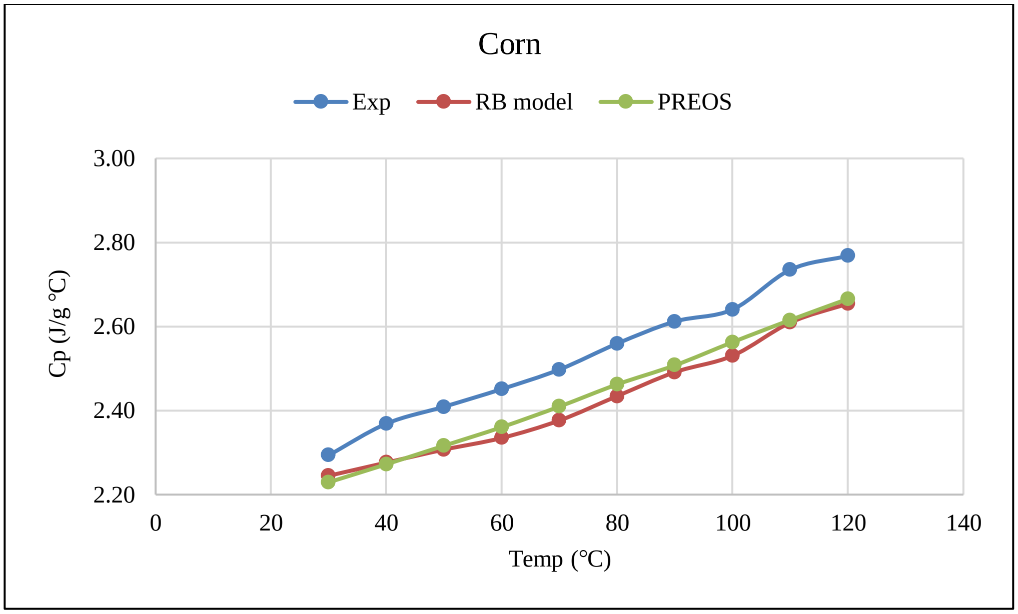


Figure 8-8 Deviation of experimental heat capacity values with respect to RB model and PREOS for corn oil

Table 8-11 Error percent of RB model and PREOS heat capacity values with respect to experimental values for corn 2H oil

Temp (°C)	Experimental	RB model	PREOS	Error[1]	Error[2]
30	2.3221	2.2575	2.2572	2.78	2.80
40	2.3586	2.3224	2.2996	1.53	2.50
50	2.3889	2.3491	2.3408	1.66	2.01
60	2.4622	2.3778	2.3845	3.43	3.16
70	2.5250	2.4158	2.4330	4.32	3.64
80	2.5674	2.4728	2.4828	3.69	3.30
90	2.6411	2.5190	2.5301	4.62	4.20
100	2.6938	2.5730	2.5810	4.49	4.19
110	2.7512	2.6162	2.6332	4.90	4.29
120	2.8089	2.6801	2.6830	4.58	4.48

Note: Error[1] is the error percentage or deviation of RB model C_p values w.r.t experimental values while Error[2] is the error percentage or deviation of PREOS C_p values w.r.t. experimental values.

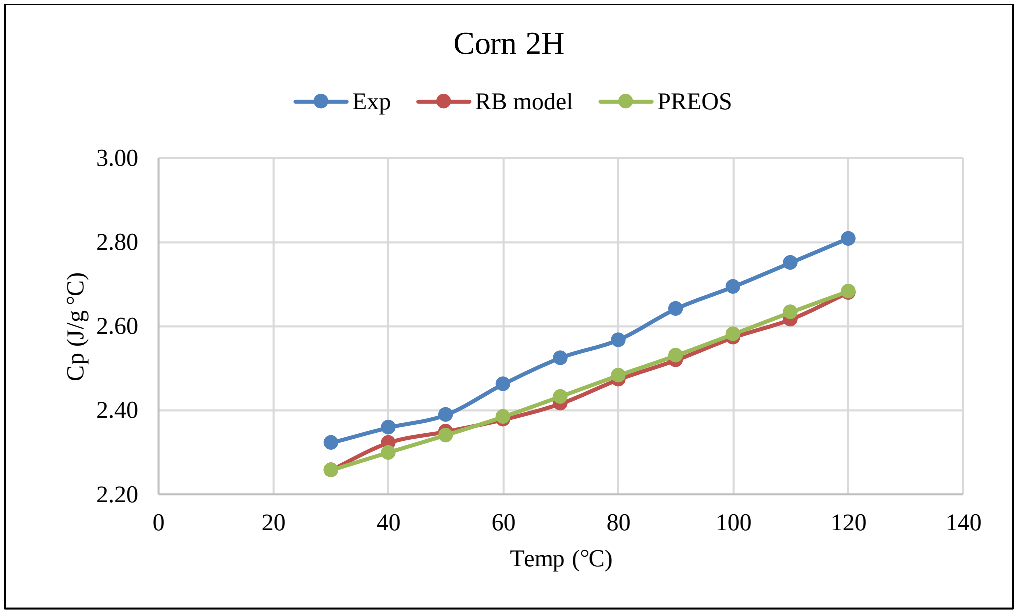


Figure 8-9 Deviation of experimental heat capacity values with respect to RB model and PREOS for corn 2H oil

Table 8-12 Error percent of RB model and PREOS heat capacity values with respect to experimental values for corn 5H oil

Temp (°C)	Experimental	RB model	PREOS	Error[1]	Error[2]
30	2.3366	2.2939	2.2866	1.83	2.14
40	2.3893	2.3179	2.3289	2.99	2.53
50	2.4234	2.3508	2.3712	3.00	2.15
60	2.4866	2.4071	2.4188	3.19	2.72
70	2.5490	2.4357	2.4665	4.44	3.23
80	2.6154	2.5082	2.5168	4.10	3.77
90	2.6802	2.5609	2.5698	4.45	4.12
100	2.7520	2.6214	2.6201	4.74	4.79
110	2.8107	2.6849	2.6744	4.47	4.85
120	2.8812	2.7423	2.7394	4.82	4.92

Note: Error[1] is the error percentage or deviation of RB model C_p values w.r.t experimental values while Error[2] is the error percentage or deviation of PREOS C_p values w.r.t. experimental values.

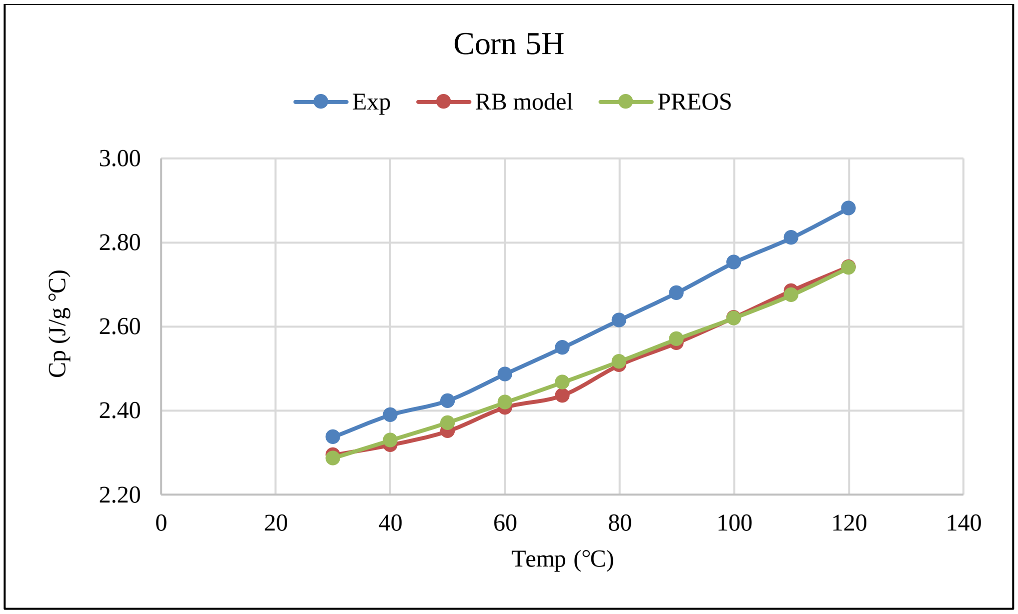


Figure 8-10 Deviation of experimental heat capacity values with respect to RB model and PREOS for corn 5H oil

