

# The influence of adsorbents on the oxidative stability of biodiesel and the deterioration of engine oil

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## Abstract:

This study focuses on the influence of adsorbents in augmenting the oxidative stability of biodiesel and its influence on engine oil deterioration. Engine oil performance is affected by the use of biodiesel as it results in a short period of oil drain intervals. Neat base oil, 80 % blended with biodiesel, 20 % is thermo oxidatively aged. The adsorbents Magnesium aluminum hydroxycarbonate and 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene are applied and the formation of oligomers in the base oil-RME mixture was monitored. The analysis with FTIR showed about 90 % less the formation of oligomers. About 90 % reduction in the total acid number. There was 50% reduction in viscosity increment. The adsorbents therefore, have an enhanced influence on the oxidative stability of biodiesel and its blends.

**Keywords:** Biodiesel, dilution, adsorption, suppression, oligomers, oxidation

## 1.0 Introduction

There has been the search for variety of energy sources because the crude oil reserves at the present rate of consumption could be depleted soon [1]. But more urgently is the need to mitigate climate change. Biodiesel, a methyl ester of vegetable oil is a renewable, low environmental impact and a green alternative fuel for diesel engine [2, 3]. Biodiesel fuel is chemically fatty acid methyl ester (FAME) derived from different plant oils and vary slightly in

molecular structures due to the degree of unsaturation of the fatty acids in the different sources as compared to conventional diesel fuel [4].

Despite the advantages offered by biodiesel, the use of it as fuel is introducing challenges into engine oil functions. Biodiesel fuels contain significant amounts of esters of oleic, linoleic or linolenic acids, which influence their oxidative stability. Small percent amount of more highly unsaturated fatty compounds have a disproportionately strong effect in reducing oxidation stability thereby promoting oligomers formation. Polyunsaturated esters are much more susceptible to oxidation than saturated esters. This is due to the presence of the double bonds in the fatty acid esters [5-9]. It is the oxidation products of the biodiesel in the engine oil which influence the degradation of the lubrication oil. The biodiesel therefore, promotes oxidation of lubrication oils when it comes into contact with it in the engine sump. These are the technical concerns with biodiesel or its blends coming into contact with engine lubrication oil. Hence biodiesel or its blends impact lubrication oil changing intervals [10-13].

This present work assess the influence of adsorbents on the formation of oligomers. To avoid the influence of additives on the oil oxidation in this work, base oil and rapeseed oil methyl ester (RME) without additives are used in the aging studies.

The oil samples used in this study were mixed with the adsorbents and aged in order to verify the influence the adsorbents in stabilizing the oil against oxidation. The level of degradation or oligomerization was assessed by monitoring the area under the carbonyl bands in the FTIR spectrum before and after aging. Other physio-chemical properties such as acid number, kinematic viscosity and buildup of molecular masses of oligomers were also determined [14, 15].

## **2.0 Technical background**

### **2.1 Oil aging**

Oxidation is a common phenomenon, which affects the useful life of lubricating oils. When oil is being used in a machine, it gets oxidized over a period of time depending on the type of oil, the operational and environmental conditions. Therefore, oxidation can have negative effects on lubrication system leading to serious consequences.

Oxidation is said to be a complex chemical degradation process in the base oil. Hence, it can be viewed as a chemical breakdown of base oil molecules in contact with oxygen from the air. Temperature, wear transition metals, water and contaminants (in general and oxidation products) all promote oxidation or aging of oil.

The oxidation process consists of a series of phases involving chain reactions, which end up with acidic products. These acid compounds undergo further reactions resulting in polymeric compounds which lead to oligomers formation. It is generally assumed that aging of oil proceeds in three phases namely initiation, propagation and termination phase. These phases are illustrated in Figure 1.

In the initiation phase, hydrocarbons react with oxygen to produce hydrocarbon free radicals. The oxidation starts with an oxygen based radical abstracting an allylic hydrogen atom from a carbon chain leading to the formation of a double allylic radicals. This initial reaction is very crucial and is catalysed by temperature, oxygen from air or traces of transition metal ions like copper, iron, etc. [14, 15]. This phase can be seen on the top left of Figure 1.

Next is the Propagation phase which is illustrated on the bottom left of Figure 1. In this phase, the hydrocarbon free radicals formed react with oxygen to form peroxide radicals. These radicals are highly reactive and therefore, react further with other hydrocarbons from the oil. Alkoxy radicals form on the carbon chain by breaking the hydroperoxide bond formed giving rise to a hydroxyl radical and an oxygen centred alkoxy radical. The breaking of the oxygen radical from the carbon chain results in an aldehyde and carbon centred radical. The carbon centred radical can therefore abstract another hydrogen atom from a hydrocarbon to perpetuate the cycle or undergo other reactions leading to the subsequent aldehyde [15]. However, the oxygen centred radical on the other hand can also abstract a hydrogen atom to form a corresponding alcohol. Radical reactions by their nature generate other radicals which triggers a chain reaction. The chain reactions involve the radical species stabilizing themselves by reacting with other species to create a more stable molecule. In the process of stabilizing itself, another radical could be produced, which can participate in the propagation reaction. Propagation reactions therefore ensures the radical cycle to continue by providing continually new species of radicals to react [16-18].

