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OIL EXTRACTS FROM SPENT COFFEE GROUNDS AND WASTE COOKING OIL TO MODIFY THE PHYSICAL PROPERTIES OF RECYCLED ASPHALT BINDER

by

RITA MAURICE JALKH

A thesis

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AN ABSTRACT OF THE THESIS OF

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Title: Oil Extracts from Spent Coffee Grounds and Waste Cooking Oil to Modify the Physical Properties of Recycled Asphalt Binder

Interest in recycling has been on the rise in the past decades accompanied with research for sustainable practices to mitigate the negative impact of various wastes on the environment. Accordingly, this study explores the use of spent coffee grounds (SCG) and waste cooking oil (WCO) as rejuvenators for reclaimed asphalt pavements (RAP). The food wastes, SCG and WCO, were collected from local catering establishments and used either as is or after further oxidation/modification.

The extracted SCG oil and WCO were further oxidized by heating to 150^{o}C accompanied by pumping air into the samples for 6, 9, 12, 24 and 48 hours. The oxidized oils were then physically and chemically characterized. Consequently, the modified oils were mixed at different percentages with PG 58-XX (unaged) and artificially aged PG 76-XX binders. The rheological properties of the blends were studied using dynamic shear testing and multiple stress creep and recovery testing according to ASTM and AASHTO standards. The addition of the oils to the asphalt binders restored the linear viscoelastic behavior of the binders which was lost during the artificial aging process. This addition has softened rejuvenated binder thus decreasing its high temperature PG grade. Finally, compared to the control unaged binder, oil-rejuvenated artificially aged asphalt shows higher strain recovery at low stress levels, i.e. showing lower susceptibility to permanent deformation.

CONTENTS

TABLES

ILLUSTRATIONS

ABBREVIATIONS

%	Percentage
°C	Degrees Celsius
AV	Acid Value
CGA	Chlorogenic Acid
cm	Centimeters
DHR	Discovery Hybrid Rheometer
FAO	Food and Agriculture Organization Of The United Nations
FTIR	Fourier Transform Infrared Spectroscopy
g	Grams
G'	Storage Modulus
G"	Loss Modulus
G*	Dynamic Shear Modulus
HMA	Hot Mix Asphalt
hr	Hours
Hz	Hertz
IV	Iodine Value
Jnr	Non-Recoverable Creep Compliance
kg	Kilograms
L	Liters
meq	Milliequivalent
mg	Milligrams
MSCR	Multiple Stress Creep Recovery
oxy	Oxidized
Pa	Pascale
PG	Performance Grade
PV	Peroxide Value
RAP	Recycled Asphalt Pavement

s	Seconds
SCG	Spent Coffee Grounds
TFO	Thin Film Oven
WCO	Waste Cooking Oil

CHAPTER I

THE IMPACT OF OXIDATION ON THE PHYSICOCHEMICAL AND RHEOLOGICAL PROPERTIES OF WASTE COOKING AND SPENT COFFEE GROUND OILS

A. Introduction

Increased environmental awareness combined with an ever-growing concern of depleting natural resources have encouraged researchers to explore new methods of waste reduction, recycling and the reuse of material and by-products of industries. Waste Cooking Oil (WCO), comprising of residual oils generated from the food industries and households, and Spent Coffee Ground (SCG), a solid waste that remains after brewing coffee, are two food wastes that are largely produced and have hazardous environmental effects. It is estimated that more than 18 million tons of WCO (Li and Wang 2015) are produced worldwide per year and 8.8 million tons of coffee traded annually (ICO 2015). WCO is considered to have detrimental effects on the environment mainly by altering oxygen levels of water by forming a layer which covers the surface. Moreover, toxic compounds have been found to get released during the degradation of WCO which then get ingested by aquatic animals and get transmitted back to the human food chain (Kabir, Yacob et al. 2014). Similarly, SCG uses large quantities of oxygen during its decomposition and was found to discharge organic matter and contaminants as caffeine, tannins and polyphenols (Mussatto, Machado et al. 2011, Vardon, Moser et al. 2013). For those reasons and in attempts to reduce the use of petroleum products and competition with oils from food sources, numerous studies have focused on the recycling and reuse of waste oils, especially waste vegetable oil, mainly in the production of biodiesel and lubricants (Kulkarni and Dalai 2006, Yaakob, Mohammad et al. 2013, Li and Wang 2015). Similarly, oil from SCG has been studied as a potential green source of biodiesel (Kondamudi, Mohapatra et al. 2008, S.Caetano, Silvaac et al. 2012, Vardon, Moser et al. 2013) but was also analyzed as a source for antioxidant phenolic compounds in pharmaceuticals (Mussatto, Ballesteros et al. 2011) and biochar to be applied with fertilizers to amend soils or as a carbon storage medium (Vardon, Moser et al. 2013). Recently, studies have been exploring the use of waste oils as rejuvenators in the asphalt industry, including waste cooking oil (Zargar, Ahmadinia et al. 2012) and recycled motor oil (Romera, Santamaría et al. 2006). Asphalt binders, by-products of the petroleum industry used to pave roads, were found to harden during storage, mixing, transport and paving due to oxidation and loss of their volatiles and oil fraction leading to cracking problems after paving (Petersen 2009). Desirable properties were usually restored using commercial rejuvenators rather than dumping the damaged pavement. Recently, natural oils were analyzed as potential natural rejuvenators including waste cooking oil and recycled motor oil. It was found that 3-4% of waste cooking compared to 20% recycled motor oil is required to restore the physical properties of the original binder (Zargar, Ahmadinia et al. 2012). These findings helped highlight waste oils as rejuvenators thus aiding in reducing the use of virgin petroleum materials (asphalt) and natural resources (quarry aggregates) as well as dumping of damaged asphaltic material and oils in the environment. However; although WCO was found to be 2 to 3 times cheaper than fresh oils (Li and Wang 2015), the heterogeneous nature of the oil and its diverse applications in the food industry and households were found to vary its physical properties

(Sanli, Canakci et al. 2011). This is why it is interesting to characterize the physicochemical properties of WCO and SCG subjected to different levels of oxidation, the major contributor to oil degradation, prior to its use in different applications. This will further help explore the potential of induced oxidation in modifying the physical properties of oils to desirable levels which may present a benefit in the customization of the physical properties of asphalt blends, especially when little research exists on this topic.

The objectives of this study were to investigate the effect of oxidation on the physicochemical and rheological properties of Spent Coffee Grounds (SCG) and Waste Cooking Oils (WCO) in order to evaluate their potential use as binder rejuvenators from reclaimed asphalt pavements.

B. Materials and Methods

1. Materials

Various samples of spent coffee ground (SCG) were collected from coffee shops in Beirut, Lebanon pertaining to four different international chains. Similarly, samples of waste cooking oil (WCO) were collected from local restaurants around Beirut, Lebanon. Hexane (purity ≥98%), Potassium Iodide powder, 2-propanol (Isopropyl alcohol) and Chloroform were purchased from Sigma-Aldrich Corp (Saint Louis, MO, US). Magnesium Sulfate anhydrous powder as well as Carbon Tetrachloride (purity ≥99.5%) were acquired from Uni-chem chemical reagent. Prepared Iodine Solution – Wij’s was purchased from Fisher Scientific UK (Bishop Meadow Road, Loughborough, Leics, LE11 5RG, UK). Toluene and acetic acid were purchased from VWR (201 Rue Carnot, F-94126 Fontenay-sous-Bois, France). Standard reagents as Sodium thiosulfate (0.1 M), Hydrochloric acid

(0.5M) and Potassium hydroxide (0.1M) were acquired from FLUKA Analytical/Sigma-Aldrich Corp (Saint Louis, MO, US).

2. Oil Extraction and Collection

Upon receipt, SCG were tested for their moisture content, after which they were dried for three hours at 105°C to remove residual moisture. Determination of oil content was performed using a Soxhlet with hexane as a solvent. Following extraction, the hexane-oil solution was passed over magnesium sulfate powder to remove any residual moisture. Hexane was next distilled out of the extract using a rotary evaporator at 335 mbar and 55 °C. Oil samples for oxidation and physico-chemical characterization were collected using reflux extractors. Waste cooking oil collected from different sources were mixed together in equal quantities then similarly passed over magnesium sulfate powder prior to the oxidation process.

3. Oil Oxidation

SCG oil and WCO were oxidized for 6, 9, 12, 24 and 48 hours at 135℃ and a continuous air flow at a rate of 3L/hr (Figure 1).

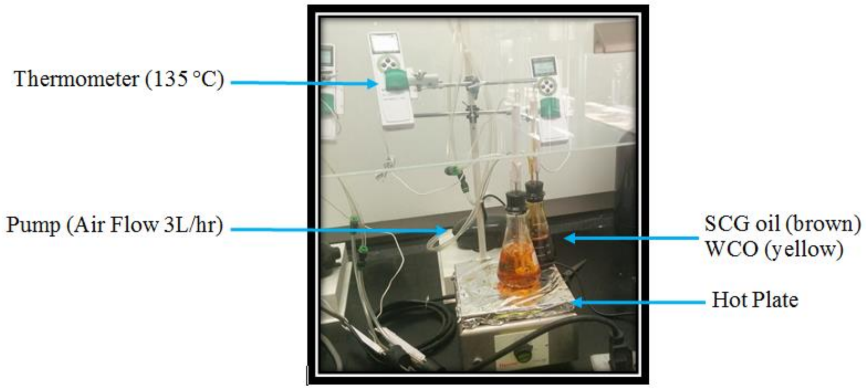

Figure 1: Laboratory setup used for the oxidation of SCG oil and WCO.

4. Oil Physicochemical Characterization

SCG oil and WCO were first chemically characterized for their Peroxide Value (PV) - AOAC 965.33, Acid Value (AV) - AOCS Cd 3d-63 and Iodine Value (IV) - AOCS Cd 1-25. Titration for the above tests was performed using a 916 Ti-Touch (Metrohm, Ionenstrasse, Herisau, Switzerland) with five replicates. Next, in order to explore the changes in functional groups, Fourier Transform Infrared Spectroscopy (FTIR) was performed using a Nicolet 4700 FT-IR Spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) with KBr plates, and analyzed using OMNIC data processing software. The spectra were collected in the 4,000 – 650 cm^{-1} range, in triplicates.