Table 8-13 Error percent of RB model and PREOS heat capacity values with respect to experimental values for carinata oil

Temp (ºC)	Experimental	RB model	PREOS	Error[1]	Error[2]
30	2.0530	1.9869	1.9958	3.22	2.78
40	2.1058	2.0158	2.0483	4.27	2.73
50	2.1283	2.0339	2.0980	4.44	1.42
60	2.2411	2.1443	2.1491	4.32	4.11
70	2.2943	2.1895	2.2015	4.57	4.05
80	2.3212	2.2136	2.2553	4.64	2.84
90	2.3818	2.2639	2.3104	4.95	3.00
100	2.4203	2.3216	2.3668	4.08	2.21
110	2.5112	2.4007	2.4220	4.40	3.55
120	2.5927	2.4956	2.4744	3.75	4.56

Note: Error[1] is the error percentage or deviation of RB model C_p values w.r.t experimental values while Error[2] is the error percentage or deviation of PREOS C_p values w.r.t. experimental values.

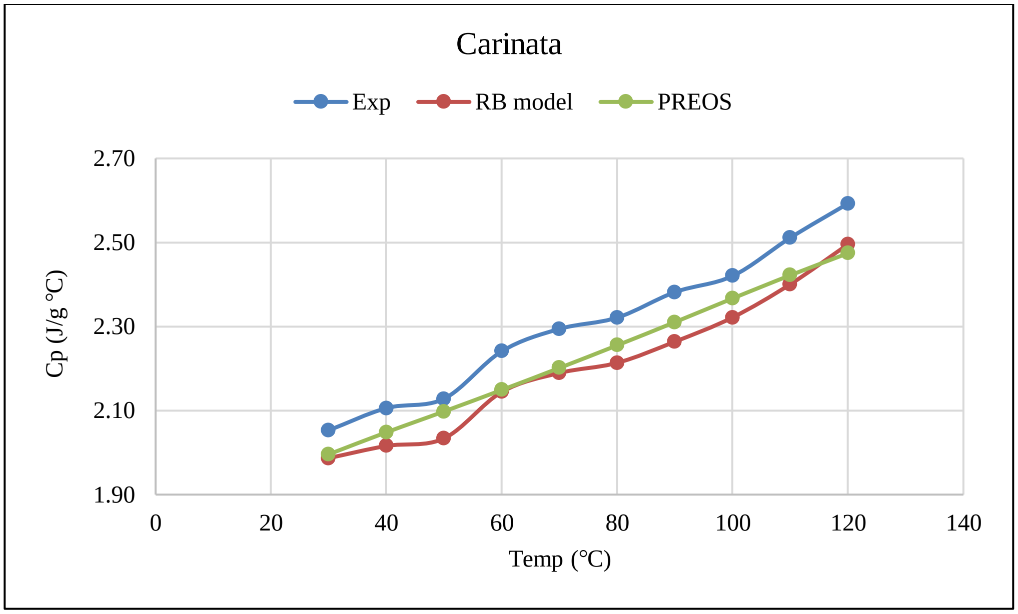


Figure 8-11 Deviation of experimental heat capacity values with respect to RB model and PREOS for carinata oil

Table 8-14 Error percent of RB model and PREOS heat capacity values with respect to experimental values for carinata 2H oil

Temp (°C)	Experimental	RB model	PREOS	Error[1]	Error[2]
30	2.0758	1.9932	1.9966	3.98	3.82
40	2.1282	2.0854	2.0499	2.01	3.68
50	2.1927	2.1327	2.0999	2.74	4.23
60	2.2634	2.1845	2.1646	3.49	4.37
70	2.3395	2.2399	2.2292	4.26	4.71
80	2.4096	2.2985	2.2971	4.61	4.67
90	2.4680	2.3491	2.3618	4.82	4.30
100	2.5271	2.4041	2.4265	4.87	3.98
110	2.6009	2.4807	2.4943	4.62	4.10
120	2.6616	2.5463	2.5606	4.33	3.80

Note: Error[1] is the error percentage or deviation of RB model C_p values w.r.t experimental values while Error[2] is the error percentage or deviation of PREOS C_p values w.r.t. experimental values.

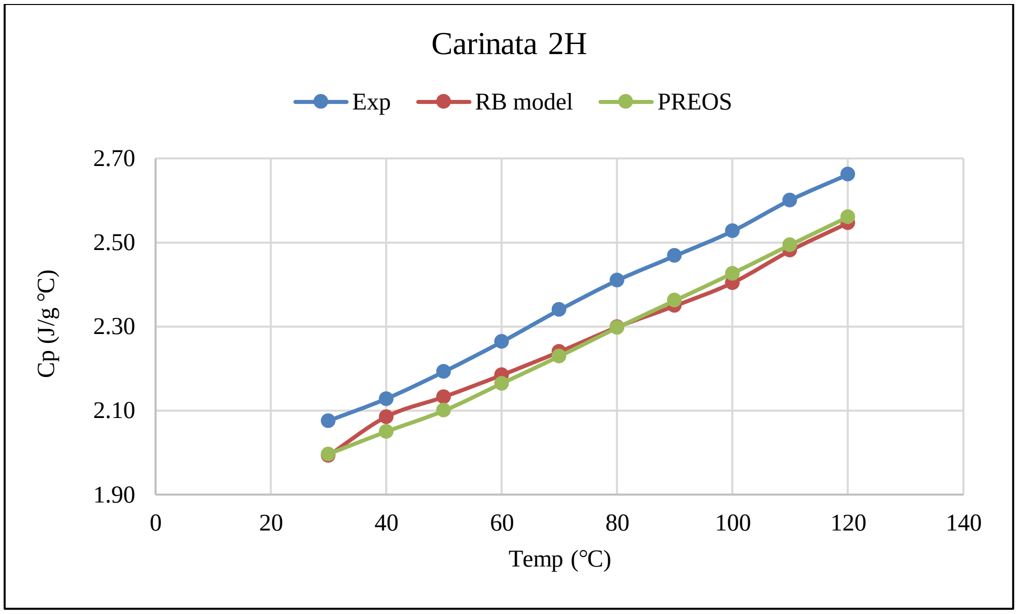


Figure 8-12 Deviation of experimental heat capacity values with respect to RB model and PREOS for carinata 2H oil

Table 8-15 Error percent of RB model and PREOS heat capacity values with respect to experimental values for carinata 5H oil

Temp (ºC)	Experimental	RB model	PREOS	Error[1]	Error[2]
30	2.0977	2.0207	2.0383	3.67	2.83
40	2.1633	2.0804	2.0995	3.83	2.95
50	2.2176	2.1270	2.1310	4.08	3.91
60	2.3053	2.2068	2.1959	4.27	4.75
70	2.3808	2.2804	2.2641	4.22	4.90
80	2.4610	2.3636	2.3524	3.96	4.41
90	2.5303	2.4162	2.4059	4.51	4.92
100	2.6064	2.4834	2.4824	4.72	4.76
110	2.6408	2.5446	2.5424	3.64	3.72
120	2.7084	2.6167	2.6107	3.39	3.61

Note: Error[1] is the error percentage or deviation of RB model C_p values w.r.t experimental values while Error[2] is the error percentage or deviation of PREOS C_p values w.r.t. experimental values.