The termination phase is illustrated at right side of Figure 1. During this phase, the hydroperoxides formed in the propagation phase may homolytically cleave and form some oxygenated products such as aldehydes, ketones, alcohols and water. These low molecular products formed can react further leading to organic acids and then high molecular weight polymeric compounds. Polycondensation and/or polymerisation of these products lead to formation of insoluble products called sludge. The sludge formed lead to increase in oil viscosity **[14, 15, 17, 18]**.

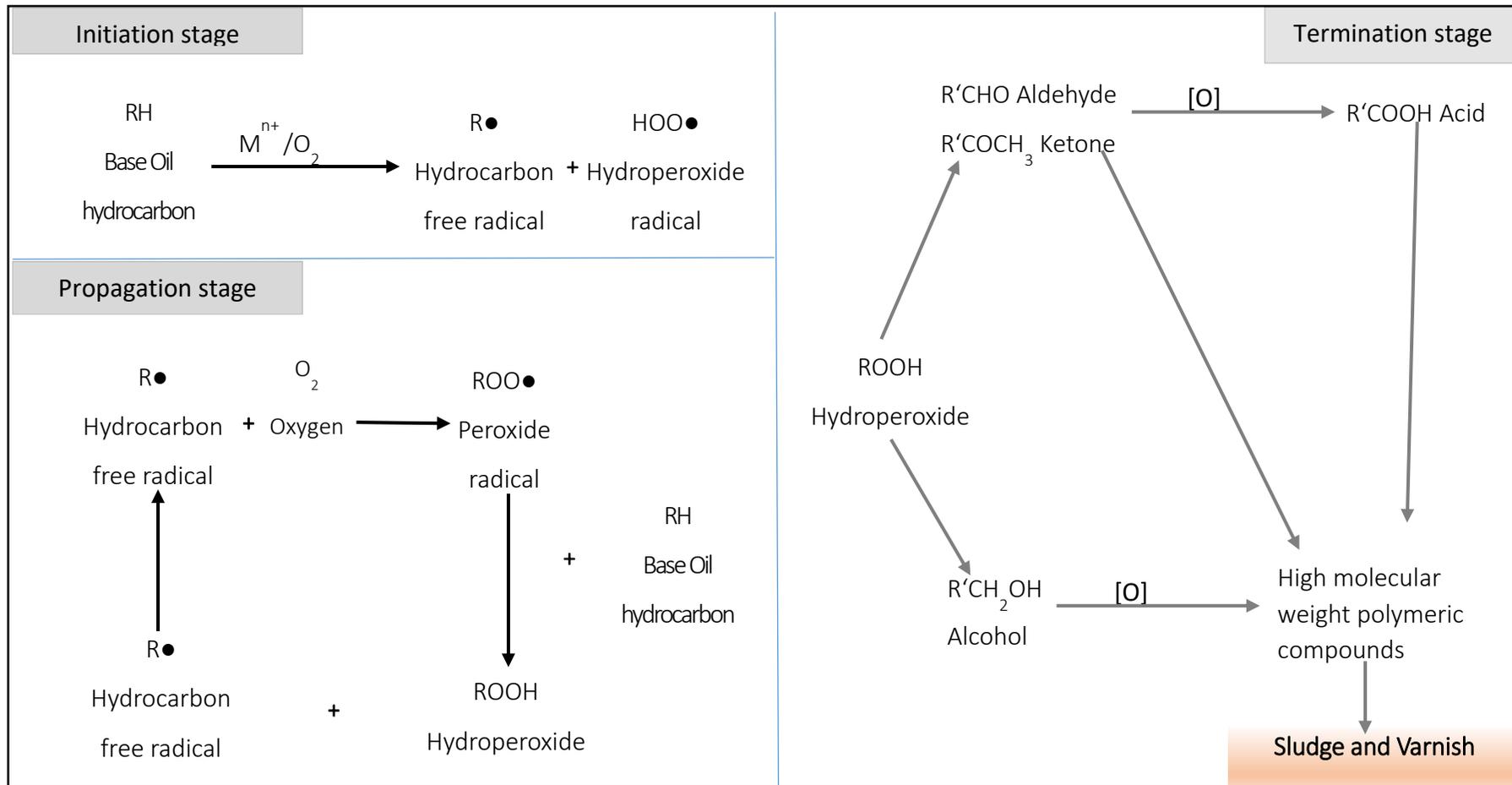


Figure 1 Oxidation process of oil [14]

## 3.0 Materials and methods

### 3.1 Chemicals

Magnesium-aluminum hydrotalcite and 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene are ordered from Sigma Aldrich Chemie GmbH, Taufkirchen, Germany. Tetrahydrofuran (99.9 %), toluene (99.8 %) and isopropanol (99.9 %) all ultraviolet (UV) / infrared (IR) grade, methanol (99.9 % p.a), and KOH in (0.1 mol/L (0.1 N)) isopropanol volumetric standard solution, nitric acid (supra quality), and hydrogen peroxide (ultra quality) are delivered by Carl Roth GmbH+Co. KG, Karlsruhe, Germany. All the chemicals were used without any modification.