Oils were next physically characterized at 40℃ and 100℃ for their linear viscoelastic behavior (frequency 1Hz – strain ranging from 0.0125 to 12.5%), viscosities (ASTM D2270-10e1) and storage/loss moduli (with 0.1% strain as determined to belong in the linear viscoelastic range, with a frequency ranging from 0.01 to 50 Hz). Tests were conducted using a Discovery Series Hybrid Rheometer – DHR (TA-Instruments, New Castle, DE, USA) equipped with 25mm parallel plates. Samples were tested in duplicates as the standard error did not exceed 5% between replicates.

C. Results and Discussion

1. *Oil Extraction from SCG*

SCG were received with 58% initial moisture content. This value was found consistent with some studies (Kondamudi, Mohapatra et al. 2008, Vardon, Moser et al. 2013, Pichai and Krit 2015), but different from others that reported values ranging from 12%, 25% and 40% (A.Deligiannis, A.Papazafeiropoulou et al. 2011, Ammerlaan, Barrière et al. 2012, S.Caetano, Silvaac et al. 2012). This may be related to the different brewing and extraction methods which usually utilize pressure during the preparation of coffee.

Soxhlet extraction yielded 14% by weight of oil which fits with earlier studies which reported oil content of SCG to range between 11% and 20% by weight depending on the type of coffee and solvent, with an average of 15% (Mussatto, Machado et al. 2011, Al-Hamamre, Foerster et al. 2012, S.Caetano, Silvaac et al. 2012, Abdullah and Bulent Koc 2013).

2. *Oil Physicochemical Characterization*

Table 1 presents the peroxide value, acid value and iodine value of SCG oil and WCO at reception compared to values obtained from literature. Results show that at reception, SCG oil was less oxidized (6.73 meq peroxide/kg) than WCO (64.47 meq peroxide/kg) but more acidic, with a recorded AV of 10.92 mgKOH/g as compared to 3.39 mgKOH/g for WCO. This could be related to the higher processing and refining of WCO as well as its repeated use as frying oils in the food industry as compared to SCG, which in turn exposes the oil to higher levels of oxidation caused by contact with air (auto-oxidation) and water from food (hydrolytic oxidation). Moreover, the higher acidity in SCG oil is mainly due to the higher concentration of acids in coffee such as chlorogenic acids (CGAs) as well as organic acids such as malic, citric, lactic and quinic acids (Farah 2012). And since the Food and Agriculture Organization of the United Nations (FAO) and CODEX (Alimentarius 1999) denote the PV up to 10 meg peroxide/kg in refined vegetable oils, then WCO at reception is officially considered as a waste oil, being non-compliant with the specified standard. It is also noticed that the chemical parameters were affected by the oxidation process, as observed in Figures 2, 3 and 4. As oxidation time increased, the acidity of both oils also increased. This could be related to the release of free fatty acids during heating. Fox and Stachowiak (2007) described the increase of free fatty acids in degrading oils after their release from triglycerides by β hydrogen elimination and hydrolysis. The opposite trend was observed for IV, which is an indication of the number of double bonds, thus level of unsaturation. Beyond 12 hours of oxidation, a significant decrease in the iodine value was noticed for both oils, a phenomenon associated with the breaking of double bonds. A similar trend was observed by Paschke and Wheeler (1954) where the IV decreased when linseed oil was polymerized at 300℃ for a time ranging between 1.5 and 6 hours. Fox and Stachowiak (2007) stated that oils having greater levels of unsaturation are more susceptible to oxidation, making WCO, having a higher IV value than SCG throughout the entire oxidation process, more prone to degradation and thus physical alterations. As for the peroxide value, a maximum value of 13.35 meq peroxide/kg for SCG oil and 174.25 meq peroxide/kg for WCO were recorded after 6 hours of oxidation, followed by a constant decrease until a plateau was reached at 10 meq peroxide/kg for both oils. The latter followed a typical trend where the peak value represents the maximum level of primary oxidation metabolites as hydroperoxides, followed by their degradation into secondary metabolites as epoxides and high molecular weight compounds. It is these secondary metabolites that cause major physical changes in vegetable oils, especially increased viscosity (Fox and Stachowiak 2007).

Table 1: Chemical parameters of SCG and WCO at reception.

Oil Type	**SCG**		**WCO**	
	Tested	**Literature**	**Tested**	**Literature**
PV (meg peroxide/kg)	6.73	5.2[1]	64.47	50.61[3]
AV (mgKOH/g)	10.92	7.1[2]	3.39	3.6[3]
IV ($gI_2/100g$)	95.04	97.6[1]	117.34	109.19[3, 4]

[1]*(Khan and Brown 1953);* [2]*(Obruca, Petrik et al. 2014);* [3] *(Sanli, Canakci et al. 2011);* [4] *(Wen, Yu et al. 2010)*

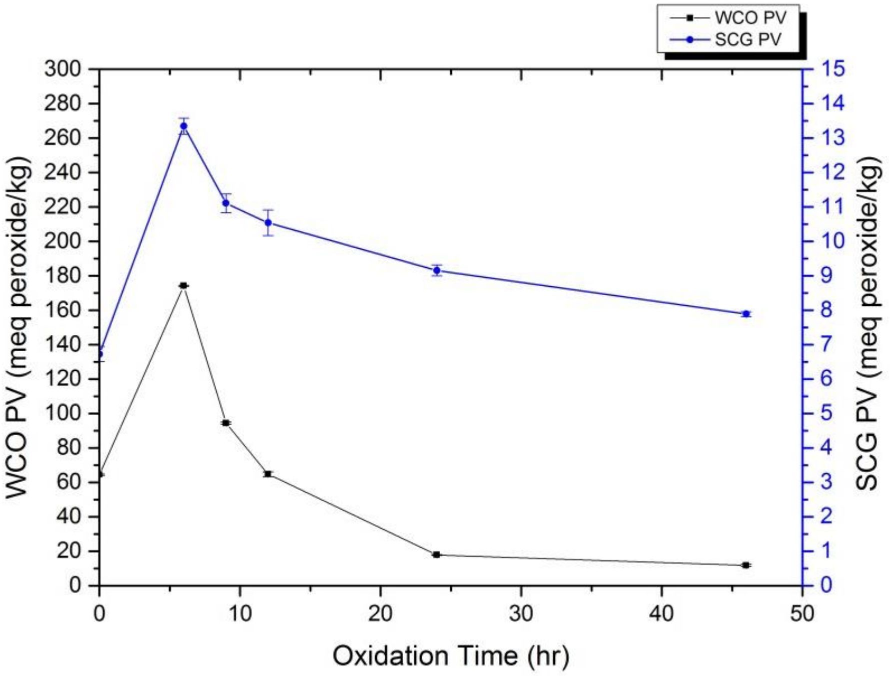

Figure 2: Peroxide Values (PV) for SCG oil and WCO versus oxidation time.

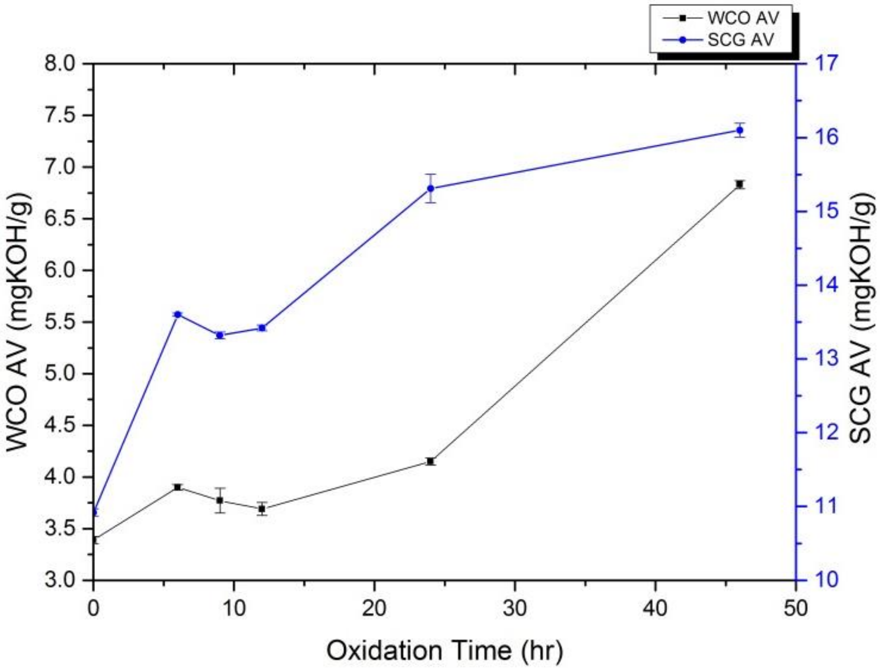

Figure 3: Acid Values (AV) for SCG oil and WCO versus oxidation time.

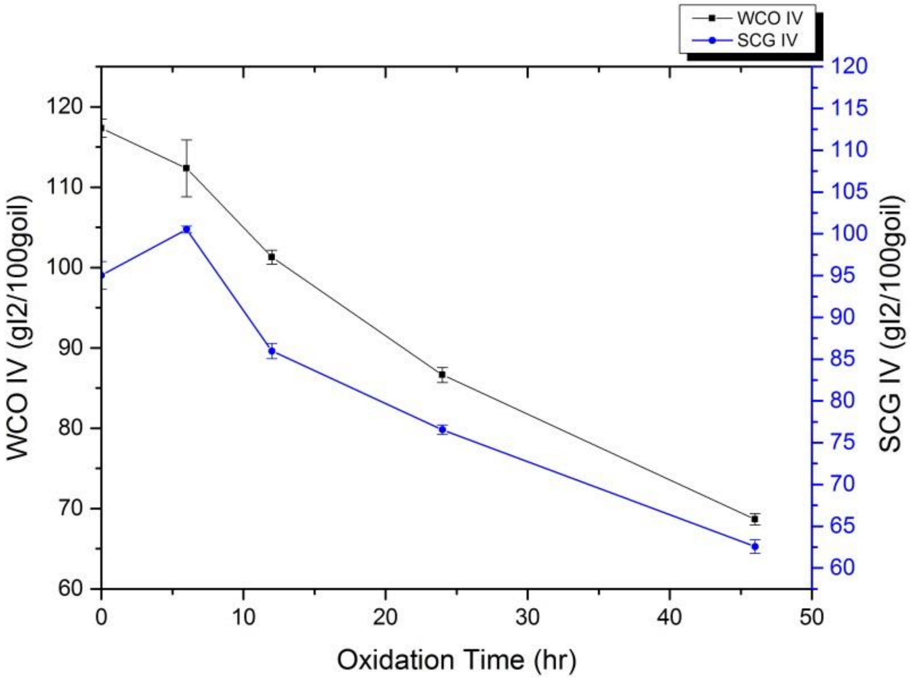

Figure 4: Iodine Values (IV) for SCG oil and WCO versus oxidation time.

