

**LUBRICANT QUALITY AND OXIDATIVE STABILITY OF
CRUCIFERAE OILS**

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By

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ABSTRACT

In the current research, oil derived from several *Brassica* species, and related oilseeds, was investigated for use as a lubricant base-oil. Oils obtained from *B. rapa* L. were selected because of their superior cold temperature performance over *Sinapis alba* L., *B. carinata* A., *B. napus*, and *B. juncea* L. The commercial antiwear additive zinc dialkyl dithiophosphate (ZDDP) was added (800 ppm) to *B. rapa* oils to determine the impact on oxidative stability and lubricity. It was found that the *B. rapa* oil ACS-C7 had a low cloud and pour point. *B. rapa* oils had poor oxidative stability at 97.8 °C when compared to a mineral oil (petroleum-based) standard. ZDDP had little effect on oxidative stability and cloud point. It was concluded that *B. rapa* oils have sufficient low temperature performance for use as a lubricant base oil. However, for continued use in a motor oil formulation, further modification of the oxidative stability will be necessary. All *B. rapa* oils with and without ZDDP were subjected to lubricity testing in a Plint High Frequency Wear Tester (TE-77). Lubricity testing simulates the high temperature and pressure in a motor system. The coefficient of friction and resultant wear scar width were measured. *B. rapa* oils lower coefficients of friction and decrease wear scar widths when compared with a mineral oil standard. Addition of ZDDP to *B. rapa* oils slightly increased lubricity performance of the oils. The wear scars produced on the polished stainless steel disk were subjected to X-ray Absorption Near Edge Structure (XANES) analysis using two synchrotron beamlines at the Canadian Light Source. XANES analysis confirmed the presence of a lubricating tribofilm on the surface of the stainless steel disks following *B. rapa* lubricity testing. These results indicate that *B. rapa* oils are suitable candidates as lubricant base oils for motor oil formulation.

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TABLE OF CONTENTS

PERMISSION TO USE	i
ABSTRACT	ii
ACKNOWLEDGMENT	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF ABBREVIATIONS	ix
LIST OF CHEMICALS	x
1. INTRODUCTION.....	1
2. OBJECTIVES	2
3. LITERATURE SURVEY	3
3.1 Motor Oils in the Automotive Industry	3
3.2 Motor Oil and the Environment	4
3.3 Internal Combustion Engine.....	5
3.4 Tribology	8
3.5 Motor Oil Composition	9
3.6 Chemistry of Lubrication and Lubricants	12
3.7 Measurement of Lubricant Performance	14
3.8 Plant Oil-based Lubricants	15

3.9 Canola-Oil-Based Lubricants	16
4. MATERIALS AND METHODS	23
4.1 Raw Materials.....	23
4.1.1 Oil Base Stock	23
4.1.2 Substrates for Tribology Studies	25
4.2 Methods	25
4.2.1 Solvent Extraction	25
4.2.2 Cold Press Extraction	25
4.2.3 Moisture Content.....	25
4.2.4 Oil Content by Goldfish Extraction.....	26
4.2.5 Whole Seed Pycnometry	26
4.2.6 Fatty Acid Profile (25 mg) by Gas Chromatography	26
4.2.7 Iodine Value of <i>Cruciferae</i> Oil	26
4.2.8 Chemical and Physical Properties of <i>Cruciferae</i> and <i>B. rapa</i> Oils	27
5. RESULTS.....	29
5.1 Composition of <i>Cruciferae</i> oilseeds.....	31
5.2 Fatty Acid Profile of <i>Cruciferae</i> and <i>B. rapa</i> Oils	31
5.3 Iodine values of <i>Cruciferae</i> Oils	33
5.4 Chemical and Physical Properties of <i>Cruciferae</i> and <i>B. rapa</i> Oils	39
5.4.1 Density of <i>Cruciferae</i> and <i>B. rapa</i> Oils	39
5.4.2 Viscosity of <i>Cruciferae</i> and <i>B. rapa</i> Oils.....	39
5.4.3 Cold Temperature Properties of <i>Cruciferae</i> and <i>B. rapa</i> Oils	49
5.4.4 Oxidative Stability of <i>Cruciferae</i> and <i>B. rapa</i> Oils.....	49
5.4.5 Refractive Index of <i>Cruciferae</i> Oils	52
5.4.6 Wear Scar and Tribofilms	52
6. DISCUSSION	73
6.1 Composition of <i>Cruciferae</i> Oilseeds	73
6.2 Fatty Acid Profiles of <i>Cruciferae</i> and <i>B. rapa</i> Oils	74

6.3 Iodine Value	76
6.4 Chemical and Physical Properties of <i>Cruciferae</i> and <i>B. rapa</i> Oils	76
6.4.1 Density of <i>Cruciferae</i> and <i>B. rapa</i> Oils	76
6.4.2 Viscosity of <i>Cruciferae</i> and <i>B. rapa</i> Oils.....	78
6.4.3 Cold Temperature Properties of <i>Cruciferae</i> and <i>B. rapa</i> Oils	79
7. SUMMARY AND CONCLUSIONS.....	86
8. REFERENCES.....	90

LIST OF TABLES

Table 4.1	<i>Cruciferae</i> oilseed sample data.....	24
Table 5.1	Moisture content, oil content, and density of whole <i>Cruciferae</i> oilseeds.....	24
Table 5.2	Composition of GLC-68D reference standard.....	34
Table 5.3	Fatty acid profile of <i>Cruciferae</i> oils	35
Table 5.4	Fatty acid profile of <i>B. rapa</i> oils.....	36
Table 5.5	Iodine values (IV) of <i>Cruciferae</i> oils.....	37
Table 5.6	Iodine values (IV) of <i>B. rapa</i> oils	38
Table 5.7	Effect of temperature on the density of select <i>Cruciferae</i> oils	41
Table 5.8	Effect of temperature on the density of <i>B. rapa</i> oils.....	43
Table 5.9	Effect of temperature on the viscosity of select <i>Cruciferae</i> oils.....	45
Table 5.10	Effect of temperature on the viscosity of <i>B. rapa</i> oils.....	47
Table 5.11	Cold temperature properties of select <i>Cruciferae</i> oils.....	50
Table 5.12	Cold temperature properties of <i>B. rapa</i> oils	50
Table 5.13	Mean oxidative stability of <i>B. rapa</i> oils	51
Table 5.14	Coefficients of friction of <i>Cruciferae</i> oils during wear scar production	53
Table 5.15	Coefficients of friction of <i>B. rapa</i> oils during wear scar production.....	55
Table 5.16	Mean wear scar width at 100× magnification of <i>Cruciferae</i> oils	59
Table 5.17	Mean wear scar width at 20× magnification of <i>B. rapa</i> oils	60

LIST OF FIGURES

Figure 3.1	General structure of zinc ZDDP.	11
Figure 5.1	Density of <i>Cruciferae</i> oil at temperatures between 0 °C and 100 °C.	42
Figure 5.2	Density of <i>B. rapa</i> oil at temperatures between 0 °C and 100 °C	44
Figure 5.3	Viscosity of <i>Cruciferae</i> oils at temperatures between 0 °C and 100 °C.	46
Figure 5.4	Viscosity of <i>B. rapa</i> oils at temperatures between 0 °C and 100 °C.	46
Figure 5.5	Friction trace for mineral oil without ZDDP	53
Figure 5.6	Friction trace for mineral oil with ZDDP.....	53
Figure 5.7	Mean and maximum coefficients of friction for <i>Cruciferae</i> oil samples.....	54
Figure 5.8	Mean and maximum coefficients of friction for <i>B. rapa</i> oil samples.....	55
Figure 5.9	<i>S. alba</i> wear scar width at 100× magnification.....	56
Figure 5.10	<i>B. napus</i> wear scar width at 100× magnification.....	57
Figure 5.11	<i>B. juncea</i> wear scar width at 100× magnification.....	57
Figure 5.12	<i>B. carinata</i> wear scar width at 100× magnification.....	58
Figure 5.13	<i>B. rapa</i> wear scar width at 100× magnification.....	58
Figure 5.14	<i>B. rapa</i> wear scar width at 20× magnification.....	61
Figure 5.15	<i>B. rapa</i> + ZDDP wear scar width at 20× magnification.....	61
Figure 5.16	Fe L-edge TEY of <i>Cruciferae</i> oils.....	63
Figure 5.17	Fe L-edge FY of <i>Cruciferae</i> oils.....	64
Figure 5.18	O K-edge TEY of <i>Cruciferae</i> oils.....	65
Figure 5.19	O K-edge FY of <i>Cruciferae</i> oils.....	66
Figure 5.20	C K-edge TEY of <i>Cruciferae</i> oils.....	67
Figure 5.21	C K-edge FY of <i>Cruciferae</i> oils.....	68
Figure 5.22	P L-edge TEY of <i>B. rapa</i> oils.....	69
Figure 5.23	P L-edge FY of <i>B. rapa</i> oils.....	70
Figure 5.24	P K-edge TEY of <i>B. rapa</i> oils.....	71
Figure 5.25	P K-edge FY of <i>B. rapa</i> oils.....	72

LIST OF ABBREVIATIONS

AES	Auger electron spectroscopy
FY	Fluorescence yield
HPLC	High Performance Liquid Chromatography
OSI	Oxidative stability index
TEY	Total electron yield
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy
ZDDP	Zinc dialkyl dithiophosphate

LIST OF CHEMICALS

Purchased from EMD Chemicals, Inc. (Gibbstown, NJ)

Hexane	HPLC grade
Isooctane	
Methanol	HPLC grade
NaCl	Reagent grade

Purchased from Sigma-Aldrich (St. Louis, MO)

Boron Trifluoride (BF₃)
C_{23:0} methyl ester

Provided by Chevron Oronite (San Ramon, CA)

Mineral oil
800 ppm ZDDP in mineral oil

CHAPTER 1

INTRODUCTION

Motor oils are typically composed of base oil, derived from petroleum sources, and functional additives. The base oil is produced through distillation and refining of petroleum products. Petroleum base oils are composed primarily of hydrocarbons, but are not suited for use as lubricants alone. In order to produce motor oil that meets all lubrication needs, additive packages are included. For example, to increase the lubricity of motor oil, the anti-wear additive zinc dialkyl dithiophosphate (ZDDP) is often included with the base oil (Lambert & Johnson, 1999). Some formulae include micronized nylon or modified vegetable oils to improve lubricant properties (Lambert & Johnson, 1999). These latter oils are referred to as “synthetic oil” or “blended synthetic oil”. Synthetic oils, often referred to as synthetic esters, may be derived from vegetable, animal or other plant sources (Bergstra, 2004). Recently, there has been much interest in the use of vegetable oils as lubricant base oil. Whether petroleum-based, synthetic, or vegetable-based, lubricant base oils must be compatible with additive packages, and must fulfill all tribological requirements of the engine and its operating conditions (Kreivaitis *et al.*, 2009).

The effectiveness of commercial antiwear additives is attributed to the elemental makeup of the additives (Sharma, Adhvaryu & Erhan, 2009). Phosphorus, sulphur, nitrogen and zinc, the active elements in many antiwear additives, affect the adsorption and stability of the tribofilms at metal-on-metal contact surfaces. These elements are released from ZDDP and into the motor oil as continuous wear occurs. The used motor oil is removed during routine engine maintenance, and if improperly disposed of, terminate in the environment. Elements such as phosphorus, sulphur and zinc may pose considerable risk to the environment and to human health because they are easily volatilized during engine operation and terminate in the atmosphere and water systems.

CHAPTER 2

OBJECTIVES

In order to produce an “environmentally friendly” lubricant, such as oils from non-petroleum-based oil, many vegetable oils have been tested for their suitability as a lubricant base stock. To date, canola/rapeseed oils, as well as other vegetable oils, have been identified as potential oil sources due to their superior lubricating qualities, including reduced friction and wear. However, most vegetable oils suffer from several drawbacks, diminishing their prospective use in automotive lubricant formulae.

Vegetable oils, specifically canola oils, are known to decompose *via* oxidative degradation, resulting in changes to the quality of the oils and, therefore to their efficiency as a lubricant. Canola oils also suffer from poor low temperature behaviour, a property that must be ameliorated in order for a motor oil to be used in cooler climates. As a result, much research is being performed to identify oil with sufficient lubricant properties and adequate chemical properties to create an “environmentally-friendly” lubricant. Therefore, it is the focus of this research was to:

- (1) To identify a canola oil (*Brassica* family and related species) with optimal cold temperature properties;
- (2) To compare the lubricant potential of each oil sample with and without commercial anti-wear additives; and
- (3) To confirm to formation of an antiwear film during simulated wear conditions using sample oils.

CHAPTER 3

LITERATURE SURVEY

3.1 Motor Oils in the Automotive Industry

In 2005, it was estimated that the automotive and industrial lubricant industry consumed over nine billion litres of motor oil each year (Erhan, Sharma & Perez, 2006). The North American market consumes one third of global lubricant production (Salimon, Salih & Yousif, 2010). As worldwide consumption of automotive and industrial lubricants increases, the waste created by these lubricants also increases. Approximately 50 per cent of all lubricants sold worldwide terminate in the environment through total loss applications, volatility, spills, accidents or improper disposal (Schneider, 2006). Over 60 per cent of the lubricants sold in the United States are lost to the environment, posing a serious threat to land and water systems (Erhan, Sharma, & Perez, 2006).

Since the 1950s, mineral oil from petrochemical sources has been used for motor oil formulae. Up to 1% of the total worldwide mineral oil consumption is used to formulate lubricants (Salimon, Salih & Yousif, 2010). Used motor oils contain polynuclear aromatic hydrocarbons and high concentrations of heavy metals (Vazquez-Duhalt, 1989), which are known to be toxic to the environment. The environmental threat posed by petroleum-based lubricants can be avoided by preventing undesirable losses, reclaiming and recycling lubricants and/or using environmentally friendly lubricants (Erhan, Sharma, Liu, & Adhvaryu, 2008).

With current worldwide concern for crude oil sources and increasing lubricant consumption, several issues must be addressed. Federal legislation is requiring automotive engineers to produce vehicles with better fuel economy and reduced emissions. The automotive industry has found that the most effective method of improving fuel efficiency while reducing emissions is through the use of energy conserving engine oils (Tung & McMillan, 2004). As a result of the depletion of the world's crude oil reserves, the increasing crude oil prices and

continuing environmental concerns, there is a renewed interest in bio-based lubricants (Salimon, Salih & Yousif, 2010). Bio-based lubricants or biolubricants includes all lubricants that are biodegradable and are not harmful to humans and other living organisms (Salimon, Salih & Yousif, 2010). The current market share for biolubricants is relatively small, approximately 2% in 2008, and is estimated to grow up to 5–10% within the next decade (Erhan, Sharma, Liu & Adhvaryu, 2008).

3.2 Motor Oil and the Environment

Biolubricants use “natural oils” as base oils from plant- and animal-based sources (Salimon, Salih & Yousif, 2010). It has been found that plant oils have superior biodegradability when compared to animal or mineral oils (Salimon, Salih & Yousif, 2010), which have drawn, increased attention by the automotive and lubricant industries. Biolubricants, sometimes called environmentally-adapted lubricants, are typically considered to be (1) biodegradable, that is they are easily degraded by microorganisms in the environment, (2) renewable, requiring that the raw material can be re-grown within 100 years, (3) of low toxicity, exposure risk and toxic impact on the environment, (4) of minimal bio-accumulability, because the accumulation of certain compounds may affect the endocrine, reproductive and immunological systems of living beings, and (5) energy efficient (Norrby, 2003).

Environmental awareness has led to the evolution of biodegradable and renewable motor oils since the 1970s (Norrby, 2003), with much more interest in bio-based materials over the past two decades. The manufacture, use and disposal of bio-based materials are not considered to pose a risk to the environment or to the health of people or animals (Biresaw, Asadauskas, & McClure, 2012). Currently, the focus is on environmentally friendly lubricants because they are known to improve fuel economy and lower emissions (Norrby, 2003). Bio-based products are growing in many industries including polymers, adhesives, personal-care products, coatings and lubricants (Bergstra, 2004).

Significant improvements in engine fuel economy and engine oil efficiency have been made over the past twenty years (Korcek, Sorab, Johnson, & Jense, 2000). Many of these improvements are due to the enhanced efficiency of fuels and lubricants. Over the next few decades, further demands will be expected of motor oil including fuel efficiency, emission compatibility, extended life, high temperature capability, antiwear protection, deposit control, low temperature performance and soot control (Korcek, Sorab, Johnson, & Jense, 2000).

Moreover, automotive lubricants will be expected to last longer, work better and have less of an impact upon the environment.

3.3 Internal Combustion Engine

The internal combustion engine is the main power source for most passenger and transportation vehicles (Totten, 2006). Internal combustion engines are also popular amongst other land and marine transportation vehicles and agricultural equipment (Tung & McMillan, 2004). The popularity of the internal combustion engine is due to its performance, reliability and versatility (Tung & McMillan, 2004). Most passenger cars in North America use a highly reliable “four stroke” cycle in which many surfaces interact and wherein the conversion of chemical energy of the fuel into mechanical energy of the crankshaft creates the potential for much wear to occur (Totten, 2006).

As the crankshaft turns, contact occurs between the crankshaft and the engine block. The load of the crankshaft is transferred to journal bearings connected to the piston rod. During engine operation, the journal bearings travel through the oil reservoir with each rotation of the crankshaft. The engine oil acts as a viscous lubricating fluid at bearing interface. However, when the engine is not in operation, the shaft settles into contact with the bearing until the engine is started again. While the engine is not in use, solid particles may become entrained in the engine oil and settle throughout the oil reservoir. These may damage the shaft or bearing surfaces (Totten, 2006).

As the piston travels up and down, it is synchronized with four cycles, or strokes: 1. *Intake*: as the piston nears the top of its travel, an intake valve in the cylinder head opens as fuel and air are injected, causing the piston to move downward; 2. *Compression*: the piston moves upward as both valves are closed and the fuel/air mixture is compressed; 3. *Power*: as the piston again nears the top of its cycle, a spark plug fires (in gasoline-powered engines), resulting in combustion of the vaporized fuel. The ensuing expansion of gas drives the crankshaft to turn; and 4. *Exhaust*: the piston reaches the bottom of the power stroke, the exhaust valves open, expelling the combustion products. The piston completes the exhaust stroke by returning to the top of the travel, closing the exhaust valve and opening the intake valve, thus repeating the sequence of events (Totten, 2006). The four-stroke cycle creates a severe environment within the engine block, where engine oils experience very high temperatures and pressures.

The piston travels through the cylinder block completing a four-stroke cycle (up-down-up-down) in two rotations of the crankshaft. The contact between the piston skirt (exterior portion of the piston) and the cylinder block is one of the greatest contributors to total engine friction (Totten, 2006). The movement of the piston within the cylinder block generates high temperatures, and the piston requires additional cooling. The engine oil often acts as a coolant and also serves to reduce friction and prevent scuffing on the surface of the piston (Totten, 2006).

In a metal-on-metal contact situation, plastic deformations occur due to friction, which expose fresh surfaces on the contacting surfaces while dislodging trace materials into the lubricant. These newly exposed surfaces are sensitive to the absorption of a lubricant film. A lubricant may interact chemically and physically with the deformed metal surface, considerably altering the properties of the lubricant. There are three common regimes of lubrication in an automotive system: boundary, hydrodynamic and mixed (Biresaw, Adhvaryu & Erhan, 2003). The molecules in lubricants are divided into two groups: polar and non-polar (Kragelskii, 1965). The polar molecules under high pressure form a thin film and enter a boundary lubrication regime *via* interactions with the oxide-layer. The non-polar molecules interact weakly with the solid surface of the engine (Kragelskii, 1965).

Throughout an automotive engine, each of the components may experience one or several lubrication regimes within one cycle (Tung & McMillan, 2004). It is generally understood that journal bearings and thrust bearings operate in a hydrodynamic lubrication regime, wherein the viscosity of the oil is such that a physical wedge is created during operation that facilitates the separation of contacting surfaces (Tung & McMillan, 2004). The valve train, piston ring system and transmission clutch operate by sliding in a boundary lubrication regime, where intense surface contact often occurs (Tung & McMillan, 2004). Boundary lubrication occurs when the lubricant is unevenly distributed and extreme-contacting conditions may occur momentarily. Most lubricants are designed to work under both hydrodynamic and boundary lubrication regimes.

In boundary lubrication regimes, chemicals within the liquid lubricant physically and chemically adsorb onto the mating surfaces, offering a protective layer referred to as an antiwear film (Tan, Huang & Wang, 2004). Adsorption of the lubricant onto the friction surfaces is influenced by the functional groups of the base oil (Biresaw, Adhvaryu & Erhan, 2003). It is in

the boundary lubrication regime where friction and wear improvements are most functional (Neville, Morina, Haque & Voong, 2007). Thin oils, when used in boundary lubrication regimes, tend to leak out of the surfaces and form an insufficient oil layer. Thicker oils do not penetrate the space between moving parts and do not act as friction reducers. As a result of improper lubricant distribution, fuel consumption increases, and the operating temperature of the engine increases (Acarogly, Oguz, & Ogut, 2001). The thickness, or viscosity, of engine oil tends to change with temperature, and has a direct effect on the reduction of friction. Therefore, one of the most important technical properties of engine oil is its viscosity over the range of normal engine operating temperatures (Ellinger, 1976). Viscosity also has important implications with the formation of antiwear films on the surface of contacting metals. In addition to lubricating the engine parts in which the engine oil contacts, it must also protect the automotive components it lubricates (Tung & McMillan, 2004). A lubricant must have sufficient viscosity to transport protective elements to the site at which they are needed, and remove waste products from the site at which they are generated (Tung & McMillan, 2004). Lubricants must also form a satisfactory antiwear film that tolerates the elevated temperatures and high pressures experienced during engine operation. The strength of the antiwear film and the extent of lubricant adsorption and ultimately the efficiency of the lubricant, and is measured as the friction coefficient and wear rate (Sharma, Adhvaryu, & Erhan, 2009).

One of the major drawbacks of an internal combustion engine is the relatively low mechanical and thermal efficiency. Much of the fuel energy is lost as heat or friction (Tung & McMillan, 2004). The internal combustion engine also emits hydrocarbons, particulates and NO_x (nitrogen oxides), which contribute to atmospheric pollution (Tung & McMillan, 2004). Friction loss within an internal combustion engine may account for up to 48% of the energy produced by the fuel (Tung & McMillan, 2004). Up to 66% of the energy lost during engine operation is due to the friction of the piston skirt, piston rings and bearings, and 34% due to the valve train, crankshaft, transmission and gears (Tung & McMillan, 2004). The total energy losses depend upon engine type, operating conditions, engine lubricants and service history of the vehicle (Tung & McMillan, 2004). In order to alleviate some of the losses due to heat and friction, all engines are designed to operate with a liquid lubricant (Tung & McMillan, 2004).

The surfaces of solids have microscopic irregularities that make the surface rough and wavy (Kragelskii, 1965). When in contact, the interacting surfaces are deformed in elastically

(Kragelskii, 1965). When a load is applied between two contacting surfaces, the surfaces continue to deform in elastically, but as load increases these deformations eventually become plastic (Kragelskii, 1965). At these contact points a high temperature is also generated, which aides in the formation and breaking of “frictional bonds” or welded junctions. Deformation of the contacting surfaces is inevitable, leading to scratching and scuffing (Kragelskii, 1965). The type of destruction that occurs depends on the properties of the contacting surfaces and upon the rubbing conditions, including load, speed and temperature (Kragelskii, 1965). In order to reduce the effect of catastrophic wear on automotive engines, the volume of metal deformed *via* metal-on-metal contact and the resultant debris must be minimized. The reduction of metal deformation and metal debris is accomplished by minimizing the contact between two metal surfaces using a liquid layer of lubricant (Tarasov, Kolubaev, & Tepper, 2002).

To ensure adequate distribution of oil throughout the main components of an internal combustion engine, a pressurized lubrication system is used – typically this is an oil pump. Oil is drawn in through the pump from the oil sump (reservoir) and delivered through a filter to the engine block (containing the pistons), crankshaft, camshaft and valve lifters. Oil returns to the sump *via* gravity through the cylinder block (Totten, 2006). The purpose of the oil filter is to remove particles from the oil that may damage the engine during operation. Oil is circulated throughout the engine *via* the pump/gravity cycle until it is removed and replaced during routine maintenance.

3.4 Tribology

Tribology is defined as “the science and technology of interacting surfaces in relative motion and of related subjects and practices” (Bhushan, 1999). The word “tribology” is derived from the Greek words “tribos” and “ology”, meaning “the study of rubbing, wearing and friction” (Dasic, Franek, Assenova, & Radovanovic, 2003). One of the core disciplines of tribology is chemistry, termed “tribochemistry”, which attempts to understand the mechanisms of rubbing contact and the protective film formation process (Nicholls et al., 2007). Furthermore, the field of tribology attempts to minimize and eliminate the losses resulting from friction and wear (Bhushan, 1999). Tribology is an interdisciplinary science that also draws on physics, mechanics, material science and lubrication technology (Dasic, Franek, Assenova, & Radovaovic, 2003).

Tribology has identified the two greatest factors of wear as heat and friction. In order to minimize the heat generated by friction and protect the sliding surfaces against deformation, a thin lubricant film, which may be liquid or solid, is placed between the two contacting surfaces. When two metal surfaces are in rubbing contact, there are small areas where micro welding may occur. These micro-welds quickly break and re-weld, releasing abrasive particles into the surrounding fluids, which results in scuffs and scratches on the surface of the metals. A lubricating film allows for sliding friction to occur between two solid surfaces without allowing them to rigidly weld together (Kragelskii, 1965).

