1 Introduction

The research described in this dissertation focuses on developing a process to remove oligomers and suppress their formation by intercepting the aging procedure's precursors using adsorbents when biodiesel and its blends are used as fuel. There has been the search for various energy sources due to the increasing awareness of the depletion of fossil fuel resources, environmental issues, and more urgently is the need to mitigate climate change. Biodiesel has become more attractive in recent times (Daming et al. 2012, Abdullah et al., 2007) as an alternative fuel. Biodiesel, a methyl ester of vegetable oil, is a renewable, low environmental impact, green alternative fuel for diesel engines (EU Regulation, 2012, Ghosh and Dutta, 2012). In addition to its renewable status, biodiesel, compared to fossil fuel, has advantages such as its biodegradability, reduced exhaust emissions, higher cetane number, lubricity, and safer distribution and storage due to its higher flash point (Pereira et al. 2015, Monyem and Van Gerpen, 2001). Biodiesel fuel is chemically fatty acid methyl ester (FAME) derived from different plant oils. It varies slightly in molecular structures due to the degree of unsaturation of the fatty acids in the different sources compared to conventional diesel fuel (Pereira et al. 2015, 2013, Sharma and Singh, 2009). Biodiesel fuels contain significant amounts of esters of oleic, linoleic, or linolenic acids, which influence their oxidative stability. A small percentage of more highly unsaturated fatty compounds have a disproportionately strong effect in reducing oxidation stability and promoting oligomers formation. The oxidation products of the biodiesel in the engine sump influence the degradation of the lubrication oil.

Irrespective of biodiesel's advantages, it is clear from the above that biodiesel comes with attendant problems, especially its oxidation stability. One of the main hindrances of biodiesel is its degradability during storage and usage. This oxidative degradability essentially alters biodiesel's desirable properties and diminishes its applicability as fuel for long-term use.

Biodiesel as fuel introduces challenges into engine oil functions as biodiesel affects engine lubrication through fuel dilution (Zdrodowski et al., 2010). The fuel in oil reduces the oil’s life expectancy and hence its effectiveness. But when the motor oil is manufactured, the main goal is to achieve maximum durability of the motor and preserve all motor properties as long as possible (Sejkorová and Glos, 2017). The lubricant used in an internal combustion engine operates under extremely aggressive conditions and must perform its roles efficiently over the prescribed length of time. Degradation changes the lubricating oil's physical and chemical properties during service, resulting in deterioration of performance. One important factor affecting lubricating oil in recent times is the dilution of the oil by unburnt fuel, especially ester-based like biodiesel and its blends. Because fuel is a natural solvent, fuel dilution in motor oil causes a decrease in viscosity, increasing engine wear. When fuel contaminates the oil in the crankcase, the consequences include reduced oil film strength, increased volatility, reduced oil viscosity, increased engine wear, weakened lubricant detergency, accelerated lubricant oxidation, sludge, and acid formation (TOTAL, 2017; Syntheticoils, 2009; AMSOIL, 2009). Biodiesel accumulates in the engine sump oil, especially in vehicles fitted with a diesel particulate filter (DPF) system (Zdrodowski et al., 2010). Unlike diesel fuel which will evaporate from the lubricating oil under average operating temperatures, biodiesel with long-chain fatty acid esters will not evaporate because of its higher boiling temperature range, 160 °C to 375 °C compared with petroleum diesel fuel, about 175 °C (Tschöke et al., 2009) but rather oxidizes leading to a significant increase in the viscosity. Since the chemical and physical properties of biodiesel are pretty different from fossil diesel fuel, the biogenic components turn to remain in the engine oil leading to problems in the engine lubricant (Rodriguez-Fernández et al., 2016; Tschöke et al., 2009; He et al., 2011; Goodrum, 2002). In addition to the low evaporative rate, biodiesel tends to have higher fuel dilution rates of the lubrication oil than diesel fuel (Bannister et al., 2011). Hence the level of unburnt fuel in the engine oil can build up (Beercheck, 2008). There is always a certain amount of unburnt fuel (Shanta, 2011; Yüksek et al., 2009). The fuel in the oil reduces the oil's viscosity, degrades its oxidation resistance, and shortens its useful service life (Schneider et al., 2013).