Peak identification of FTIR spectra (Colorado) determined the presence of O-H, C-H and C=O shown by the presence of the following major bands; 3473 cm^{-1}, 2925 cm^{-1} and 1745 cm^{-1}; respectively. Other bands showed the presence of amine and C-H on the 1465 cm^{-1}, 1162 cm^{-1} and 717 cm^{-1}. Various spectra showed no change in peaks of both SCG oil and WCO with increased oxidation time, as illustrated in Figure 5, except for the C=O which presented a linear increase. This increase (R^2= 0.64 for SCG oil; R^2=0.94 for WCO), presented in Figure 6 could be related to the breaking of C=C with the introduction of oxygen upon induced oxidation.

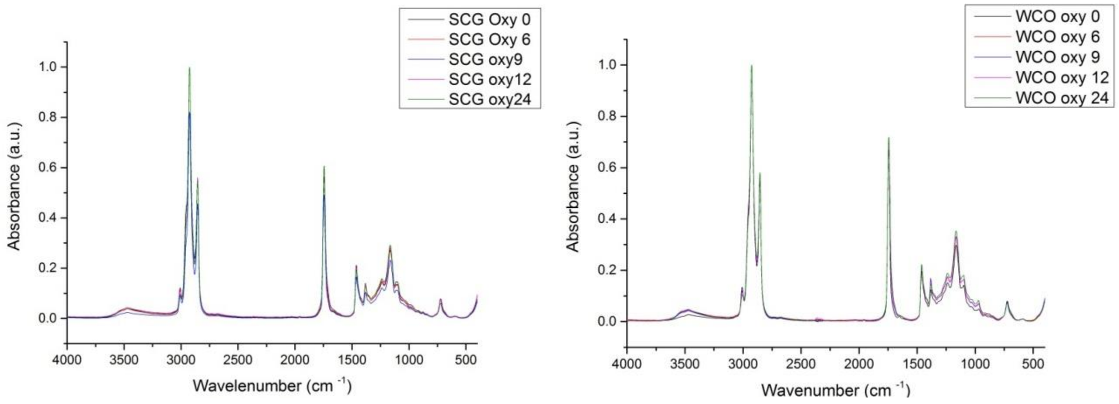

Figure 5: FTIR spectra for (left) non-oxidized SCG and SCG oxidized for 6, 9, 12 and 24 hours, (right) non-oxidized WCO and WCO oxidized for 6, 9, 12 and 24 hours.

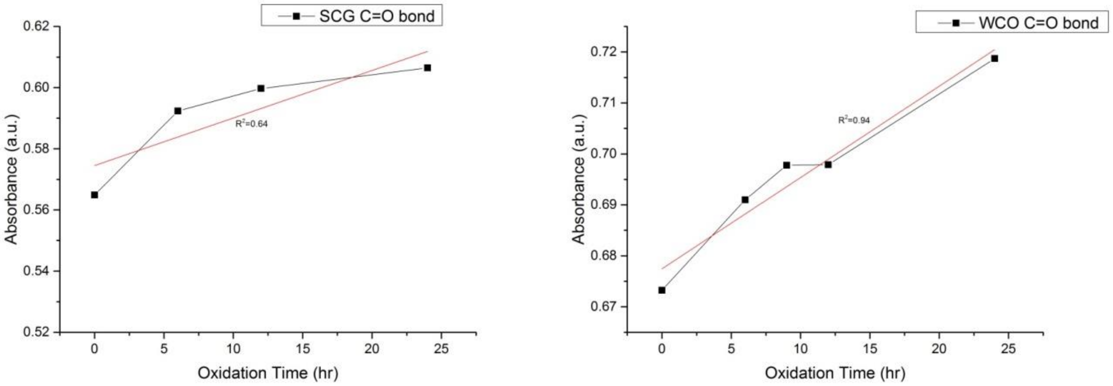

Figure 6: (left) Increased absorbance for C=O bonds in SCG oil (R^2=0.64) with increased oxidation time, (right) Increased absorbance for C=O bonds in WCO (R^2=0.94) with increased oxidation time.

In order to perceive the changes observed in the chemical tests, physical characterization of both oils was performed. Linear visco-elastic behavior was first determined at 0.1% strain as determined by the DHR tests. This value was thereafter used for the remaining physical tests to obtain representative results. Mainly, both SCG oil and WCO exhibited a Newtonian flow behavior regardless of the level of oxidation and temperature, as shown in Figure 7. This behavior was evident from plots of shear stress versus shear rate obtained from flow sweep tests which were performed during the determination of the viscosity. A linear relationship (r^2=0.999) is observed thus indicating that the viscosity is independent of the shear rate. This shows that despite induced oxidation for long periods of time (up to 48 hours), the behavior of the flow does not change.

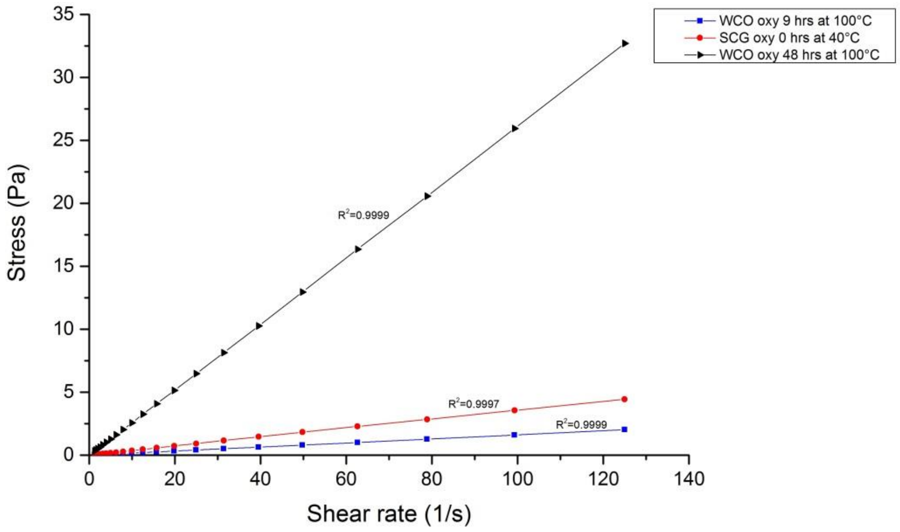

Figure 7: Stress-strain curve of tested samples of SCG oil and WCO at 40℃ and 100℃.

Values of viscosity of both SCG oil and WCO at 40°C and 100°C are presented in Table 2 and show the significant increase after 12 hours, caused by induced oxidation. Viscosities were reported to increase by more than 2 folds after 24 hours of oxidation and exceeded 10 folds after 48 hours. This increase in the oils' viscosities could be related to the changes in the physical structure of the oil molecules and the phenomenon of polymerization (Santos, Santos et al. 2005) caused by extensive oxidation over time. This is mainly due to the production of high molecular weight compounds which result from cyclisation and polymerization at high temperatures (Fox and Stachowiak 2007), evident from the decrease in peak values of PV after 6 hours of oxidation, and indicate final phases of oxidation. The correlation between the changes in PV of SCG oil and WCO with their subsequent viscosity is represented in Figure 8. It can thus be noticed that PV reaches a peak at a low viscosity of the oil followed a constant decrease of PV with increasing viscosity. Another factor which may be contributing to the increased viscosities is the breaking of double bonds (C=C), marked by the decrease in IV, which leads to the gradual formation of more saturated fatty acid chains having a higher viscosity. Viscosities are also noticed to decrease with increasing temperatures. This is due to the dependence of the viscosities of liquid foods on their temperature and composition as stated by Rao (1977). As temperature increases, intermolecular forces are weakened which in turn increase molecular thermal movement and eases flow within the oil, thus reducing the viscosity. Such decrease in viscosity versus increasing temperatures has been reported in several vegetable oils (Noureddini, Teoh et al. 1992, Tangsathitkulchai, Sittichaitaweekul et al. 2004, Santos, Santos et al. 2005, Fasina and Colley 2008, Esteban, Riba et al. 2012, Diamante and Lan 2014). Additionally, statistical analysis showed no significant difference between the viscosities of SCG oil and WCO at 100°C but not at 40 °C. This shows that at relatively low temperatures, bonds between the oil molecules are stronger unlike at high temperatures. Hence it can be concluded that regardless of the physical changes witnessed within the two different oils, the performances of SCG oil and WCO at high temperatures, close to the mixing temperatures of asphalt binders, are considered similar.

Table 2: Reported viscosities for SCG oil and WCO.