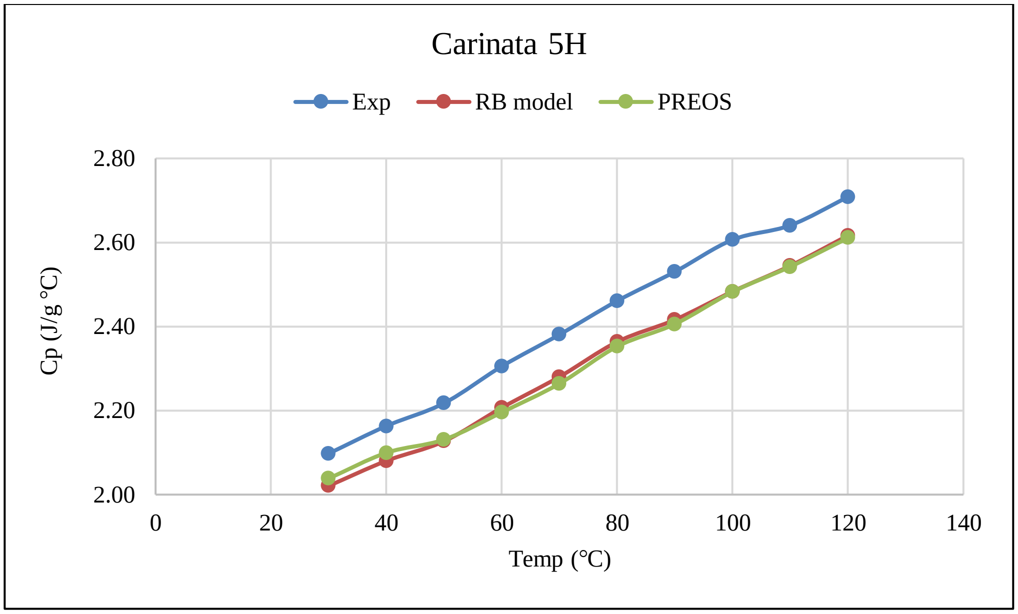


Figure 8-13 Deviation of experimental heat capacity values with respect to RB model and PREOS for carinata 5H oil

Additionally, it is observed that the heat capacity goes on increasing at higher temperature. This observation can be verified by using the conclusion from the literature experiment of oil and water. For oil, the rise in temperature is gradual at initial level while the heat makes the oil less viscous. Subsequently, as the oil becomes relatively less viscous the heating and temperature rise becomes greater at higher temperatures. Therefore, the error percent is observed to be greater towards higher temperatures. Another reason is that the models only ascertain for ideal compositions or structures, qualities and operating as well as surrounding conditions without taking into consideration any practical anomalies or uncertainties. Therefore, some error is expected to exist as the qualities determined by different strategies vary due to different methods and models used. Also, the quality and the quantity of sample used to study affects the derived values. The heat capacity of an oil therefore can be said to be changing simultaneously with temperature and composition. The difference may or may not be that significant as it is observed that the heat capacity for any edible oil lies in the range of 2.3 J/g ^{o}C to 2.8 J/g ^{o}C whereas the oil that is used to make jet fuel is slightly lower compared to edible oils and lies within 2.0 J/g ^{o}C to 2.7 J/g ^{o}C.

As it was discussed earlier in physical property estimations, a substance’s its structure and composition contribute distinctively in determining the properties. Thus, change in heat capacity can be attributed to the change in fatty acid composition of the oils after use. In addition to this, since the used oils are more saturated than the unused oils, they can be expected to produce biofuel with relatively higher oxidative stability.

CHAPTER 9: CONCLUSIONS AND FUTURE WORK

On the basis of the calorimetry and composition analysis results given and verification carried out using mathematical model by Rowlison-Bondi and Peng Robinson equation of state method and after interpreting the results, conclusions can be deduced as follows.

9.1 Conclusions

The study on determining whether the heat capacities for waste oil changes with respect to unused oil was carried out. Two vegetable oils, canola and corn oils that are commonly and popularly used in kitchens across households and restaurants and an inedible oil, carinata oil, were taken into consideration for this purpose. Thus, all three oils in three different forms were studied viz unused, twice used/heated (2H) and five times used/heated (5H) and results were listed. As per the results, the heat capacity changes as the oil is heated and is reported to increase with an increase in number of times the oil has been used. Though the C_p for used oil is more than that of the unused oil, the increase in these values were within acceptable ranges. It is assumed and theorized that the changes in the heat capacity are a result of change composition of the oil as compared to their original composition; attributing to the actualization done by *Poling, Prausnitz and O'Connell* in their book [26] that physical properties of a liquid or any substance are a significant function of the compound structure, intermolecular forces and bonding. Further to confirm the extent of composition change in oils, GC-MS analysis for all the oils was carried out and was essentially found that the composition of oils does change significantly with every heating cycle. The SFA and MFA were observed to increase while the PuFA were observed to decrease. This can be explained as the PuFA undergo saturation and to form relatively saturated FA and break down to lower molecular fatty acids. Thus, the increase in heat capacity is a function of increasing temperature as well as changing composition on reheating the oils.

9.2 Future Work

The study on changing heat capacities and the composition for waste oils as compared to unused oils serves a good motivation for further work on this project. To further inspect the pattern and reason behind changing heat capacities, the fatty acids comprising the oil can be studied in depth. Although the mathematical models give a fair validation to experimental results, they cannot be held completely reliable. As the parameters of acentric factor and reduced temperature needed to mathematically calculate the heat capacities may have deviations; the values generated using the calculation methods cannot be held accountable to verify the experimental results entirely. In order to further understand the changing heat capacities for reheated oils, the components of oil could be focused to study. The calorimetry for individual and desired composition mixture of fatty acids can be expected to indicate an insight on the thermodynamic property of oils and the alteration on subject to reheating.

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APPENDIX A: NOMENCLATURE

SFA: Saturated Fatty Acids

MFA: Monounsaturated Fatty Acids

PuFA: Polyunsaturated Fatty Acids

DSC: Differential Scanning Calorimeter

Un. O: Unused Oil

2H: Twice Used Oil

5H: Five times Used Oil

RB: Rowlison-Bondi

PREOS: Peng Robinson equation of state

w.r.t: with respect to

H_r: Integrated heat for a blank run

H_s: Integrated heat for a sample run

ΔT: Temperature ramp

W: Weight of the sample

APPENDIX B: CALCULATIONS

B.1 Fatty Acid Composition in Purchased Oils

The oils bought from the local grocery store for experimental purpose did not have the percent composition for a specific fatty acid but the total amount of saturated, monounsaturated and polyunsaturated fatty acids as a category on whole present in grams was printed in the nutritional facts, shown in tables B-1 and B-2 below.

Table B-1 Nutritional fact for canola oil based on container (from [11])

Total fat	14 g
Saturated fat	2 g
Monounsaturated fat	8 g
Polyunsaturated fat	4 g

Note: The fat amount specified above is for 1 serving size of 1 tbsp = 14 g

Table B-2 Nutritional fact for corn oil based on container (from [11])

Total fat	14 g
Saturated fat	2 g
Monounsaturated fat	4 g
Polyunsaturated fat	8 g

Note: The fat amount specified above is for 1 serving size of 1 tbsp = 14 g

The amount under each category of fatty acid was converted into percentage. The number so obtained was the total weight percent of that particular category of fatty acid.