Engine oils also serve to decrease the frictional force by forming antiwear films between moving parts, thereby preventing and reducing power loss (Acaroglu, Oguz, & Ogut, 2001). During rubbing, the temperature at the contacting surface may reach a critical value and the lubricating film present may become dissociated (Kragelskii, 1965). As a lubricant breaks down, molecular chains become disoriented, causing the lubricant to lose its protective properties (Kragelskii, 1965).

3.5 Motor Oil Composition

Most motor oil formulae contain base oil, to which certain functional chemicals are added. There are four categories of base fluids used in lubricant manufacturing mineral oils, synthetic fluids, vegetable-based wax esters and triglyceride vegetable oils (Norrby, 2003). Mineral oils are derived from the heavier fractions of crude oil after the low-boiling fractions, including gasoline, kerosene and diesel, have been removed *via* distillation (Okpokwasili & Okorie, 1990). Crude oils are produced from fossil raw materials, which have formed millions of years ago from forests and other plant biomass (Willing, 2001). Mineral oils are complex mixtures of very long chain, hydrocarbon compounds (20–50 carbons in length) (Salimon, Salih, & Yousif, 2010) and contain linear alkanes (waxes), branched alkanes (paraffinics), and alicyclic (naphthenic), olefinic and aromatic species. These molecules affect important lubricant characteristics such as volatilization, flash point, viscosity and density (Salimon, Salih, & Yousif, 2010).

Synthetic lubricant base oils are often used when performance requirements cannot be attained by mineral oil formulations (Salimon, Salih, & Yousif, 2010). Synthetic fluids include polyglycols (from ethylene or propylene molecules), polyalphaolefins, and synthetic esters from either petrochemical or natural origins (Norrby, 2003). Friedel and Crafts produced the first

synthetic oils in 1877 using aluminum trichloride as the catalyst (Nagendramma & Kaul, 2012). The first 100% synthetic oil was marketed in 1975 in the United States (Nagendramma & Kaul, 2012). Today, all major automotive lubricant producers, including Mobil, Quaker State, Castrol, Valvoline and Pennzoil, offer full synthetic alternatives to petroleum-based lubricants (Nagendramma & Kaul, 2012).

Full synthetic and semi-synthetic (or synthetic ester) based lubricants have been used for over 50 years (Nagendramma & Kaul, 2012). Their use as lubricant base stocks is preferred because their predictable properties, as a result of the carefully controlled molecular structure (Nagendramma & Kaul, 2012). Synthetic esters are generally comparable to mineral oils, and are easily blended with additive packages intended for mineral-based oils. Modern synthetic oils are considered to be minimally toxic.

Most additives used in commercial formulae are derived from petroleum products that may be toxic to the environment (Sharma, Adhvaryu, & Erhan, 2009). Lubricant formulae contain additives that perform several vital functions, including reducing wear, reducing oxidation, optimizing viscosity, providing detergency, inhibiting corrosion, deactivation of metal surfaces, depression of pour point and dispersion of liquids and solids. Up to 10% of the total volume in motor lubricants is additives (Salimon, Salih, & Yousif, 2010). The most common lubricant additive is ZDDP (Figure 3.1), which forms a strong antiwear film on the surface of engine components *via* chemical and physical adsorption. However, lubricant films on contacting surfaces are also subject to wear by the same mechanisms as other materials during severe engine service. The protective effects of ZDDP and the total additive package depend upon the rate of film formation and the rate of film removal (Morina, Neville, & Priest, 2003). ZDDP and other antiwear/antioxidant agents become degraded throughout engine operation, producing byproducts which may accelerate engine wear and have detrimental effects on other engine parts, such as deactivation of the catalytic converter in the exhaust system.

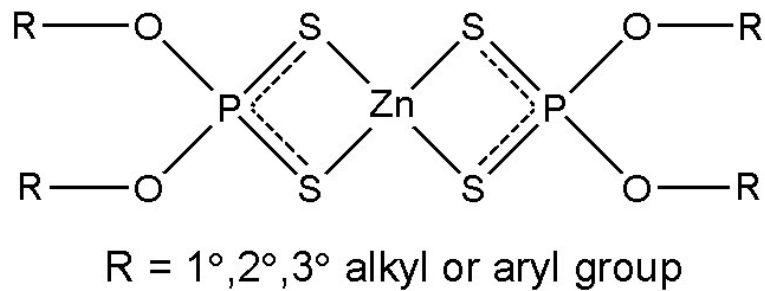


Figure 3.1 General structure of zinc ZDDP. The R-group structure is proprietary and brand specific (Spikes, 2004).

In order to reduce the environmental impact of automotive lubricants, the automotive industry is decreasing the content of inorganic elements, such as phosphorus and sulphur, in engine oil formulae (McQueen, Gwo, Black, Gangopadhyay, & Jensen, 2005). Consequently, the content of ZDDP, whose structure is largely composed of phosphorus and sulphur, is being decreased to reduce the negative impact of motor oils on the environment. The acceptable limit of phosphorus in fully formulated passenger car oil is 0.08%. There is no single replacement additive for ZDDP that is known to be effective for modern internal combustion engines (Nicholls, Do, Norton, Kasrai, & Bancroft, 2005). ZDDP in engine oil has several functions including acting as an antioxidant, antiwear/extreme pressure additive, and corrosion inhibitor (McQueen, Gwo, Black, Gangopadhyay, & Jensen, 2005). ZDDP often interacts with other additives in motor oil formulae due to high temperatures, and may cause sludge deposits and corrosive intermediates, which further increase the wear of the engine and the degradation of the motor oil (Totten, 2006).

ZDDP is the most widely used and cost effective multifunctional additive in automotive lubricants (Zhang, Najman, Kasrai, Bancroft, & Yamaguchi, 2005). The mechanisms of action of ZDDP are a highly researched subject. It is well known that lubricants containing sulphur additives generate a thin film layer under sufficiently high temperatures (Kragelskii, 1965). It is hypothesized that the phosphorus in ZDDP forms a glass-like layer that acts to protect the underlying surface. It is also well known that at the onset of metal-on-metal contact wear first increases with increasing pressure, followed by a reduction of measured wear and at the highest

pressure there is another slight increase in pressure. Many believe that the measured reduction in wear is attributed to the antiwear film formation. In a study performed by Mailänder and Dies (1943), it was found that the reduction in wear was associated with the formation of iron oxide (Fe_2O_3), which protects the surface from damage (Spikes, 2004). ZDDP also acts as a mild extreme pressure additive, which likely results from its ability to form iron sulphide during rubbing contact (Spikes, 2004).

3.6 Chemistry of Lubrication and Lubricants

The mechanisms of formation of the antiwear films and their action against wear are poorly understood (Nicholls, Do, Norton, Kasrai, & Bancroft, 2005). The antiwear film formed by ZDDP on the surface of metals has been found to contain various amounts of zinc, phosphorus, sulfur, and oxygen (Nicholls, Do, Norton, Kasrai, & Bancroft, 2005). It appears that the phosphorus in antiwear films occurs as both short- and long-chain polyphosphates (Fuller *et al.*, 1997). Morina, *et al.* (2003) suggest that the boundary wear films on steel surfaces form a layered structure, with long-chain zinc polyphosphates forming the upper wear film, a mixture of iron and zinc short-chain polyphosphates in the bulk of the film, and a base layer composed of iron oxysulfides. Often unreacted ZDDP also is found in antiwear films (Fuller *et al.*, 1997).

It is postulated that the effectiveness of ZDDP in wear reduction is due to the physical separation of the two metal surfaces, as well as the reduced friction caused by the formation of an antiwear film with a thickness of 50-150 nm on steel surfaces (Morina & Neville, 2007). Although film thickness varies with load, rubbing time and ZDDP concentration (Spikes, 2004), it is the chemical composition of the film that confers protection to the engine surfaces. It has been found that hydrocarbon solutions that contain ZDDP, such as motor oil formulations, undergo degradation *via* three mechanisms: (1) thermal, (2) catalytic and (3) oxidative (Martin, 1999). The degradation of ZDDP yields volatile products, including mercaptides, alkyl sulphides, hydrogen sulphide and olefins (Spikes, 2004), all of which cause further degradation of the motor oil and are potential toxins when released into the environment. Following ZDDP decomposition, a glassy insoluble product remains, containing phosphorus, oxygen, zinc and trace amounts of sulphur (Spikes, 2004).

The first stage in antiwear film formation is the precipitation of ZDDP from solution (Spikes, 2004). The ZDDP diffuses and adsorbs onto the iron surface of the metal *via* the sulfur

atom of ZDDP at the P = S bond (Spikes, 2004). At temperatures above 60 °C, zinc ions are lost into solution and adsorption becomes irreversible. Irreversible adsorption occurs *via* an iron dithiophosphate bond or by hydrolysis of surface water to produce free dithiophosphoric acid. At temperatures above 178 °C, the decomposition products of ZDDP become effective in forming a surface film which acts to prevent corrosion and wear (Spikes, 2004).

The antiwear film produced in the rubbing track grows to a thickness of ZDDP approximately 50–150 nm on steel surfaces, at which point it stabilizes and begins to protect the metal parts during wear situations (Spikes, 2004). It is important to distinguish an antiwear films from thermal films. A thermal film is formed when steel, copper, and other metals are exposed to ZDDP in solution, at temperatures above 100 °C. The reaction between the metal surface and ZDDP solution produces a transparent, solid film on the metal surface. Like antiwear films, thermal films contain an outer layer of polyphosphate. Unlike antiwear films, thermal films produced on metal show very little evidence of adsorption; and are, therefore, less likely to remain on the metal surface (Spikes, 2004).

Antiwear films or tribofilms, especially those containing ZDDP, form at temperatures much lower than those required for the formation of thermal films. However, the rate of antiwear film formation increases with increasing temperature (Spikes, 2004). Tribofilms are chemically similar to thermal films but are mechanically stronger (Spikes, 2004). The protective action of ZDDP is proposed to act in three ways: (1) as a protective film, providing mechanical antiwear properties; (2) by removing harmful molecules, including corrosive peroxides and peroxy-radicals; and (3) by degrading iron oxide particles, which may cause harmful abrasion on metal surfaces (Spikes, 2004).

ZDDP is a multifunctional additive that acts as both antiwear agent and antioxidant. It has been recognized since World War II that ZDDP acts as an effective oxidation inhibitor (Spikes, 2004). The proposed mechanism by which ZDDP acts as an inhibitor is by acting as an effective metal deactivator. ZDDP has the ability to sequester copper, lead and iron into soluble inert complexes, thereby preventing the release of pro-oxidant ions into the lubricant (Spikes, 2004). ZDDP also has the ability to decompose hydroperoxides and peroxy-radicals (Spikes, 2004) thereby preventing and delaying the onset of oxidation. The reaction products of ZDDP with hydroperoxide and peroxy radicals are also themselves effective oxidation inhibitors (Spikes, 2004).

3.7 Measurement of Lubricant Performance

Several techniques have been employed for surface analysis of antiwear film properties, including X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) (Fuller, Fernandes, Mossoumi, Lennard, Kasrai, & Bancroft, 2008). Fuller, et al. (2000) have shown that the surface analytical technique XANES (X-ray Absorption Near Edge Structure) spectroscopy can be used to study the chemistry and composition of the antiwear film produced by ZDDP. XANES is a powerful technique that can identify the elements and oxidation states at the surface and in the bulk of antiwear films using both total electron yield (TEY) and fluorescence yield (FY) techniques (Li, Pereira, Kasrai, & Norton, 2007). XANES is particularly useful fingerprinting tool for probing carbon, oxygen, phosphorus and sulphur in tribofilms, providing information on the geometry and oxidation state of the constituent elements (Nicholls, Morina, Haque, & Voong, 2007).

XANES spectroscopy uses synchrotron radiation to produce soft X-rays for the excitation and promotion of core-level electrons to unoccupied valence states in the anti-bonding orbitals (Najman, Kasrai, & Bancroft, 2004). The characteristic binding energies of the atomic core electrons provide element specific information (Najman, Kasrai, & Bancroft, 2004). The x-ray absorption spectra near the absorption edge of each element provide non-destructive information on the bonding state and local geometry of the absorbing atom (Najman, Kasria, & Bancroft, 2004). The surface of a sample may be probed using TEY mode, which measures P and S L-edges at up to a depth of 5 nm while the FY mode measures the surface emissions at a depth of 50 nm.

Synchrotron radiation excites and ejects core electrons within the sample, which results in the absorption of X-rays. Auger electrons fill the vacant orbitals, causing a cascade of scattering events. TEY mode measures all electrons produced during electron scattering. Electron scattering occurs at the surface of a solid sample, therefore, TEY measures the chemistry of the first few nanometers of a sample (Zhang, Najman, Kasrai, Bancroft, & Yamaguchi, 2005). FY mode measures the fluorescence photons emitted per incident photon and is, therefore, capable of measuring the sample at greater depths (Kasrai, Lennard, Brunner, Bancroft, Bardwell, & Tan, 1996).

XANES experiments performed by Martin (1999) at the phosphorus L-edge, using both TEY and FY detection modes, has shown that the multilayer structure of ZDDP films has a

short-chain phosphate layer below a thin long-chain polyphosphate layer. XANES, in combination with other analytical techniques, including AES, SIMS and XPS, has shown that the main cation present in the upper layer of ZDDP tribofilms is zinc (Martin, 1999). XANES has also revealed that the proportion of iron (a major component of stainless steel used in automotive engines and ZDDP experimentation) to zinc increases throughout the tribofilm towards the surface of the metal (Spikes, 2004). It has also been shown, through XANES experimentation, that sulphur is present in the tribofilms as zinc sulphide (Spikes, 2004). All such information elucidated from XANES spectroscopy is beginning to develop a picture of the chemistry of ZDDP films. However, to date, much of the XANES work has been performed on lubricants containing ZDDP that are composed of mineral and synthetic oils.

3.8 Plant Oil-based Lubricants

It is well known that when vegetable oil is added to automotive lubricant formulae, lubricity often improves. Lambert & Johnson (1999) have found that liquid lubricants composed principally of vegetable oils may be used in place of petroleum-based oils. Many vegetable oils and vegetable oil products are sources for additives and other lubricant components (Norrby, 2003). Without additives, most vegetable oils outperform petroleum-based oils in antiwear and friction, scuffing load capacity and fatigue resistance (Fox & Stachowiak, 2007). There are five biodegradable base stocks currently used in lubricant formulae: (1) highly unsaturated or high oleic vegetable oils; (2) low viscosity polyalphaolefins (PAOs); (3) polyalkylene glycols (PAGs); (4) dibasic acid esters (DEs); and (5) polyol esters (PEs) (Nagendramma & Kaul, 2012).

Because of environmental and toxicological considerations, there is growing demand for a lubricating oil that has excellent biodegradability and improved lubricating performance (Zhan, Song, Ren, & Liu, 2004), which has prompted the use of vegetable oils in lubricating oil formulae. Vegetable oils have a triacylglycerol structure, which confers good lubricity as well as high viscosity index, high flash point and low evaporative loss (volatility), all of which are desirable lubricant base oil properties (Jayadas, Prabhakaran Nair, & Ajithkumar, 2007). However, vegetable oils have several undesirable base oil characteristics, including poor low temperature properties, poor thermal and oxidative stability, and high wear rate (Jayadas, Prabhakaran Nair, & Ajithkumar, 2007). It is suggested that these preferred properties are due to the naturally occurring long chain fatty acid structures in vegetable oils (Lambert & Johnson, 1999).

The major component of vegetable oils is triacylglycerols, also called triglycerides. Triglycerides are composed of a glycerol backbone to which three long chain (usually) fatty acids are attached *via* ester linkages at the hydroxyl groups (Fox & Stachowiak, 2007). Most fatty acids in triglycerides range from 14 to 22 carbons long, with varying levels of unsaturation. The long chain fatty acids have different sites of functionality, including double bonds, allylic carbons and ester groups that are sites for possible chemical modifications. These sites also affect the chemical and physical interactions occurring between the fatty acids and their surroundings. The long chain fatty acids of triglycerides provide high strength to lubricant films (Fox & Stachowiak, 2007). The most common fatty acyl groups in plant triglycerides are derived from unsaturated fatty acids including [oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3)] and saturated fatty acids such as [palmitic acid (C16:0) and stearic acid (C18:0)]. The amount and type of fatty acids present in oil also affects stability and performance in an engine system during operation.

3.9 Canola-Oil-Based Lubricants

Lambert & Johnson (1999) suggest a high percentage of 16- to 22- carbon fatty acids is desirable in vegetable-based lubricating oils. Preferred sources of long chain fatty acids include canola and rapeseed (*Brassicaceae* family), as well as sunflower, safflower (*Compositae* family), flax (*Linaceae* family), and soybean (*Leguminosae* family) oils (Lambert & Johnson, 1999). Aside from their value as lubricant base oils, vegetable oils have several molecules with additional potentially useful properties. Phospholipids may act as antioxidants and may be useful for water dispersion in the oil (Lambert & Johnson, 1999). Other molecules present in vegetable oils, such as aliphatic alcohols, terpenoids and saponins function as detergents (Lambert & Johnson, 1999). There are also several naturally occurring antioxidants, including vitamins (tocopherols), pyrazines and other pigment molecules in vegetable oils (Lambert & Johnson, 1999). Additionally, all vegetable oils contain amphiphilic compounds that consist of a hydrophilic polar head, and a nonpolar hydrophobic chain (Adhvaryu, Biresaw, Sharma, & Erhan, 2006 Vol 45). These amphiphilic molecules might orient themselves during sliding contact situations in layers that are purported to increase lubrication. The polar groups of waxes and hydroxyl fatty acids in vegetable oil may also aid in bonding the oil to the metal surface, a suggested mechanism in the formation of an antiwear film, thereby reducing metal-on-metal contact (Lambert & Johnson, 1999).

In comparison to petroleum-based oils, vegetable-based lubricants are much more biodegradable, but they also may have several inferior technical characteristics. Vegetable-based lubricants typically have poor oxidative stability and low temperature flow properties (OSI and pour point, respectively). Erhan & Asadauskas (2000) reported that vegetable oils have oxidative stability that is an order of a magnitude less than mineral/petroleum or synthetic basestocks. Additional secondary problems associated with vegetable oils include poor hydrolytic stability, foaming and poor filtering properties. These properties will negatively affect the utility of a vegetable-oil-based lubricant during storage and in use (Nagendramma & Kaul, 2012). These problems can be partially or wholly remediated with lubricant additives. Sharma, Adhvaryu, Liu, & Erhan (2006) note that vegetable oil base fluids, combined with suitable additives, demonstrate equivalent oxidative stability when compared with mineral-oil-based lubricant formulae. Therefore, there is a need for an ideal lubricant base stock from vegetable oil sources that satisfies the technical demands of a motor oil formulation, or that may be chemically modified to eliminate or minimize oxidation susceptibility and the formation of crystals at low temperatures (Erhan & Asadauskas, 2000).

Vegetable oils are often subjected to chemical and genetic modifications so as to overcome their shortcomings and increase their usability in lubricant formulae (Sharma, Adhvaryu, Liu & Erhan, 2006). To date, vegetable oils are most often used in total loss applications, including chainsaw oils for the forestry industry, and in outboard marine engines (Nagendramma & Kaul, 2012). In order to increase the oxidative stability of vegetable oil and improve its function as a lubricant base oil, considerable investigation of leaching, catalytic hydrogenation and sulfurization of vegetable oils, in particular canola and cottonseed oil, has been conducted (Kuliev, Kuliev, Mutalibova, & Julieva, 2006). None of the attempted methods have proven to be completely successful in improving the oxidative stability of vegetable oils for industrial purposes (Kuliev, Kuliev, Mutalibova, Julieva, 2006). Unmodified vegetable oils undergo oxidative degradation, which results in an undesirable change in viscosity, colour and lubricity.

The process by which vegetable oils degrade *via* oxidation is well known. The presence of *bis*-allylic protons in the fatty acid structures of vegetable oils results in an active site for free radical attack, followed by oxidative degradation and the formation of polar oxygen containing compounds (Erhan, Sharma, & Perez, 2006). Vegetable oils are also highly susceptible to

hydrolytic breakdown due to the presence of ester functionality (Erhan, Sharma, & Perez, 2006). Oxidative degradation and hydrolytic breakdown result in the formation of insoluble deposits and an increase in oil acidity and viscosity, both of which are undesirable during engine operation. Polar oxygen containing compounds also result in the formation of insoluble deposits (Murilo, Luna, Rocha, Rola Jr., & Albuquerque, 2011).

Unsaturated fatty acids in vegetable oils are susceptible to oxidative attack by a one-electron transfer process, which results in a free radical intermediate. These intermediates subsequently react with molecular oxygen in the free radical chain reaction (Schneider, 2006) producing hydroperoxides. The unstable hydroperoxides may polymerize and thus increase viscosity, release water or produce aldehydes, ketones or carboxylic acids. Severe oxidation leads to the formation of sediments in the lubricant (Schneider, 2006). The *bis*-allylic hydrogens of the fatty acids are the most susceptible to oxidative attack.

It has been found that vegetable oils containing triglycerides with a lower degree of unsaturation will have better oxidative stability than those with a higher degree of unsaturation (Biresaw, Adhvaryu, & Erhan, 2003). A vegetable oil with acceptable oxidative stability must have a low content of polyunsaturated fatty acids (C18:2 and C18:3), and should have at least one fatty acid with a double bond present, such as oleic acid (C18:1) so as to inhibit low temperature solidification (Schneider, 2006). Oleic acid, with one double bond is somewhat stable against oxidation. Linoleic and linolenic acids, with two and three double bonds, respectively, are much more sensitive to oxidative attack (Schneider, 2006). Unfortunately, as oxidative stability increases, biodegradability decreases and the pour point of the oil also increases (Schneider, 2006). Consequently, a compromise must be made when considering performance and environmental friendliness of vegetable-oil-based lubricants.

Antioxidants inhibit peroxides or scavenge free radicals when added to lubricant base oils and, thereby, retard oxidation (Barnes, Bartle, & Thibon, 2001). Free radical scavengers act by reacting with peroxy radicals in solution and inhibiting propagation of free radical chain reactions (Barnes, Bartle, & Thibon, 2001). Peroxide inhibitors react with hydroperoxide molecules preventing the formation of peroxy radicals (Barnes, Bartle, & Thibon, 2001). ZDDP achieves both oxidation pathways in vegetable oil.

The interactions between ZDDP and vegetable oil oxidation products are thought to result in a decrease in ZDDP antioxidant activity (Barnes, Bartle, & Thibon, 2001). However, the

degradation of ZDDP in an engine depends upon many factors, primarily the operating temperature of the engine (Barnes, Bartle, & Thibon, 2001). The degradation products of ZDDP have been found to be less effective as antiwear agents than intact ZDDP additives (Barnes, Bartle, & Thibon, 2001). However, it is believed that the breakdown products of ZDDP affect anti-wear film thickness and, therefore, may contribute to antiwear protection at points of contact (Barnes, Bartle & Thibon, 2001).

Automotive lubricants are required to function over a wide range of temperatures. Most petroleum-based lubricants function satisfactorily at temperatures below $-25\text{ }^{\circ}\text{C}$ (Asadauskas & Erhan, 1999). The usability of a lubricant is limited by its flash point at high temperatures and by its pour point at low temperatures (Boyde, 2002). Many reports for vegetable oils indicate cloudiness, precipitation, poor flowability, poor pumpability and even solidification at a temperature of $-15\text{ }^{\circ}\text{C}$ (Asadauskas & Erhan, 1999). The lowest temperature at which oil will flow freely under its own weight is the pour point (Chen, Zhao, & Yin, 2010). It is been determined that the low temperature solidification of vegetable oils is due to low molecular weight saturated fatty acids in triglycerides. The geometries of various fatty acids within a triglyceride offer stearic hindrance, which also affects low temperature solidification (Asadauskas & Erhan, 1999). At least one *cis* double bond fatty acid is required in a vegetable oil for improved low-temperature behaviour; therefore, a high content of oleic acid is desired (Schneider, 2006). Pour point also is improved when a vegetable oil contains branched fatty acids (Schenider, 2006). Most motor oil formulae, including those with vegetable oil base stocks, have pour point depressants in their additive package so as to improve low temperature performance (Asadauskas & Erhan, 1999).

The viscosity of the base oil has a large impact upon the performance of motor oil at low temperatures. Vegetable oils owe their relatively high viscosity to the intermolecular interactions of the fatty acids on the glyceride backbone (Noor Azian, Mustafa Kamel, Panau, & Ten, 2001). Furthermore, vegetable oils have low volatility due to the high molecular weight of the triglyceride structure (Erhan, Adhvaryu & Liu, 2003). The oil viscosity generally increases as fatty acid chain length (and molecular weight) increases (Schneider, 2006). Ideally, lubricant viscosity would change very little across a wide variety of temperatures. At lower temperatures, the viscosity of vegetable oils increases to near solidification, often due to the presence of saturated fatty acids within the triglyceride structures (Asadauskas, & Erhan, 1999).

Solidification of vegetable oils is poorly understood and complex. It is hypothesized that the fatty acid chains of the triglyceride molecules have a bend in their structure, which facilitates stacking of the molecules during the cooling process (Adhvaryu, Erhan, & Perez, 2003). Solidification of vegetable oils also results in the precipitation of higher molecular weight molecules, such as waxes, from the oil. Contaminants and foreign bodies in vegetable oils act as nucleation centers, encouraging crystallization and low temperature gellation (Asadauskas & Erhan, 1999). The appearance of waxy crystals causes an agglomeration of molecules, which results in further crystallization and the solidification of oil. Many lubricant formulae include pour point depressants in their additive package so as to discourage large crystal formation during exposure to low temperatures (Asadauskas & Erhan, 1999). The transition of liquid oils to solid oils due to precipitation and crystallization does not occur at one particular temperature, but rather over a range of temperatures (Adhvaryu, Erhan, & Perez, 2004). Most commercial motor oil formulae include pour point depressants that prevent the formation of crystals around nucleation centers in the oil.