### 3.2 Adsorbents

#### 3.2.1 Hydrotalcite

Magnesium aluminum hydrotalcite ( $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ ) is a double layered hydroxide with many applications including oil adsorption. The hydrotalcite compound has hydroxide ions ( $\text{OH}^-$ ) and carbonate ions ( $\text{CO}_3^{2-}$ ) as anionic components between its layers. It is a solid powder with a melting point of  $T > 250\text{ }^\circ\text{C}$  [19, 20]. It has a chemical composition of  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ . Magnesium aluminum hydrotalcite releases ions when in oil while adsorbing anions also. Although it is weakly basic, it contains relatively small amount of hydroxide ions and relatively large amount of carbonate ions. It is therefore able to adsorb the acids formed during the oil aging [21].

#### 3.2.2 1,3,5-Trimethyl-2,4,6-Tris(3,5-Di-Tert-Butyl-4-Hydroxybenzyl)Benzene

1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene is a radical scavenger and readily donates hydrogen atoms to radicals. This donation allows the generation of stable products and thus breakdown the chain reaction mechanism of the oxidation by inhabiting the process [22]. As a radical trapping agent, it has the ability to inhibit oxidation by intercepting the oxidation factors such as free radicals, which are the precursors for the production of oligomers. It thus intercepts the peroxide radical preventing it from creating another radical by the autoxidation mechanism. The adsorbent contains an easily abstracted

hydrogen. The free radical of the adsorbent therefore, reacts to form a stable molecule that does not contribute to the oxidation process. The oxidation chain reaction is therefore interrupted. The hydrotalcite compound is thus used in conjunction with 1,3,5-Trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene in ratio of 1:2 respectively to inhibit oil degradation[22].

### 3.3 Fuel samples

In this work, the following oil and fuel components are employed:

- 1) Base oil without additives,
- 2) Rapeseed oil methyl ester (RME), without additives,

Base oil was obtained from a project partner. Rapeseed oil methyl ester was ordered from ADM, Hamburg, Germany. For the aging experiments, a mixture of pure neat base oil with rapeseed oil methyl ester (RME) was used. The mixture had 80 % base oil and 20 % RME all by percent volume. This is a simulation of 20 % oil dilution. The physical parameters of viscosity at 40°C and 100 °C and density of the fuel and oil are listed in Table 1.

Table 1: The physical parameters of base oil and RME used in this project

Sample	Base oil	RME
Kinematic viscosity at 40 °C	30.97 mm <sup>2</sup> /s	4.52 mm <sup>2</sup> /s
Kinematic viscosity at 100 °C	5.91 mm <sup>2</sup> /s	1.77 mm <sup>2</sup> /s
Density at 15 °C	0.87 kg/m <sup>3</sup>	0.88 kg/m <sup>3</sup>

### 3.4 Aging

The Rancimat was used for the aging of the samples. While maintaining the prescribed air flow of 10 L /h, a temperature of 170 °C and a volume of 30 ml of sample was used for the aging process. The results of an engine oil usage for a distance coverage of 30,000 km can be achieved in the laboratory with a constant temperature of 170 °C for 40 h duration [23]. Different amounts of the adsorbents, 0.225 g, 0.45 g and 0.675 g in the ratio of 1:2 (hydrotalcite : 1,3,5-Trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene) were added into 30 mL of fresh sample of base oil and RME mixture and aged at 170 °C for 80 h

duration giving rise to simulated distance of 60,000 km. The effects of the different amounts of the adsorbent on pertinent parameters relating to oxidative product build up, total acid number, changes in chemical structure and viscosity were monitored.

### **3.5 Analytical methods**

The buildup of aging products were detected and analyzed using Fourier transform infrared spectroscopy (FTIR), size-exclusion-chromatography (SEC), kinematic viscosity measurement and their acid values were treated using Metrohm potentiometric titrator.

#### **3.5.1 Fourier Transform Infrared Spectroscopy (FTIR)**

For Fourier transform infrared (FTIR) spectroscopy analysis, a Nicolet 6700 FTIR from thermo scientific company was used. The thermo scientific omnic software was used for the evaluation of the measurements. This instrument is equipped with an ATR-crystal for ATR spectroscopy. FTIR is a receptive method used for identifying organic and some inorganic molecular compounds present in a sample. The samples are analyzed to determine the changes in the chemical structure. The chemical molecules absorb light in infrared region of electromagnetic spectrum, which corresponds to the bonds in the molecules. Infrared spectrometry takes advantage of the natural vibrations in molecules which lead to changes in their dipole moments. This forms the principle of IR spectroscopy and the molecular vibrations absorb electromagnetic waves at certain wavelengths. Therefore, the impact of the adsorbents on the aging of the samples will show in the difference in the spectra before and after aging and with and without the use of the adsorbents. The crystal needs just a drop of the sample which is sufficient for analysis. A DTGS detector is in use in the machine. It has an XT-KBr beam splitter. The background and sample were each scanned 16 times.