Canola oil consists of, total Fat = 14g

Saturated fat = 1g

This 1g was converted to percent as: x= (1/14)* 100 = 14.28%

Similarly, Monounsaturated fat= 8g ; Therefore, (8/14)* 100 = 57.14%

Polyunsaturated fat= 4g ; Therefore, (4/14) *100 = 28.57%

Container based compositions in tables 3-1 and 3-2 were calculated by following these steps.

Next, under each category, these total percent were used to calculate the percent of each fatty acid under the corresponding category by assuming the same ratio as that of the literature composition.

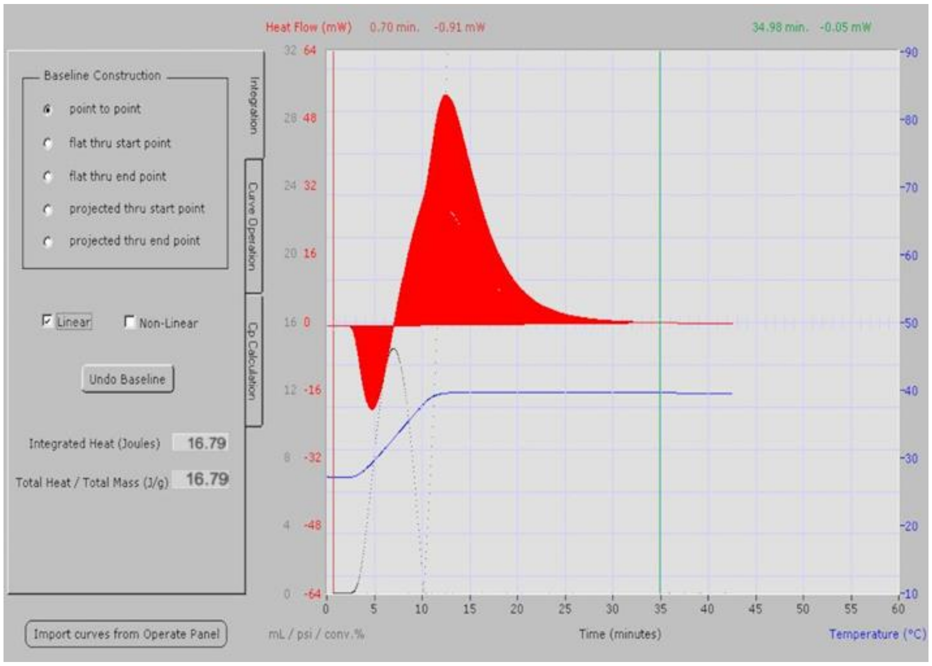
B.2 Calculating Experimental Heat Capacity

Looking at the analyzed curve on the calorimeter, the integrated heat for a blank vial at 40 °C is -21.63 J/ °C and that for the unused oil sample is 77.51 J/ °C. The values so generated at by ramping the temperature by 10 °C in every sampler run. The weight of the sample used is 4g.

So, by plugging these values in the formula noted-

$Q_r = H_r / \Delta T$ (J/ °C) = (16.79/10) = 1.679 J/ °C

$Q_t = H_t / \Delta T$ (J/ °C) = (-77.51/10) = -7.751 J/ °C

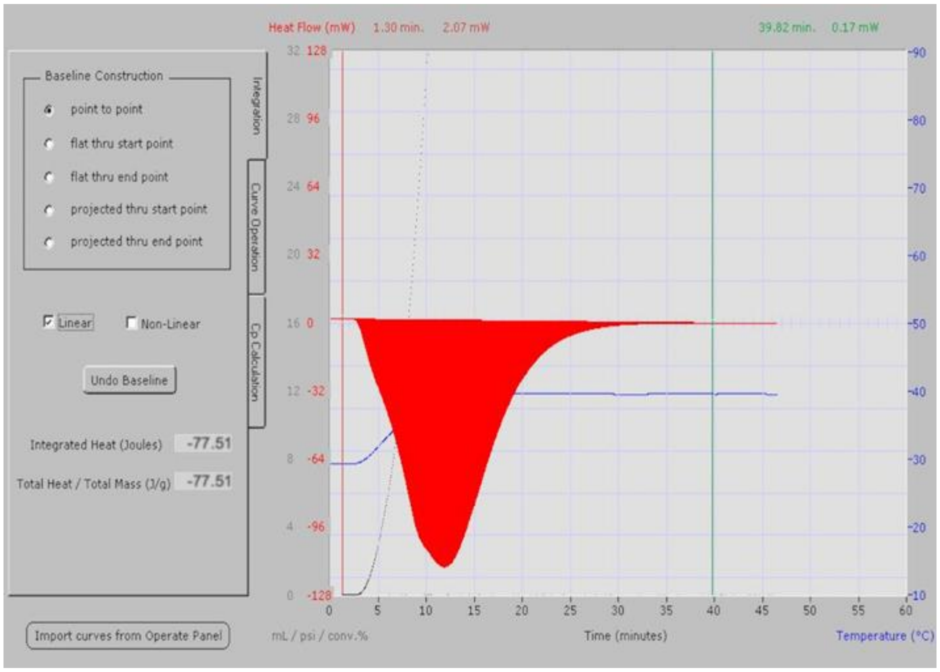


Baseline Construction
● point to point
○ flat thru start point
○ flat thru end point
○ projected thru start point
○ projected thru end point

☑ Linear ☐ Non-Linear

Integrated Heat (Joules) 16.79
Total Heat / Total Mass (J/g) 16.79

Figure B-1 Integrated heat curve for blank run


Baseline Construction

- ● point to point
- ○ flat thru start point
- ○ flat thru end point
- ○ projected thru start point
- ○ projected thru end point

☑ Linear ☐ Non-Linear

Integrated Heat (Joules) -77.51

Total Heat / Total Mass (J/g) -77.51

Figure B-2 Integrated heat curve for sample run

$C_p = (Q_t - Q_r) / W_s$

$= -2.3575$ J/g ^{o}C

Tables 8-1, 8-2 and 8-3 were developed by calculating the corresponding values by using these formulae.

The heat capacities for all the samples of unused and waste oils were calculated in similar manner and listed in the table. Now the integrated heat value for blank runs are positive indicating heat absorbed by the system. While for sample runs the integrated heat is negative indicating the system is losing heat as temperature is increasing. Since after calculation, the final heat capacity is negative, heat capacity can never be negative. But is only a sign convention showing the heat is released from the system as temperature increases [14].

B.3 Rowlison-Bondi Model Based Heat Capacity Calculation

This method uses the contribution of every hydrocarbon group in a compound. The heat capacity constants for each group are listed in the paper by Rihani and Doraiswamy [12]. The necessary values for the groups under consideration for the purpose of this project are given in table B-3. A sample calculation for calculating the heat capacity constants for Palmitic acid has been shown below:

Palmitic acid is $C_{16}H_{32}O_2$. The structure is made of one $-CH_3$ group, fourteen $-CH_2$ groups and one -COOH group. Next, taking into consideration the values listed for each of these groups.

Table B-3 Heat capacity constants (from [12])

Group	a	b * 10^2	c * 10^4	d* 10^6
$-CH_3$	0.6087	2.1433	-0.0852	0.001135
$-CH_2$	0.3945	2.1363	-0.1197	0.002596
-COOH	1.4055	3.4632	-0.2557	0.006886

Now calculating ‘a’, ‘b’, ‘c’ and ‘d’ for Palmitic acid:

$a= (1* 0.6087) + (14*0.3945) + (1*1.4055) \quad = 7.5372$

$b= (1*2.1433*10^{-2}) + (14*2.1363*10^{-2}) + (1*3.4632*10^{-2}) \quad = 0.3551$

$c= (-0.0852*10^{-4}) - (14*0.1197*10^{-4}) - (1*0.2557*10^{-4}) \quad = -2.0167*10^{-4}$

$d= (0.001135*10^{-6}) + (14*0.002596*10^{-6}) + (0.006886*10^{-6}) \quad = 4.4365*10^{-8}$

Further, some additional data is required to calculate the heat capacity.