Commercial pour point depressants contain large molecules, often polymethacrylates, with a complex network of branches that act by disrupting or preventing the formation of three-dimensional wax crystal networks (Chen, Zhao, & Yin, 2010). Asadauskas and Erhan (1999) note unsatisfactory pour point performances of vegetable oils to which pour point depressants have been added at low temperatures. Asadauskas and Erhan (1999) report a mean pour point of $-18\text{ }^{\circ}\text{C}$ for canola oil. The dependence of viscosity on the temperature is referred to as viscosity index (Schneider, 2006). In general, the viscosity of a vegetable oil decreases approximately 30% for each $10\text{ }^{\circ}\text{C}$ increase of temperature (Timms, 1985). In order to remediate low temperature solidification of vegetable oil lubricant formulations, petroleum products are often added as diluents to depress the pour point (Asadauskas & Erhan, 1999). In an internal combustion engine, the oil must have a sufficiently low viscosity to allow the engine to start at even the coldest temperatures (Ellinger, 1976).

Until the early 19th century, most lubricants used vegetable oil bases (Choi, Ahn, Kwon, & Chun, 1999). Aside from thermal and oxidative stability and low temperature problems, a major limitation of vegetable oil use in motor oil formulae is their relatively high cost (Choi, Ahn, Kwon, & Chun, 1999). In general, the cost of biolubricants is up to twice that of petroleum-based lubricants (Potera, 2009). However, the price of mineral oil will continue to

increase in the future as demand increases and supply decreases. A low-cost replacement for petroleum-based products is needed (Schneider, 2006).

At present, rapeseed/canola, sunflower, and soybean oils have promise as potential lubricant base fluids (Schneider, 2006). Rapeseed oil is often chosen as a lubricant base stock due to its superior antioxidant properties when compared with other natural vegetable oils (Gong, He, & Liu, 2003). Canola, specifically *Brassica napus* L. (*B. napus*) and related species, is the second largest oilseed crop in the world (Raymer, 2002). *Brassica* oilseeds are reported to contain in excess of 40% oil (Raymer, 2002). The fatty acid compositions of many *Brassica* oilseeds are genetically altered to produce a product with a specific triglyceride profile, tailored for end use (Raymer, 2002). *Brassica* cultivars bred for non-edible purposes, specifically lubricants and hydraulic fluids, are termed “industrial rapeseed” (Raymer, 2002).

Industrial rapeseed products are required to satisfy the requisite qualities of motor oil during extended use at high operating temperatures and cold start conditions. Bartz (1998) indicated that rapeseed/canola oil is a good compromise between low temperature behaviour and oxidative stability. In order to improve the necessary criteria of a lubricant base oil, there presently are two options: (1) to increase the content of oleic acid in vegetable oils by breeding or genetic modification, or (2) to modify the vegetable oil by chemical means (Schneider, 2006). Furthermore, vegetable oils, including canola oil, have a higher solubilizing capacity for contaminants and additives than do petroleum-based oils (Erhan, Sharma, Liu, & Adhvaryu, 2008). However, petroleum-based raw materials have been studied and developed for over a century, whereas the chemistry and behaviour of canola/rapeseed-oil-based lubricants is relatively new and comparatively poorly understood (Biresaw, Asadauskas & McClure, 2012).

It is known that the polar functionality of many vegetable oils is suggested to have a positive impact on wear protection. The polar sites of triglyceride molecules strongly adsorb onto metal surfaces (Adhvaryu, Erhan & Perez, 2004). The ester chains also have strong lateral interactions, which encourage the triglyceride molecules to react with phosphate groups (in the oil and in the additives, such as ZDDP), forming a protective layer of fatty acid-phosphate complexes (Adhvaryu, Erhan, & Perez, 2004). The polarity of base oil has a profound effect on additive efficiency, specifically ZDDP (Kreivaitis et al., 2009). In addition, the triglycerides of vegetable oils are amphiphilic, allowing their use in both boundary and hydrodynamic lubrication regimes (Adhvaryu, Erhan, & Perez, 2004). Because of the many potential

environmental benefits of vegetable oils and the known advantages of vegetable oils as lubricants, canola/rapeseed oil have been investigated for their use as automotive lubricant base oils.

The choice of lubricant base stock and additive package for an automotive formulation depends upon the lubricant application, the operating conditions, technical requirements, biodegradability and recyclability (Nagendramma & Kaul, 2012). Ultimately, technical, logistic and cost barriers must be addressed and comprises made to produce practical formulae. The biggest challenge to date is finding a biodegradable base stock that performs satisfactorily and can replace mineral oils in automotive lubricants (Nagendramma & Kaul, 2012).

CHAPTER 4

MATERIALS AND METHODS

4.1 Raw Materials

4.1.1 Oil Base Stock

Selected varieties of *Cruciferae* oilseeds (*B. rapa* L., *B. carinata* A., *B. napus* L., *B. juncea* L. and *Sinapis alba* L.) were grown and maintained by Agriculture and Agri-Food Canada (AAFC), Saskatoon Research Centre, Saskatoon, SK. Samples were generously donated by Dr. Kevin Falk of the Saskatoon Research Centre. Samples included twenty-six *Cruciferae* oilseeds, twenty-three of which were of known genus, species, and variety from test plots grown near Saskatoon in 2007 (Table 4.1). These oilseed samples were used to survey several physicochemical properties. Several additional varieties of *Brassica rapa* (*B. rapa* ACS C-7, COMP-4, El Dorado, Goldrush, Parkland, Reward, Sunbeam, Tobin, TR-2, TR-3, TR-5) also were obtained from AAFC.

Table 4.1 *Cruciferae* oilseed sample data

Sample ID	Genus	Species	Cultivar	Crop ID	Plot	Rep	Code	Label	Test Group
19	<i>Sinapis</i>	<i>alba</i>	AC Base	06T22SK069					06Test22Sask
23	<i>Sinapis</i>	<i>alba</i>	AC Pennant	06T22SK097	97	4	12		06Test22Sask
2	<i>Sinapis</i>	<i>alba</i>	Andante	06T22SK068	59	3	12		05Test22Biodiesel
18	<i>Sinapis</i>	<i>alba</i>	AC Pennant		68	3	12		06Test22Sask
13	<i>Sinapis</i>	<i>alba</i>	FMK1						05Test22Biodiesel
5	<i>Sinapis</i>	<i>alba</i>	Svalof		20	1	15		0522TestBiodiesel
9	<i>Brassica</i>	<i>carinata</i>	57EM	06T22SK083	83	3	20		06Test22Saskatoon
14	<i>Brassica</i>	<i>carinata</i>		21156y/S2					06Test22Saskatoon
20	<i>Brassica</i>	<i>juncea</i>		VR03.9HTTC5928					06Test22Sask
7	<i>Brassica</i>	<i>juncea</i>		VR03.9HTTC5906	63	3	2	06T22SK063	05Test22Biodiesel
1	<i>Brassica</i>	<i>juncea</i>		VR03.9HTTC5914	61	3	1	06T22SK061	06Test22Sask
11	<i>Brassica</i>	<i>juncea</i>		VR03.9HTTC5915	65	3	4	06T22SK065	06Test22Saskatoon
22	<i>Brassica</i>	<i>juncea</i>		VR03.9HTTC5912					06Test22Sask
3	<i>Brassica</i>	<i>napus</i>	Argentine		120	4	12		06Test22Sask
21	<i>Brassica</i>	<i>napus</i>	Nugget						06Test22Sask
17	<i>Brassica</i>	<i>napus</i>	Midas						06Test22Saskatoon
6	<i>Brassica</i>	<i>napus</i>	AC Excel	06T22SK119	119	4	7		06Test22Saskatoon
16	<i>Brassica</i>	<i>napus</i>	Westar						06Test22Sask
12	<i>Brassica</i>	<i>rapa</i>	Zangyou	F1 TR8x	54	3			05Test22Biodiesel
10	<i>Brassica</i>	<i>rapa</i>	TR8		52	3	21		06Test22Saskatoon
4	<i>Brassica</i>	<i>rapa</i>		TR29	14	1	22		05Test22Biodiesel
8	<i>Brassica</i>	<i>rapa</i>	AOS-C7		51	3	24		05Test22Biodiesel
15	<i>Brassica</i>	<i>rapa</i>	AC Sunbeam						05Test22Biodiesel
24				21156y-495					
25				567/2					
26				200423/S2					

4.1.2 Substrates for Tribology Studies

Stainless steel coupons (ASI 52100, ~1% carbon, ~1-1.3% chromium, remainder iron) were cut and hardened (>60RC hardness) by the Department of Earth Sciences at the University of Western Ontario, London, ON. Coupons were polished to a mirror finish at the Geological Lab at the University of Western Ontario (London, ON). Stainless steel pins (ASI 52100, 11 mm length, 7 mm diameter, > 60RC hardness) were purchased from an automotive supplier and cleaned in hexanes (EMD Chemicals, Inc.) in an ultrasonic bath prior to their use.

Mineral oil and mineral oil plus 800 ppm ZDDP were generously donated by Chevron Oronite (San Ramon, CA) for use as reference oil standards. ZDDP, a standard anti-wear and antioxidant additive used by the automotive industry also was provided by Chevron Oronite for formulation in *B. rapa* oil samples.

4.2 Methods

4.2.1 Solvent Extraction

Twenty-three oil samples from the five *Cruciferae* families were obtained by hexane. Oilseeds were ground in a coffee grinder for 60 seconds. Oilseed meal (300 g) was transferred to a large beaker containing 1,800 mL hexanes (EMD Chemicals, Inc.). The solution was stirred with a stir bar on a hot plate for 2 h. The solution was allowed to settle, and the upper (liquid) layer was decanted. The liquid layer was filtered prior to rotary evaporation of the hexanes, resulting in clear sample oils.

4.2.2 Cold Press Extraction

Samples of eleven varieties of *Brassica rapa* were processed using a continuous screw press expeller (Komet Type CA59 C, IBG Monforts Okeotec GmbH & Co., Mönchengladbach, Germany) operated at a speed of 6.5 using a 6-mm dye. Collected oil was filtered using Whatmann filter paper under vacuum.

4.2.3 Moisture Content

Moisture content of the *Cruciferae* samples was determined using an oven drying method. Each variety of whole oilseed was ground in a coffee grinder prior to weighing. Ground oilseed (approximately 1 g) was placed into pre-weighed tin cups. Samples were dried in a

forced air oven at 110 °C for 2 h, cooled in a desiccator, and weighed again. Moisture content was calculated on a per weight basis.

4.2.4 Oil Content by Goldfish Extraction

Oil content of the oilseed samples was determined using a modified version of AOCS Official Method Am 2-93 (2000). Whole oilseed was ground in a coffee grinder until a uniform powder was obtained. Approximately 5 g of ground sample was weighed prior to oil extraction with hexane using a Labconco Goldfish extractor.

4.2.5 Whole Seed Pycnometry

Gas pycnometry was performed on whole oilseed samples using a Quantachrome Ultrapychnometer Ultrapyc 1200 (Boynton Beach, FL). Each sample was weighed (4.5 ± 0.5 g) prior to analysis and the density was determined by gas displacement within the calibrated pycnometer chamber. The density (ρ) of each sample was calculated electronically by the pycnometer. Each sample was analyzed three times before a mean value was calculated by the pycnometer.

4.2.6 Fatty Acid Profile (25 mg) by Gas Chromatography

Fatty acid profiles of samples were determined using oils methylated according to the AOCS Official Method Ce 1b-89 (1998). Gas chromatography was performed using a gas chromatograph (Agilent 6890, Agilent Technologies Inc., Life Sciences and Chemical Analysis, Wilmington, DE). The fatty acid methyl esters were identified by comparison with the retention times of the reference standard GLC-68D, prepared by Nu-Chek Prep, Inc. (Elysian, Minnesota). A C23:0 ($\geq 99.5\%$ purity tricosanoic acid) fatty acid internal standard (Sigma-Aldrich Canada, Ltd. Oakville, Ontario) was used for the quantification of fatty acids in oils samples. The calculated % Area of each chromatogram was used to calculate the amount of each fatty acid present in an oil sample.

4.2.7 Iodine Value of *Cruciferae* Oil

Iodine value, a measure of unsaturation of fatty acids in oil, may be calculated according to AOCS Method Cd 1c-85 (1998) (Calculated Iodine Value). Using the data obtained for fatty acid analysis, Iodine Value (IV) was calculated using Equation 3.1.

$$\text{Triglycerides, iodine value} = (\% \text{ hexadecenoic acid} \times 0.950) + (\% \text{ octadecenoic acid} \times 0.860) + (\% \text{ octadecadienoic acid} \times 1.732) + (\% \text{ octadecatrienoic acid} \times 2.616) + (\% \text{ eicosenoic acid} \times 0.785) + (\% \text{ docosenoic acid} \times 0.723) + (\% \text{ tetracosanoic acid} \times 0.663) \quad (3.1)$$

4.2.8 Chemical and Physical Properties of *Cruciferae* and *B. rapa* Oils

4.2.8.1 Density of *Cruciferae* and *B. rapa* Oils

Density of oil samples (23 *Cruciferae* oil samples, mineral oil standard with and without 800 ppm ZDDP and three selected *B. rapa* oils with and without 800 ppm ZDDP) was measured using a 25 mL glass pycnometer at 10 °C increments. Oils chilled to 0 °C were placed in a calibrated glass pycnometer and fitted with a glass stopper with a hole at the top. Oils were heated in an oil bath and removed for weighing at 10 °C increments, beginning at 5 °C. As the temperature of the oil increased, the volume also increased. Oil expelled through the hole at the top of the fitted glass stopper was wiped clean. Density of the oils was calculated using Equation 3.2.

$$\text{Density of oils (g/mL)} = (\text{weight of oil in pycnometer (g)} - \text{weight of pycnometer (g)}) / 25 \text{ mL} \quad (3.2)$$

4.2.8.2 Viscosity of *Cruciferae* and *B. rapa* Oils

Viscosity of oil samples (23 *Cruciferae* oil samples, mineral oil standard with and without 800 ppm ZDDP and three selected *Brassica rapa* oils with and without 800 ppm ZDDP) was determined using a method similar to the ASTM standard D4212 (Standard Test Method for Viscosity by Dip-Type Viscosity Cups) used for motor oil and automotive lubricants. Viscosity was measured at 10 °C increments between 0 and 100 °C, starting at 5 °C. At the desired temperature, a #3.5 Shell Viscosity Cup (Norcross[®], Pompano Beach, FL) was submerged in the oil, and drawn out. Time was measured (in seconds) from when the cup broke the surface until the oil stream broke. This time was related to the viscosity (in centipoises, cP) using a standard curve provided by the manufacturer.

4.2.8.3 Cold Temperature Properties of *Cruciferae* and *B. rapa* Oils

4.2.8.3.1 Cloud Point

Cloud point is the temperature at which oil becomes turbid and cloudy in appearance. This property is measured by visual inspection in a cold bath. Oil samples (23 *Cruciferae* samples, 12 *B. rapa* oils, 12 *B. rapa* oils with 800 ppm ZDDP, mineral oil standard and mineral

oil with 800 ppm ZDDP standard) were placed in a cold bath and inspected every 3 °C below 0 °C, following the ASTM Standard method D5773-07 (2008) (Standard Test Method for Pour Point of Petroleum Products). The temperature at which the oil became turbid and opaque was recorded as the cloud point.

4.2.8.3.2 Pour Point

Pour point was measured similarly in a cold bath following the ASTM Standards D-97 (2008) (Standard Test Method for Pour Point of Petroleum Products) and D-5853 (2008) (Standard Test Method for Pour Point of Crude Oils). Following cloud point determination, cooling off was continued, with visual inspection every 3 °C. When a sample could be tipped for 5 seconds without disturbing the oil surface, the last temperature was recorded as the pour point.

4.2.8.3.3 Oxidative Stability of *Cruciferae* and *B. rapa* Oils

The oxidative stability of *Cruciferae* and *B. rapa* oil samples was measured by accelerating the oxidation process in an oxidative stability instrument (OSI-24, Omnion Inc., Rockland, MA). The induction period of each oil sample was analyzed following the AOCS Method Cd 12b-92 (1998) (Oil Stability Index). Each oil sample (5.0 ± 0.1 g) was placed in a glass tube fitted with a rubber stopper. Air was passed through the oil sample as it was heated to 110 °C. As the oils oxidized, the volatiles released were trapped in a plastic vessel containing deionized water, increasing the conductivity of the water. The conductivity of the water was monitored by a computer, which calculated the oxidative stability index (OSI) of the oils, and reported the time to the onset of induction period.

4.2.8.3.4 Refractive Index of *Cruciferae* Oils

Refractive index is a measure of the angle of refraction of an incident beam of light at the interface between two media. Refractive index was measured using a Leica Auto ABBE Refractometer (Model 10500B, Leica Inc. Optical Products Division, Buffalo, NY). Measurements were taken at room temperature following instrument calibration with distilled water. A single analysis of each oil sample was performed.

4.2.8.4 Analysis of Wear and Lubricant Properties

4.2.8.4.1 Wear Scar Production

The lubricating film, or tribofilm, that prevents wear between two moving metal parts may be created artificially using a bench-top tester. Tribofilms were generated on polished

52100 stainless steel disks, sometimes called coupons, using a TE-77 Plint High Frequency Wear Tester (Phoenix Tribology Ltd., Newbury, U.K.). The stainless steel pins and disks were cleaned in an ultrasonic bath for one minute with hexanes before being placed in the wear-testing device. Oil was poured into the oil bath and the pin was loaded flat against the disk. A contact load of 220 N was applied to the pin, and the temperature of the oil was set to and maintained at 100 °C throughout the experiment. The pin was set in motion with a stroke length of 7 mm at 25 Hz for 1 h, following the method suggested by Zhang, Yamaguchi, Kasrai and Bancroft (2004). The coefficient of friction was monitored with a piezo electric transducer during wear scar production. After wear scar production, the oil was removed and stored for further experimentation. The pins and disks were rinsed with hexane to remove unbound oil and any remaining unreacted ZDDP. The wear scar produced on each pin was examined at 100× magnification using an optical microscope equipped with a camera. The width of each wear scar was measured at ten points across the flattened surface of the pin and the mean width was calculated for comparison of lubricant efficacy.

4.2.8.4.2 X-ray Absorption Near Edge Structure Analysis

Several techniques may be employed to measure the surface of a tribofilm/wear scar and to identify molecules present on disks following wear scar production using a Plint Tribometer. Two synchrotron beamlines at the Canadian Light Source were used to identify molecules in the tribofilm. The Canadian Light Source is a 2.9 GeV electron storage ring located at the University of Saskatchewan and was used for a series of X-ray absorption near edge structure (XANES) studies. Data was collected using the Iron L-edge, Carbon K-edge and Oxygen K-edge Spherical Grating Monochromator (SGM) beamline which covers the energy region of 200-600 eV and the Phosphorus L-edge was analyzed using the Variable Line Spacing- Plane Grating Monochromator (VLS-PGM) beamline, measuring at approximately 700 eV. Spectra on both beamlines were collected in two modes, TEY and FY. K-edge measurements result from the excitation of an $n = 1$ (1s) electron by synchrotron x-rays. L-edge measurements result from the excitation of $n = 2$ (2 s and 2 p) electrons. Simultaneous detection in both TEY and FY modes provides information on the chemical species present at the surface and throughout the bulk of the sample.

The presence of certain elements on the surface of the disks was confirmed by comparing the spectra of the vegetable oil tribofilms to those of known spectra. Iron (III) Oxide (Fe_2O_3)

was used for the detection of the substrate, therefore confirming or refuting the presence of a tribofilm on the surface of the disks. Graphite was used to calibrate the beamline Iron (III) Phosphate ($\text{Fe}_4\text{O}_{21}\text{P}_6$) was used to detect the presence of a tribofilm containing ZDDP on the surface of the disks.

Chapter 5

RESULTS

5.1 Composition of *Cruciferae* oilseeds

The moisture content, oil content, and density of 23 *Cruciferae* oilseed samples were determined (Table 5.1). Between one-quarter and one-half of each of the *Cruciferae* oilseeds was composed of oil. The *S. alba* seeds can be divided into two classes, high oil ($34.15 \pm 1.63\%$) and low oil ($25.43 \pm 0.41\%$), but in comparison to the other oilseeds sampled, *S. alba* had lower oil content. *B. carinata* ($36.3 \pm 2.1\%$), *B. rapa* ($42.9 \pm 1.4\%$), and *B. napus* ($45.5 \pm 2.4\%$) had higher oil contents than did *S. alba*, but a lower oil content than did *B. juncea* ($48.9 \pm 1.4\%$). Oilseeds with higher oil contents had lower moisture content and conversely, oilseeds with lower oil content had higher moisture content. Low-oil *S. alba* had the highest moisture content ($2.50 \pm 0.22\%$), whereas *B. juncea* had the lowest moisture content ($1.56 \pm 0.09\%$).

S. alba had the lowest measured density (1.236 ± 0.002 g/cc). Interestingly, *B. juncea* oilseeds did not have the highest mean density (1.123 ± 0.010 g/cc), as would be expected, although they did have the second highest density next to *B. napus* (4.23 ± 0.20 g/cc and 1.096 ± 0.0058 g/cc, respectively). *B. napus* had the second highest content of oil, and the second lowest moisture content. There did not appear to be a relationship between oil content and density.

5.2 Fatty Acid Profile of *Cruciferae* and *B. rapa* Oils

The composition of the fatty acid reference standard used in fatty acid analysis is shown in Table 5.2. The fatty acid profiles of *Cruciferae* oil samples are shown in Table 5.3. When comparing the five *Cruciferae* species, both C16:0 palmitic acid and C16:1 palmitoleic acid show very little variation among the different varieties sampled (2.49–3.52% for palmitic acid, and 0.07-0.33% for palmitoleic acid). Of the oils sampled, four may be quantified as low stearic acid (C18:0) oil, namely low-oil *S. alba* (1.06%), *B. carinata* (1.09%), *B. rapa* (1.42%) and *B. napus* (1.71%), and two may be quantified as high stearic acid, namely high-oil *S. alba* (6.56%), and *B. juncea* (4.74%). There was a large range in oleic acid (C18:1) content, from 10.07% (*B. carinata*) to 49.63% (*B. rapa*). Other 18-carbon fatty acids exhibited smaller measured differences concentration among samples. Vaccenic acid (C18:1) ranged from a mean content of 0.60% (*B. carinata*) to 4.29% (*B. juncea*). A range from 8.44% (high-oil *S. alba*) to 20.85% (*B.*

Table 5.1 Moisture content, oil content, and density of whole *Cruciferae* oilseeds ($n = 3$)

Sample ID	Genus/species	Moisture (%)	Mean Moisture (%)	Oil (%)	Mean Oil (%)	ρ (g/cc)	Mean ρ (g/cc)
19	<i>S. alba</i>	2.5		24.9		1.236	
23	<i>S. alba</i>	2.8	$2.50 \pm$	25.4	$25.43 \pm$	1.239	1.236 ± 0.002
2	<i>S. alba</i>	2.3	0.22	25.5	0.41	1.236	
18	<i>S. alba</i>	2.4		25.9		1.233	
13	<i>S. alba</i>	2.0	$2.15 \pm$	33.0	$34.15 \pm$	1.189	1.190 ± 0.001
5	<i>S. alba</i>	2.3	0.21	35.3	1.63	1.191	
9	<i>B. carinata</i>	2.5	$2.35 \pm$	35.1	36.6 ± 2.12	1.181	1.185 ± 0.006
14	<i>B. carinata</i>	2.2	0.21	38.1		1.189	
20	<i>B. juncea</i>	1.5		46.5		1.136	
7	<i>B. juncea</i>	1.5		49.3		1.119	
1	<i>B. juncea</i>	1.5	$1.56 \pm$	49.4	$48.94 \pm$	1.117	$1.1225 \pm$ 0.010
11	<i>B. juncea</i>	1.6	0.09	49.6	1.38	1.112	
22	<i>B. juncea</i>	1.7		49.9		1.125	
3	<i>B. napus</i>	1.8		41.4		1.105	
21	<i>B. napus</i>	1.7		45.6		1.093	
17	<i>B. napus</i>	1.7	$1.66 \pm$	46.4	$45.58 \pm$	1.098	1.096 ± 0.006
6	<i>B. napus</i>	1.6	0.11	47.0	2.44	1.095	
16	<i>B. napus</i>	1.5		47.5		1.088	
12	<i>B. rapa</i>	2.2		41.2		1.149	
10	<i>B. rapa</i>	2.1		41.8		1.134	
4	<i>B. rapa</i>	1.7	$1.90 \pm$	43.1	$42.92 \pm$	1.140	1.138 ± 0.007
8	<i>B. rapa</i>	1.7	0.23	43.8	1.43	1.133	
15	<i>B. rapa</i>	1.8		44.7		1.135	

rapa) was determined for linoleic acid (C18:2). The content of linolenic acid (C18:3) ranged from 6.76% (high-oil *S. alba*) to 14.8% (*B. carinata*). The long chain fatty acid eicosenoic acid (C20:1) had a measured mean range of 3.59% (*B. rapa*) to 10.49% (low-oil *S. alba*). Erucic acid (C22:1) had a very large measured range of fatty acid content, from 21.3% (*B. rapa*) to 37.8% (*B. carinata*). All other fatty acids measured were summed and categorized as “others”. *B. rapa* had a low mean of “others” fatty acids (1.12%), whereas *B. carinata* had the highest mean “others” content (4.99%).