Therefore, a proportion of fuel in vehicles always finds its way into the lubricating oil leading to dilution. This fuel dilution is increasingly significant in vehicles equipped with diesel particulate filters. Diesel vehicles fitted with diesel particulate filters (DPFs) require active regeneration via late injection of fresh fuel. This regeneration brings about an increase in the amount of biodiesel in the sump oil. In these engines, fuel is post-injected during the expansion stroke into the cylinder to increase the exhaust gas temperature and stoichiometry in a diesel particulate filter. The regeneration is done to help burn carbon-based deposits. During the post-injection for after-treatment system regeneration, some of the fuel is sprayed on cylinder walls and then is scraped by the piston's oil ring into the engine's crankcase. The fuel carried into the engine oil evaporates in the crankcase, particularly the lighter molecular weight fuel. The heavier molecular weight fuel remains in the oil and accumulate. Biodiesel accumulates in the lubricating oil, and unlike mineral diesel fuel, the biodiesel does not evaporate at the average operating temperature of the oil and will instead accumulate. Therefore, when biodiesel degrades within the oil, the degradation products eventually form, leading to a significant increase in the oil viscosity, potentially impacting lubrication oil durability (Bannister et al., 2010). Therefore, the presence of biodiesel in engine oil leads to dilution of the oil, increasing viscosity, oxidation of lubricating oil, and finally, the premature formation of sludge and deposits in the crankcase resulting in a short period of oil drain interval (Knorr et al., 2016; Karavalakis et al., 2011; Bannister et al., 2010; Thornton et al., 2009; Yüksek et al., 2009; Beercheck, 2008; Fang et al., 2007; Andreae et al., 2007). The lubricant performance, service intervals, and engine oil durability are impacted by biodiesel and engine oil interaction.

In Europe and according to EN 590, diesel fuel can contain up to 7 % biodiesel (FAME), but in other places such as America, higher percentages of up to 20 % biodiesel can be found. Biodiesel, derived from rapeseed, soybean, waste oils, etc., comprises a range of saturated and polyunsaturated esters. Therefore, it has a typical fatty acid pattern that differs in chain length and double bond content depending on the vegetable oil product used. The fatty acid pattern has an apparent influence on the physical and chemical properties of the fuel. A high proportion of double bonds can improve cold stability, but such fuels are more susceptible to oxidation. The susceptibility of the different fatty acid esters to oxidation differs according to the number of double bonds in the sample. Polyunsaturated compounds are more prone to oxidation than monounsaturated esters, which are more reactive than saturated esters. On exposure to air, these esters are prone to oxidative degradation. Additionally, the esters in FAME are hydrolyzed, resulting in high concentrations of weak acids in lubricants.

As biodiesel is relatively unstable compared to mineral diesel fuel, it readily degrades and aids the lubricating oil's oxidative degradation (Daming et al., 2012; EU Regulation 2012; Abdullah et al., 2007). Biodiesel, therefore, accelerates the degradation of crankcase oil (Pereira et al., 2015, 2013; Ghosh and Dutta, 2012; Shanta, 2011; Yüksek et al., 2009; Sharma and Singh, 2009; Andreae et al., 2007; Monyem and Van Gerpen, 2001).

The share of renewables in Germany’s transport is relatively low at around 5 % since most biofuels are currently consumed as blends, typically 10 % or less by volume with mineral fuels. However, biodiesel consumption has increased by 8.6 % (Le Seigneur, 2019; Germany 2020 Energy Policy Review). Its consumption is further projected to be 21,770 ktoe in 2020 (NREAP, 2019).

Various standards cover the use of biodiesel. In Europe, low-level biodiesel/diesel fuel blends, B5, B7 blends, are covered by EN 590, while EN 14214 focuses on biodiesel specifications for diesel engines. EN14214, introduced in 2012, expanded the scope to cover blends up to B10. With EN 16709 introduced in 2015, B20 and B30 blends for use by captive fleets are covered. The FAME component in EN 16709 must satisfy EN 14214, while the diesel component complies with EN 590 (Dieselnet std.php).