#### **3.5.2 Size Exclusion-Chromatography (SEC)**

Size exclusion chromatograms (SEC) were measured using Agilent Technologies 1260 Infinity quaternary LC Systems with a column length of 30 cm, pore size 5 microns, porosity of 100 Å, refractive index detector and using tetrahydrofuran (THF) as solvent. Three columns were used in series with a flow rate of 0.5 mL/min at 45 °C. SEC is a method which separates molecules based on their size by filtration through a gel and equipped with a refractive index detector. In this separation process, the column used is filled with material containing many pores. Therefore, when dissolved molecules of different sizes flow into the column, smaller

dissolved molecules flow more slowly through the column due to their penetration deep into the pores. The larger dissolved molecules on the other hand, will flow quickly through the column since they do not enter the pores and therefore, elute from the column's void volume. Consequently, larger molecules elute from the column sooner and smaller molecules later, which effectively sorts the molecules by size. This leads to obtaining the average molecular weight values. This is the separation principle of size exclusion chromatography.

Calibration was done with polyethylene glycol standards (Agilent PEG calibration kit Part No.: PL2070-0100) with different molecular masses between 106 and 4040 Da. Using PEG for calibration, the molar mass of methyl oleate was determined to be about 335 Da though the actual molar mass of methyl oleate is 296.45 Da. Since the molecular size of the calibration standards and the analytes were not identical, it has therefore become difficult to make quantitative statements. The SEC measurements were done with 10 mg of the sample mixed with 1000  $\mu$ L THF.

### **3.5.3 Potentiometric determination of the Total Acid Number (TAN)**

Total acid number was measured using a fully automated measurement system developed by Metrohm (Titrando 888). The potentiometric determination was carried out according to ASTM D664. The entire TAN determination procedure is described elsewhere in [24]. The acid number is a useful tool in monitoring degradation of biodiesel since the acid number increases with degradation.

### **3.5.4 Determination of kinematic viscosity**

Kinematic viscosity was measured using an Anton Paar Stabinger viscometer SVM3000. In this, the measurement is done in a small test tube located in a temperature controlled chamber. The kinematic viscosity was measured at temperatures of 40 °C and 100 °C and in  $\text{mm}^2/\text{S}$ .

## **4.0 Results and discussion**

### **4.1 Aging of neat base oil with RME**

Figure 2 shows the IR-spectra of the mixture during the aging process of the base oil and RME and the various amounts of adsorbents used in this study. The FTIR spectra represents results from the entire phases of the oil aging processes as illustrated in Figure 1. The key portions of the spectra have been integrated. The region between 1600 and 1900  $\text{cm}^{-1}$  registered an

enhanced absorption as seen in Figure 2 and Figure 3. The base oil mixed with RME before aging showed an ester vibration. With the aging proceeding, the aged samples showed wider carbonyl bands than a mere ester vibration. A broad band centered around  $1750\text{ cm}^{-1}$  is due to the presence of carbonyl containing degradation products. These products, which are illustrated at the right side of Figure 1, include but not limited to aldehyde, ketone, and alcohol. The presence of these variety of oxidation products in the mixture aged without the adsorbents broadens the peak registered. The OH band can be visualized in Figure 2 between the regions of  $3000\text{ to }3600\text{ cm}^{-1}$  and is attributable to the organic compounds including water, alcohol, hydroperoxide and carboxylic acids with OH functional group. The increase in these signals of the mixture aged without the use of the adsorbents translates into higher acid content and this collaborates with the total acid number determined in this study. A decrease of the CH, CH<sub>2</sub> and CH<sub>3</sub> vibrations in the sample aged without the use of the adsorbent were detected within the range of  $2800\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$ . The broadness of the peak registered in the regions of  $1600\text{ to }1900\text{ cm}^{-1}$  and  $3000\text{ to }3600\text{ cm}^{-1}$  and also the decrease in signals within the regions of  $2800\text{ to }3000\text{ cm}^{-1}$  for the mixture aged without the adsorbent are absent or small in amount in the mixture aged with the adsorbent. The adsorbents used thus resulted in significant effect on the signals. This signifies the influence of the adsorbents on the oxidation of the mixture. The exact point in the phases of the oxidation where the adsorbents thus acted cannot be concluded with only the FTIR results. However, the adsorbents have demonstrated some positive impact on the stability of the oil.