The fatty acid profile of the selected *B. rapa* oils differed very little across the 12 varieties sampled (Table 5.4). The palmitic acid content varied from 3.1% (Goldrush) to 3.8% (El Dorado). El Dorado also had the highest (1.8%) content of stearic acid amongst all *B. rapa* oils sampled. ACS-C7 had very low stearic acid content, 0.17%. COMP-4 had the highest oleic acid content of 59.2%, while Parkland had the lowest oleic acid content (53.2%). The vaccenic acid content ranged from 1.5% (ACS-C7) to 3.2% (Reward). Parkland had very low linoleic acid content, at 12.2%, whereas all other samples had linoleic acid contents of 21.0% (COMP-4) to 22.9% (ACS-C7). El Dorado had a slightly lower linolenic acid (C18:3) content (9.1%) than other *B. rapa* oils, which ranged from 10.1% (COMP-4) to 13.8% (Reward). All *B. rapa* oils had low eicosanoic acid contents, ranging from 0.9% (TR3) to 1.6% (Sunbeam). COMP-4 had the lowest content of “other” fatty acids at 0.9%, while Tobin had the highest content of “other” fatty acids (1.3%).

5.3 Iodine values of *Cruciferae* Oils

The iodine value (IV) was determined using the gas chromatography for fatty acid profiling data (Table 5.5 and Table 5.6). IV is a predictor of the oxidative stability of oil. Oil with a higher IV will be less stable. *B. rapa* oil has the highest calculated iodine value (118.08 ± 4.49), and, therefore, would be expected to be the least oxidatively stable. Similarly, *B. carinata* had an IV of 117.29 ± 3.51 , and would also be expected to have poor oxidative stability. Conversely, *S. alba* has the lowest IV (97.62 ± 0.98) and is, therefore, expected to be the most resistant to oxidative degradation. Oil that is susceptible to oxidation reactions will require the addition of anti-oxidants to conserve motor oil stability.

Table 5.2 Composition of GLC-68D reference standard

Fatty Acid	Common Name	Composition (%)
C14:0	Methyl Myristate	6
C14:1	Methyl Myristoleate	1
C16:0	Methyl Palmitate	16
C16:1	Methyl Palmitoleate	5
C18:0	Methyl Stearate	8
C18:1	Methyl Oleate	13
C18:1	Methyl Vaccenate	4
C18:2	Methyl Linoleate	2
C18:3	Methyl Alpha Linolenate	2
C20:0	Methyl Arachidate	1
C20:1	Methyl 11-Eicosenoate	9
C20:2	Methyl 11-14-Eicosadienoate	1
C20:3	Methyl Homogamma Linolenate	–
C20:4	Methyl Arachidonate	3
C20:5	Methyl Eicosapentanoate	10
C22:0	Methyl Behenate	1
C22:1	Methyl Erucate	3
C22:6	Methyl Docosahexanoate	12
C24:0	Methyl Lignocerate	1
C24:1	Methyl Nervonate	1

Table 5.3 Fatty acid profile of *Cruciferae* oils ($n = 3$)

Sample ID	Genus/species	C16:0 Palmitic Acid	C16:1 Palmitoleic Acid	C18:0 Stearic Acid	C18:1 Oleic Acid	C18:1 Vaccenic Acid	C18:2 Linoleic Acid	C18:3 Linolenic Acid	C20:1 Eicosenoic Acid	C22:1 Erucic Acid	Others
19	<i>S. alba</i>	3.05	0.17	1.09	26.9	1.26	9.16	11.5	11.3	31.6	3.52
23	<i>S. alba</i>	2.81	0	1	24.5	11.3	9.53	10.6	10.3	35.8	3.77
2	<i>S. alba</i>	2.82	0.16	1.06	23.5	1.11	10	11.2	9.85	35.8	3.88
18	<i>S. alba</i>	2.94	0.17	1.09	25.5	1.14	9.6	10.7	10.5	34.1	3.83
Mean		2.91	0.13	1.06	25.1	3.70	9.57	11.0	10.49	34.3	3.75
13	<i>S. alba</i>	2.52	0.51	12.1	23.1	4.69	8.79	4.89	4.56	20.6	4.4
5	<i>S. alba</i>	2.45	0.15	1.03	22.7	0.92	8.08	8.62	9.16	42.4	3.94
Mean		2.49	0.33	6.56	22.9	2.81	8.44	6.76	6.86	31.5	4.17
9	<i>B. carinata</i>	3.48	0	1.23	11.9	1.18	18.2	16.1	8.78	33.7	4.65
14	<i>B. carinata</i>	3.19	0.13	0.95	8.23	0.01	18.2	13.5	6.95	41.9	5.33
Mean		3.34	0.07	1.09	10.1	0.6	18.2	14.8	7.86	37.8	4.99
20	<i>B. juncea</i>	2.10	0	1.06	17	0.91	17.2	9.38	7.6	39.8	4.29
7	<i>B. juncea</i>	2.30	0	1.02	19.3	0.86	18.4	8.86	7.47	37.3	1.73
1	<i>B. juncea</i>	2.39	0	1.04	17.2	0.74	18.4	9.4	7.28	38.9	3.84
11	<i>B. juncea</i>	2.51	1.13	19.6	0.85	18.2	9.55	0.75	0.83	35.6	4.36
22	<i>B. juncea</i>	2.33	0.00	0.99	17.4	0.75	17.5	9.02	7.45	40	3.9
Mean		3.23	0.23	4.74	14.4	4.29	16.2	7.48	6.13	38.3	3.62
3	<i>B. napus</i>	3.15	0.08	1.19	17.7	1.2	13.8	9.08	11.6	39.2	2.22
21	<i>B. napus</i>	3.10	0.16	1.5	21	1.34	12.7	7.3	13.1	37	2.24
17	<i>B. napus</i>	3.85	0.17	1.92	60.8	2.49	18.8	8.97	1.48	0.29	0.83
6	<i>B. napus</i>	3.78	0.19	2.05	62.1	3.02	16.9	8.71	1.68	0.67	0.48
16	<i>B. napus</i>	3.73	0.17	1.9	62.2	2.63	16.9	8.04	2.26	1.41	0.46
Mean		3.52	0.15	1.71	44.8	2.14	15.8	8.42	6.02	15.7	1.25
12	<i>B. rapa</i>	2.70	0.00	1.23	33	1.75	18.2	9.54	9.55	21.3	2.19
10	<i>B. rapa</i>	3.33	0.17	1.53	54.9	2.61	21.0	12	1.87	1.51	0.70
4	<i>B. rapa</i>	3.31	0.18	1.5	54.9	2.68	21.3	21.3	1.69	1.31	0.84
8	<i>B. rapa</i>	3.40	0.18	1.43	55.7	2.69	21.4	12.1	1.24	0.94	0.60
Mean		3.19	0.13	1.42	49.6	2.43	20.9	11.4	3.59	6.27	1.12

Table 5.4 Fatty acid profile of *B. rapa* oils (n = 3)

Sample ID	Palmitic Acid (C16:0)	Stearic Acid (C18:0)	Oleic Acid (C18:1)	Vaccenic Acid (C18:1)	Linoleic Acid (C18:2)	Linolenic Acid (C18:3)	Eicosanoic Acid (C20:1)	Others
ACS-C7	3.56	0.17	54.93	1.47	22.85	13.37	1.01	1.40
COMP-4	3.45	1.60	59.22	2.68	21.01	10.06	1.00	0.91
El Dorado	3.76	1.79	59.09	2.71	21.26	9.14	1.04	1.16
Goldrush	3.05	1.47	54.20	3.08	22.81	12.91	1.14	1.25
Parkland	3.34	1.37	53.17	3.05	12.20	13.84	0.96	1.18
Reward	3.44	1.53	54.89	3.21	22.46	12.29	0.93	1.26
Sunbeam	3.55	1.58	55.76	2.79	21.43	11.05	1.57	1.22
Tobin	3.33	1.54	55.50	3.06	22.09	12.33	1.01	1.32
TR2	3.25	1.48	55.07	2.97	21.46	13.62	1.02	1.22
TR3	3.68	1.49	55.53	3.1	21.50	12.61	0.89	1.20
TR5	3.27	1.50	57.49	2.76	21.86	11.31	0.96	0.96

Table 5.5 Iodine values (IV) of *Cruciferae* oils ($n = 3$)

Sample ID	Genus	Species	Cultivar	IV	Mean IV
19	<i>Sinapis</i>	<i>alba</i>	AC Base	104.10	
23	<i>Sinapis</i>	<i>alba</i>	AC Pennant	102.44	
2	<i>Sinapis</i>	<i>alba</i>	Andante	104.12	
18	<i>Sinapis</i>	<i>alba</i>	AC Pennant	102.78	103.36 ± 0.88
13	<i>Sinapis</i>	<i>alba</i>	FMK1	98.31	
5	<i>Sinapis</i>	<i>alba</i>	Svalof	96.93	97.62 ± 0.98
9	<i>Brassica</i>	<i>carinata</i>	57EM	119.77	
14	<i>Brassica</i>	<i>carinata</i>		114.81	117.29 ± 3.51
20	<i>Brassica</i>	<i>juncea</i>		107.24	
7	<i>Brassica</i>	<i>juncea</i>		107.43	
1	<i>Brassica</i>	<i>juncea</i>		109.35	
11	<i>Brassica</i>	<i>juncea</i>		108.67	
22	<i>Brassica</i>	<i>juncea</i>		106.81	107.90 ± 1.07
3	<i>Brassica</i>	<i>napus</i>	Argentine	102.96	
21	<i>Brassica</i>	<i>napus</i>	Nugget	98.59	
17	<i>Brassica</i>	<i>napus</i>	Midas	112.01	
6	<i>Brassica</i>	<i>napus</i>	AC Excel	110.02	
16	<i>Brassica</i>	<i>napus</i>	Westar	108.86	106.49 ± 6.23
12	<i>Brassica</i>	<i>rapa</i>	Zangyou	110.68	
10	<i>Brassica</i>	<i>rapa</i>	TR8	120.30	
4	<i>Brassica</i>	<i>rapa</i>		120.47	
8	<i>Brassica</i>	<i>rapa</i>	ACS-C7	120.87	118.08 ± 4.94

Table 5.6 Iodine values (IV) of *B. rapa* oils ($n = 3$)

Cultivar	Iodine Value
ACS-C7	127.43
COMP-4	120.26
El Dorado	118.54
Goldrush	125.56
Parkland	128.83
Reward	125.19
Sunbeam	122.02
Tobin	125.03
TR-2	126.81
TR-3	125.03
TR-5	123.01

5.4 Chemical and Physical Properties of *Cruciferae* and *B. rapa* Oils

5.4.1 Density of *Cruciferae* and *B. rapa* Oils

The density of each *Cruciferae* oils was determined at temperatures between 0 °C and 100 °C (Table 5.7). At temperatures near 0 °C, *S. alba* had the lowest density (0.908 g/mL), and *B. juncea* the highest density (0.924 g/mL). As the temperature increased, the density of all oils decreased following a linear relationship (Figure 5.1). At temperatures near 100 °C, *B. carinata* had the highest density (0.880 g/mL) and *B. rapa* the lowest (0.847 g/mL).

The densities of three selected *B. rapa* oils also were determined at temperatures between 0 °C and 100 °C (Table 5.8). At temperatures near 0 °C, the densities of the oils were very similar (0.926 g/mL for both ACS-C7 and COMP-4, and 0.925 g/mL for Sunbeam). As the temperature increased, the densities of all three oils decreased linearly, but differed very little amongst the three oil samples. All three vegetable oils followed a similar linear trend when the motor oil additive ZDDP was added (Figure 5.2). The density of mineral oil and mineral oil + ZDDP was significantly lower than that of the three vegetable oils, but also followed an inverse linear trend at temperatures between 0 °C and 100 °C. The densities of *B. rapa* oils decreased by up to 0.061 g/mL as temperature increased. With the addition of ZDDP to the *B. rapa* oils, the decrease in density with increasing temperature ranged from 0.047–0.067 g/mL.

5.4.2 Viscosity of *Cruciferae* and *B. rapa* Oils

The viscosity of each *Cruciferae* oil was determined at temperatures between 0 °C and 100 °C (Table 5.9). At low temperatures, *S. alba* and *B. rapa* had relatively low viscosities (76 cP), while *B. carinata* and *B. juncea* had high viscosities (107 and 120 cP, respectively). As temperature increased, the viscosity of all oils decreased following an inverse exponential relationship (Figure 5.3). At temperatures near 100 °C, the viscosity of the oils dropped to 14 cP, with the exception of *B. juncea*, which a viscosity of 16 cP at 100 °C.

The viscosity of *B. rapa* oils also was determined at temperatures between 0 °C and 100 °C (Table 5.10). At 5 °C, the viscosity of *B. rapa* ranged from 82 cP (ACS-C7) to 96 cP (COMP-4). The addition of ZDDP decreased the viscosity of all oils slightly (79 cP for ACS-C7 + ZDDP, and 86 cP for COMP-4 + ZDDP). As the temperature increased, the viscosity of all oils, with or without ZDDP, decreased. As temperatures approached 100 °C, the viscosity of all

oils, with or without ZDDP, became relatively low, ranging from 12 cP (COMP-4 + ZDDP) to 15 cP (COMP-4). The viscosity of mineral oil at 5 °C was 60 cP, and 57 cP with the addition of ZDDP. Mineral oil and mineral oil + ZDDP also demonstrated an inverse exponential decrease with increasing temperature, to a minimum of 12 cP, at 75–95 °C (Figure 5.4). It is important to note that the minimal limit of the viscosity cups used to measure the viscosity of the oil samples was 12 cP.

Table 5.7 Effect of temperature on the density (g/mL) of select *Cruciferae* oils

Temperature (°C)	<i>S. alba</i>	<i>B. napus</i>	<i>B. juncea</i>	<i>B. carinata</i>	<i>B. rapa</i>
5	0.908	0.916	0.924	0.918	0.917
15	0.896	0.912	0.919	0.917	0.899
25	0.892	0.906	0.912	0.911	0.894
35	0.887	0.903	0.906	0.908	0.891
45	0.881	0.901	0.899	0.905	0.884
55	0.879	0.886	0.891	0.901	0.877
65	0.874	0.879	0.885	0.891	0.869
75	0.873	0.868	0.879	0.89	0.862
85	0.868	0.863	0.875	0.884	0.855
95	0.866	0.857	0.872	0.88	0.847

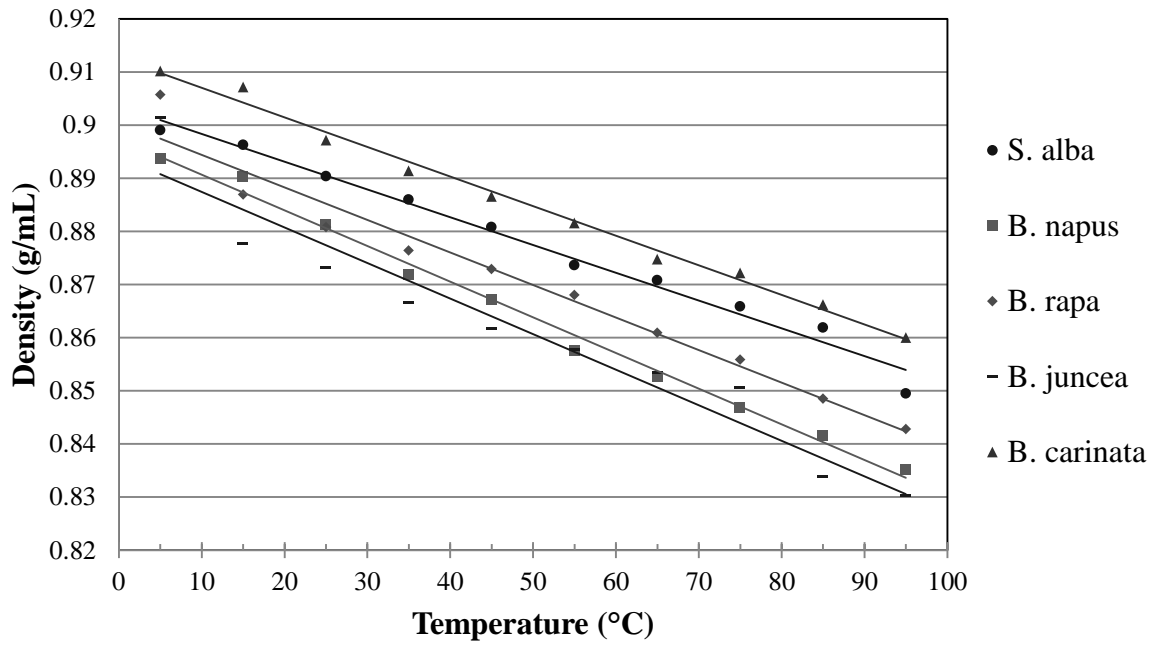


Figure 5.2 Density of *Cruciferae* oil at temperatures between 0 °C and 100 °C.

Table 5.8 Effect of temperature on the density (g/mL) of *B. rapa* oils

Temperature (°C)	ACS-C7	ACS-C7 + ZDDP	COMP-4	COMP-4 + ZDDP	Sunbeam	Sunbeam + ZDDP	Mineral Oil	Mineral Oil + ZDDP
5	0.926	0.922	0.926	0.93	0.925	0.93	0.861	0.865
15	0.919	0.923	0.917	0.92	0.916	0.924	0.852	0.853
25	0.908	0.915	0.91	0.911	0.91	0.919	0.842	0.946
35	0.905	0.908	0.902	0.903	0.903	0.909	0.837	0.838
45	0.897	0.905	0.894	0.897	0.896	0.904	0.831	0.833
55	0.89	0.896	0.88	0.887	0.888	0.898	0.823	0.825
65	0.884	0.889	0.881	0.88	0.882	0.894	0.816	0.819
75	0.879	0.887	0.875	0.875	0.878	0.887	0.81	0.814
85	0.871	0.88	0.868	0.869	0.871	0.881	0.804	0.808
95	0.865	0.875	0.864	0.863	0.865	0.876	0.798	0.802

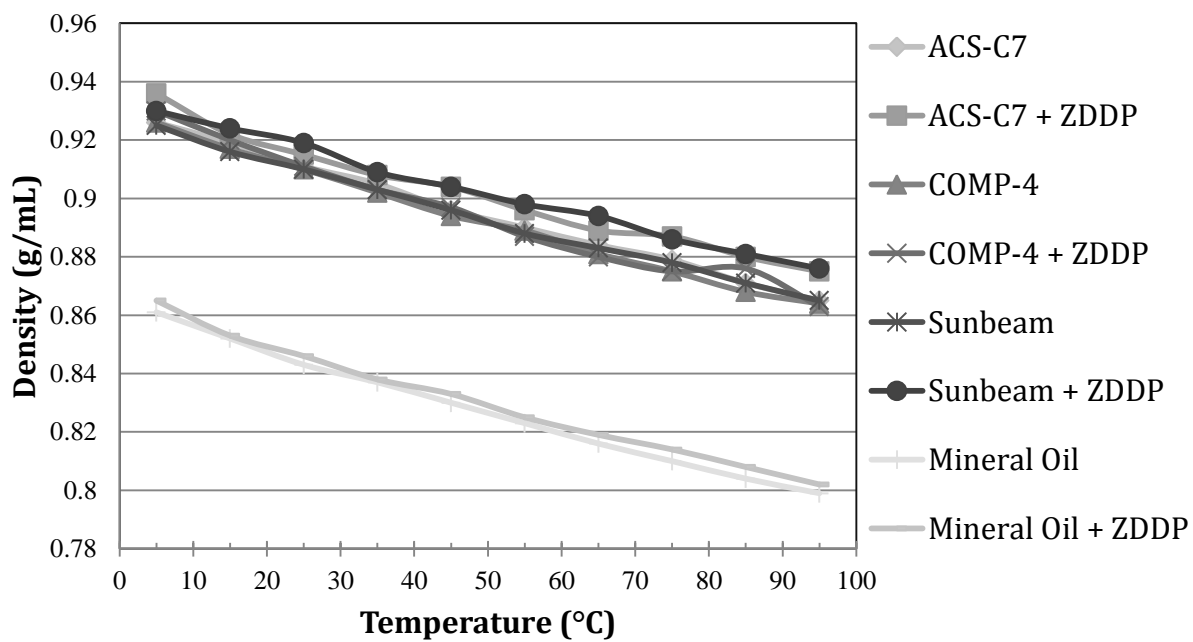


Figure 5.3 Density of *B. rapa* oil at temperatures between 0 °C and 100 °C.

Table 5.9 Effect of temperature on the viscosity (cP) of select *Cruciferae* oils ($n = 3$)

Temperature (°C)	<i>S. alba</i>	<i>B. napus</i>	<i>B. juncea</i>	<i>B. carinata</i>	<i>B. rapa</i>
5	76	81	120	107	76
15	60	72	88	76	56
25	42	64	68	55	40
35	36	42	46	38	34
45	32	32	38	30	30
55	30	28	28	24	26
65	28	25	21	19	24
75	22	22	18	17	22
85	17	14	16	17	14
95	14	14	16	14	14

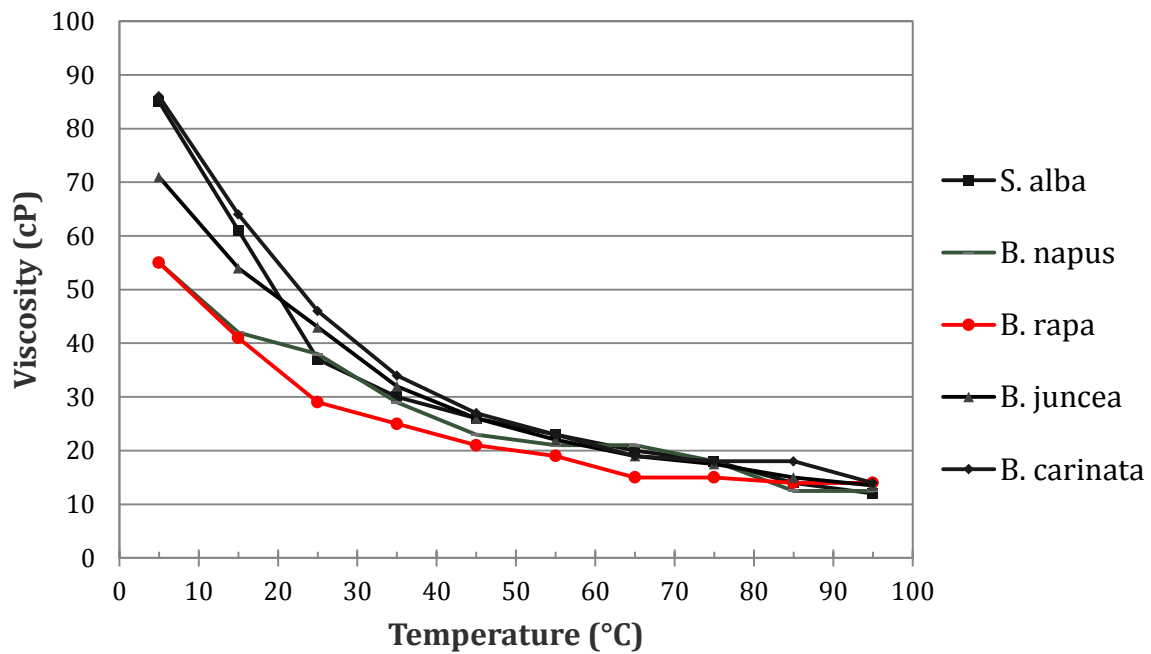


Figure 5.4 Viscosity of *Cruciferae* oils at temperatures between 0 °C and 100 °C.

Table 5.10 Effect of temperature on the viscosity (cP) of *B. rapa* oils

Temperature (°C)	Mineral Oil	Mineral Oil + ZDDP	ACS-C7	ACS-C7 + ZDDP	COMP-4	COMP-4 + ZDDP	Sunbeam	Sunbeam + ZDDP
5	60	57	82	79	96	86	93	83
15	44	48	69	66	82	76	80	68
25	33	35	57	53	63	43	59	56
35	22	27	41	41	45	33	44	40
45	16	19	30	32	34	25	33	32
55	14	15	26	26	28	20	27	25
65	13	13	22	22	23	15	23	19
75	12	12	18	16	20	14	19	15
85	–	–	15	15	15	12	15	14
95	–	–	14	14	15	–	13	12

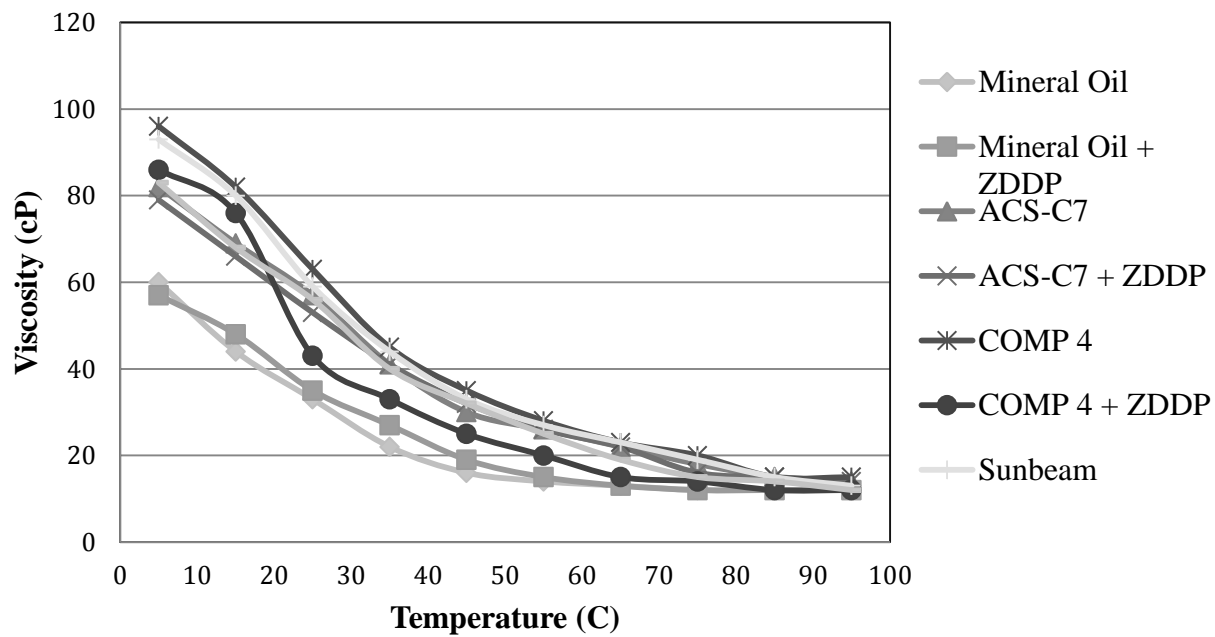


Figure 5.4 Viscosity of *B. rapa* oils at temperatures between 0 °C and 100 °C.