Oxidation Time (hr)	**Viscosity (Pa.s)**			
	SCG Oil		**WCO**	
	40°C	**100°C**	**40°C**	**100°C**
0	0.0449^{a}	0.0082^{a}	0.0375^{a*}	0.0079^{a*}
6	0.0717^{a}	$0.0115^{a,b}$	0.1185^{a}	0.0174^{b}
12	$0.1199^{a,b}$	0.0161^{b}	0.1200^{a}	0.0202^{b}
24	0.2039^{b}	0.0236^{c}	0.3023^{a}	0.0352^{c}
48	1.7144^{c}	0.1066^{d}	3.5545^{b}	0.2523^{d}

Different letters indicate significant differences between groups per column (P<0.05) (ANOVA, Tuckey's HSD).
**Compared to 0.0367Pa.s at 40℃ and 0.0085Pa.s at 100℃ (Li and Wang 2015).*

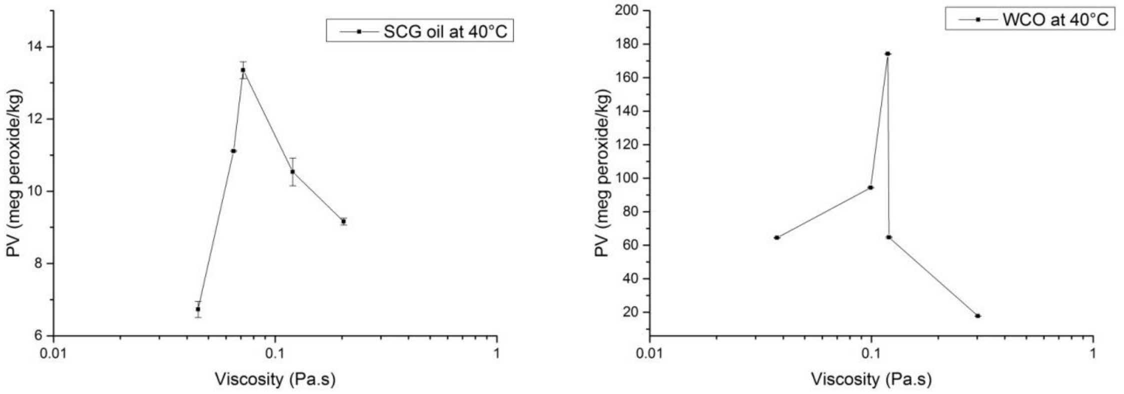

Figure 8: Peroxide Value of SCG oil (left) and WCO (right) versus viscosity for different oxidation times.

A qualitative analysis of the dynamics of the elastic (G'; storage modulus) and viscous (G"; loss modulus) components of the oils throughout oxidation is represented by tanδ (G"/G') versus oscillatory frequency in Figure 9. Results show that at low frequencies, both SCG and WCO oils exhibited higher viscous behavior than elastic which then decreased with increasing angular frequency. This is reflected by an increased elastic behavior with increased angular frequency as portrayed in Figures 10 and 11.

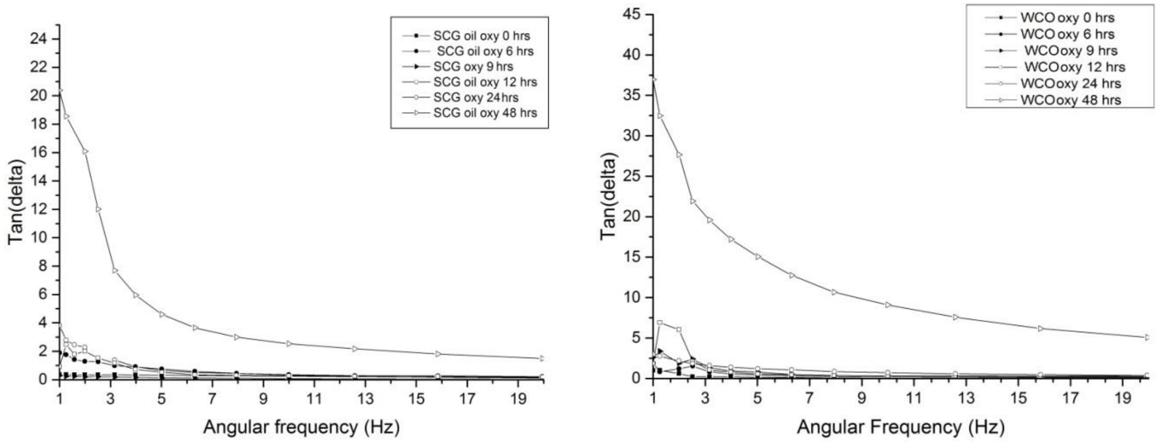

Figure 9: Storage and loss moduli presented as tanδ versus angular frequency of SCG oil (left) and WCO (right) throughout oxidation.

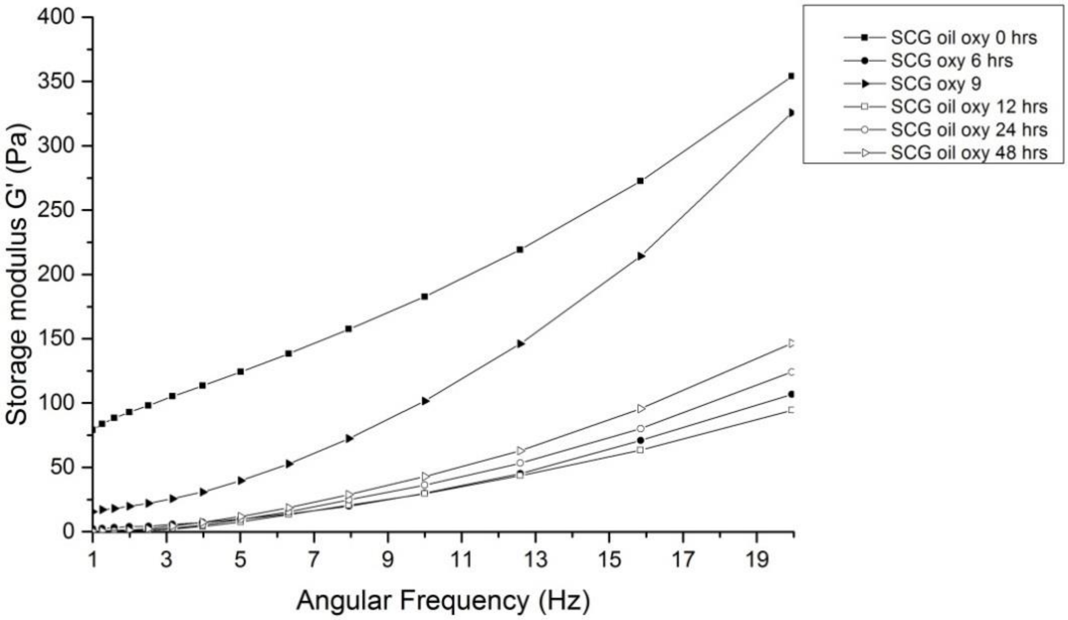

Figure 10: G’ curve versus angular frequency of SCG oil throughout oxidation.

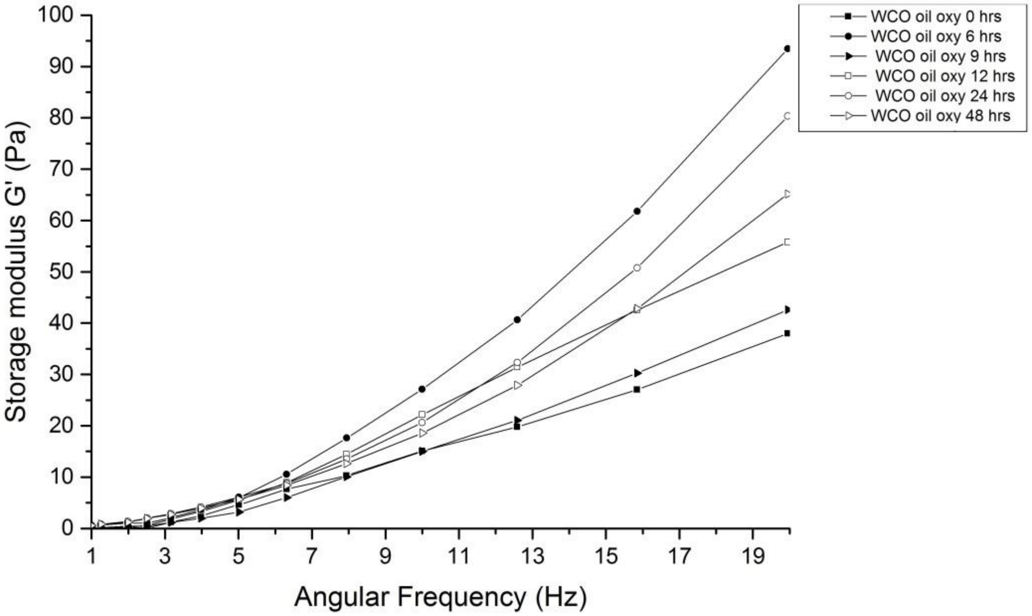

Figure 11: G’ curve versus angular frequency of WCO throughout oxidation.

D. Conclusion

After exposing SCG oil and WCO to induced oxidation and characterizing their physicochemical properties in an attempt to explore their potential as sustainable asphalt rejuvenators, the following can be concluded:

- Chemical properties were affected by oxidation and demonstrated an increase in peroxide value to a certain peak followed by a decrease reaching a plateau, with acid values increasing while iodine values decreased as a result of the release of free fatty acids and the breaking of double bonds.
- No major differences were noted in the FTIR peaks of the oils' spectra upon oxidation.
- Regardless of oxidation, both SCG oil and WCO exhibited a Newtonian behavior.
- Oil viscosities presented a significant increase after 12 hours of oxidation. At low temperatures, oils exhibit different viscosities which however behaved similarly at higher temperatures, close to the mixing temperatures of asphalt binders.
- Both oils at low oscillation frequencies showed a higher viscous component followed by an increased elastic component with increasing angular frequencies.

As oxidation played a major factor in modifying the physical and chemical properties of oils, it can be concluded that SCG oil and WCO may be considered as potential sustainable and natural with a customizable range of viscosities for rejuvenating aged asphalt binders; ultimately aiding in the decrease of both asphaltic and food wastes. This is especially true since the oils possess desirable properties as being user friendly, have a high flash point thus being safe, have been reported to improve the physical properties of aged asphalt and being wastes of renewable feedstock.