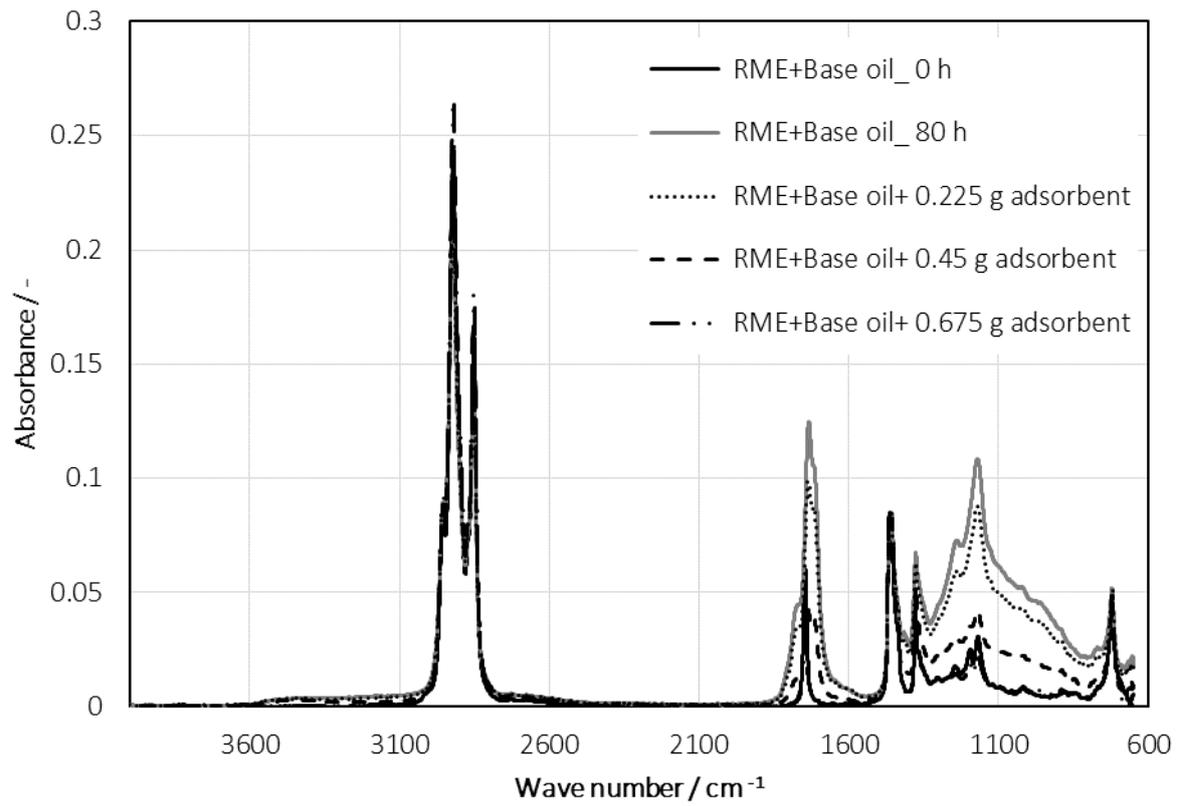


Figure 2: FTIR spectrum of base oil mixed with RME with and without adsorbent and aged at 170 °C for 80 h