5.4.3 Cold Temperature Properties of *Cruciferae* and *B. rapa* Oils

The mean temperatures at which the *Cruciferae* and *B. rapa* oils became cloudy are listed in Tables 5.11 and 5.12, respectively. The cloud points and pour points of the five *Cruciferae* oil samples varied widely. *S. alba* had the highest (and therefore least desirable) cloud point and pour point, at $-4\text{ }^{\circ}\text{C}$ and $-22\text{ }^{\circ}\text{C}$, respectively. *B. juncea* also had higher values for cloud point ($-8\text{ }^{\circ}\text{C}$) and pour point ($-23\text{ }^{\circ}\text{C}$). *B. napus* and *B. carinata* had moderate cloud points, both at $-15\text{ }^{\circ}\text{C}$, and their pour points were $-26\text{ }^{\circ}\text{C}$ and $-25\text{ }^{\circ}\text{C}$, respectively. *B. rapa* had the lowest cloud and pour points, $-21\text{ }^{\circ}\text{C}$ and $-31\text{ }^{\circ}\text{C}$, respectively.

As a result of their cloud and pour points, *B. rapa* oils were selected for further analysis. Oils from eleven varieties of *B. rapa* were tested for their suitability as a lubricant base oil. The mean cloud points and pour points of the 11 *B. rapa* oil samples are listed in Table 5.12. COMP-4 and Sunbeam had the highest measured cloud point ($-18\text{ }^{\circ}\text{C}$) and pour point ($-27\text{ }^{\circ}\text{C}$), respectively. ACS-C7 had both the lowest cloud point and the lowest pour point, $-20\text{ }^{\circ}\text{C}$ and $-33\text{ }^{\circ}\text{C}$, respectively. Further experimentation was performed on these three oils (*B. rapa* ACS-C7, COMP-4 and Sunbeam), selected to represent both poor cold-temperature and superior cold-temperature samples.

5.4.4 Oxidative Stability of *Cruciferae* and *B. rapa* Oils

The oxidative stabilities at $97.8\text{ }^{\circ}\text{C}$ of five *Cruciferae* oils were measured. Oil from *B. carinata* had the lowest OSI at 5.2 h, and would therefore be the least oxidatively stable. *B. rapa* also had a relatively low OSI at 5.8 h. *S. alba* (both high and low oil varieties) had the highest oxidative stability at 16.2 h.

The oxidative stabilities of selected *B. rapa* oils were measured with and without the addition of ZDDP (Table 5.13). Oil from Sunbeam had an oxidative stability of 15.5 ± 0.8 h without ZDDP and 26.1 ± 6.3 h with the addition of ZDDP. Oil from ACS-C7 had an OSI of 17.6 ± 1.0 h, and ACS-C7 + ZDDP had an OSI of 27.3 ± 8.8 h. The highest measured OSI was from COMP-4 at 18.6 ± 8.4 h, and COMP-4 + ZDDP at 79.9 ± 6.5 h. Oxidative stability measurements were stopped at 95 h for both mineral oil and mineral oil with ZDDP.

Table 5.11 Cold temperature properties of select *Cruciferae* oils ($n = 3$)

Sample ID	Mean Cloud Point (°C)	Mean Pour Point (°C)
<i>S. alba</i>	-4	-22
<i>B. napus</i>	-15	-26
<i>B. juncea</i>	-8	-23
<i>B. carinata</i>	-15	-25
<i>B. rapa</i>	-21	-31

Table 5.12 Cold temperature properties of *B. rapa* oils ($n = 3$)

Sample ID	Mean Cloud Point (°C)	Mean Pour Point (°C)
ACS-C7	-20	-33
COMP-4	-18	-27
El Dorado	-19	-31
Goldrush	-21	-31
Parkland	-21	-31
Reward	-17	-31
Sunbeam	-18	-24
Tobin	-23	-30
TR2	-23	-31
TR3	-19	-31
TR5	-23	-28

Table 5.13 Mean oxidative stability of *B. rapa* oils (*n* = 3)

Sample	Additive	OSI at 97.8 °C (h)
Mineral oil	NO	Stopped at 95 h
	ZDDP	Stopped at 95 h
ACS-C7	NO	17.6 ± 1.0
	ZDDP	27.3 ± 8.8
COMP-4	NO	18.6 ± 8.4
	ZDDP	79.9 ± 6.5
Sunbeam	NO	15.5 ± 0.8
	ZDDP	26.1 ± 6.2

5.4.5 Refractive Index of *Cruciferae* Oils

The refractive indices of the *Cruciferae* oils as are 1.472 (*S. alba*), 1.472 (*B. napus*), 1.473 (*B. juncea*), 1.472 (*B. carinata*), and 1.472 (*B. rapa*). There is very little variation in the measured values, ranging from 1.472 (*B. napus*) to 1.473 (*B. juncea*).

5.4.6 Wear Scar and Tribofilms

5.4.6.1 Coefficient of Friction

The mean and maximum coefficients of friction of triplicate analysis measured during wear scar production are listed for the *Cruciferae* oils in Table 5.14 and for *B. rapa* oils in Table 5.15. The coefficient of friction as measured during wear scar production for mineral oil without ZDDP is shown in Figure 5.5. In comparison, Figure 5.6 shows a coefficient of friction trace as measured during wear scar production for mineral oil with 800 ppm ZDDP. Graphical representations of these data sets are shown in Figures 5.6 and 5.7. The *B. napus* oils had the highest mean (0.0313 ± 0.0073) and highest maximum (0.0973 ± 0.0101) coefficients of friction of all *Cruciferae* oils. Both *B. juncea* and *B. rapa* had the lowest mean and lowest maximum coefficients of friction (mean coefficient of friction = 0.0231 ± 0.0104 and maximum coefficient of friction = 0.0833 ± 0.0170 for *B. juncea* and mean coefficient of friction = 0.0231 ± 0.0123 and maximum coefficient of friction = 0.0834 ± 0.0221 for *B. rapa*).

The oil from *B. rapa* Sunbeam had the lowest mean coefficient of friction with (0.087 ± 0.0044) and without (0.048 ± 0.0040) ZDDP. Sunbeam also had the lowest maximum coefficient of friction with (0.097 ± 0.0036) and without (0.091 ± 0.0035) ZDDP. COMP-4 had slightly higher results for both mean coefficient of friction (0.048 ± 0.0056 without ZDDP and 0.087 ± 0.0134 with ZDDP) and maximum coefficient of friction (0.090 ± 0.0055 without ZDDP and 0.097 ± 0.0106 with ZDDP). ACS-C7 had the highest mean coefficient of friction (0.063 ± 0.0018 without ZDDP and 0.090 ± 0.0038 with ZDDP) and maximum coefficient of friction (0.093 ± 0.0023 without ZDDP and 0.097 ± 0.0026 with ZDDP). Interestingly, all three *B. rapa* oils had the same value for maximum coefficient of friction with the addition of ZDDP (ranging from 0.097 ± 0.0026 to 0.097 ± 0.0106). In comparison, mineral oil had a mean coefficient of friction of 0.108 ± 0.0017 , and 0.116 ± 0.0007 with ZDDP, and a maximum coefficient of friction of 0.148 ± 0.0165 and 0.134 ± 0.0035 with ZDDP.

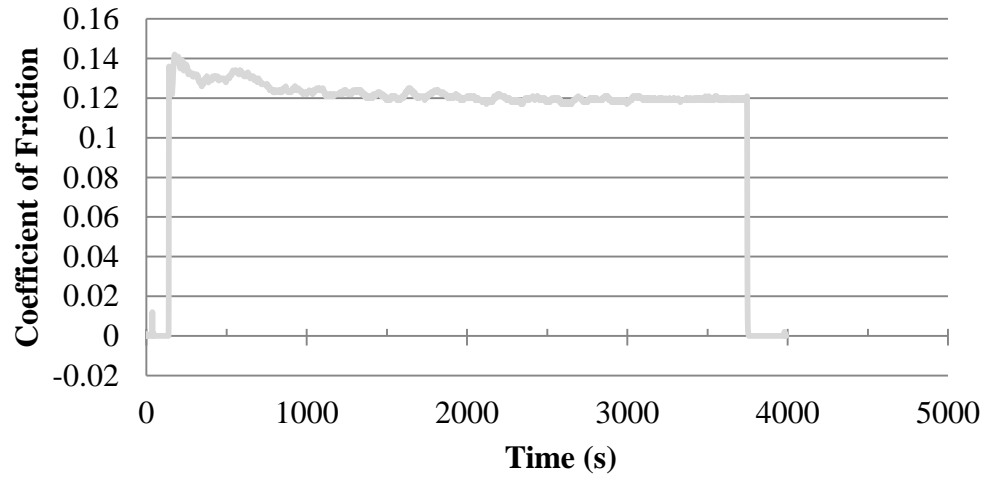


Figure 5.5 Friction trace for mineral oil without ZDDP.

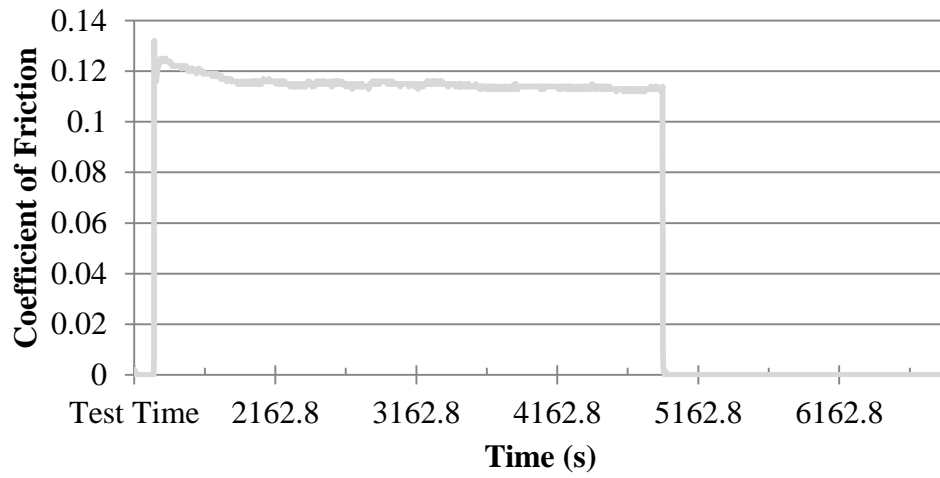


Figure 5.6 Friction trace for mineral oil with ZDDP.

Table 5.14 Coefficients of friction of *Cruciferae* oils during wear scar production ($n = 3$)

<i>Cruciferae</i> oil	Mean Coefficient of Friction	Maximum Coefficient of Friction
<i>S. alba</i>	0.0281 ± 0.0067	0.0949 ± 0.0070
<i>B. napus</i>	0.0313 ± 0.0073	0.0973 ± 0.0101
<i>B. rapa</i>	0.0231 ± 0.0123	0.0834 ± 0.0221
<i>B. juncea</i>	0.0231 ± 0.0104	0.0833 ± 0.0170
<i>B. carinata</i>	0.0261 ± 0.0003	0.0875 ± 0.0092

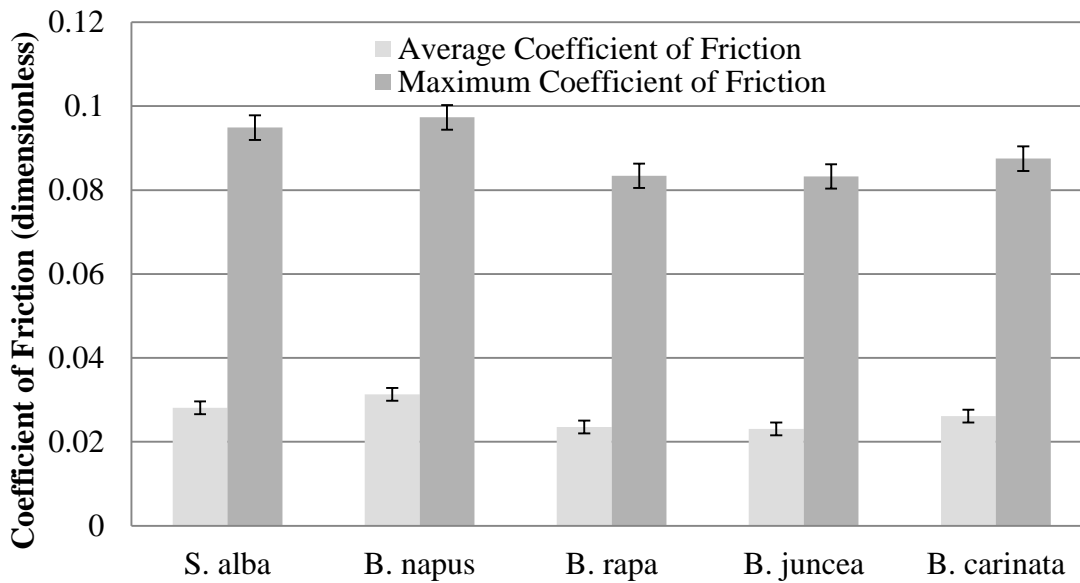


Figure 5.7 Mean and maximum coefficients of friction for *Cruciferae* oil samples.

Table 5.15 Coefficients of friction of *B. rapa* oils during wear scar production ($n = 3$)

<i>B. rapa</i> Oil	Mean Coefficient of Friction	Maximum Coefficient of Friction
ACS-C7	0.063 ± 0.0018	0.093 ± 0.0026
ACS-C7 + ZDDP	0.090 ± 0.0038	0.097 ± 0.0026
COMP-4	0.048 ± 0.0056	0.090 ± 0.0055
COMP-4 + ZDDP	0.087 ± 0.0134	0.097 ± 0.0106
Sunbeam	0.048 ± 0.0040	0.091 ± 0.0035
Sunbeam + ZDDP	0.087 ± 0.0044	0.097 ± 0.0036
Mineral oil	0.108 ± 0.0017	0.148 ± 0.0165
Mineral oil + ZDDP	0.116 ± 0.0007	0.134 ± 0.0035

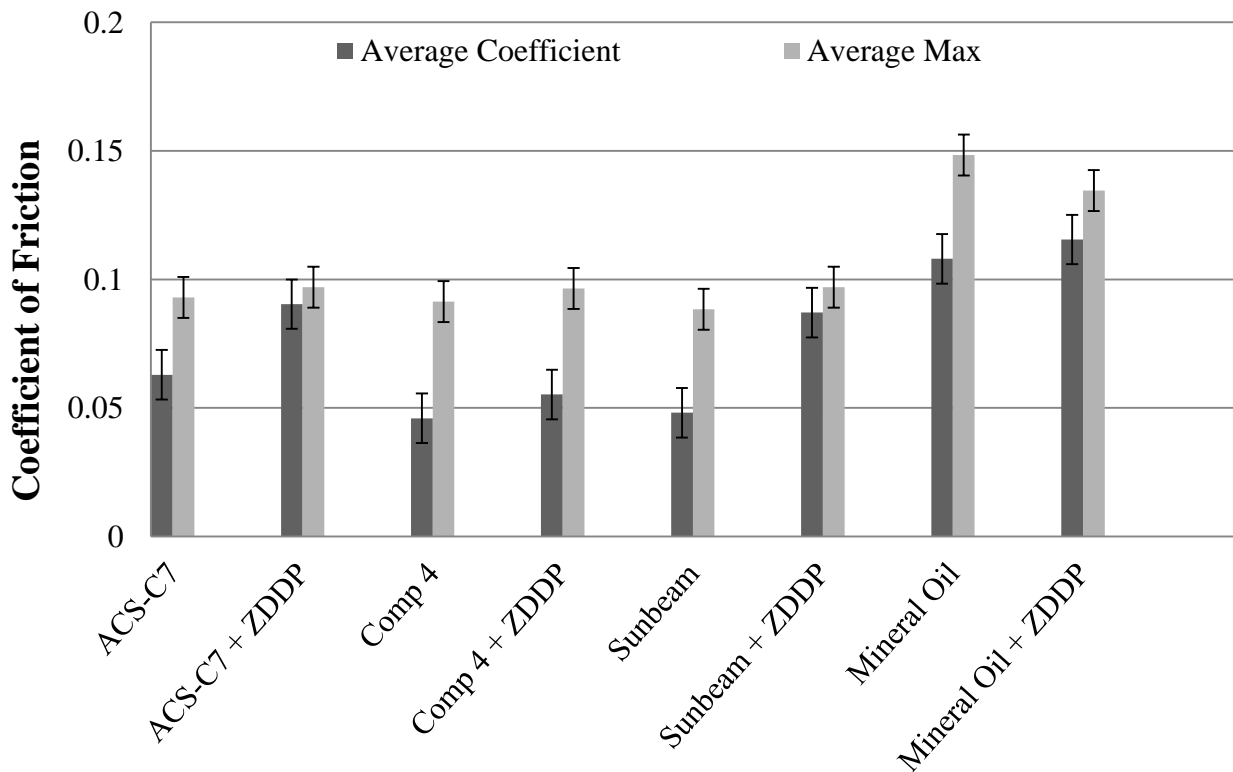


Figure 5.8 Mean and maximum coefficients of friction for *B. rapa* oil samples

5.4.6.2 Wear Scar Width

The width of the scar created on the pin by friction against the stainless steel during Plint Tribometer testing was measured at 100× magnification for *Cruciferae* oils (Tables 5.16 and 5.17, Figures 5.9–5.14). Measurements were taken at ten (10) points along the flattened side of the pin, and the mean wear scar width was calculated. *S. alba* oils had the largest measured wear scar width (591 μm). *B. juncea* also had a large wear scar, measuring 541 μm. *B. carinata* and *B. rapa* had similar mean wear scars widths at 517μm and 514μm, respectively. *B. napus* had the smallest mean wear scar width (482 μm).

There was a large range in mean wear scar widths measured across the different *B. rapa* varieties. The *B. rapa* oil ACS-C7 had the smallest measured wear scar width, both with (252 μm, Figure 5.15) and without (222 μm) ZDDP. COMP-4 also had a small wear scar 247 μm and 277 μm with ZDDP. Sunbeam had the largest wear scar without ZDDP (269 μm) and with ZDDP (547 μm). Mineral oil, without ZDDP, had a wear scar width higher than most *B. rapa* oils with and without ZDDP, at 461 μm. When ZDDP was added to the mineral oil, the wear scar width was 501 μm. It must be noted that some variation will occur across the length of the pin due to uneven loading into the Plint Tribometer.

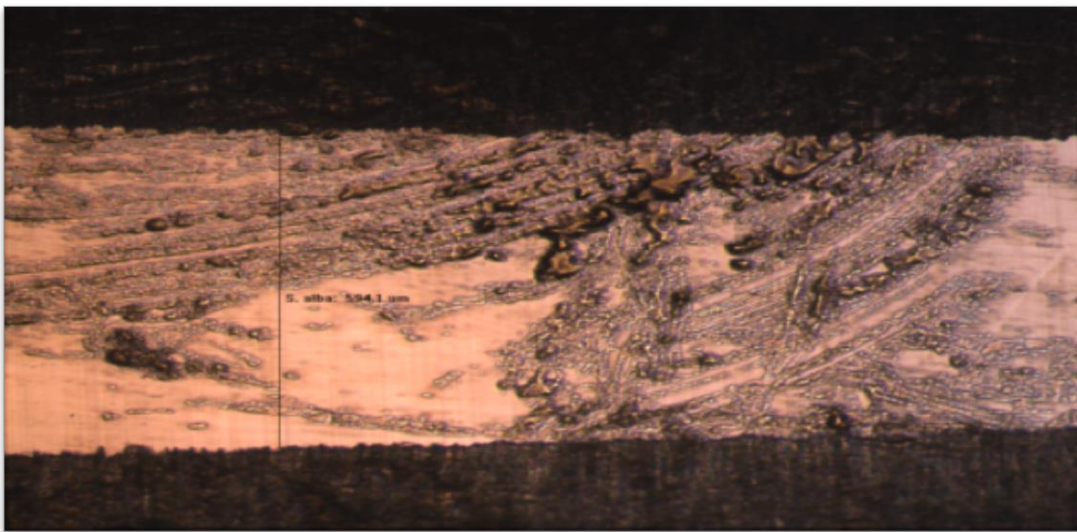


Figure 5.9 *S. alba* wear scar width at 100× magnification.

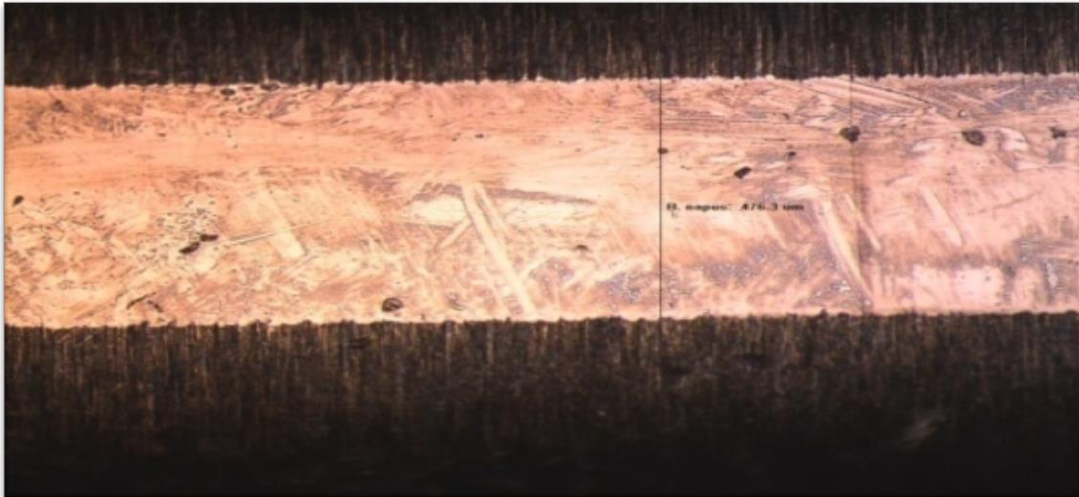


Figure 5.10 *B. napus* wear scar width at 100× magnification.

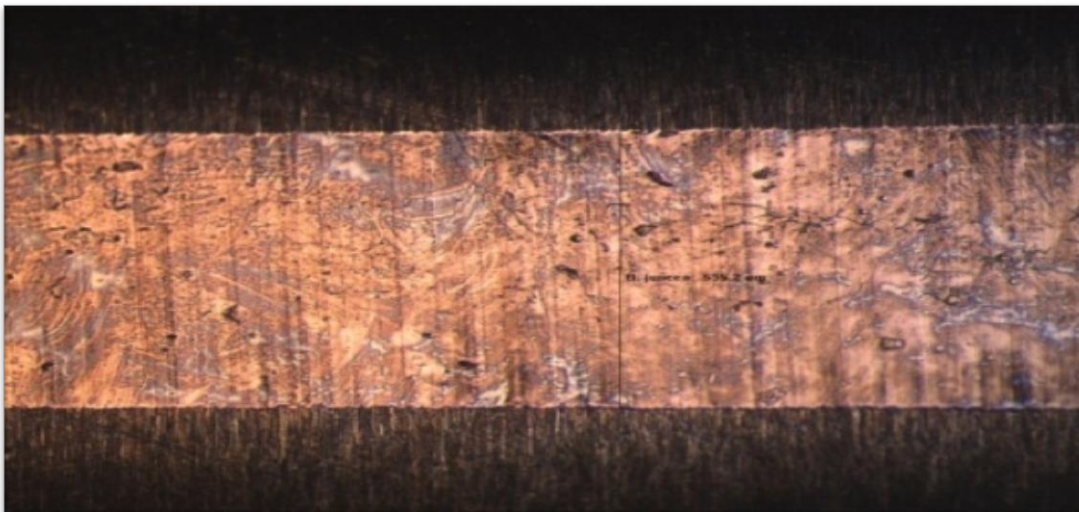


Figure 5.11 *B. juncea* wear scar width at 100× magnification.