CHAPTER II

SUSTAINABLE ASPHALT BINDER REJUVENATORS FROM SPENT COFFEE GROUNDS AND WASTE COOKING OILS

A. Introduction

Green energy is gaining interest due to increasing fuel costs, limited crude reserves and environmental awareness. These changes pushed for sustainable asphalt production and paving practices to reduce carbon emissions, the need for landfill areas, and increased cost effectiveness. For these reasons, recent studies have focused on using recycled material to be incorporated in binders and asphalt mixes. Asphalt binders are by-products of the petroleum industry that, regardless of their depleting natural resources, are still being extensively used with aggregate mixes to pave roads. It was found that during storage, mixing, transport and paving, oils found in the asphalt oxidize and evaporate. This leads to hardening of the pavement and in turn causes deformation and cracking problems. Traditionally, such damaged material used to be dumped in landfills and only new asphaltic mixes were used to re-pave roads. But since asphaltic wastes were found to leach toxic chemicals to the environment especially underground water and render them un-exploitable, agencies initiated the use of Recycled Asphalt Pavement (RAP) in Hot Mix Asphalt (HMA). Researchers have concentrated on the use of RAP in different proportions in mixes, rather than continuously dumping old pavements deteriorated by oxidative aging and constructing new ones. However; the application of RAP was limited to 15% due to its aged and damaged nature. For this reason, asphalt rejuvenators were introduced to modify

RAP, restore its desirable properties (Chen, Chen et al. 2015) and help improve its performance thus increasing its application to 80%. Commercial rejuvenators mainly soften asphalt and improve the maltene/asphaltene fractions as well as restoring volatiles while attaining adhesion. At this moment, alternative binders are being produced from biomasses (Wen, Bhusal et al. 2013) which constitute one of the largest sources of energy worldwide. It supplies about 10 % of primary energy globally (Kucuk Mm 1997, Kaltschmitt M 2007, MF 2010). An additional benefit is by utilizing biomass residues such as waste cooking oil (Zhang, Dubé et al. 2003, Shi and Bao 2008), and spent coffee ground (Kondamudi, Mohapatra et al. 2008). The latter is a solid waste that remains after coffee is brewed. The International Coffee Organization reported more than 8 billion kilograms of coffee being exported worldwide (ICO 2015). Moreover, studies on spent coffee ground reported high percentages of oil mostly lipid constituting around15 % by dry weight (Kondamudi, Mohapatra et al. 2008, Mussatto, Machado et al. 2011). Other studies explored the antioxidant effect of spent coffee ground on the rheology and aging of asphalt properties, especially for the hardening effect caused by oxidative aging, but were found to serve as a solvent rather than an antioxidant (Zofka and Yut 2012), with no change in temperature susceptibility being recorded. On the other hand, waste cooking oil produced from a range of vegetable oils is being extensively used in biodiesel production in the United States (Radich 2004, Eidman 2006). The most important source for waste cooking oil is food sectors where their disposal is considered problematic. Approximately 3 billion gallons of waste cooking oil are collected from food establishments as stated by U.S Environmental Protection Agency (EPA 2014) . This oil is usually polymerized to produce oil-based bio-asphalt. In 2013, it was found that the incorporation of waste cooking oil bio-asphalt reduced the stiffness and resistance of Hot Mix Asphalt (HMA) to rutting and fatigue cracking but increased its resistance to thermal cracking (Wen, Bhusal et al. 2013).

Since it was demonstrated that large amounts of oil can be potentially used from spent coffee ground and waste cooking oil; it is then of interest to explore the rejuvenating effects of these oils on the rheology and physical properties of aged asphalt while evading their hazardous disposal and minimizing the use of natural resources. Therefore, the main purpose of this study is to decrease the environmental impact of two problematic food wastes, spent coffee grounds (SCG) and waste cooking oil (WCO) by providing an innovative solution and new potential uses for their recycling.

B. Objectives

The study presents tasks conducted on two complementary objectives that promote sustainability by effectively recycling, in conjunction, wastes from two industries: food and construction. The objectives aim at:

- Minimizing environmental impact of two problematic food wastes (SCG and WCO) by providing an innovative solution for their recycling, and
- Producing binder rejuvenators from SCG and WCO for use in enhancing the performance of recycled asphalt binder from reclaimed pavements (RAP), thus allowing its effective incorporation in new asphalt-aggregate mixtures.

Succeeding in the above-stated objectives fosters sustainable development through minimizing the environmental and social impacts of improper handling of waste, relieving pressure on landfills and incineration plants, decreasing illegal dumping, and limiting the mining of natural resources.

C. Scope

In order to investigate the feasibility and effectiveness of rejuvenation and amelioration of the physical properties of recycled asphalt binders, two types of binders (un-aged PG58-XX and aged PG76-XX) were mixed under laboratory conditions with various percentages of two waste oils from the food industry; spent coffee grounds (SCG) and waste cooking oil (WCO).

The scope of this chapter covers the following tasks:

- Evaluating the softening effect of oils on asphalt binders by mixing various percentages of both types of un-oxidized and oxidized oils with un-aged PG58-XX binder and test for changes in its physical properties, including linearity, high temperature performance grading and creep behavior;
- Laboratory aging of the PG58-XX binder to produce a higher temperature grade binder, specifically, PG 76-XX;
- Repetition of the aforementioned suite of tests on the aged PG76-XX binder to investigate the rejuvenating effectiveness of the oils.

D. Materials and Experimental Design

1. Materials

The original asphalt binder used was Pen 60/70 asphalt meeting PG grade of PG 58-XX high temperature based on the results obtained from the dynamic shear rheometery testing conducted according to ASTM-D7175-08. All chemicals used in this research were procured from Sigma Aldrich (St. Louis, MO, USA).

2. *Experimental Design*

a. Un-aged PG58-XX binder

For the experiments conducted on un-aged PG 58-XX binder as per Figure 12, oxidized oils from SCG and WCO were mixed in 5%, 7% and 10% with the binder and tested for linearity, performance grading and recovery using the Linearity check test, Complex Shear Modulus test and Multiple Stress Creep Recovery check; respectively.

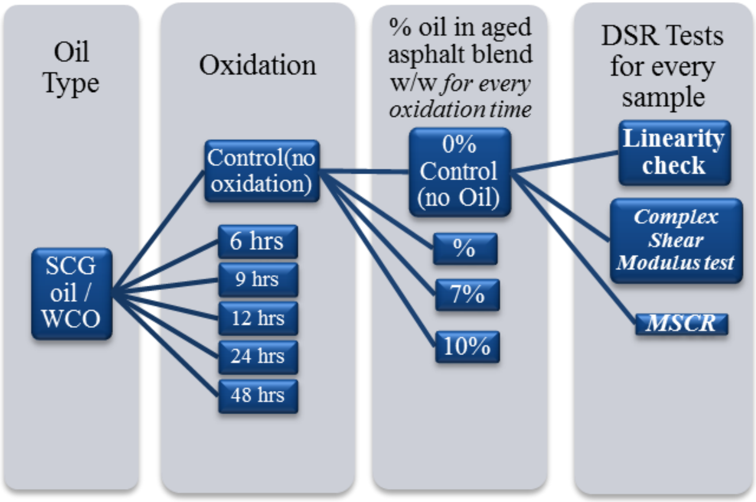

Figure 12: Experimental program conducted to study the effect of oxidation on oil characteristics as well as the effect of mixing oils on the physical properties of asphalt binder.

b. Aged PG76-XX binder

Based on the results for the un-aged PG 58-XX binder, SCG oil and WCO were mixed with aged PG 76-XX binder at 1%, 5%, 10%, 12% and 15% w/w as per Figure 13. The same rheological tests were conducted as for the un-aged binder.

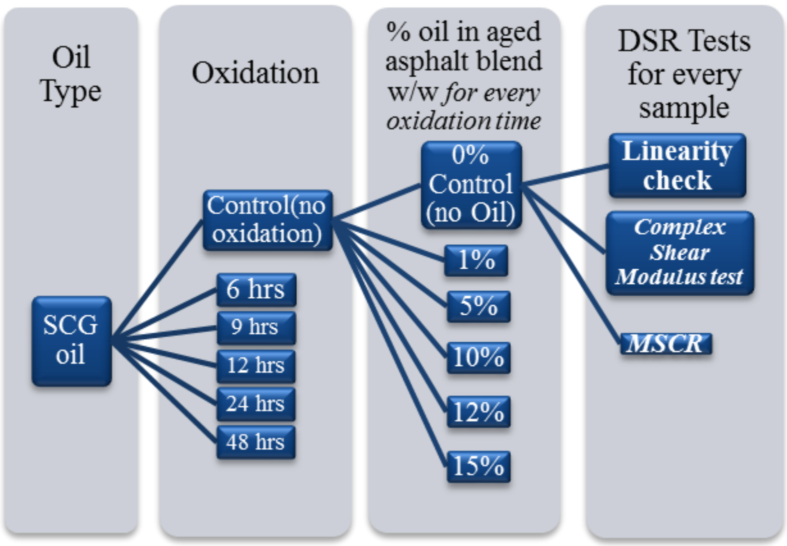

Figure 13: Experimental program conducted to study the rejuvenating effect of SCG oil on the physical properties of aged or recycled asphalt binder.

3. *Methodology*

a. Binder Aging and Oil Mixing

Following ASTM D1754/D1754M − 09, thin layers of un-aged PG 58-XX binder were poured in plates and aged in a Thin Film Oven (TFO) for 24 hours at 165°C in order to increase the PG by two grades, thus yielding a grade of PG 76-XX. Oils were then incorporated in the un-aged and aged binders following the experimental design. Blending the bio-asphalt was performed using a warring mixer to obtain a homogenous mix, inspected visually.

b. Characterization of Bio-asphalt Binder

All rheological measurements – linearity tests, complex shear moduli tests and multiple stress creep recovery tests of bio-asphalt blends were performed using a Discovery

Hybrid Rheometer – DHR 3 (TA-Instruments, New Castle, DE, USA) equipped with an upper heated plate, 25mm. Tests were conducted in duplicates as the error was less than 5%.

i. Bio-asphalt Binder Linearity Check

A linearity check was first performed on all bio-asphalt blends in order to conduct the rheological measurements in the linear viscoelastic range. Tests were performed at 58℃ with 10 rad/s angular frequency, strain ranging from 2% to 16% and 2% increment (ASTM D7175 − 08).

ii. Complex Shear Modulus Test

After confirming the bio-asphalt's linear viscoelastic behavior, oscillatory tests were conducted in order to determine the dynamic shear modulus (|G*|) and the phase angle (δ) in order to analyze the rutting factor and performance grade (|G*|/sinδ) (ASTM D7175 − 08). The tests were conducted under 52, 58, 64, 70 and 76℃ with 12% strain and angular frequency ranging from 100 to 0.1 rad/sec. To meet a specific performance grade, the value of |G*|/sinδ at the high temperature of the grade should exceed 1 for unaged samples and 2.2 after 5 hours of aging.

iii. Multiple Stress Creep Recovery – MSCR – Test

The MSCR tests were conducted following ASTM-D7405. The temperatures used for the bio-asphalt blends were those identified by the oscillation tests. Stress levels of 100 Pa and 3200 Pa were applied with a creep time of 1 second and a recovery time of 9 seconds, repeated 10 times each.