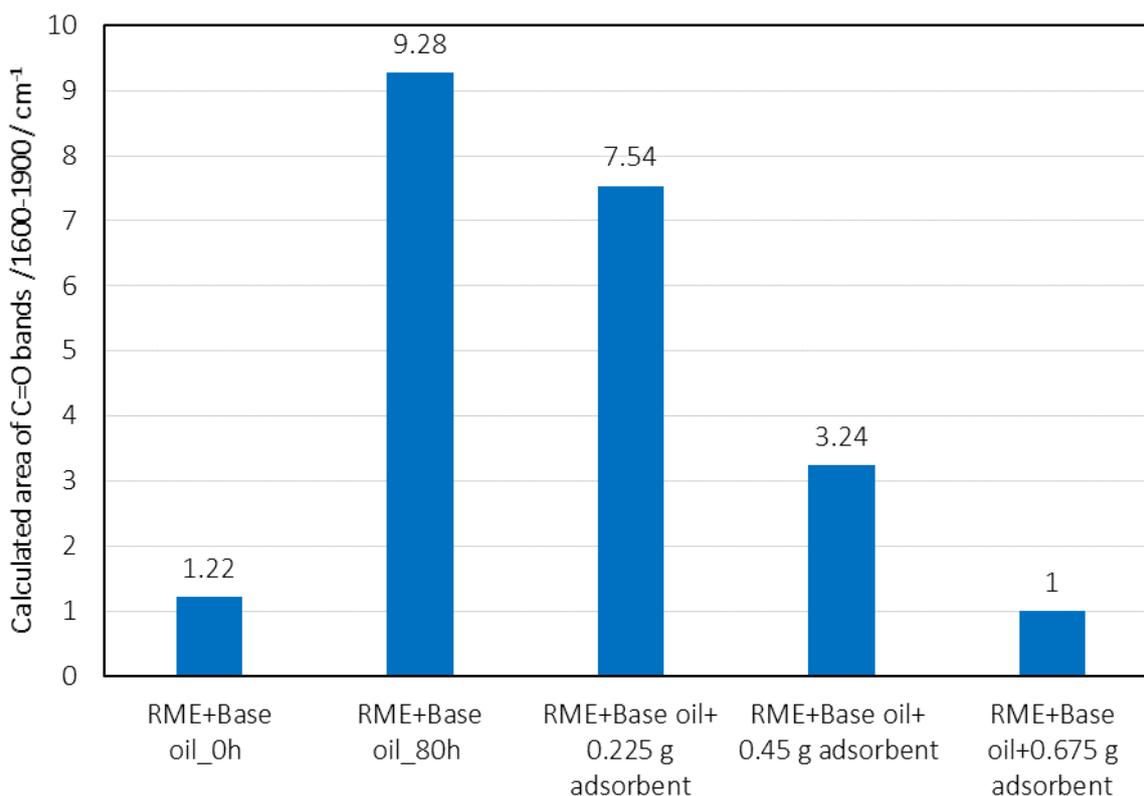


Figure 3: Calculated area of C=O bands of the FTIR spectrum of the aged mixtures

## 4.2 Size Exclusion Chromatography

The FTIR results cannot illustrate the presence of bigger molecules, oligomers formed. However, it is imperative to show the evidence of their formation or otherwise using size exclusion chromatography (SEC). The presence of higher molecular mass substances focuses on the termination step of the aging process, which is illustrated at the right side of Figure 1 and is the reaction step of higher molecular mass formation. The SEC analysis detects the change in molar mass of molecules formed during the aging procedure. In Figure 4, neat base oil and RME mixture with and without adsorbent added and aged for 80 h are shown. In this figure, while the mixture aged without the use of the adsorbents had bigger molecules with relative molar masses of about 1200 g/mol at the end of the aging period, the mixtures aged with the adsorbents have molecular masses between 800 and 1000 g/mol depending on the mass of the adsorbent used. The highest amount of the adsorbent used reduced about 90 % of the oligomers formed.