Table B-4 Palmitic acid additional data required for heat capacity calculation

Critical Temperature, T_c (K)	799.88
Acentric factor, ω	1.109
Molecular weight, MW (g/mol)	256.42
Correction factor, Fc	-0.27
Universal constant, R (J/mol K)	8.314

For instance, we calculate the heat capacity for 40 ^{o}C;

T = 40 ^{o}C = 313 K,

T_r (reduced temperature) = T/T_c= 0.39,

Using the heat capacity formula: $C_p = a + bT + cT^2 + dT^3$, and

Ideal gas specific heat capacity,

$C_p^o = (7.5372) + (0.3551*313) + (-2.0167*10^{-4}*313^2) + (4.4365*10^{-8}*313^3)$

= 100.30 cal/mol K

= 419.96 J/mol K

Final specific heat capacity is calculated by rearranging the formula stated by to solve for C_p,

$(C_p - C_p°) /R = 1.45+ 0.45 (1 -T_r)^{-1}+ 0.25\omega [17.11+ 25.2 (1 - T_r)^{1/3} T_r^{-1}+ 1.742 (1 -T_r)^{-1}]$,

Rearranging and solving this formula for C_p at 40 ^{o}C;

$C_p= \{1.45 + 0.45 (1 -T_r)^{-1} + 0.25\omega [17.11+ 25.2 (1 - T_r)^{1/3} T_r^{-1}+ 1.742 (1 -T_r)^{-1}]\}*R + C_p°$

$C_p= \{1.45+ 0.45(1-0.39)^{-1} + 0.25*1.109* [17.11+25.2*(1-0.39)^{1/3}0.39^{-1} + 1.742* (1-0.39^{)-1}]\} *8.314 + 419.96$

=596.21 J/mol K

Hence, Palmitic acid C_p = 596.21/256.42 =2.33 J/g K

In similar way, heat capacities for other fatty acids of the oil, that is stearic acid, oleic acid, linoleic acid and alpha- linolenic acid were calculated for the temperature range of 30 ^{o}C to 120 ^{o}C.

Now another sample calculation for the heat capacity of the oil based on the component heat capacities at that temperature and weight percent composition:

Table B-5 Weight composition, mass fraction and heat capacities for composing fatty acids of canola oil at 40 °C

Fatty acid	Weight composition	Number of moles	Mass fraction	C_p (J/g °C)
Palmitic acid	5.11	0.02	0.04	2.3271
Stearic acid	2.52	0.01	0.02	2.3308
Oleic acid	63.79	0.22	0.61	2.3104
Linoleic acid	20.91	0.07	0.22	2.2507
Linolenic acid	7.79	0.03	0.10	2.2423

Number moles = weight of the component/ molecular weight= 4/256.42= 0.02

Mass fraction = number of moles/ total number of moles

= 0.02/ (0.02+0.01+0.22+0.07+0.03) =0.02/ 0.35 = 0.057

C_p for Canola oil at 40 °C by

= (2.3271*0.04) + (2.3308*0.02) + (2.3104*0.61) + (2.2507*0.22) +(2.2423*0.1)

= 2.2684 J/g °C

The RB model values for all oils from tables 8-7 to 8-15 were calculated similarly.

B.4 Calculating Error Percent

As a sample calculation for the error percentages in tables 8-7 to 8-15 is shown below. Keeping it consistent, again Canola oil at 40 °C is considered. The heat capacity values for Canola oil at 40 °C by all three methods are listed in the table below.

Table B-6 Sample calculation for error percent for heat capacities of canola oil at 40 °C by different methods

Temp (°C)	Experimental	RB model	PR method	Error[1]	Error[2]
40	2.3575	2.2624	2.2701	4.03	3.71

Error percent = ((Expected value- Achieved value) / Expected value) * 100

Hence, for RB model, error percent = ((2.3575-2.2624) / 2.3575) * 100 = 4.03%

For PRWS, error percent = ((2.3575-2.2701) / 2.3575)*100 = 3.71%

B.5 Procedure Related Error

For the *weight of sample*, the expected weight was 4 g and most of the samples were weighed to 4 g, there was some inconsistency while weighing some of the samples. A maximum error in weighed tolerated was +0.05 g

Hence the error percent for samples is,

((Expected value- Achieved value) / Expected value) * 100

= ((4-4.05) / 4) * 100 = -1.25%

For *weight of vials*, it is recommended that both vials, reference and sample, have the same weight for more accuracy. Though during this project, the two vials used as sample vial and reference vials were kept the same for consistency, but it was noticed that their weights were not exactly the same. The starting weight of sample vial was 13.642 g while that of reference vial was 13.639 g.

Hence the error percentage in the difference of weights between reference and sample vial weights is

= ((13.642-13.639) / 13.642) * 100 = 0.02%

For ramp temperature difference, the project involved heating run of oil from 20 ^{o}C to 120 ^{o}C and each of these runs consisted for 10 ^{o}C ramps. That is, for example a ramp would starts at 30 ^{o}C and end at 40 ^{o}C. Even though, it was noticed that the calorimeter temperature reading was not exactly starting at 30 ^{o}C and ending at 40 ^{o}C. The actual calorimeter temperatures read 29.6 ^{o}C and 39.5 ^{o}C thus making the temperature difference to be 9.9 ^{o}C. This error can be attributed to the calorimeter controller error. The difference between initial and final value of temperature, that is the ramp size deviated by ±0.3 ^{o}C from actual desired ramp size of 10 ^{o}C. The measured ramp size varied from 9.7 ^{o}C to 10.2 ^{o}C. Hence, the ramp size error for temperature difference is

= ((10-9.7) / 10) * 100 = 3% or ((10-10.2) / 10) * 100= -2%

Table B-7 below lists all the procedure related errors that were encountered throughout the project also the difference values mentioned above remained the same in between every ramp and did not deflect more than the numbers mentioned.

Table B-7 List of unavoidable errors encountered while performing experiments

Error Type	Percentage
Weight of sample	-1.25%
Weight of vials	0.02%
From start to end	0.08%
In between runs	0.01%
Ramp Temperature Difference	±3 %

B.6 C_p Calculation Error Propagation

The relation used for calculating C_p is as stated earlier- $(\Delta Q/ \Delta T)$

$$C_p = ((C_{pt}- C_{pr})/ W_s)$$

$$= ((Q_t/ \Delta T- Q_r/ \Delta T)/ W_s)$$

$$= (Q_t- Q_r)/ (\Delta T* W_s)$$

Table B-8 List of approximated and measured parameters

Variable	Approximated values	Measured to
ΔT (°C)	10	±0.3 °C
W_s (g)	4	+0.05

Q_t and Q_r are not considered as variables since those are the integrated the heat curve values generated by WinCRC software that is equipped with the calorimeter. To do the error propagation, method specified in the book Applied Mathematics in Chemical Engineering [reference] was used. The expression for propagation of error is as follows-

Desired quantity is related to several directly measured quantities as M = gamma $(m_1, m_2\ldots m_n)$

The most probable values of M (with errors) is denoted by Z = gamma $(z_1, z_2,\ldots.z_n)$

The differential changes in each of z gives an overall change of Z and is expressed as-