The Renewable Energy Directive (RED) requires the EU to achieve a binding target whereby 20 percent of its overall energy use would be powered from renewable sources by 2020. The RED also requires that the transport sector reach a renewable energy-use target of 10 percent. However, in RED II, the overall EU target for renewable energy source consumption by 2030 is raised to 32 %, with a minimum of 14 % target on road and rail transport by 2030. With this, the use of biodiesel is gradually increasing in proportion, and for biodiesel to be fully integrated into the fuel mix, the problem of its impact on lubrication oil changing interval must be overcome. While there have been significant research studies highlighting the effects of biodiesel on engine oil performance (Zdrodowski et al., 2010; Devlin et al., 2008; Andreae et al., 2007; Waynick, 2005; Blackburn et al., 1983; Thornton et al., 2009; Gulzar et al., 2016), understanding the autoxidative mechanisms of biodiesel (Christensen and McCormick, 2014; Flitsch et al., 2014; Ogawa et al., 2009; Fang et al., 2006), there is much to be done in combating the formation and removal of oligomers. The suppression of oligomer formation shall be the focus of this project.

1.1 Objectives

So far, there has been no attempt to cause the stabilization of biodiesel and its blends using adsorbents from open literature. This investigation is one of the first studies on the use of adsorbents to mitigate biodiesel and diesel fuel's stability behavior–biodiesel blends and the removal of oligomers or suppressing the formation of high molecular mass species in aging oil.

This study's primary aim has been achieved by several experimental measurements that provided results on adsorbents' effect on fuel oxidative stability, especially ester-based fuel like biodiesel and its blends. The chemical composition and some critical rheological analyses of the samples have been measured to understand their role in the oxidation of the sample by comparing the presence and absence of the adsorbents during the aging process.

Furthermore, it aims to use adsorbents to suppress oligomers' formation and remove them in aging oil due to the influence of biodiesel and its blends.

The research project also seeks to stabilize fuel, especially ester-based fuel like biodiesel, and its blends using the adsorbents. The adsorbents' application will enhance biodiesel's oxidative stability and its blends during long-term storage or application, focusing on its use in plug-in hybrid vehicles, emergency power plants, and generators. The combustion engine only starts in plug-in hybrid vehicles if the battery cannot supply energy on longer journeys. As a result, the fuel remains longer in plug-in hybrid vehicles. Fuels that are exposed to heat and oxygen over an extended period can form aging products. These aging products lead to the formation of deposits, especially in the case of diesel fuels mixed with biodiesel content, and can, therefore, endanger the operational safety of the vehicle in critical components such as injectors or filter units (Schroder et al., 2017; Christensen and McCormick, 2014; Flitsch et al., 2014; Ogawa et al., 2009; Fang et al., 2006).

This work's primary focus is adsorbents' use to suppress oligomers formation in aging oil and biodiesel fuel and its blends. A combined adsorbent of hydrotalcite compound and radical trapping agent are applied to interfere with sludge precursors' production and, therefore, suppress oligomers' formation. Other deactivated adsorbents would be applied to remove oligomers when it gets formed in aging oil. The use of adsorbents to remove the oligomers and other potential unstable components of the oil aging procedure resulting from the influence of biodiesel and its blends in the engine sump would promote and prolong the changing interval of lubricating oil in an engine fueled by biodiesel or its blends. The use of adsorbents in this process also makes it possible to increase the proportion of biodiesel or blends used as fuel in the transport sector or emergency power plants. The adsorbents' application in this process will enhance biodiesel's storage stability for a more extended period of duration.