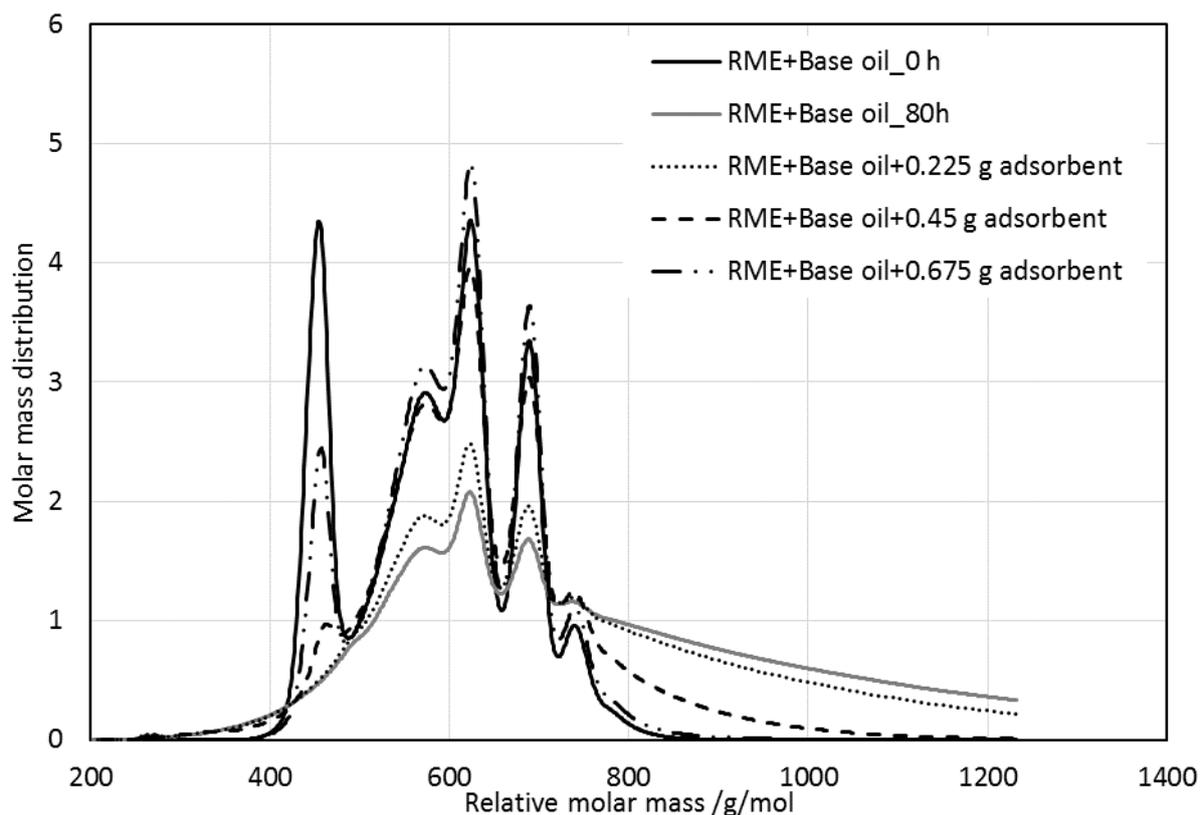


Figure 4: SEC of aged base oil and RME with and without adsorbents

### 4.3 Viscosity

The impact of the adsorbents on aging of the mixture was determined by the viscosity index (VI) as defined in the standard ASTM D2270. This is illustrated in Figure 5. As shown in the right side of Figure 1, in the termination phase, the buildup of oligomers/sludge would result in higher viscosity of the oil. The viscosity index is a measure of change in viscosity with temperature fluctuations. Therefore, the viscosity index tells how well a viscosity is protected during changes in temperature. The higher the viscosity index, the “better” the oil because the oil changes less in viscosity with temperature [25]. High-VI oils are less affected by temperature changes. The viscosity index of the sample aged without the adsorbent had the lowest value while the samples aged with the adsorbents had higher values, see Figure 5. This could be explained that the use of the adsorbents retarded the formation of higher molecular weight substances leading to low viscosities registered. This then gives the oil more resistance to any increase in viscosity and hence more useful service life. Therefore, the increased admixture of the adsorbent improves the life-time of the base oil by maintaining improved viscosity index values over aging.

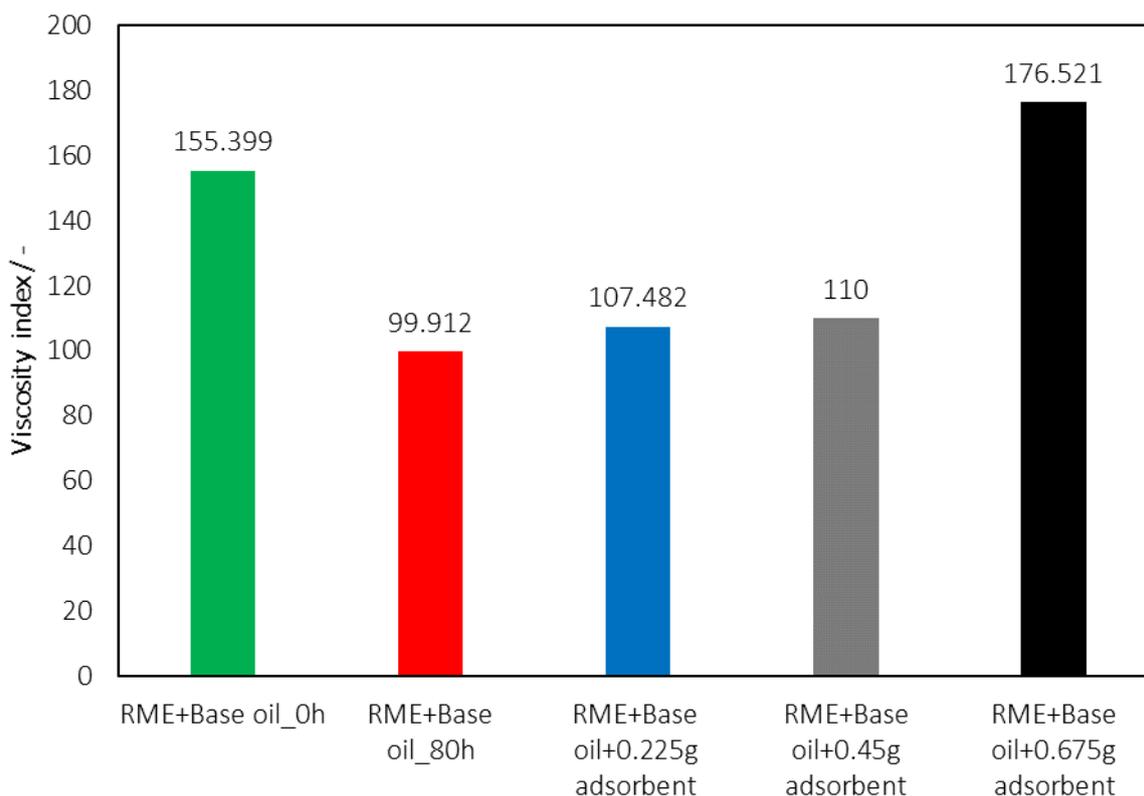


Figure 5: The viscosity index of base oil mixed with RME and aged with and without the use of the adsorbents

#### 4.4 Total Acid Number (TAN)

Figure 6 illustrates the acid values of the samples over the entire aging period of 80 h. The acid values is a focus on the termination phase of the aging procedure of the oil as seen in Figure 1. There is a low to insignificant buildup of the total acid number in the samples aged with the adsorbent. While the sample aged without the adsorbent had 41.3 mg KOH/g acid value, the samples which were aged together with the adsorbent had 29.6, 1.9 and 1.3 mg KOH/g respectively. The acid values relates to the level of degradation or oxidation products. The higher the degradation, the higher the acid values. The acid values of the samples aged with the adsorbent again indicates that the amount of the adsorbent used thus play a key role in the buildup of higher molecular mass substances. The 29 %, 95 % and 97 % respectively recorded acidic product buildup thus signifies that the adsorbents have an influence on the formation of oxidative products in base oil-RME mixture. The use of the adsorbents on the other hand might have interrupted the breaking down of the fatty acid ester molecules, thereby preventing the complex secondary oxidation reactions which would have led to the

formation of more reactive aldehydes. It is these reactive aldehydes which then oxidizes into acids increasing the acid value.