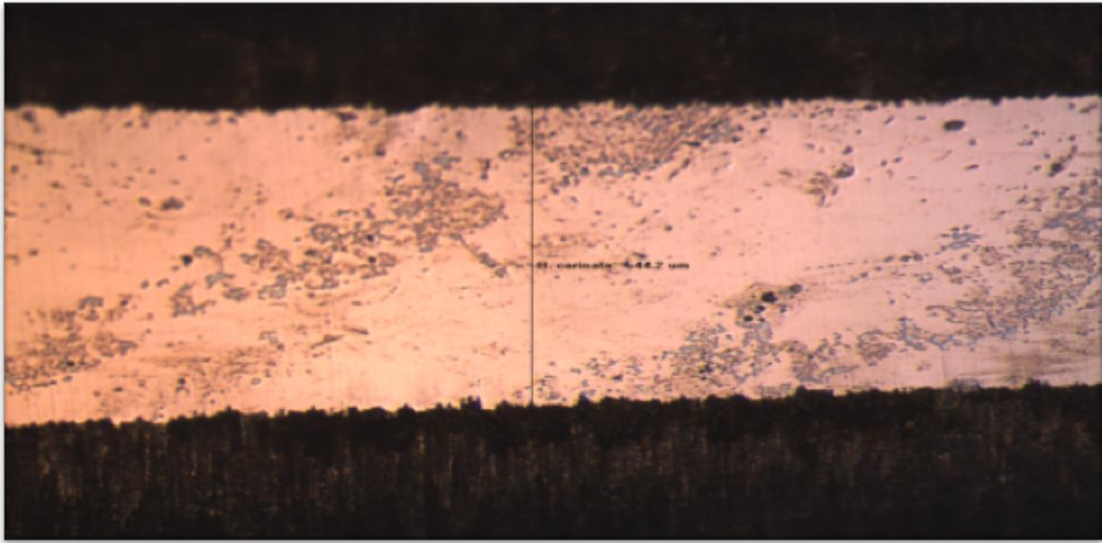


Figure 5.12 *B. carinata* wear scar width at 100× magnification.

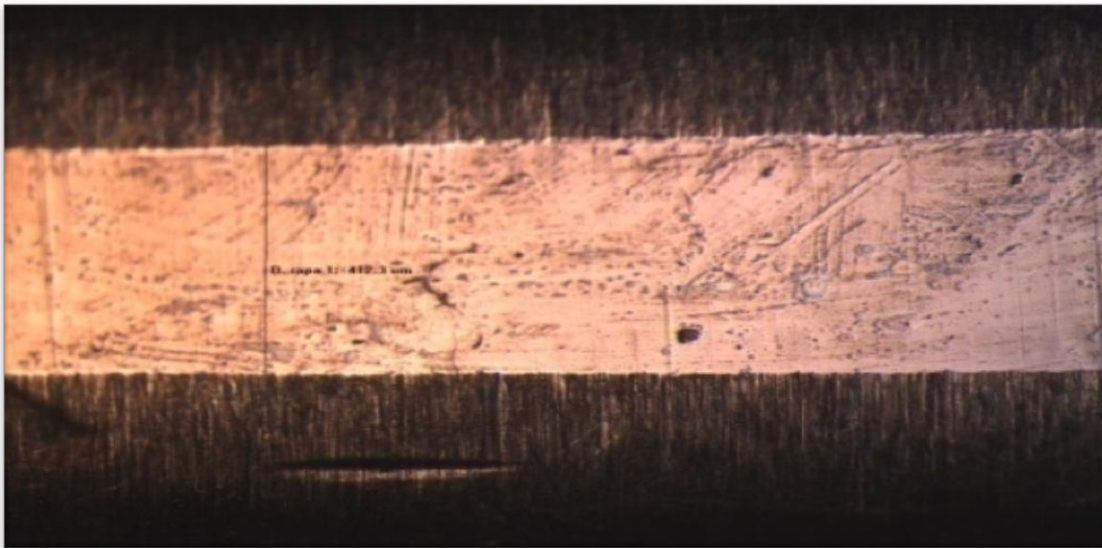


Figure 5.13 *B. rapa* wear scar width at 100× magnification.

Table 5.16 Mean wear scar width (μm) at 100 \times magnification of *Cruciferae* oils

Sample	Mean wear scar width (μm)
Mineral oil	435 \pm 128
Mineral oil with ZDDP	511 \pm 55
<i>S. alba</i>	602 \pm 30
<i>B. napus</i>	546 \pm 47
<i>B. rapa</i>	496 \pm 49
<i>B. juncea</i>	506 \pm 55
<i>B. carinata</i>	540 \pm 84

Table 5.17 Mean wear scar width (μm) at 20 \times magnification of *B. rapa* oils

Sample	Additive	Mean wear scar width (μm)
Mineral oil	NO	461 \pm 43
	ZDDP	265 \pm 5
ACS-C7	NO	222 \pm 14
	ZDDP	252 \pm 30
COMP-4	NO	247 \pm 25
	ZDDP	277 \pm 14
Sunbeam	NO	269 \pm 39
	ZDDP	547 \pm 213

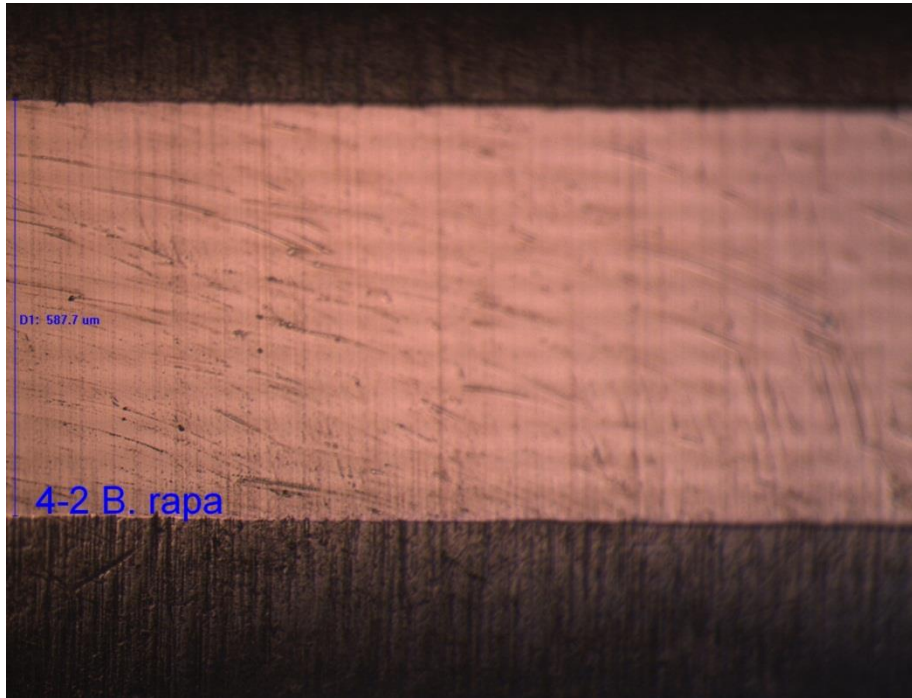


Figure 5.14 *B. rapa* wear scar width at 20× magnification.

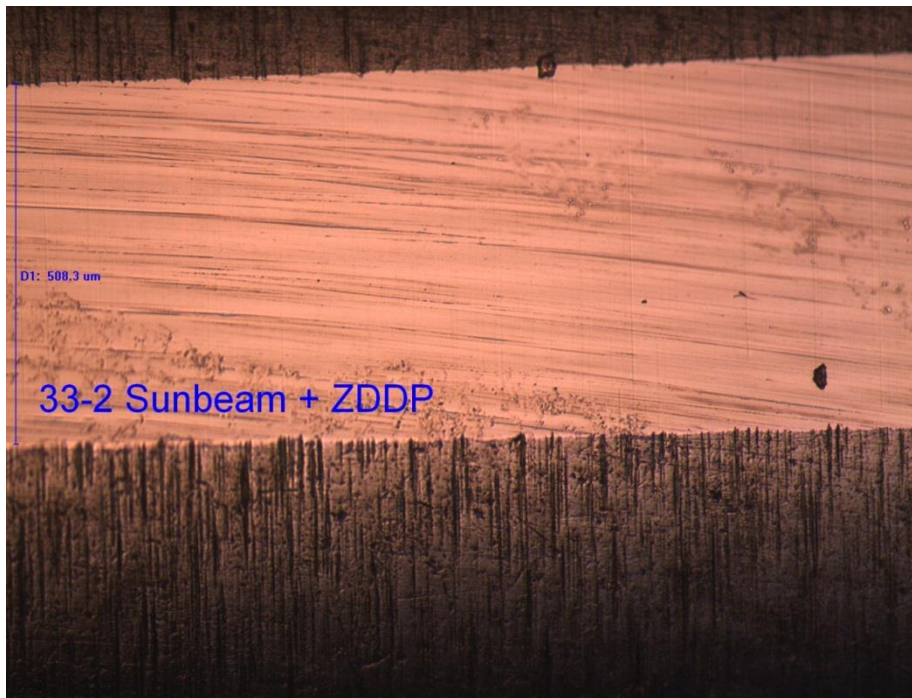


Figure 5.15 *B. rapa* + ZDDP wear scar width at 20× magnification.

5.4.6.3 X-ray Absorption Near Edge Spectroscopy

In order to confirm the presence of the tribofilms within the wear scar, each sample was compared to a known reference standard. Figures 5.16–5.21 show the spectra of five *Cruciferae* oil samples and the reference standards Iron (III) Oxide (Fe_2O_3) and graphite.

In the Fe L-edge (TEY) spectra, all five *Cruciferae* oils show a small double peak at 710 eV, similar to the double peak of the Iron (III) Oxide reference standard. The most pronounced double peak was the *B. napus* peak. The Iron (III) Oxide reference standard also has a double peak at approximately 728 eV. The *Cruciferae* oil spectra show a very small feature at 725 eV, but no distinguishable peaks were observed. The O K-edge spectrum in TEY mode shows a double peak at 535 eV and a broad peak at 545 eV for the Iron (III) Oxide reference standard. Each *Cruciferae* oil sample showed a single peak (*B. napus* had a slight shoulder) at 535 eV. All five vegetable oil samples also had a very large single peak over the range of 540–560 eV. The five C K-edge TEY *Cruciferae* oil spectra have a double peak at 290 eV, while the graphite reference standard has a double peak at 295 eV.

The spectra shown in Figure 5.22 and 5.23 are the P L-edge spectra for oil from *B. rapa* Parkland. The purpose of these spectra was to confirm the presence and form of phosphate in the tribofilm. The *B. rapa* peaks in Figure 5.24 (P K-edge TEY) and Figure 5.25 (P K-edge FY) reveal that phosphorus was present at the surface of the tribofilms.

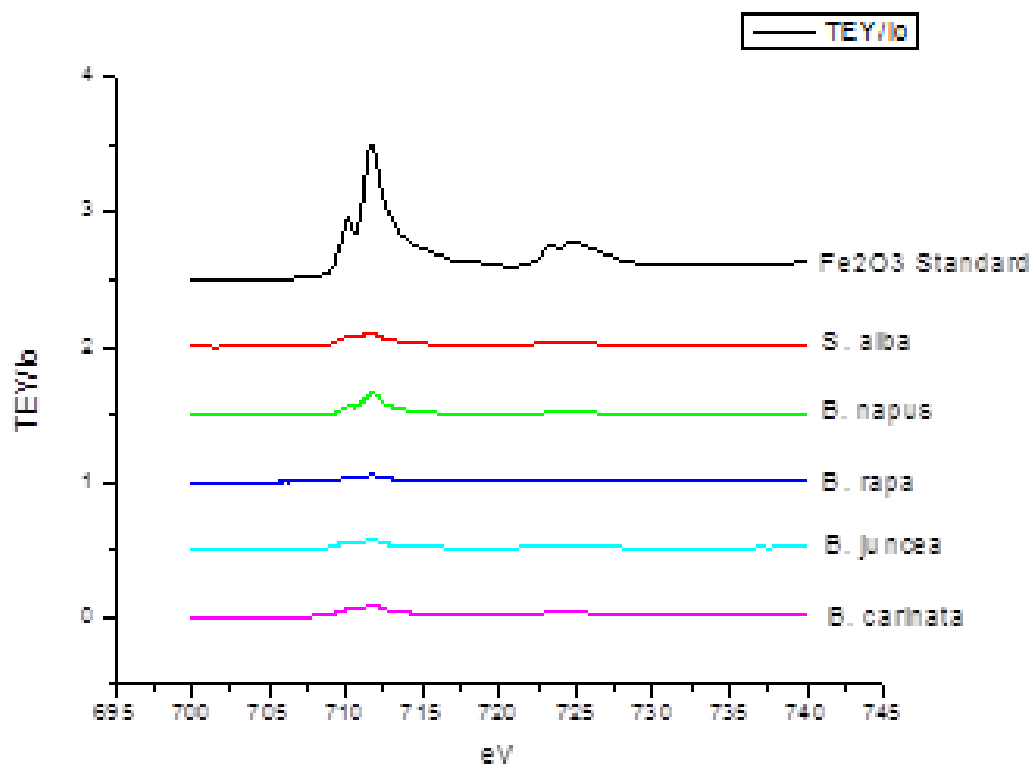


Figure 5.16 Fe L-edge TEY of *Cruciferae* oils.

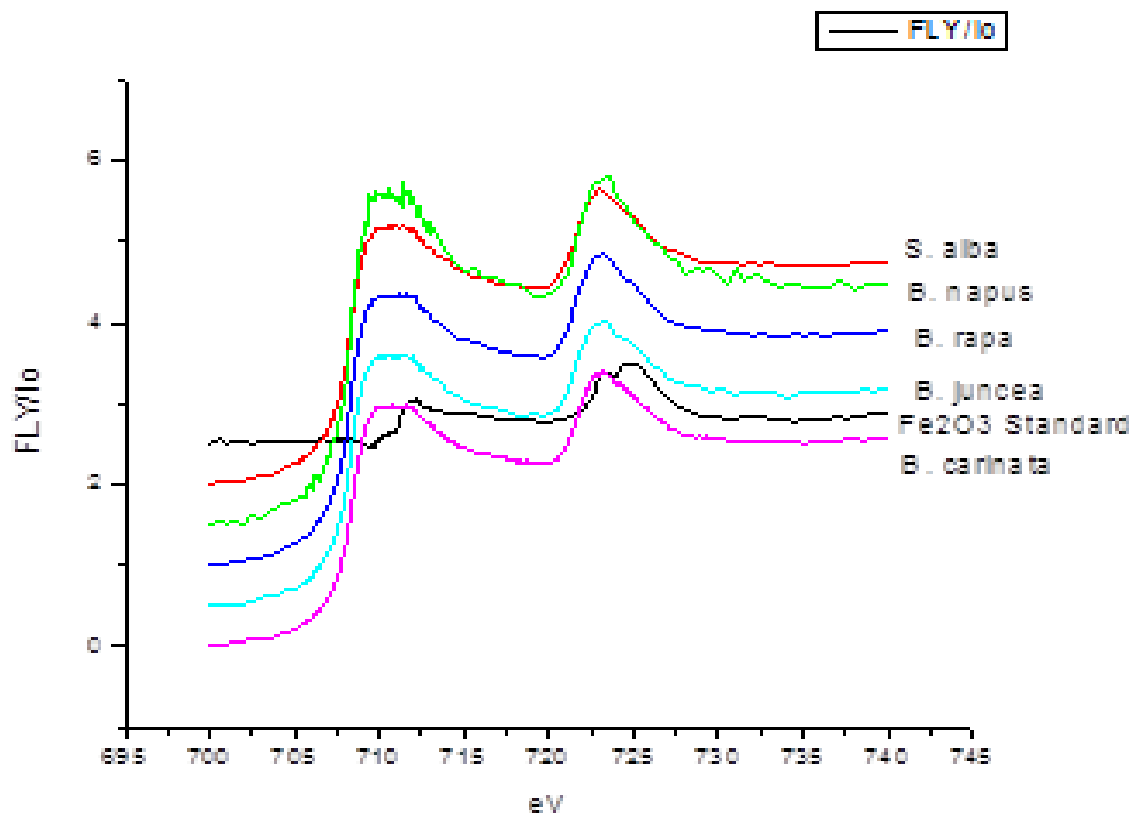


Figure 5.17 Fe L-edge FY of *Cruciferae* oils.

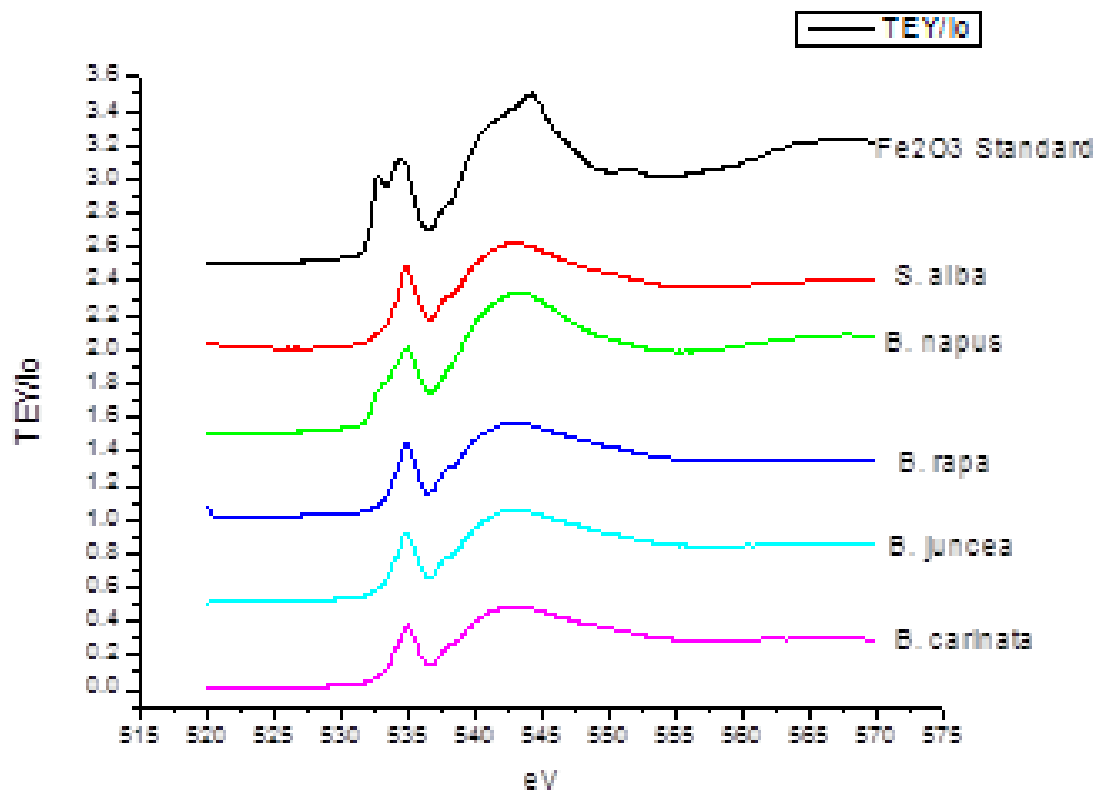


Figure 5.18 O K-edge TEY of *Cruciferae* oils.

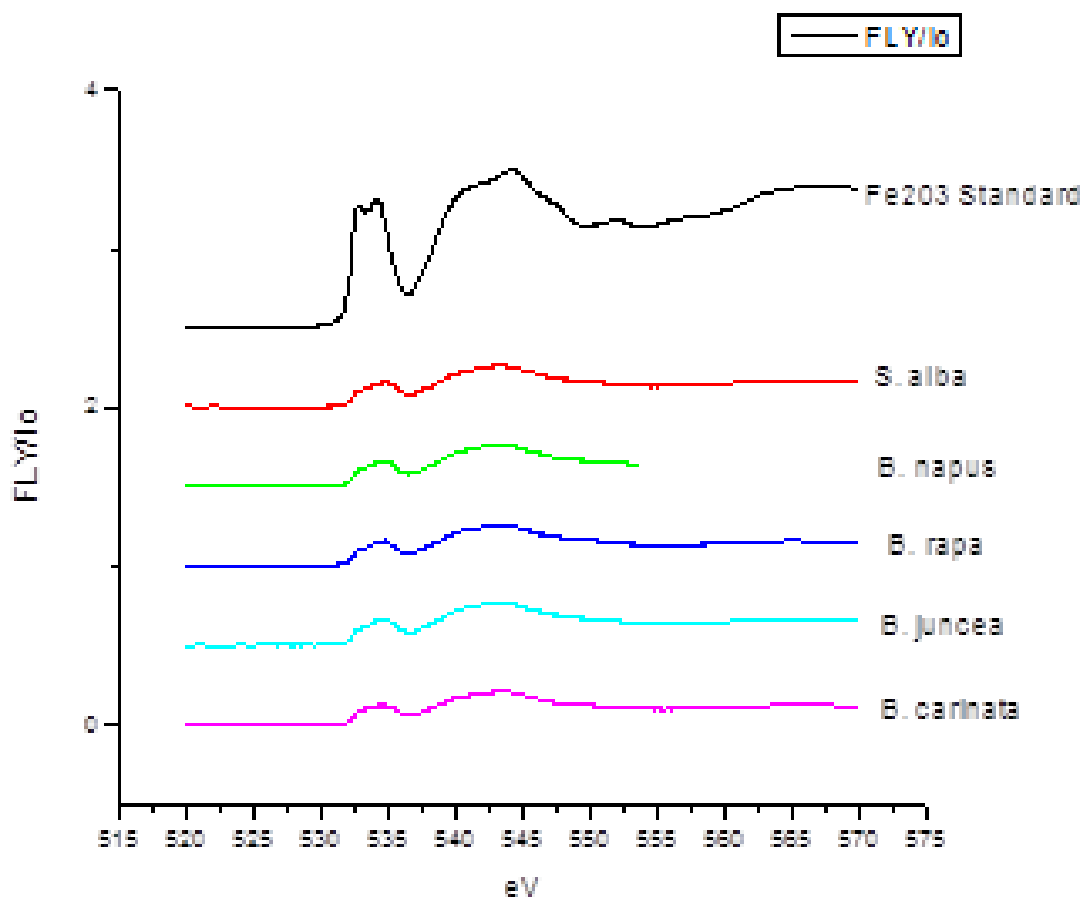


Figure 5.19 O K-edge FY of *Cruciferae* oils.

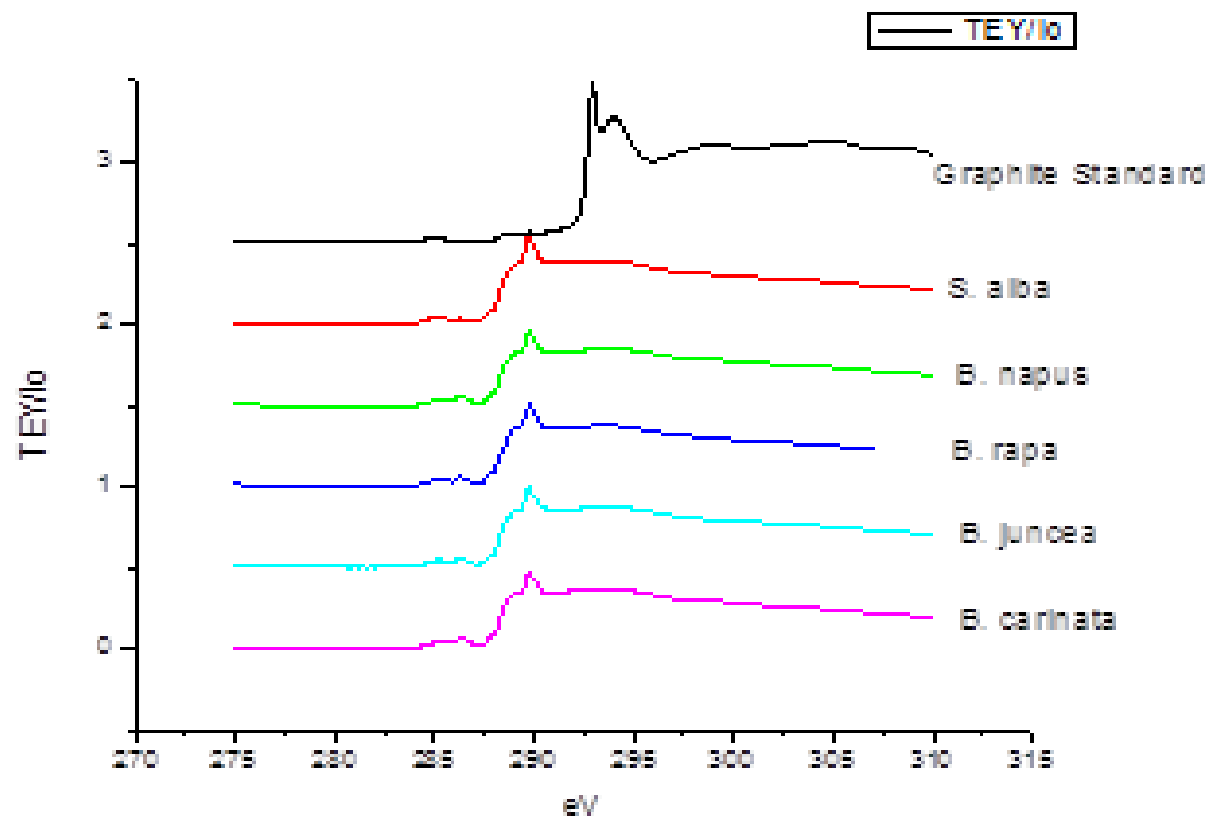


Figure 5.20 C K-edge TEY of *Cruciferae* oils.