$\Delta Z = (\partial gamma/ \partial z_1).\Delta z_1 + (\partial gamma/\partial z_2). \Delta z_2 + \ldots. +(\partial gamma/ \partial z_n). \Delta z_n$

Following this equation for Cp relation-

$(\partial C_p/\partial \Delta T) = -(Q_t-Q_r)/ (W_s. \Delta T^2)$

$(\partial C_p/\partial \Delta Ws) = -(Q_t-Q_r)/ (W_s^2. \Delta T)$

To obtain maximum error,

$(\Delta C_p)_{max} = (-(Q_t-Q_r)/ (W_s. \Delta T^2)) * \Delta(\Delta T)) -(Q_t-Q_r)/ (W_s^2. \Delta T)) * \Delta W_s)$

$= (-(-77.51 – 21.63) / 4 * 10^2) * \Delta(\Delta T)) – ((-77.51 – 21.63) / 4^2 * 10) * \Delta W_s)$

$= -(-0.2357 * \Delta(\Delta T)) - (-0.5893 * \Delta W_s)$

$= (0.2357* 0.3) + (0.5893 * 0.05)$

$=0.1001$

Here $\Delta(\Delta T)$ and ΔW_s are the measurement up to deviations and are taken in positive to obtain maximum probable error.

Approximate C_p for this set of numbers is-

$= (-77.51 – 16.79)/ (4 * 10)$

$= -2.3575$

The negative value of C_p indicated the heat lost by the system as the temperature increases.

Hence, the maximum percentage error is

$= \pm (\Delta C_{pmax}/ C_p) * 100$

$= \pm (0.1001/2.3575) * 100$

$= \pm 4.25 \%$

B.7 Composition Analysis Calculation

A sample calculation for mass% and mole % composition of canola oil from table 7-3 is shown below. Compositions for all oils were calculated similarly.

Table B-9 Canola oil composition

		Canola				
	Molecular Weight (g/mol)	Area	Mass %	Amount of FA	No. Of moles	Mole %
Palmitic acid	270	4367636	5.11	5.11	0.0189	5.56
Stearic acid	298	2151620	2.52	2.52	0.0084	2.48
Oleic acid	296	54509562	63.79	63.79	0.2155	63.26
Linoleic acid	294	17864478	20.91	20.91	0.0711	20.87
Linolenic acid	292	6653373	7.79	7.79	0.0267	7.83
Internal Standard (IS)		33483797				
Total (w/o IS)		85447320	100.12	100.12	0.3407	100

Amount of oil sample weighed = 100mg

Amount of internal standard added= 20 mg

Internal Response factor (IRF) = [area$_{is}$ X amount$_{s}$]/ [amount$_{is}$ X area$_{s}$]

= [33483797 * 100]/[20 * 85447320]

= 1.96

Mass % of methyl esters = [area of methyl ester/ total area w/o IS] *100

For eg- mass % of methyl palmitate = [4367636/85447320] * 100

= 5.11%

Amount of fatty acid methyl ester = [amount$_{is}$ X area$_{s}$ X IRF]/ area$_{is}$

= [20 * 4367636 * 1.96]/ 33483797

= 5.11 mg

No. of moles = [Amount of fatty acid methyl ester/molecular weight]

= [5.11/ 270]

= 0.0189

Mole % = [no. of moles/ total no. of moles] * 100

= 5.56 %

Tables 7-3, 7-4 and 7-5 were developed by following these formulae and calculations.

The pattern to determine change in composition was calculated using mass composition from tables 7-3 to 7-5. The tables 8-3 to 8-6 were developed by simple subtraction of weights of fatty acid groups at every heating stage. Sample calculation for canola oil is shown below. Since saturated and monounsaturated fatty acids are increasing,

Amount of SFA/MFA fatty acid increased at 2H heating cycle =

(SFA/MFA in canola 2H) – (SFA/MFA in canola)

= (6.05 + 3.62 + 66.39)g – (5.11+ 2.52 + 63.79)g = 4.64 g

Amount of PuFA fatty acid decreased at 2H heating cycle =

(PuFA in canola) – (PuFA in canola 2H)