1.2 Thesis Outline

This dissertation consists of 12 chapters, the introductory Chapter 1, where the motivation, problem statement, and objectives for this research work are outlined. Chapter 2 discusses relevant publications on lubricants, biodiesel, oxidation, and the techniques of preventing or delaying oxidation. The different methods for measuring the level of degradation of biodiesel are looked at here. The effect of biodiesel on lubrication oil and previous work carried out within the research group have been summarized. The theoretical framework, essential functions of lubricants, and the lubrication chemistry are highlighted, followed by a summarized description of the production, composition, and means by which the fuel finds its way into the sump are covered in Chapter 3. The underlying mechanism by which the samples or fuel and oil mixture degrade is covered in this chapter. Chapter 4 builds on the basic experimental techniques applied to study the effect and impact of the adsorbents on the degradation of the fuel and oil mixtures. Chapter 5 outlines the focus of this work. The various degradation processes of the oil and fuel mixtures are carried out at relevant temperatures and durations of aging to establish the impact or effectiveness of the adsorbents in suppressing oxidation. While chapter 6 covers the selection of the adsorbents. This chapter provides the theoretical groundwork on which the adsorbents act to achieve the desired goals. The materials and methods applied in this work are covered in chapter 7. This chapter also looks at the measurement and instrumental techniques employed in this study. In chapter 8, the discussion of the trends in the results, while chapter 9 concludes the dissertation with a focus on the significant findings and perspectives for further work. The relevant publications reviewed and referenced in this dissertation are in chapter 10. The appendix, chapter 11, covers the results of experiments that are not discussed in this dissertation. In chapter 12, the glossary is covered.

2 Literature Review

Introduction

In this chapter, background information on biodiesel and its related oxidation and stability issues is discussed. This elucidates biodiesel's effect on engine lubricating oil and the different approaches for retarding its oxidation. Therefore, this literature review highlights various techniques presently used to subdue oxidation and hence allow the importance of this current study to be put into perspective.

2.1 Previous Work

The oxidative stability of biodiesel, especially the ester base, is associated with its application as fuel. Oxidation stability is the tendency of a fuel to react with oxygen at temperatures near ambient, and it describes the relative susceptibility of the fuel to degradation by oxidation (Christensen and McCormick, 2014). Biodiesel is susceptible to oxidation due to its high proportion of double bonds than diesel fuel during application and long-term storage. The oxidation stability of biodiesel is lower than that of petroleum-based diesel fuel (Botella et al., 2014; Dantas et al., 2011; Jain and Sharma, 2011; Karavalakis et al., 2011; Kivevele et al., 2011), and this hinders its application and long-term storage. It tends to deteriorate via hydrolytic and oxidative reactions because of its high degree of unsaturation (Singer et al., 2014; Abdullah et al., 2007; Fang et al., 2006; Duffield et al., 1998). In long-term storage or application, most biodiesel begins to oxidize immediately during storage. Biodiesel will very likely go out of specification regarding stability within four months. The oxidation stability of biodiesel has been evaluated through many experimental techniques. The Rancimat method is the standardized accelerated oxidation test, EN14112 and ASTM D6751 (Botella et al., 2014). The PetroOXY method is another way biodiesel's oxidation stability is determined and is described in the prEN16091 standard. The European standard for biodiesel (EN 14112) sets a limit of 6 h as the minimum induction period determined by using the Rancimat method (Karavalakis et al., 2010). The Rancimat test method indicates the length of time the fuel can be stored before producing acids, indicating that the fuel is becoming unstable or degrading (Karavalakis et al., 2010). The time that passes until the appearance of these secondary reaction products is called induction time or induction period, which is an indicator for oxidation stability and characterizes the fuel's resistance to oxidation. At only four months, biodiesel with induction times more extended than seven hours is reported out of specification for oxidation stability (McCormick and Westbrook, 2010). Biodiesel oxidation leads to increased acid value and oligomers' formation (Bannister et al., 2010). Many recent studies have focused on the problem of oxidation stability of biodiesel and its blends and their polymerization effects (TOTAL, 2017; Moser et al., 2013; Bannister et al., 2010; AMSOIL, 2009; Yüksek et al., 2009; Beercheck, 2008)