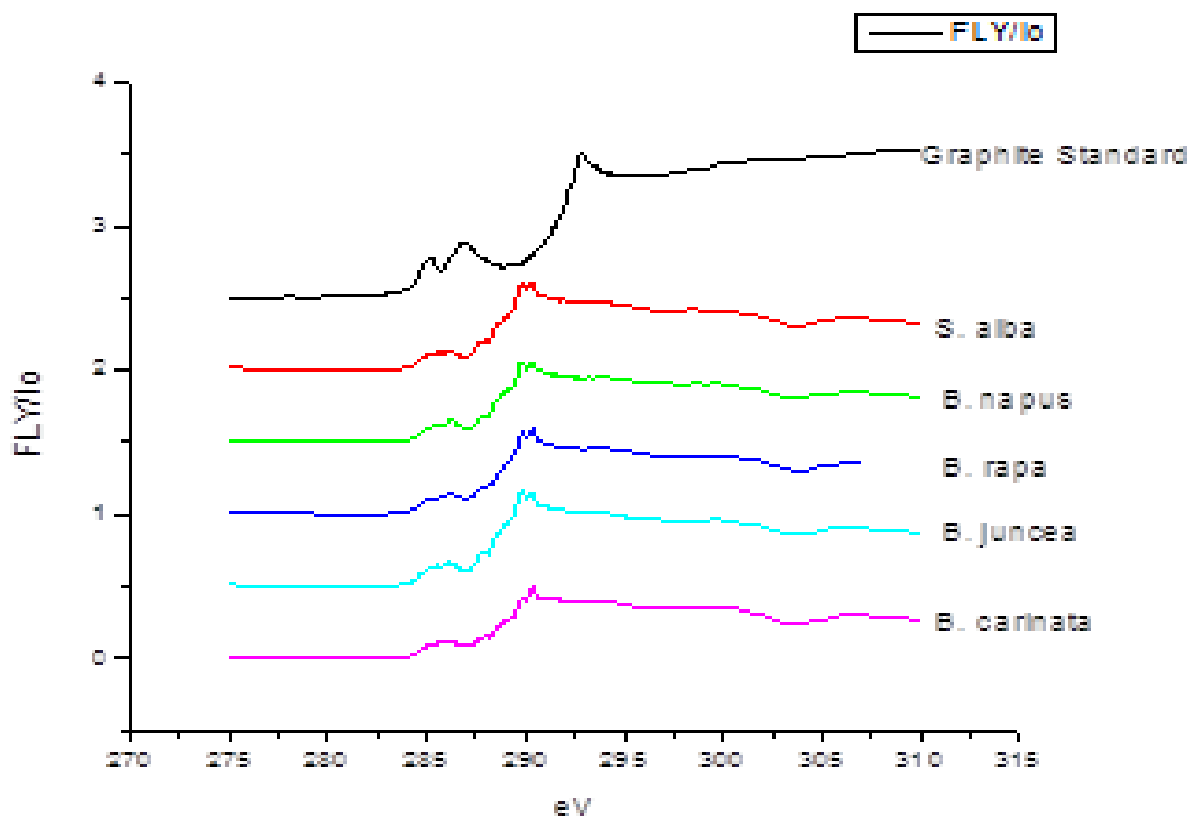


Figure 5.21 C K-edge FY of *Cruciferae* oils.

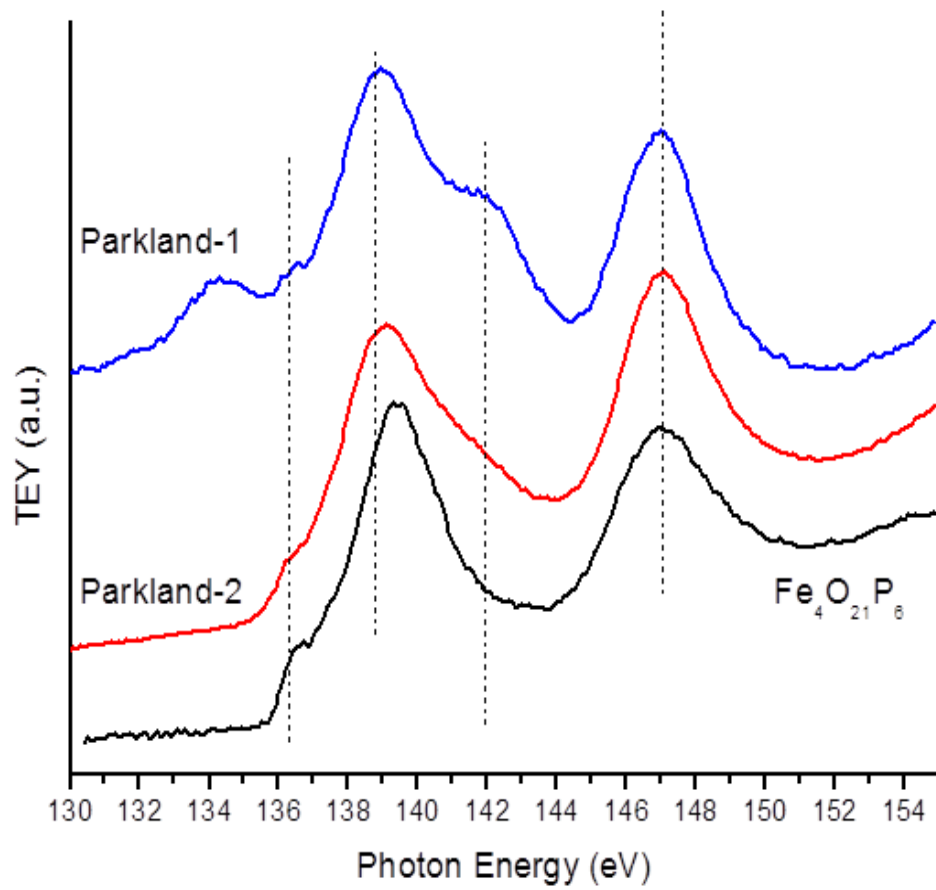


Figure 5.22 P L-edge TEY of *B. rapa* oils.

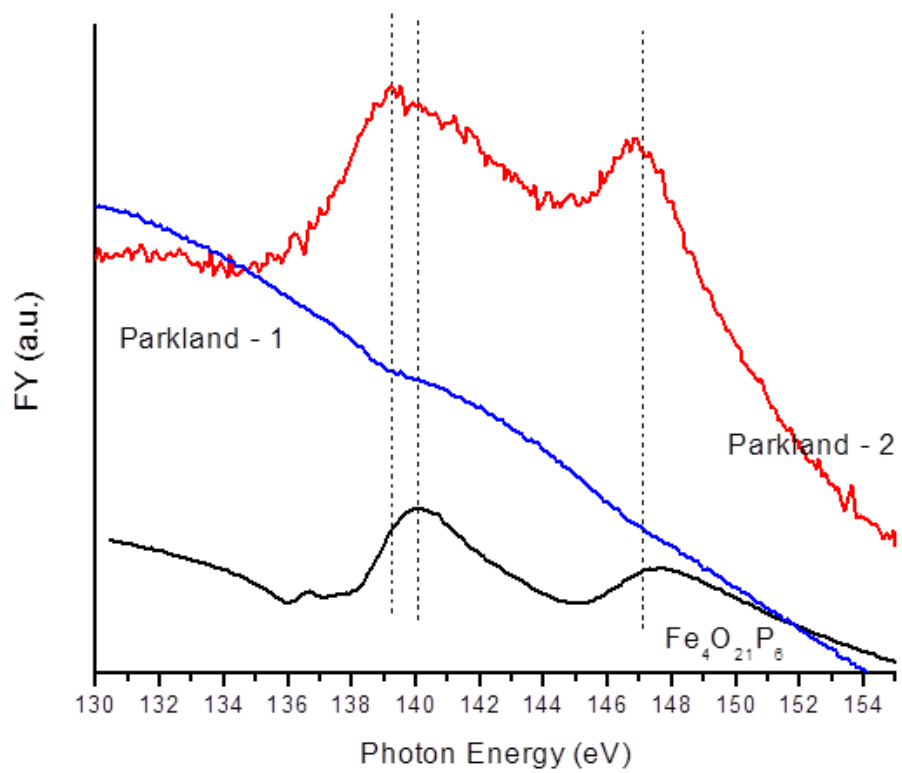


Figure 5.23 P L-edge FY of *B. rapa* oils.

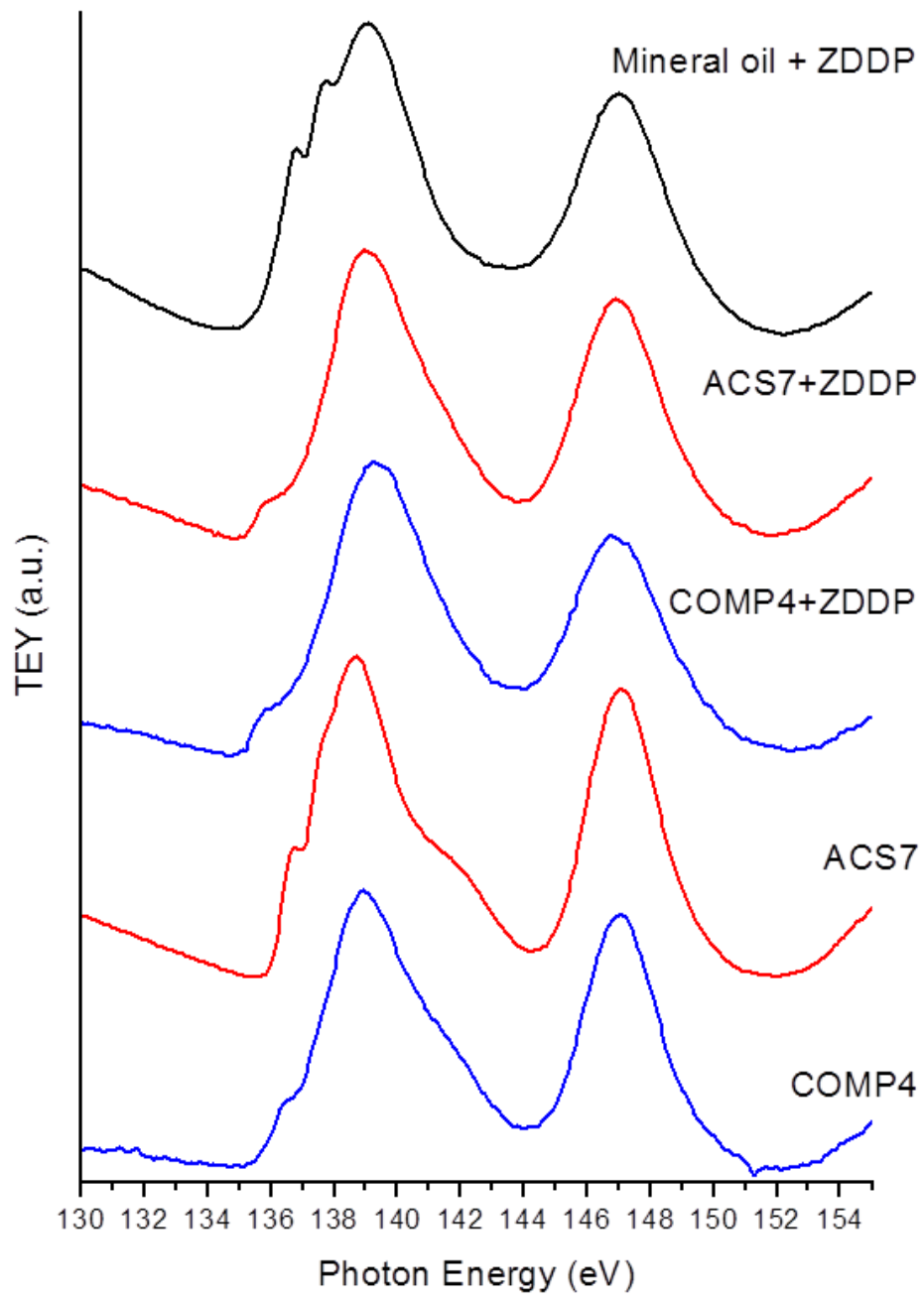


Figure 5.24 P K-edge TEY of *B. rapa* oils.

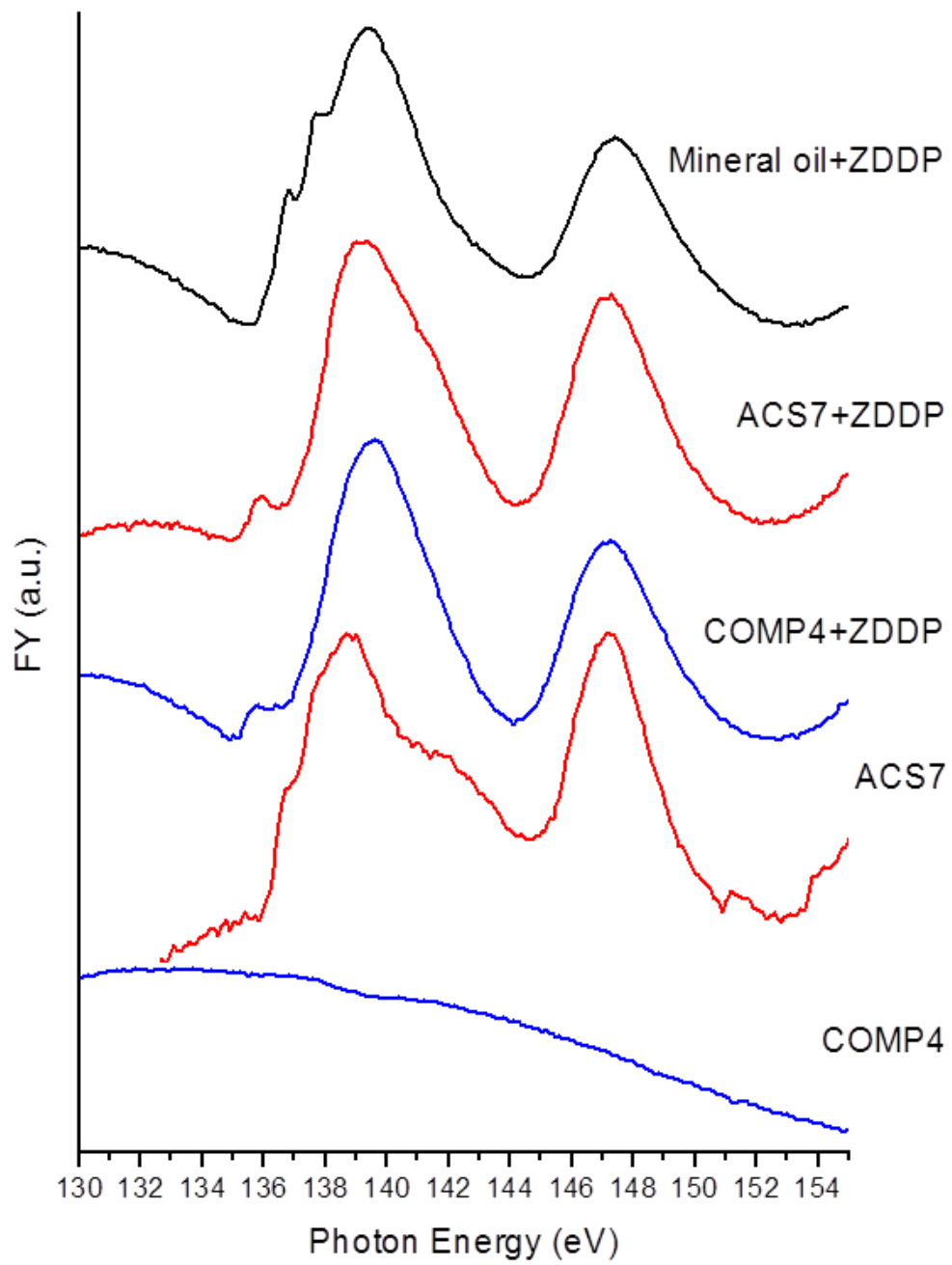


Figure 5.25 P K-edge FY of *B. rapa* oils.

Chapter 6

DISCUSSION

The *Cruciferae* family of oilseeds includes mustard and rapeseed/canola. These crops are successfully grown throughout Canada, the United States of America, and many European countries. They are known to produce oil that is suitable for both food and non-food applications. The renewed interest in environmentally friendly lubricants has brought attention to the possible use of *Cruciferae* oils as automotive lubricants (Lambert et al., 1999). In order to produce a bio-based motor oil with excellent lubricant properties, a suitable oilseed must first be identified. Properties of importance include oil content of the oilseed and oxidative stability, viscosity and low temperature fluidity of the oil. Following physical and chemical characterization of oilseed samples, it will be possible to select oilseed with a high oil content and satisfactory oxidative stability, suitable viscosity at elevated temperatures and low temperature fluidity.

6.1 Composition of *Cruciferae* Oilseeds

The five *Cruciferae* oilseeds studied (*S. alba*, *B. carinata*, *B. juncea*, *B. napus*, and *B. rapa*) are potential candidates for lubricant formulae because of the relatively high oil content in each oilseed. Low-oil *S. alba* had the lowest measured oil content (25%), followed by high-oil *S. alba*, *B. carinata*, *B. rapa*, *B. napus*, and *B. juncea* (49%). Mandal et al. (2002) reported a mean total oil content ranging from 28% (*B. carinata*) to 47% (*B. juncea*).

In each of the five *Cruciferae* oils studied, the mean % moisture had an inverse relationship with mean % oil content. That is, oilseed with high oil content had a low moisture content, and oilseed with a low oil content had a high moisture content. *S. alba* is a high moisture, low oil oilseed, and is therefore less suited for use as an inexpensive source of oil for used in motor oil. With almost half of the oilseed composed of oil, *Cruciferae* oils offer a high oil to seed weight ratio (Mandal et al., 2002).

6.2 Fatty Acid Profiles of *Cruciferae* and *B. rapa* Oils

According to Mandal et al, (2002), the seven major fatty acids present in *Cruciferae* oil samples are palmitic, stearic, oleic, linoleic, linolenic, eicosenoic and erucic acids. The fatty acids in *Cruciferae* oils are formed by stepwise biosynthetic pathways beginning with oleic acid, which is either desaturated to form linoleic acid and then linolenic acid, or is elongated to form eicosenoic acid and then erucic acid (Mandal et al., 2002).

The palmitic acid content of the five *Cruciferae* oils surveyed was between 2.5 and 3.5%. A survey of several *Cruciferae* oils by Mandal et al (2002) also resulted in palmitic oil content of approximately 3%. The same study by Mandal et al. (2002) reported a stearic acid content of approximately 1%. The five *Cruciferae* oil samples had a mean stearic acid content of 1.1–6.6%, slightly higher than the results of Mandal et al (2002). The differences in stearic acid content are likely due to the lower content of other fatty acids within the oil as a result of breeding and growing conditions.

The oleic acid content of the five *Cruciferae* oil samples was highly varied, ranging from 10.1% to 49.6%. The oleic acid content of the oilseeds sampled by Mandal et al (2002) also varied greatly, from approximately 12% to 58%. Linoleic acid and linolenic acid are formed from the precursor oleic acid, and therefore their content also varies. The linoleic acid content of the five *Cruciferae* oil samples ranged from 8.4% to 20.9%, whereas the linoleic acid content of the *Cruciferae* oils sampled by Mandal et al. (2002) ranged from 10–18%. The linolenic acid content as measured by Mandal et al. (2002) was 5–11%. The linolenic acid content of the five *Cruciferae* oils sampled was 6.7–14.8%.

The eicosenoic acid content of *Cruciferae* oils as reported by Mandal et al. (2002) was approximately 5–7%, and was considerably lower than the five *Cruciferae* oils sampled, ranging from 6.3%–38.3%. It is important to note that the data presented for the five *Cruciferae* oil samples is a mean of several varieties, which accounts for the large range of fatty acid concentration in the profile, and the differences between the different data sets.

The erucic acid contents of the five *Cruciferae* oil samples ranged from 2.0 to 34.3%. Mandal et al. (2002) reported an erucic acid content for *Cruciferae* oilseeds of approximately 8–50%. Interestingly, it has been found that oils with a low level of erucic acid also have a high percentage of palmitic and oleic acid (Mandal et al., 2002). The *Cruciferae* oil samples *B. napus* and *B. rapa* had a high oleic acid content (44.8% and 49.6%, respectively), and had very low erucic acid content at 1.3% (*B. napus*) and 1.1% (*B. rapa*). Both high-oil and low-oil *S. alba* samples had moderate erucic acid levels (33.3% and 31.5%, respectively), and had moderate oleic acid contents (25.1% and 22.9%, respectively). Interestingly, *B. juncea* and *B. carinata* had low erucic oil content, low palmitic oil content and moderate oleic acid contents (10.1–14.4%), but did have relatively high linolenic acid contents (16.2% and 18.2%, respectively). *B. rapa* oils, did have high oleic acid content (49.6%), and low palmitic acid content (3.2%), low erucic acid content (1.1%), and had the highest measured linoleic acid content (20.9%) of all *Cruciferae* oils sampled.

For the *B. rapa* oils, similar data was found for all oils sampled. *B. rapa* oils are composed primarily of oleic acid, ranging from 53% (Parkland) to 59% (COMP-4 and El dorado) of the total fatty acid content. *B. rapa* oils also contain significant amounts of linoleic acid (C18:2) at 21–23% and linolenic acid (C18:3) at 9–14%. These values are significantly higher than those for all other *Cruciferae* oils samples. All oil samples had small amounts of palmitic acid and vaccenic acid. Trace amounts of palmitoleic acid, stearic acid, arachidic acid, eicosenoic acid, behenic acid, erucic acid, lignoceric acid and nervonic acid were detected in some of the *B. rapa* samples. For the most part, these values agree with those reported by Velasco et al. (1998), with the exception of oleic acid and erucic acid. The oleic acid contents as reported by Velasco et al (1998) ranged from 8.2–33.8%, whereas the mean oleic acid contents of *B. rapa* samples in the current study was 55.9%. Erucic acid was measured at below 1% of the fatty acid profile (classified as “others”), but was reported at a mean 45.3% by Velasco et al. (1998).

Oils containing high levels of erucic acid and other long chain fatty acids are considered desirable for industrial applications, but not for food purposes (Stefansson et al., 1961). Many breeding programs have focused on the increase of oleic acid and linoleic acid and the reduction of linolenic acid and erucic acid content so as to improve the nutritional quality for human consumption, which is consistent with the results for *B. rapa* oils surveyed. In addition to the

breeding of *Brassica* oilseeds, the growing conditions may also affect the fatty acid profile of the oils. Harvey and Downey (1964) noted that many *Brassica* species grown in the northern parts of the Prairie provinces produced oils with a lower content of erucic and linolenic acids, but contained a higher percentage of palmitic, oleic, linoleic and eicosenoic acids.

6.3 Iodine Value

Using the fatty acid profile, it is possible to calculate the iodine value (IV) of each oil sample. IV is the amount of iodine (in grams) that is expended by 100 grams of oil. IV is an indicator of the amount of unsaturated fatty acids in oil because the unsaturated double bonds readily react with iodine in solution. A higher IV indicates a higher content of double bonds in the oil (Earle et al., 1960).

An oil with more double bonds is more unsaturated and, therefore is less oxidatively stable (Knothe, 2002). Therefore, IV is a predictor of the oxidative stability of oil. Oil with a higher IV will be less oxidatively stable. *B. rapa* oil had the highest calculated iodine values, and therefore would be expected to be the least oxidatively stable. Conversely, *S. alba* has the lowest IV and therefore would be the most resistant to oxidative degradation. Oil that is susceptible to oxidation will require the addition of anti-oxidants to conserve motor oil stability.

Przybylski et al. (2005) reported that low- and high-erucic acid canola oils had a mean IV of 97–126. In the current study, *B. rapa* oil samples had IV values over the range of 118–128. The oils *B. rapa* ACS-C7 and *B. rapa* Parkland had the highest IV values, and would be expected to have the poorest oxidative stability. The oils COMP-4 and El dorado would be expected to have better oxidative stability than other *B. rapa* oils due to their lower IV.

6.4 Chemical and Physical Properties of *Cruciferae* and *B. rapa* Oils

The chemical and physical properties of *Cruciferae* and *B. rapa* oils were analyzed so as to predict their suitability as lubricant base oil.

6.4.1 Density of *Cruciferae* and *B. rapa* Oils

Oil density is an important property for motor oils. A less dense or “light” oil will float on water, while a heavier, or less dense, oil will sink to the bottom of the container. Oil density directly affects oil’s ability to lubricate moving parts. Furthermore, a lubricating oil is expected to operate over a range of temperatures in an engine system (Chun, 2003).

Demirbas (2008) reported that canola/rapeseed oil at approximately 35 °C had a density of 0.912 g/mL whereas mustard oil had a density of 0.913 g/mL. The density of the five *Cruciferae* oils at 35 °C ranged from 0.887 g/mL to 0.908 g/mL, slightly lower than the values obtained by Demirbas (2008).

The density of a vegetable oil has an inverse relationship with its molecular weight, that is oil with higher molecular weight would be less dense, and oil with lower molecular weight would be denser (Chun, 2003). The density of vegetable oils also has a direct relationship with the degree of unsaturation. Oil with a high degree of unsaturation would be expected to be denser, whereas oil with a lower degree of unsaturation would be expected to be less dense (Giannelos et al, 2002).

At room temperature (25 °C), oil from *B. juncea* was the densest and had high levels of the unsaturated fatty acids linoleic acid, linolenic acid and erucic acid. Oils from *B. carinata* and *B. rapa* also had higher densities than the other *Cruciferae* oils due to a higher content of unsaturated fatty acids. Conversely, oils from *S. alba* had the least dense oil at room temperature (both high-oil and low-oil varieties) and had a lower degree of unsaturation. However, *S. alba* did have high amounts of long chain fatty acids, including eicosenoic acid and erucic acid, and would therefore have a high molecular weight.