= (20.91 + 7.79)g – (16.34 + 7.37)g = 4.99g

APPENDIX C: ADDITIONAL FIGURES

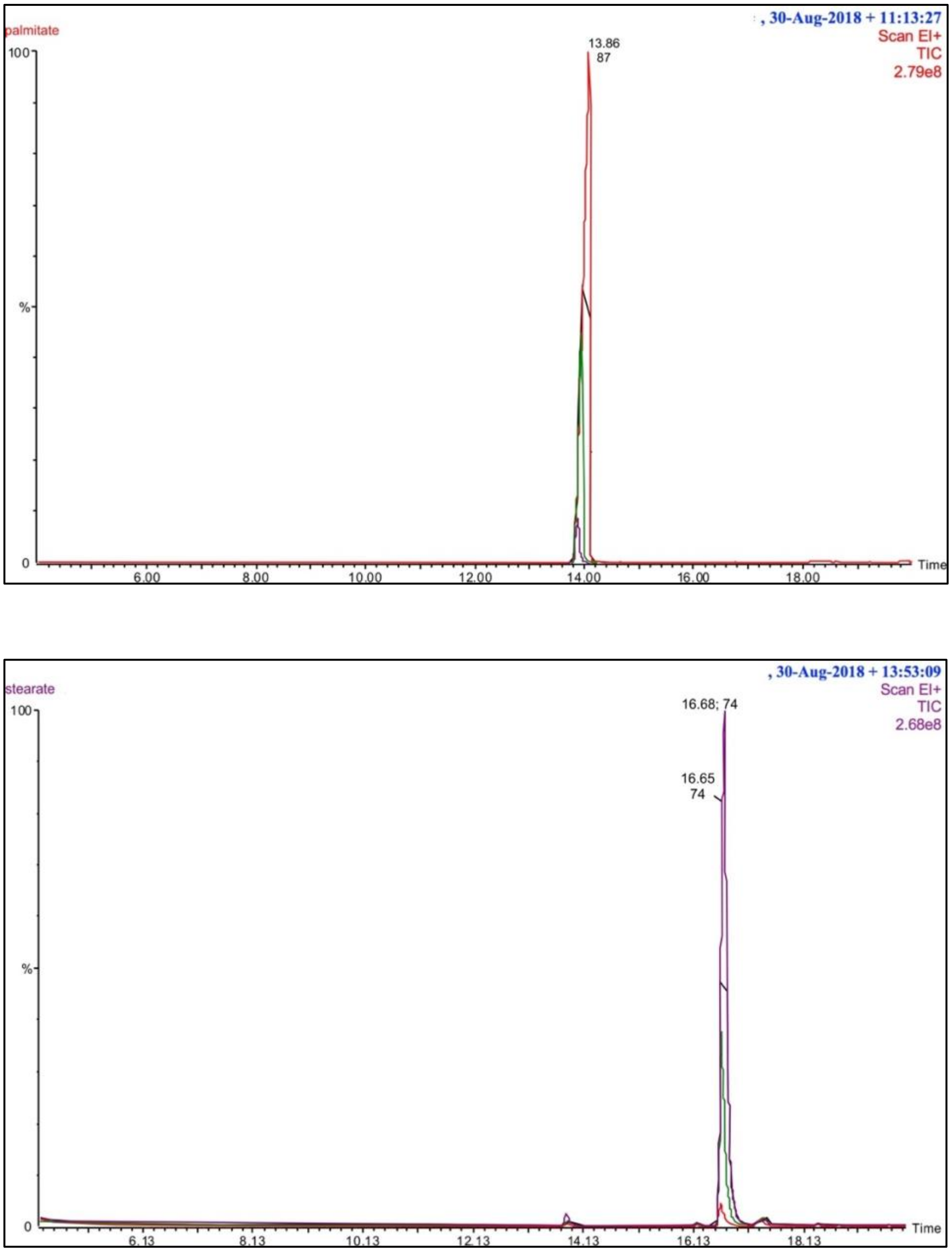
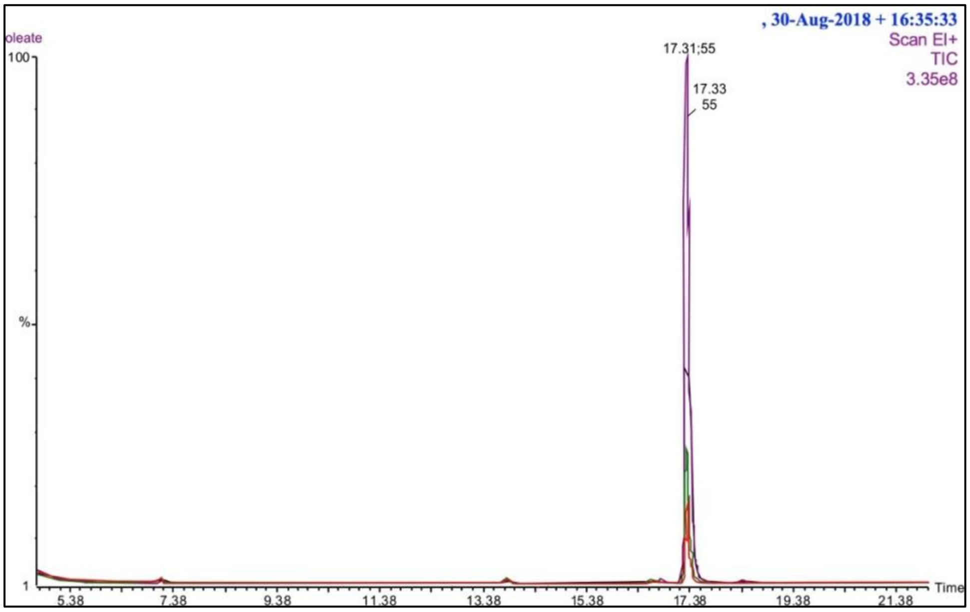
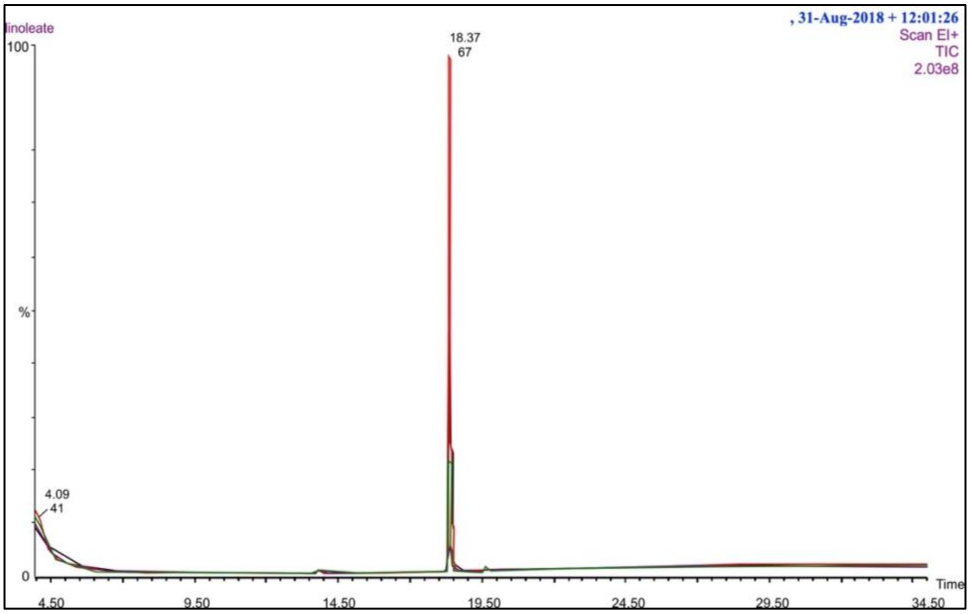


Figure C-1 Methyl ester standards calibration chromatograms





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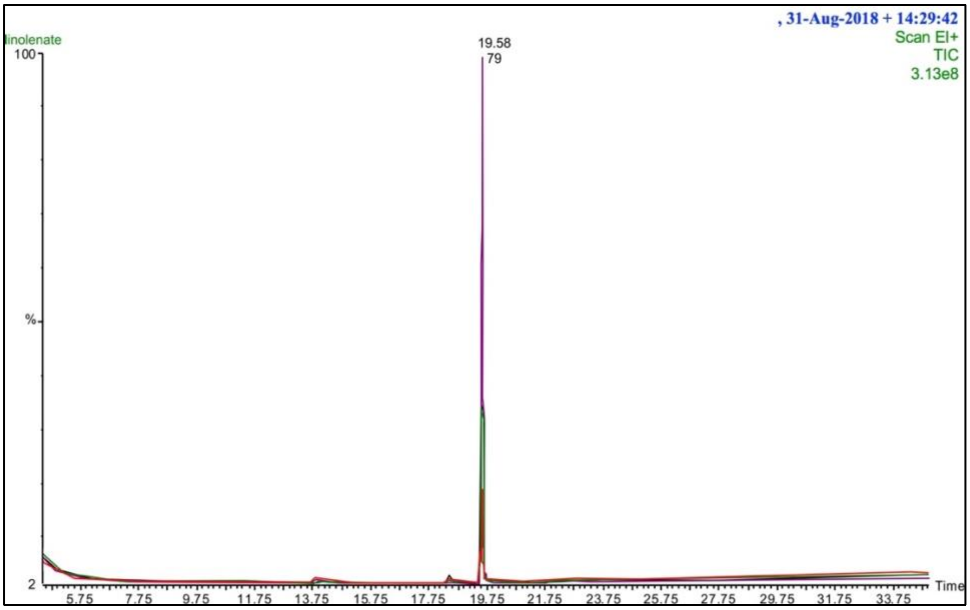


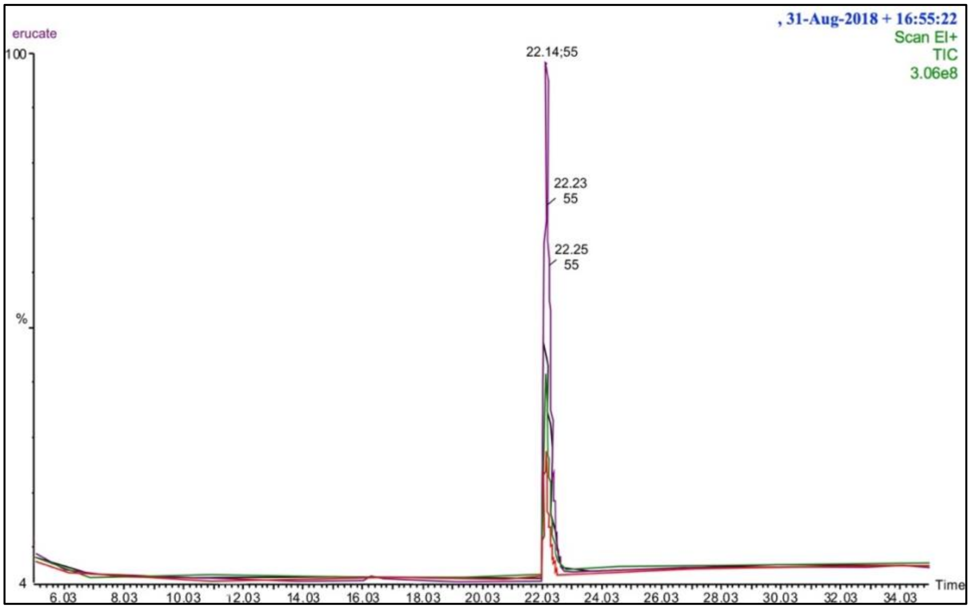


Figure C-1 (continued)