4. Results and Discussion

a. DSR Analysis of Bio-asphalt Blends

i. Bio-asphalt Binder Linearity Check

Un-aged PG 58-XX Binder:

To confirm linearity, the percentage difference of the dynamic shear modulus (|G*|) between 2% and 12% oscillation strains was calculated. Linearity was confirmed when all tests resulted in less than 2% difference. All bio-asphalt blends belonged in the linear viscoelastic range.

Aged PG 76-XX Binder:

Aged binder was noticed to retain linearity up to 12 hours of aging where the binder belonged in the linear viscoelastic range. However, after 24 hours of aging, non-linear behavior was evident. It was noticed that mixing SCG oil and WCO as low as 1% w/w was effective enough to restore linearity to the aged binders as seen in Figure 14.

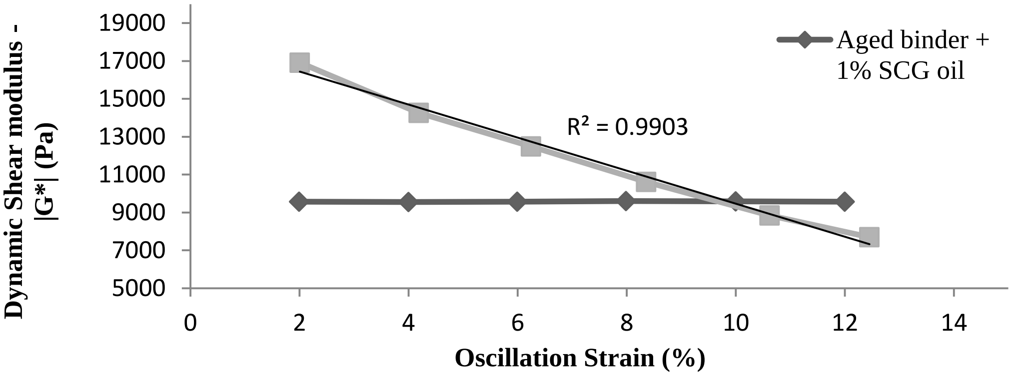

Figure 14: Loss in linear behavior in binder aged for 24 hours, illustrated by a difference greater than 2% between strains of 2% and 12%; followed by the restoration of linear behavior by the addition of 1% SCG oil to the aged binder.

ii. Complex Shear Modulus Test

The oscillatory tests conducted on the control unaged binder classified it as potentially having a high PG of 64-XX; however, after aging the sample for 5 hours the values of $|G^*|/\sin\delta$ were less than 2.2 at 64°C. Consequently, the unaged binder used in this study was classified as PG 58-XX.

The oscillatory tests conducted on the rejuvenated binder blends under the same testing conditions resulted in decreased values of $|G^*|/\sin\delta$ in comparison to the control unaged binder which may be correlated to potential fatigue cracking under field conditions as demonstrated by Daniel and Chehab (2008). The tests further illustrate that blending SCG oil and WCO has a significant effect on softening the asphalt. Un-oxidized SCG oil and WCO at 5% and 7% w/w reduced the high performance grade of the control binder from PG 58-XX to PG 52-XX, whereas the blend containing 10% SCG oil reduced the PG even lower, except for the oils that were oxidized for 24 hours. It is thus noticed that as the oil percentage increases in the asphalt blends, the degree of softening increases thus increasing susceptibility to permanent deformation but reducing susceptibility to fatigue cracking. This is however not the case for highly oxidized oils. This is where the evident effect of oxidation is reflected in the increased viscosity which in turn limits the softening effect of the oil. The reduction in $|G^*|/\sin\delta$ of SCG oil blends at 52°C are presented in Figure 15. Comparison of means between values of $|G^*|/\sin\delta$ of both SCG oil and WCO showed no significant difference, indicating that both oils behaved similarly and soften the asphalt blends equally. For this reason, SCG oil was chosen to be tested as the innovative potential oil to modify aged asphalt binder.

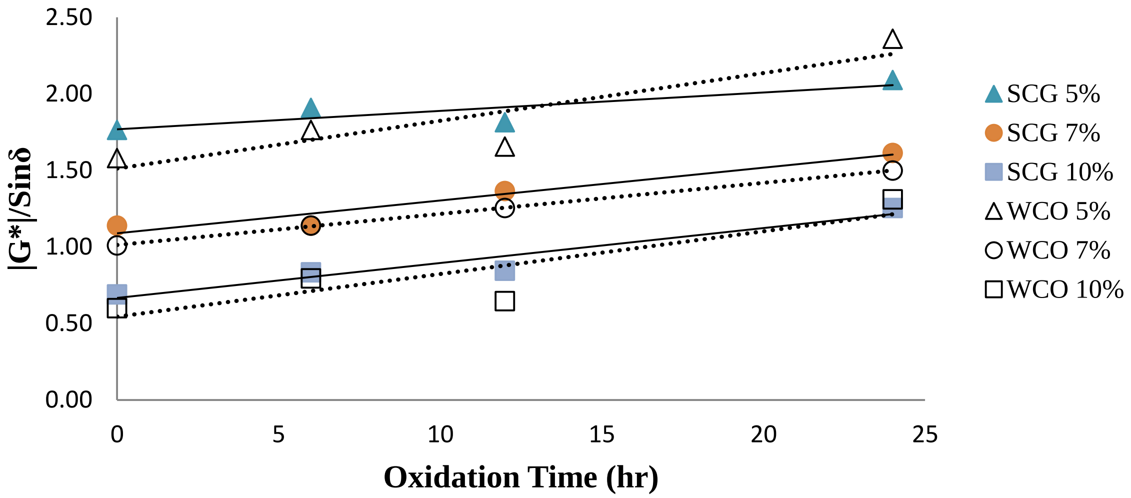

Figure 15: Values of |G*|/sinδ for SCG and WCO blends at 52°C.

In comparison to the unmodified binder, mixing SCG oil or WCO, either oxidized or not at any percentage, decreased the stiffness of bio-asphalt blends by decreasing the values of the dynamic shear modulus (|G*|) from 6,342 Pa. This was further elaborated when statistical analysis using SPSS showed the significant decrease in stiffness caused by the increased percentage of added oil, reflected by the values of (|G*|), but not on the elastic behavior (phase angle, δ). This is when the blends were seen to soften and become more prone to deformation, as reflected by the decreased ratio of |G*|/sinδ. This was also demonstrated by Wen, Bhusal et al. (2013) when waste cooking oil-based bio-asphalt also decreased the resistance of conventional binder to permanent deformation.

The oscillatory tests conducted on the aged control binder concluded its high performance grade as PG 76-XX. Oscillatory tests conducted on asphalt blends with non-oxidized and oxidized SCG oil under the same testing conditions resulted in decreased values of |G*|/sinδ in comparison to the aged control binder, confirming that mixing SCG oil softened the asphalt. Extracted and oxidized SCG oil in 1, 5, 10, 12 and 15% w/w blends modified the high performance grade of the control binder from PG 76-XX depending on the oil content and level of oxidation, as shown in Table 3. It can be noticed that PG grading increases vertically with increasing oxidation time whereas it decreases horizontally when the oil percentage increases. It is thus noticed that 10% of un-oxidized SCG oil, having the lowest viscosity, is required to bring back the PG of the aged asphalt to the initial PG of the control. In order to better comprehend the behavior of the asphalt, the dynamics of the complex modulus (|G*|) were analyzed in function of oxidation time at the grade temperature of the control binder (58℃), as demonstrated in Figure 16 and identified the different grade zones. Figure 17 represents the changes in |G*|/sinδ with increased percentage of un-oxidized SCG oil at a constant temperature. This model representation could be used to interpolate the quantity of required un-oxidized SCG oil to reach a certain preferred PG.

Table 3: Comparison in Performance Grade (PG) of control to that of asphalt/SCG oil blends. 10% SCG oil required to bring back the aged binder to its initial PG.

Oil Percentage **Oxidation Time**	**1**	**5**	**10**	**12**	**15**
0	70	64	**58**	58	58
6	70	70	70	64	64
9	76	76	70	64	64
12	76	76	70	64	64
24	76	76	70	70	64

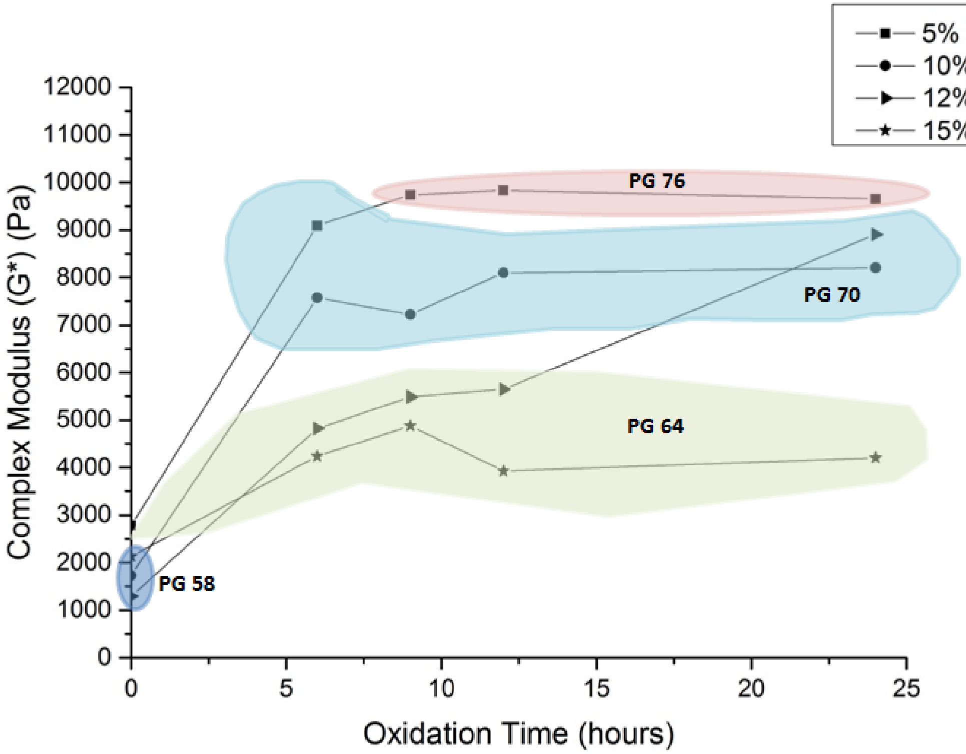

Figure 16: Different PG zones identified from the dynamics of the complex modulus (|G*|) versus oxidation time.