As stated in the introduction (section 1.0), biodiesel accumulates in the engine sump oil, severely impacting engine lubrication oils. The use of biodiesel leads to substantial lubrication oil dilution, which is not desirable since it affects various tribosystems of the engine (Molina et al., 2014; Gili et al., 2011) and lowers viscosity initially while increasing oil oxidation and causing biodiesel fuel itself and the lubricating oil to oxidize, leading to increased viscosity, premature formation of sludge and deposits in the crankcase resulting in a short period of oil drain interval (Ljubas et al., 2010; Karavalakis et al., 2010; Yüksek et al., 2009; Devlin et al., 2008; McTavish, 2008; Larsson, 2007; Sappok and Wong, 2007; Fang et al., 2006; Devlin et al., 2008; Knothe and Dunn, 2003). Sufficient work has been done for the understanding of the extent of biodiesel dilution in lubricants and its impact on oxidative stability of lubricating oils and sludge formation (Ljubas et al., 2010; Cowart et al., 2008; McTavish, 2008; Devlin et al., 2008; Marsh and Corradi, 2007; Fang et al., 2007; Andreae et al., 2007; Burgeoning, 2007; Infineum, 2007; Fetterman, 2007; Sappok and Wong, 2007; Larsson, 2007; Fang et al., 2006; Agarwal, 2005; Sharp et al., 2000). Shortening of the recommended oil drains between 30 % and 60 % due to biodiesel dilution with a corresponding increase in deposit formation has been reported (Gili et al., 2011). Through the dilution of biodiesel, acidity and viscosity are increased, thereby degrading lubricating oil performance. This oil dilution shortens oil drain intervals (Watson and Wong, 2008; Devlin et al., 2008) though oil with FAME content exceeding 6 % has been recommended for an oil change (Gili et al., 2011). There is an increase in sludge build-up resulting from oxidation due to a significant increase in engine oil dilution by biodiesel fuel (Shanta et al., 2011; Watson and Wong, 2008; Devlin et al., 2008; Avinash, 2003). However, there are varied results from studies on fuel dilution. Rapeseed methyl ester, 50 %, was used in heavy trucks and light vehicles and did not result in increased deposits (Dairene Uy et al., 2011). Therefore, fuel dilution is attributed to the biodiesel type used. Using soybean methyl ester (SME) recorded a significant increase in oxidation and deposits in fuel-diluted engine oil (Devlin et al., 2008), while Thornton et al. (2009) had no noticeable lubricant aging effects attributable to biodiesel. Sappok and Wong (2008) accelerated oil aging and reported an increased degradation of biodiesel.

The adverse effects of fuel dilution on properties and performance of lubrication engine oils have been extensively researched in recent times (Wakiru et al., 2018; Shanta, 2011; Bannister et al., 2010; Yüksek et al., 2009; Thornton et al., 2009; Beercheck, 2008; Watson and Wong, 2008; Sappok and Wong, 2008). While there has been much research on lubricant dilution, few researchers focused on biodiesel's influence on lubricating oil degradation. Knorr et al. (2016), Singer et al. (2014), and Schumacher (2013) went beyond the concept of dilution and simulated with model substances to trace the influence of biodiesel on the accelerated aging of lubricating oil.

Early work on the oxidation stability of biodiesel took a critical approach to suppress oxidation of biodiesel (Kumar, 2017; Zuleta et al., 2012; Rhet de Guzman et al., 2009; Fang et al., 2006; Duffield et al., 1998). It focused on using ester and polyglycol based formulations (Sharma and Singh, 2009; Woydt et al., 2008), thin-film coatings that may offer wear robustness between FAME and lubricant oil, and ring metallurgies and coatings that may offer wear robustness (Woydt et al., 2009). Sem (2004), in his study, concluded that increased deposits resulting from biodiesel dilution could be reduced with higher amounts of additives in the engine lubricating oils.

Researchers have proposed biodiesel mixtures (Sierra-Cantor and Guerrero-Fajardob, 2017; Serrano et al., 2014; Zuleta et al., 2012), structural modification, antioxidant usage, and blending with diesel fuel. Some researchers (Kumar, 2017; Zuleta et al., 2012; Karavalakis et al., 2011) have reported altering the fatty acid profile with an enhanced saturated fatty acid leading to improved oxidative stability. Here, oil with high saturated fatty acid content for biodiesel production is used compared to the unsaturated portion. Also, a combination of elevated oleic acid with increased stearic acid but critically, such biodiesel exhibits poor cold flow properties due to the level of saturates in the fuel (Sierra-Cantor and Guerrero-Fajardob, 2017). Singh et al. (2019) critiqued this concept and