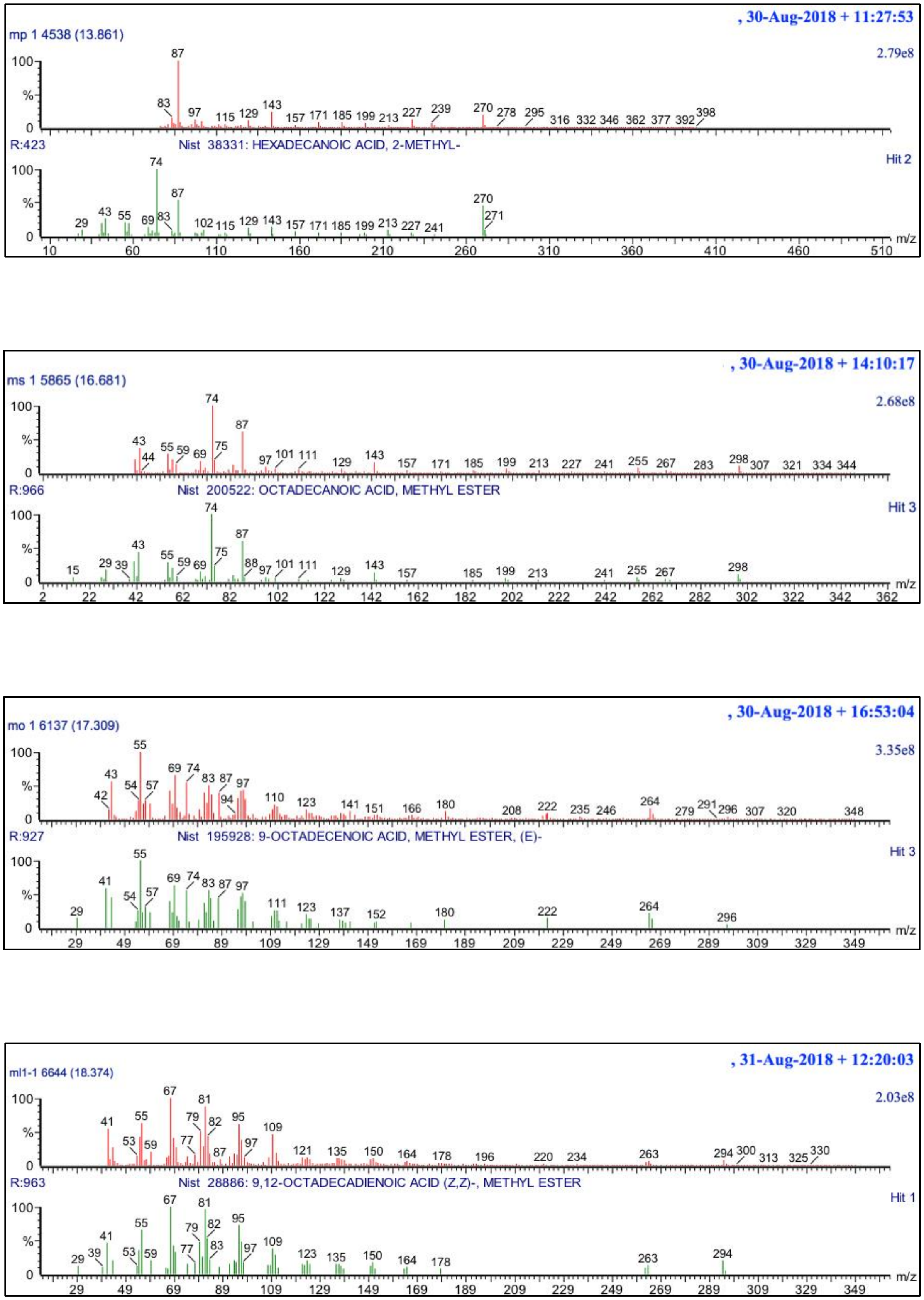
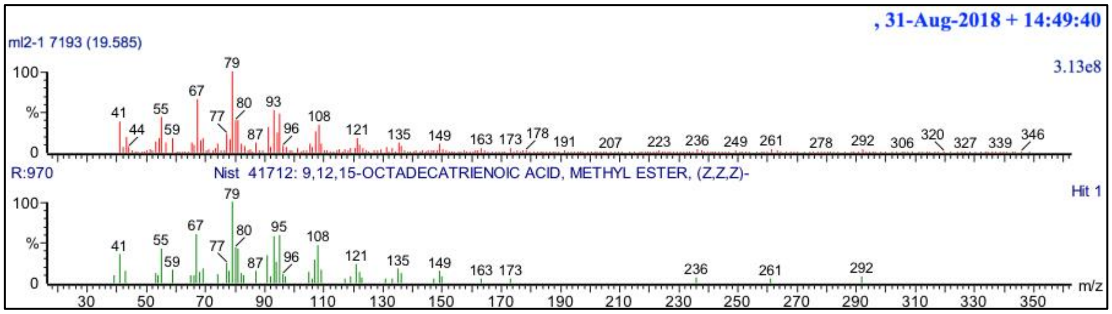


Figure C-2 Methyl esters spectra



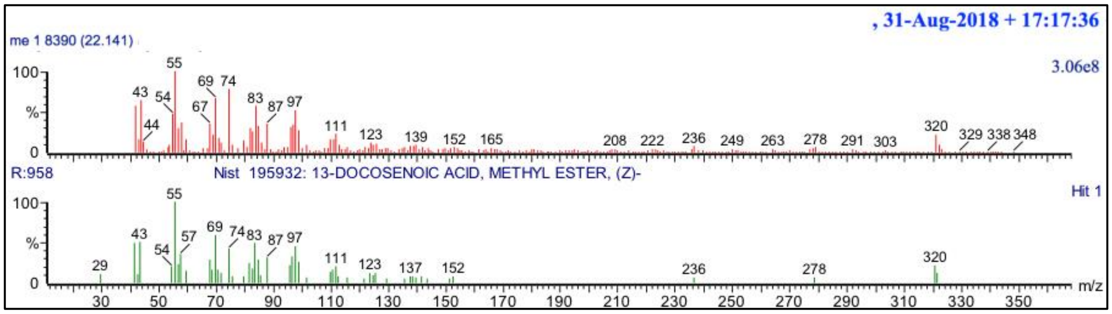


Figure C-2 (continued)

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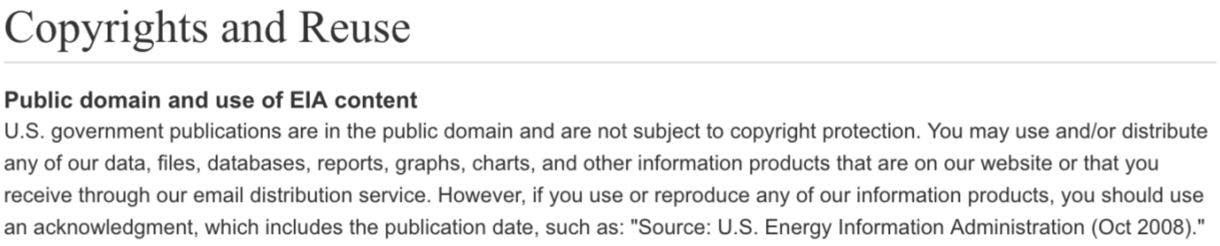

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