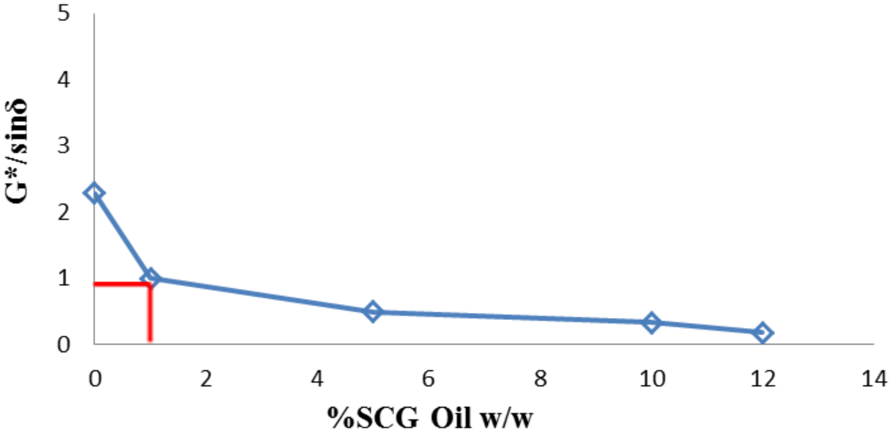

Figure 17: A model representation of the percentage of un-oxidized SCG oil required to reach PG 70-XX, starting from PG 76-XX.

iii. Multiple Stress Creep Recovery – MSCR – Test

MSCR tests were conducted for PG 58-XX samples at temperatures where |G*|/sinδ exhibited values larger than 1. MSCR is a relatively new method that helps evaluate the elastic behavior of binders. During an MSCR test, a binder gets subjected to a low and high stress levels (0.1 kPa and 3.2 kPa) by applying 10 loading and unloading stresses at each level. A creep load is applied for one second, followed by a nine second release which will allow the sample to relax and recover; during which the recovered and unrecovered strains will be measured. An MSCR measures the Non-Recoverable Creep Compliance (J_{nr}), which represents the amount of residual strain remaining in the sample after the repeated cycles of creep and recovery are applied. J_{nr} can be considered as an indicator of permanent deformation.

In comparison to the control unaged PG 58-XX binder which recorded J_{nr} values of 9.18 kPa^{-1} at 0.1kPa and 10.37 kPa^{-1} at 3.2kPa, all blends with oil exhibited lower values of J_{nr} thus higher recovery at 0.1 and 3.2 kPa. Figure 18 presents the changes in J_{nr} values with increasing SCG oil percentage in aged asphalt blends. It can be noticed that even the blend containing 10% un-oxidized SCG oil, which decreased the performance grade of aged asphalt to levels similar to the control, had lower J_{nr} values indicating higher resistance to permanent deformation. It can also be seen that the increased quantity of un-oxidized SCG oil resulted in the highest increase in J_{nr} values, gradually lowering the recovery due to the fluid nature of the oil. Similar results were obtained by Wen, Bhusal et al. (2013) when waste cooking oil bio-asphalt was used. However; oxidized SCG oils did not considerably lower the levels of recovery, although modifying the PG, since oxidation increased viscosities and the solid component of the oils. This characteristic may hold the potential to customize asphalt binders to desirable physical properties depending on the needs and geographical location which depict certain requirements on binders. Figure 19 additionally represents the calculated percent difference in non-recoverable creep compliance between 0.100 kPa and 3.200 kPa.

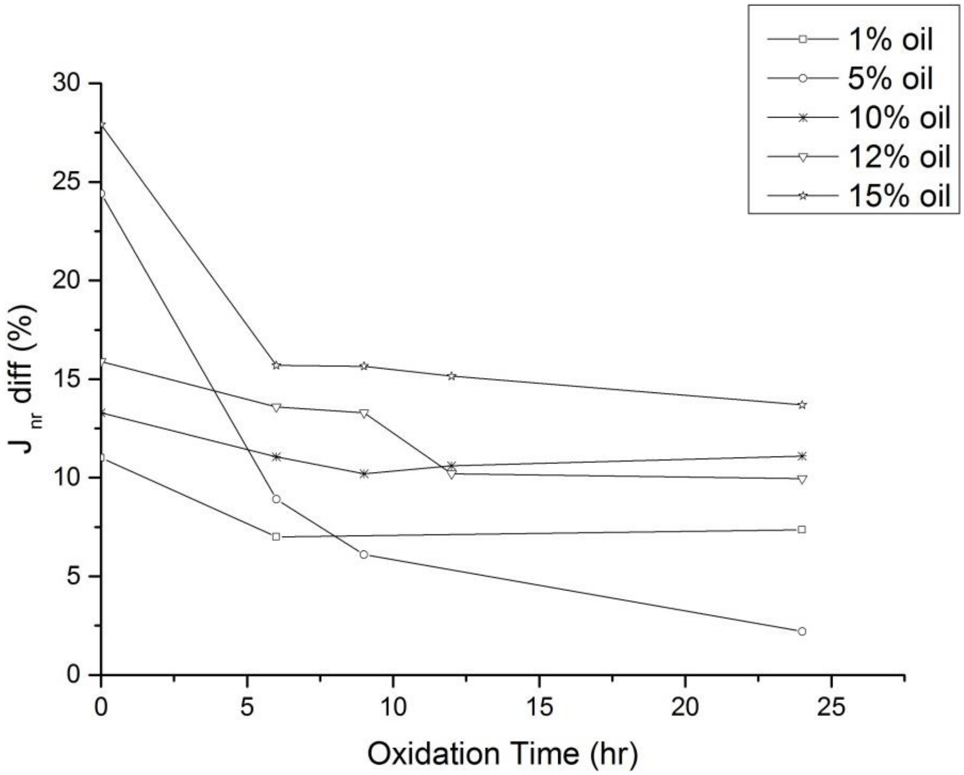

Figure 18: Changes in J_{nr} values with increasing un-oxidized and oxidized SCG oil percentage in asphalt blends.

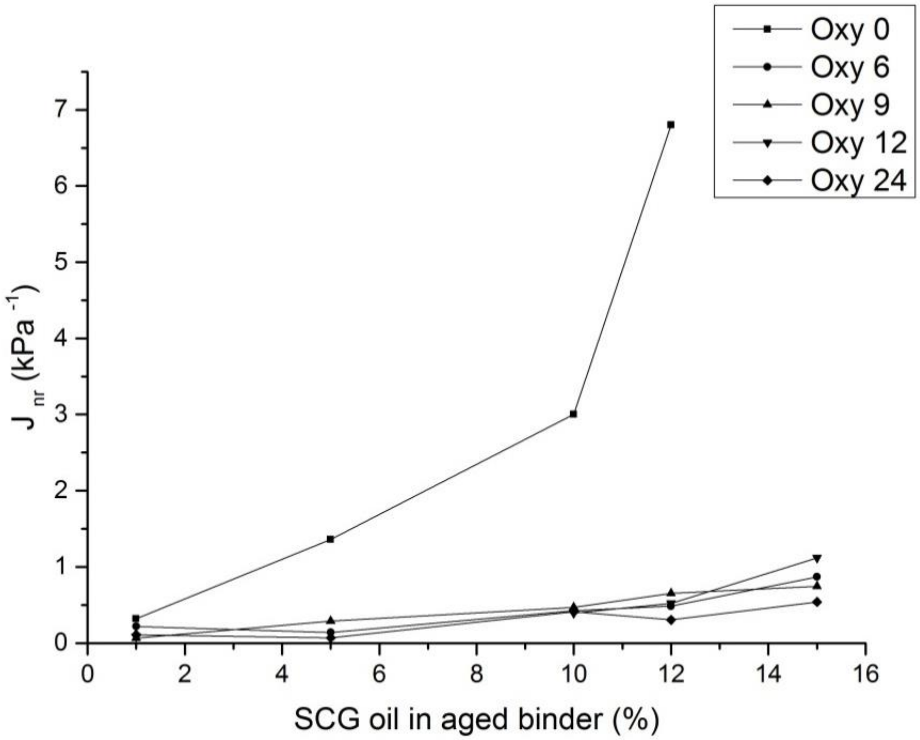

Figure 19: Values of J_{nrDiff} with oxidation time. $\mathbf{JnrDiff} = \frac{(\mathbf{Jnr\ 3.2 - Jnr\ 0.1}).\mathbf{100}}{\mathbf{Jnr\ 0.1}}$

E. Conclusion

Global studies highlighted the importance of recycling and the use of renewable energy in order to decrease environmental impacts. Decreasing crude oil reserves and technical difficulties in modifying asphalt properties additionally draw attention to further needs. For that reason, oil from Spent Coffee Grounds (SCG) and Waste Cooking Oil (WCO), two food wastes having hazardous disposal, were introduced to un-aged PG 58-XX and aged PG 76-XX asphalt binder to change their physical properties. The blending was studied to assess the feasibility of using SCG oil and WCO to modify and enhance recycled asphalt binder. The use of SCG oil and WCO in asphalt binder was found to restore linear behavior which was lost upon the aging process. SCG oil and WCO were also found to increasingly soften the asphalt with increasing quantities of oil thus decreasing its PG, with 10% oil required to return the binder to its initial PG. This characteristic could possibly be used to modify and customize new or recycled asphalt to a PG that suits specific needs and preferences related to geographical location or other technical reasons. Finally, MSCR tests showed that all blends had lower values of non-recoverable creep compliance (J_{nr}), even for the same PG as the control, thus lowering susceptibility to permanent deformation compared to un-aged asphalt with an increasing J_{nr} with increased percentage of SCG oil.