The density of vegetable oils also tends to change as temperature changes. Since a vegetable oil would be expected to operate over a range of temperatures in an engine system, it is important to understand the effect temperature has on the density of *Cruciferae* and *Brassica rapa* oils. The density of all five *Cruciferae* oil samples decreased by as little as 0.038 g/mL up to 0.070 g/mL as the temperature increased. A very small change in density over a large range of temperatures indicates that each of the *Cruciferae* oil samples would be suitable as a lubricant during engine operation.

At room temperature, oil from *B. rapa* ACS-C7 had the lowest density, while COMP-4 and Sunbeam had the highest densities. However, the difference in the measured densities of these oils was only 0.003g/mL, and it is unlikely that any measured differences were due to either the molecular weight or the degree of unsaturation because each of these oils had similar fatty acid profiles. It was noticed that the density of all vegetable oils, as well as the mineral oil sample, increased upon the addition of ZDDP. This increase in density is likely attributed to the density of the carrier oil in which the ZDDP was delivered.

The density of all *B. rapa* oils with and without ZDDP at temperatures between 0 °C and 100 °C were only slightly higher than the densities of mineral oil with and without ZDDP. These results indicate that the *B. rapa* oils selected would be suitable base oils in an engine system over a large range of operating temperatures. Rodenbush et al. (1999), confirm a linear relationship between decreasing density and increasing temperature. It is also suggested that there is a linear trend between increasing density with increasing levels of unsaturation, as well as a decrease in density with increasing molecular weight of the oil samples.

6.4.2 Viscosity of *Cruciferae* and *B. rapa* Oils

The viscosity of oil is its “thickness” or resistance to flow. Viscosity is one of the most important properties of oils in engine lubrication (Agoston et al., 2005). Oil must have sufficient viscosity to properly lubricate moving parts, while maintaining a satisfactory flow so as to adequately coat and cover all parts. A lower viscosity oil will pour more easily at a low temperature, whereas a high viscosity oil is “thicker” and, therefore, better suited for higher temperature applications. An ideal lubricant base oil would have a viscosity which is high enough to allow cold temperature pumping and start-up, and low enough at high temperatures to allow sufficient distribution of the oil throughout the engine system.

At low temperatures, *B. juncea* had the highest initial viscosity. As temperatures approached room temperature, the viscosities of all oil samples became very similar. At temperatures approaching 100 °C, there was very little measured difference in the viscosity of the *Cruciferae* oils. Nouredini *et al.* (1992) present a range of viscosities for rapeseed (canola) oil approximately 80 cP at 24 °C to approximately 10 cP at 100 °C. The values for *Cruciferae* oil samples ranged from 68 cP at 25 °C to 14 cP at 95 °C. The results obtained by Nouredini et al. (1992) are slightly higher than the values obtained in the current study for *Cruciferae* oils. The differences are likely due to the use of different methods for measuring viscosity during data collection.

Of the five *Cruciferae* oils sampled, *B. rapa* oils had the lowest viscosities over the range of temperatures. At low temperatures, all *B. rapa* oils sampled had viscosities higher than that of mineral oil. The addition of ZDDP to *B. rapa* and mineral oils decreased the viscosity of the oils to a small degree. Again, this difference in viscosity upon the addition of ZDDP was likely due to the viscosity of the carrier oil. As temperature increased, the viscosity of both the mineral oils

and the *B. rapa* oils decreased, to a minimum of 12–15 cP. Rodenbush et al. (1999) confirm a decrease in vegetable oil density with increasing temperature.

At low temperatures, the viscosities of *B. rapa* oils were somewhat higher than those of mineral oils. This would result in more resistance to flow by the *B. rapa* oils than by the mineral oils. Many lubricant formulae include viscosity modifiers in their additive packages so as to alleviate low temperature resistance to flow. At higher temperatures, *B. rapa* oils had viscosities similar to those of mineral oils, and would act much the same in a lubricating situation.

6.4.3 Cold Temperature Properties of *Cruciferae* and *B. rapa* Oils

6.4.3.1 Cloud Point

At low temperatures, certain components in vegetable oils with higher melting points begin to precipitate out of solution, resulting in a cloudy appearance (Imahara et al., 2006). These precipitated components are potentially hazardous to engine systems, as they may plug oil filters, inhibit pumping, and cause large deposits which may contribute to the wear of moving metal parts. An ideal vegetable oil for automotive lubricant formulae would have a low cloud point, and subsequently a low pour point, so as to facilitate optimal lubrication, enable pumping, and prevent friction and wear.

Of the five *Cruciferae* oils sampled, oils from *B. rapa* had significantly lower cloud points than all other vegetable oils sampled. It is for this reason that *B. rapa* oil was selected for further testing to assess the suitability of several varieties for use as a base motor oil. Quinchia et al. (2012) reported that rapeseed oil had a mean cloud point of $-22\text{ }^{\circ}\text{C}$. The measured cloud point of the *B. rapa* oils ranged from $-17\text{ }^{\circ}\text{C}$ to $-23\text{ }^{\circ}\text{C}$. Each of these *B. rapa* oils are potential candidates for automotive formulation, as they would not show the cloudy appearance of precipitates at cooler temperatures.

6.4.3.2 Pour Point

Pour point is the temperature at which oil will not flow when disrupted (Srivastava et al, 2000). This is the temperature at which oil or lubricant cannot be readily pumped through an engine system. The pour point of the five *Cruciferae* oil samples ranged from $-22\text{ }^{\circ}\text{C}$ to $-31\text{ }^{\circ}\text{C}$. In most climates, these pour points would be sufficient for motor oil formulation. However, in northern climates, a lower pour point is desirable, and therefore *B. rapa*, the oil with the lowest pour point ($-31\text{ }^{\circ}\text{C}$) was selected for further experimentation.

The measured range for pour point of all *B. rapa* oil samples was $-24\text{ }^{\circ}\text{C}$ to $-33\text{ }^{\circ}\text{C}$. Continued experimentation revealed that the lowest pour point measured was $-37\text{ }^{\circ}\text{C}$ (ACS-C7). Quinchia et al. (2012) reported a pour point of $-54\text{ }^{\circ}\text{C}$ for rapeseed oil. However, this value is a result of a different method for determining the pour point, and it is not mentioned which varieties were included in these data points. Low temperature performance is one of the main constraints for all lubricant base oils, including mineral oils, synthetic oils and vegetable oils. *B. rapa* ACS-C7 has a pour point sufficiently low for motor oil formulae.

When looking at the *B. rapa* oil samples, it becomes apparent that the oil from ACS-C7 had the lowest pour point, and also had the lowest stearic acid content. ACS-C7 also had a higher concentration of linoleic acid and linolenic acid. Conversely, oils with the highest pour point had higher stearic acid contents; and lower linoleic acid and linolenic acid contents. It is likely that the multiple conjugations of the linoleic and linolenic acid prevents the physical stacking of triacylglycerol molecules as temperature drops, thereby preventing the increase in viscosity and the “freezing” of the oil.

6.4.3.3 Oxidative Stability of *Cruciferae* and *B. rapa* Oils

Lipid oxidation, which often leads to rancidity, is one of the main limiting factors in the use of vegetable oils in motor oil formulae (Aldrich et al., 2003). Oil rancidity alters the viscosity, low temperature operation and long-term storage/use of vegetable oils. The oxidative stability test is an accelerated oxidation test which estimates the stability or susceptibility of the sample oil to oxidation. The oxidative stability results for *Cruciferae* and *B. rapa* oils are reported as an induction period in hours. This is the time over which the rate of oxidation is slow and the oil resists oxidation (Isbell et al., 1999). Following the induction period, the rate of oxidation in oil increases dramatically. The purpose of an Oxidative Stability Instrument (OSI) is to accelerate the onset of oxidation in sample oils, measuring their resistance to oxidation as induction period, or time to onset of oxidation.

When comparing the five *Cruciferae* oil samples, it is clear that *B. carinata* and *B. rapa* have very poor oxidative stability, as their time to induction of oxidation is very low (5.2 h and 5.8 h, respectively). Oils from *B. napus* and *S. alba* had longer induction periods (12.1 h and 16.2 h, respectively) and therefore are more oxidatively stable. Chu and Kung (1997) reported an OSI for canola oil of 3.7 h, significantly lower than the results obtained for the *Cruciferae* oils. The discrepancy between the canola oil values from Chu and Kung (1997) and the results

for the five *Cruciferae* oils may be due to prior storage conditions, the oil extraction method and/or the varieties of oils used for sources of oil.

The OSI results for the selected *B. rapa* oils are considerably higher than those obtained during *Cruciferae* oil testing, ranging from 15.50 ± 0.76 h to 18.60 ± 8.36 h. Again, these results differ from the low values obtained during *Cruciferae* oil sampling likely because of the different varieties used. As expected, the oxidative stability of each *B. rapa* oil increased greatly upon the addition of the antioxidant/antiwear additive ZDDP. The induction period of the vegetable oils increased by as little as 10 h, to as much as 60 h, when ZDDP was added to the oils. However, the OSI values for all *B. rapa* oils with and without ZDDP are still significantly lower than those obtained for mineral oil and mineral oil + ZDDP. As with all motor oil formulae, there are compromises which must be made. In order to formulate a vegetable-oil-based lubricant, the oxidative stability of the product will be compromised, in comparison to formulae based on mineral oils. In order to remediate the poor oxidative stability of vegetable oils in automotive lubricants, anti-oxidants such as ZDDP are often included in additive packages.

6.4.3.4 Refractive Index of *Cruciferae* Oils

The refractive index of oil is often used to predict the density of the oil. The refractive indices of select oil samples were measured so as to determine the correlation between these two properties. Refractive index is a measure of the angle of refraction of an incident beam of light at the interface between two media. Single analysis of the oils did not show any conclusive evidence for a strong or significant correlation between refractive index and density.

6.4.4 Wear Scar and Tribofilms

6.4.4.1 Coefficient of Friction

The coefficient of friction is a dimensionless measurement of the force of contact between an object and a surface and the frictional force that resists motion of the object. A low coefficient of friction is desirable in an engine system, indicating less wear during metal-on-metal contact. The purpose of a Plint Tribometer (TE-77) is to simulate metal-on-metal wear by rubbing a horizontal pin at high frequencies against a polished stainless steel disc. The friction created by the rubbing creates a wear scar on the disc and a flat wear surface on the pin, and is measured with a piezo electric transducer during wear scar production. A lubricating oil will

build a tribofilm during the wear process that will decrease the coefficient of friction between the pin and the disc (Minfray et al., 2006).

Crawford et al. (2010) suggested that vegetable oils have superior lubricity over mineral oils in many lubrication regimes during short term use. It is expected that the coefficients of friction measured for vegetable oils would be lower than those of mineral oils, indicating superior lubricant potential. The results for *Cruciferae* oil wear scar formation demonstrated the superior lubricity of all vegetable oil samples in comparison with mineral oil samples.

B. juncea oil had the lowest coefficient of friction as measured during Plint Tribometer testing, at a mean of 0.023 ± 0.010 , and a maximum of 0.083 ± 0.017 . Oil from *B. rapa* also had a very low mean coefficient of friction and maximum coefficient of friction, 0.023 ± 0.012 and 0.083 ± 0.022 , respectively. Sharma et al. (2009) reported that the maximum coefficient of friction of vegetable oils, specifically soybean oil, was approximately 0.0950. The data for all *Cruciferae* oils agree with the data reported by Sharma et al. (2009). Because of superior cold temperature performance and its superior coefficient of friction, oil from *B. rapa* is a potential candidate for lubricant formulation.

The mean and maximum coefficients of friction for all *B. rapa* oils were significantly lower than those measured for mineral oils. The addition of ZDDP to vegetable oils increased the coefficient of friction, as well as that of mineral oil. However, the coefficient of friction for *B. rapa* oils + ZDDP was still lower than for mineral oil or mineral oil + ZDDP. These results suggest that the boundary layer formed by vegetable oils alone is more efficient in decreasing friction than are the films created by vegetable oils with the antiwear additive ZDDP, and the tribofilms created by mineral oil with and without ZDDP. Sharma et al (2009) stated that the triglyceride molecules in vegetable oils bind to metal surfaces and that the polar functional groups have physical and chemical interactions which minimize friction. It was also suggested that the vegetable oils minimize friction and wear by decreasing the pressure of contact between metal surfaces and by reducing the area of contact, thereby minimizing the wear scar produced during metal-on-metal sliding.

6.4.4.2 Wear Scar Width

In all metal-on-metal contact situations, some wear will occur. The purpose of a lubricant is to minimize wear and to delay catastrophic failure. Modern lubricant formulae use mineral oil as their base oil because of its excellent performance at high and low temperatures.

However, much attention has been paid recently to vegetable oils as lubricant base oils because of their low environmental impact and their purported efficiency in minimizing the damage caused during metal-on-metal wear (Siniawski et al., 2007).

The mean wear scar width of vegetable oils was comparable to that of unformulated mineral oil and mineral oil with ZDDP. The five *Cruciferae* oils had a mean wear scar widths ranging from 482 μm to 591 μm . The mean wear scar width of mineral oil was 454 μm . Based upon these results, it may be concluded that vegetable oils have lubricant properties suitable for their use as base oil for reducing wear between contacting metal surfaces. Oils from *B. napus* and *B. rapa* had the lowest measured wear scar widths, 482 μm and 514 μm , respectively. Because of the excellent cold temperature performance, superior coefficient of frictions, and a low wear scar width, *B. rapa* was chosen for further tribofilms experimentation.

The selected *B. rapa* oils protected metal coupons efficiently as measured wear scar widths were considerably smaller than observed for coupons in mineral oil. The addition of ZDDP to *B. rapa* oils resulted in a slight increase in measured wear scar width for coupons immersed in oil from both ACS-C7 and COMP-4. The addition of ZDDP resulted in a large increase of mean wear scar width for coupons in oil from the cultivar Sunbeam (it is likely this increase is due to uneven wear on the surface of the pin throughout wear testing). The addition of ZDDP to mineral oil greatly decreased the measured wear scar width. However, the wear scar widths of coupons in *B. rapa* oils with and without ZDDP were still generally lower than those of mineral oil with and without ZDDP.

Ito et al. (2006), suggest that a multi-layered tribofilm form on the iron oxide surface of a stainless steel sample ranging from 30–130nm. The lower layer contains zinc, iron, sulfur, phosphate and oxygen, while the top layers contain zinc, sulfur and phosphate. It is also suggested that the middle layers contain high amounts of carbon. It is hypothesized that the mechanism of low friction may be attributed to the iron oxide on the surface of the sample (Ito et al. (2006). The lower measured wear scar widths of sample oils without ZDDP may indicate complex interactions between the oil and the iron oxide surface of the sample in a low-friction tribosystem.

Adhvaryu and Erhan (2002) hypothesized that the excellent lubricity of vegetable oils is due to their ester functionality. The polar heads of the fatty acids in triacylglycerols attach themselves to the metal surface of the engine, whereas the non-polar tails of the fatty acids orient

away from the surface. The long chain structure of the non-polar tails (-CH₂-) form the lubricating layer between contacting metal surfaces which provides a sliding surface, preventing metal-to-metal contact. Contact between the metal surfaces results if a tribofilm is not formed, and may result in adhesion and micro-welding between moving parts.

6.4.4.3 X-ray Absorption Near Edge Spectroscopy

The purpose of XANES spectroscopy using synchrotron light was to confirm the presence of tribofilms formed on stainless steel disks during wear scar production. The spectra produced by XANES are used as a fingerprint to identify the chemical nature of the tribofilms by comparison to known reference standards. In recent years, XANES has been used to elucidate the lubrication properties of antiwear additives and the mechanisms by which tribofilms are formed (Nicholls et al., 2007).

The Fe L-edge TEY spectra of the five *Cruciferae* oil seeds are very similar to the spectra produced by the Iron (III) Oxide reference standard. This indicates that the tribofilm present is very thin, as the iron surface of the substrate is being detected. At greater depths (FY mode), the Fe L-edge spectra confirm the presence of an Iron (III) Oxide species on the surface of the disk for all *Cruciferae* oil samples.

The O K-edge spectra show that an oxygen species exists at the surface (TEY mode) similar to that of the Iron (III) Oxide reference standard. The shapes of the spectra differ somewhat between the five *Cruciferae* oil samples and the model standard. These observed differences (single peak for *Cruciferae* samples versus a double peak for the reference standard) are perhaps due to a change in the oxygen species at the surface of the tribofilms.

The C K-edge TEY spectra for each of the five *Cruciferae* oil sample indicates the presence of carbon on the surface of the tribofilms. The shapes of the five *Cruciferae* oils was the same, but differed from that of the graphite reference standard. It is likely that the carbon present in the tribofilms remains from the vegetable oils, and is of an organic nature, whereas the graphite is an inorganic carbon structure. Carbon is also present at the depth of the tribofilm created by all five *Cruciferae* oil samples, as indicated by the C K-edge FY spectra.

The results of *Cruciferae* oil XANES spectroscopy indicate that a tribofilm is formed by each of the vegetable oils on the surface of the stainless steel disks during simulated wear conditions. Each tribofilm contains iron, oxygen and carbon, as confirmed by the reference

standards. These results have also confirmed that *Cruciferae* oil tribofilms may be detected using XANES spectroscopy.

The P L-edge spectra (Figure 5.20, TEY mode) suggest several events have occurred within the wear scar track. Both *B. rapa* Parkland oils developed a phosphate film, likely an iron phosphate, which closely resembled the $\text{Fe}_4\text{O}_{21}\text{P}_6$ standard. The slight peak at ~142 eV indicates the possibility of a CaPO_4 ion within the tribofilm. The broadening of the peak at ~139 eV, as well as the slight shift at this energy range, suggests that there may be multiple forms of a phosphorus species present in the tribofilm. The slight pre-edge trace at ~134 eV suggests that some of the phosphate present in the original *B. rapa* oil may have been absorbed onto the surface of the wear scar area but has remained unreacted.

Similarly, the P L-edge spectra (Figure 5.21) of *B. rapa* Parkland (FY mode) suggest that a tribofilm has been formed on the surface of the metal disks during wear scar production when lubricated with vegetable oils. The loss of the FY signal in the Parkland-1 sample confirms the presence of unreacted phosphorus species within the tribofilm. The noticeable peak at ~142 eV in FY mode relative to that in TEY mode suggests that CaPO_4 may be present throughout the bulk of the tribofilm. The broadening of the peak at ~147 eV demonstrates the complex chemical interactions within the tribofilm throughout the bulk of the sample, and also suggests a complex interaction at the interface of the metal disk and the vegetable oil.

The results in Figure 5.22 for *B. rapa*, P K-edge (TEY mode) specifically compare the tribofilms created during simulated engine wear using mineral oil with ZDDP and two *B. rapa* oil samples with and without ZDDP. All spectra show similar results, and therefore it can be concluded that the surfaces of each tribofilm have similar chemistry for the phosphorus species present. At the surface of the stainless steel disk (FY mode, Figure 5.23), all vegetable oils, with the exception of COMP-4, had similar spectra, indicating that a thin film was present, and the surface of the substrate was easily detected. These results demonstrate that *B. rapa* oils produce a tribofilm much like that produced by mineral oil with ZDDP, a model of modern motor oil formula. These results also conclude that the addition of ZDDP to vegetable oils does not greatly affect the tribofilm formed. It is likely that the chemical structures detected using XANES spectroscopy are glass-like polyphosphate structures not unlike those that have been detected by others.

Chapter 7

SUMMARY AND CONCLUSIONS

For over 50 years, most automotive lubricants have been composed of petroleum-based oils to which specific chemical additives have been added so as to maximize the performance of the engine during normal operating conditions. In recent decades, it has become clear that petroleum oil has a detrimental effect upon the environment. Furthermore, petroleum oil sources are becoming limited and will not be able to supply the growing demand for motor oils in the automotive industry. Therefore, a suitable replacement for motor oils is being sought. Many have suggested that vegetable oils are potential candidates as motor oil replacements (Korcek, 2000). It has been shown that oils from the *Cruciferae* oilseed family have suitable properties for use as lubricant base stock oils. Oils derived from five species of *Cruciferae* and five selected *Brassica rapa* cultivars were analyzed for their suitability as lubricant base stock oils.

Composition of Cruciferae Oils

It was found that *Cruciferae* oilseeds contained a high amount of oil and had contained very low moisture content. The oils from *Brassica juncea*, *Brassica napus*, and *Brassica rapa* contained the highest concentration of oil, and could potentially supply an environmentally friendly oil for the lubricant industry.

Fatty Acid Profile of Cruciferae Oils

The chemical composition of *Cruciferae* oils directly affects their performance as lubricant base stock oils. *Cruciferae* oils are composed of triacylglycerols which contain a variety of fatty acids. Certain fatty acids affect the lubricant potential, oxidative stability and low temperature performance of the oil. Oil with a high amount of unsaturated fatty acids is susceptible to free radical attack which results in oxidative degradation. Most *Cruciferae* oils had high levels of unsaturated fatty acids, and were consequently, less oxidatively stable. The

oxidative stability of *Cruciferae* oils must be addressed through the use of chemical additives during motor oil formulation or through chemical modification of the oil itself.

Chemical and Physical Properties of Cruciferae Oils

The physical properties of oil, specifically density and viscosity, directly affect usability as a component of formulated motor oil. The oil density, or lightness, affects the distribution of the oil throughout the engine, and thereby affects access to engine parts that require lubrication. The viscosity, or thickness, of oil affects the efficiency of formation of lubricating films on metal surfaces within the engine. Motor oil is expected to operate across a wide range of temperatures. Therefore, the density and viscosity must behave as predicted at both low and high engine temperatures. The density and viscosity of *Cruciferae* oil was satisfactorily at all temperatures between 0 °C and 100 °C and similar to petroleum-based mineral oil.

At very cold temperatures, motor oils become very thick and “freeze”, restricting their function as lubricants. *Cruciferae* oils, like mineral oils, are required to operate under cold conditions in certain climates. Oil constituents may precipitate below temperatures specific to each oil causing a cloudy appearance (cloud point), and eventually the movement of the oil is completely arrested (pour point). Of the *Cruciferae* oils analyzed, *B. rapa* had the lowest cloud point and pour point, and therefore, would be the most suitable oil for automotive lubricant use. Therefore, the *B.rapa* oils ACS-C7 (lowest cloud points and pour points), COMP-4 and Sunbeam (highest cloud points and pour points) were chosen for further experimentation as lubricant base oils. The very low cloud points and pour points of the *B. rapa* oils make their use in motor oil formulae appealing.

Lipid oxidation, which occurs in all natural oils, leads to chemical and physical changes which alter the usability of *Cruciferae* oils as automotive lubricants. The oxidative stability of *Cruciferae* oils was measured using an accelerated oxidation test. When compared to mineral oils, *Cruciferae* oils, specifically *B. rapa* oils, had poor oxidative stability. However, motor oil formulae often include antioxidant additives, which delay the onset of oxidation and prolong the useful life of the oil.

The most common additive used in automotive lubricants is ZDDP. ZDDP is known as a multifunctional additive, and also acts as an antiwear agent.

Wear scar and tribofilms

The efficiency of a lubricant in decreasing the amount of friction during metal-on-metal contact may be measured as a dimensionless coefficient of friction during simulated wear situations on a Plint Tribometer. Oil that provides sufficient lubrication will decrease friction experienced by creating a lubricant film, called a tribofilm. When an adequate tribofilm is created on the wear surface, the coefficient of friction is small, and less wear occurs. All *Cruciferae* oils showed very small coefficients of friction in comparison to mineral oil standards. The *Cruciferae* and *B. rapa* oils with and without the addition of the antiwear/antioxidant additive, showed superior lubrication potential to that of mineral oils with ZDDP (simulating fully formulated motor oils), and are therefore potential candidates as lubricant base stock oils.

The amount of wear that occurred during simulated metal-on-metal contact also was measured as the wear scar width on the flattened surface of a round metal pin, rubbed against a metal disk. The wear scar width for *Cruciferae* and *B. rapa* oils were comparable to the measured wear scar widths of mineral oils, again indicating that *Cruciferae* oils have desirable lubricating properties for motor oil applications.

The presence of a tribofilm in the wear tracks on the surface of the metal disks was confirmed using XANES spectroscopy using Synchrotron light at the Canadian Light Source (Saskatoon, SK). Using known reference standards as “fingerprints”, it is possible to identify the chemical nature of the tribofilms created by *Cruciferae* oils. A change in the iron and oxygen species present was detected, indicating that a chemical reaction had occurred. The presence of phosphorus species on the disks indicates that *Cruciferae* oils were creating a tribofilm that contained phosphorus, much like those created by oils containing ZDDP.

In this research, it was shown that:

- (1) *Cruciferae* oils, specifically *Brassica rapa* oils had suitable chemical and physical characteristics for use in environmentally friendly automotive lubricants. The *B. rapa* sample ACS-C7 had desirable cold temperature behaviours for engine operation in cold climates;
- (2) All *Cruciferae* oil samples had lubricant properties which were similar, if not superior, to a mineral oil standard. The addition of the commercial antiwear additive ZDDP did not greatly affect the measured lubricity of each *Cruciferae* oil sample.
- (3) XANES analysis confirmed that *Cruciferae* oils produced a tribofilm on the sample surface which is similar to that of mineral oil, with and without the use of the common

commercial additive, ZDDP. Therefore, it is recommended that *B. rapa* oils be further explored for their use in formulated engine oils.

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