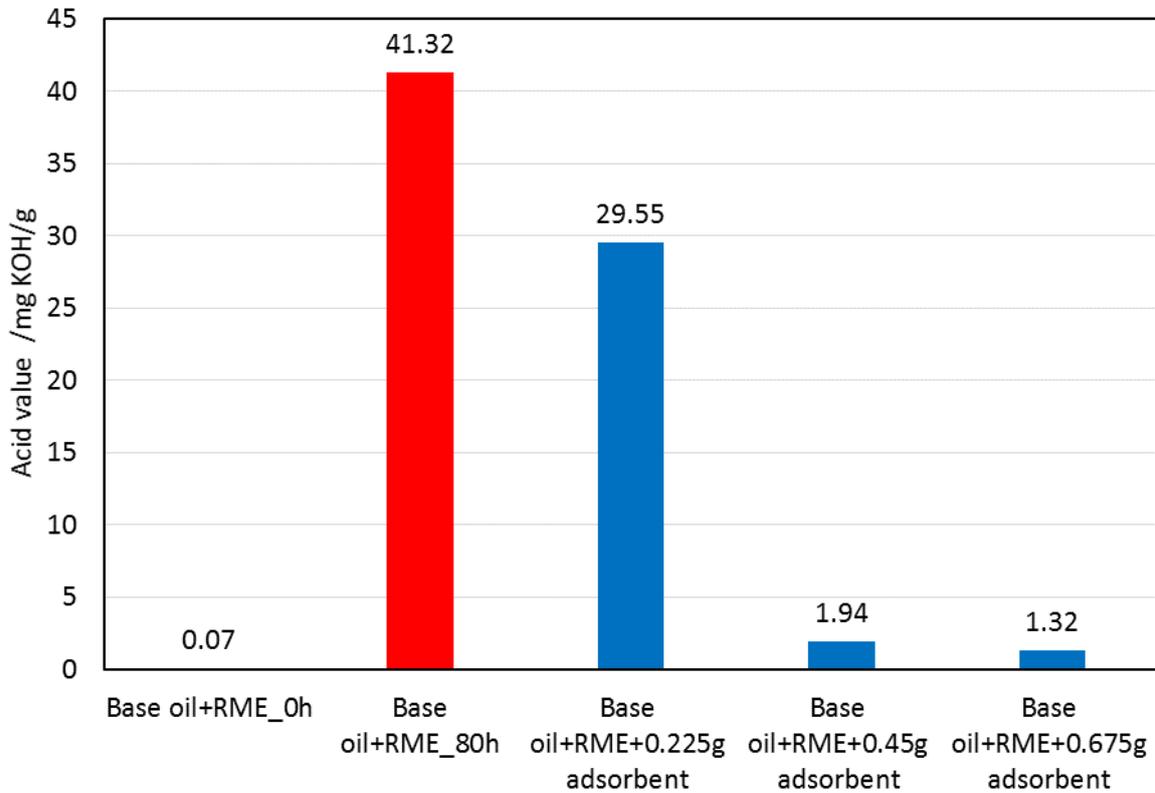


Figure 6: The acid value of the mixture of RME and base oil with and without the use of the adsorbents

## 5.0 Conclusion

The current study aimed at evaluating the impact of adsorbents on the oxidative stability of biodiesel and its blends by tracking the physio-chemical changes that occur during oxidation. The adsorbents used have demonstrated greater efficiency in stabilizing the biodiesel and its blends by retarding the aging processes. The use of the adsorbents led to between about 20 % and 90 % reduction in oligomers formation. The use of the adsorbents recorded a total acid value reduction of about 90 % and more than 50 % reduction in viscosity increment. The adsorbents must have increased the resistance of the oil towards the formation of secondary oxidation products which usually lead to increase in acid number, viscosity, density and others.

This collaborates the work of Dinkov et al. (2009) [26] where antioxidants were used to stabilize biodiesel-diesel fuel blends.

It can therefore be concluded that the adsorbents, Magnesium-aluminum hydrotalcite and 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl) benzene have an enhanced impact on the oxidative stability of biodiesel and its blends.

The adsorbents have exhibited some retardation attitudes in the oxidation of biodiesel and its blends. Considering the fact that the adsorbent is a radical scavenger and has hydrogen atoms which can be readily donated to radicals, the reaction leading to this delay in oxidation could really be due to suppression. The exact phase of the oxidation process where these retardation effect is taking is inconclusive as at now. Therefore, our next set of work will investigate the reaction mechanism of the adsorbent. This will be reported in our subsequent publication.

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