REFERENCES

A.Deligiannis, A.Papazafeiropoulou, G.Anastopoulos and F. Zannikos (2011). Waste Coffee Grounds as an Energy Feedstock. 3rd International CEMEPE & SECOTOX Conference. Skiathos.

Abdullah, M. and A. Bulent Koc (2013). "Oil removal from waste coffee grounds using two-phase solvent extraction enhanced with ultrasonication." Renewable Energy **50**(0): 965-970.

Al-Hamamre, Z., S. Foerster, F. Hartmann, M. Kröger and M. Kaltschmitt (2012). "Oil extracted from spent coffee grounds as a renewable source for fatty acid methyl ester manufacturing." Fuel **96**(0): 70-76.

Alimentarius, C. (1999). Codex Alimentarius Standards for Fats and Oils from Vegetable Sources. Section 2.

Ammerlaan, T., V. Barrière, P. Genest-Richard and S. Rabow (2012). Tales of a Forgotten Bioresource: The recycling of spent coffee grounds. Design III

BREE 495. M. U. Department of Bioresource Engineering**:** 1-58.

Chen, J.-S., S.-F. Chen, M.-C. Liao and S. W. Huang (2015). "Laboratory Evaluation of Asphalt Blends of Recycling Agents Mixed with Aged Binders." Journal of Materials in Civil Engineering **27**(4): 04014143.

Colorado, O. "Table of Characteristic IR Absorptions." Retrieved March 2016, from http://orgchem.colorado.edu/Spectroscopy/specttutor/irchart.pdf.

Daniel, J. S. and G. R. Chehab (2008). Use of RAP Mixtures in Mechanistic Empirical Pavement Design Guide. Transportation Research Board 87th Annual Meeting, Washington DC, Transportation Research Board Business Office.

Diamante, L. M. and T. Lan (2014). "Absolute viscosities of vegetable oils at different temperatures and shear rate range of 64.5 to 4835 s− 1." Journal of Food Processing **2014**.

Eidman, V. R. (2006). "Renewable Liquid Fuels: Current Situation and Prospects." Choices **21**(1): 15–19.

EPA. (2014, 2014). "Learn About Biodiesel." from http://www.epa.gov/region9/waste/biodiesel/questions.html.

Esteban, B., J.-R. Riba, G. Baquero, A. Rius and R. Puig (2012). "Temperature dependence of density and viscosity of vegetable oils." Biomass and Bioenergy **42**: 164-171.

Farah, A. (2012). Coffee Constituents. Coffee, Wiley-Blackwell**:** 21-58.

Fasina, O. and Z. Colley (2008). "Viscosity and specific heat of vegetable oils as a function of temperature: 35 C to 180 C." International Journal of Food Properties **11**(4): 738-746.

Fox, N. J. and G. W. Stachowiak (2007). "Vegetable oil-based lubricants—A review of oxidation." Tribology International **40**(7): 1035-1046.

ICO, I. C. O. (2015). Annual Report 2013 - 2014.

Kabir, I., M. R. Yacob and A. Radam (2014). "Households' Awareness, Attitudes and Practices Regarding Waste Cooking Oil Recycling in Petaling, Malaysia." IOSR Journal of Environmental Science, Toxicology and Food Technology **8**(10 ver. 3): 45-51.

Kaltschmitt M, S. W., Wiese A (2007). Renewable energy: technology, economics and environment, Springer.

Khan, N. A. and J. B. Brown (1953). "The composition of coffee oil and its component fatty acids." Journal of the American Oil Chemists Society **30**(12): 606-609.

Kondamudi, N., S. K. Mohapatra and M. Misra (2008). "Spent Coffee Grounds as a Versatile Source of Green Energy." Journal of Agricultural and Food Chemistry **56**(24): 11757-11760.

Kucuk Mm, D. A. (1997). "Biomass conversion processes " Energy Convers Manage **38**(2): 151–165.

Kulkarni, M. G. and A. K. Dalai (2006). "Waste cooking oil an economical source for biodiesel: a review." Industrial & engineering chemistry research **45**(9): 2901-2913.

Li, W. and X. Wang (2015). "Bio-lubricants Derived from Waste Cooking Oil with Improved Oxidation Stability and Low-temperature Properties." Journal of Oleo Science **64**(4): 367-374.

MF, D. (2010). "Microalgae as a feedstock for biodiesel." Energy Educ Sci Technol **25**: 31-43.

Mussatto, S., E. S. Machado, S. Martins and J. Teixeira (2011). "Production, Composition, and Application of Coffee and Its Industrial Residues." Food and Bioprocess Technology **4**(5): 661-672.

Mussatto, S. I., L. F. Ballesteros, S. Martins and J. A. Teixeira (2011). "Extraction of antioxidant phenolic compounds from spent coffee grounds." Separation and Purification Technology **83**: 173-179.

Noureddini, H., B. Teoh and L. D. Clements (1992). "Viscosities of vegetable oils and fatty acids." Journal of the American Oil Chemists Society **69**(12): 1189-1191.

Obruca, S., S. Petrik, P. Benesova, Z. Svoboda, L. Eremka and I. Marova (2014). "Utilization of oil extracted from spent coffee grounds for sustainable production of polyhydroxyalkanoates." Applied Microbiology and Biotechnology **98**(13): 5883-5890.

Paschke, R. and D. Wheeler (1954). "Inter-and intramolecular polymerization in heat-bodied linseed oil." Journal of the American Oil Chemists Society **31**(5): 208-211.

Petersen, J. C. (2009). Transportation Research Circular E-C140: A Review of the Fundamentals of Asphalt Oxidation. Transportation Research Board.

Pichai, E. and S. Krit (2015). "Optimization Of Solid-To-Solvent Ratio And Time For Oil Extraction Process From Spent Coffee Grounds Using Response Surface Methodology." Journal of Engineering and Applied Sciences **10**(16): 7049-7052.

Radich, A. (2004). "Biodiesel Performance, Costs, and Use." from http://www.eia.doe.gov/oiaf/analysispaper/biodiesel/.

Rao, M. (1977). "RHEOLOGY OF LIQUID FOODS-A REVIEW1." Journal of Texture Studies **8**(2): 135-168.

Romera, R., A. Santamaría, J. J. Peña, M. E. Muñoz, M. Barral, E. García and V. Jañez (2006). "Rheological aspects of the rejuvenation of aged bitumen." Rheologica Acta **45**(4): 474-478.

S.Caetano, N., V. F. M. Silvaac and T. M. Matab (2012). "Valorization of Coffee Grounds for Biodiesel Production." CHEMICAL ENGINEERING TRANSACTIONS **26**: 267-272.

S.Caetano, N., V. F. M. Silvaac and T. M. Matab (2012). "Valorization of Coffee Grounds for Biodiesel Production." The Italian Association of Chemical Engineering **26**: 268-272.

Sanli, H., M. Canakci and E. Alptekin (2011). "Characterization of waste frying oils obtained from different facilities." Bioenergy Technol **57**: 479-485.

Santos, J., I. Santos and A. Souza (2005). "Effect of heating and cooling on rheological parameters of edible vegetable oils." Journal of food Engineering **67**(4): 401-405.

Shi, H. and Z. Bao (2008). "Direct preparation of biodiesel from rapeseed oil leached by two-phase solvent extraction." Bioresour Technol **99**(18): 9025-9028.

Tangsathitkulchai, C., Y. Sittichaitaweekul and M. Tangsathitkulchai (2004). "Temperature effect on the viscosities of palm oil and coconut oil blended with diesel oil." Journal of the American Oil Chemists' Society **81**(4): 401-405.

Vardon, D. R., B. R. Moser, W. Zheng, K. Witkin, R. L. Evangelista, T. J. Strathmann, K. Rajagopalan and B. K. Sharma (2013). "Complete Utilization of Spent Coffee Grounds To Produce Biodiesel, Bio-Oil, and Biochar." ACS Sustainable Chemistry & Engineering **1**(10): 1286-1294.

Wen, H., S. Bhusal and B. Wen (2013). "Laboratory Evaluation of Waste Cooking Oil-Based Bioasphalt as an Alternative Binder for Hot Mix Asphalt." Journal of Materials in Civil Engineering **25**(10): 1432-1437.

Wen, Z., X. Yu, S.-T. Tu, J. Yan and E. Dahlquist (2010). "Biodiesel production from waste cooking oil catalyzed by TiO2–MgO mixed oxides." Bioresource Technology **101**(24): 9570-9576.

Yaakob, Z., M. Mohammad, M. Alherbawi, Z. Alam and K. Sopian (2013). "Overview of the production of biodiesel from Waste cooking oil." Renewable and Sustainable Energy Reviews **18**: 184-193.

Zargar, M., E. Ahmadinia, H. Asli and M. R. Karim (2012). "Investigation of the possibility of using waste cooking oil as a rejuvenating agent for aged bitumen." Journal of Hazardous Materials **233–234**: 254-258.

Zhang, Y., M. A. Dubé, D. D. McLean and M. Kates (2003). "Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis." Bioresource Technology **90**(3): 229-240.

Zofka, A. and I. Yut (2012). Investigation of Rheology and Aging Properties of Asphalt Binder Modified with Waste Coffee Grounds. Alternative Binders for Sustainable Asphalt Pavements. Washington DC, Transportation Research Board of the National Academies**:** 61-72.