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INVESTIGATION ON OXIDATION AND THERMAL STABILITY OF JATROPHA OIL

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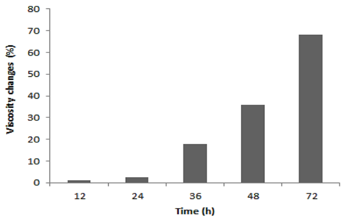
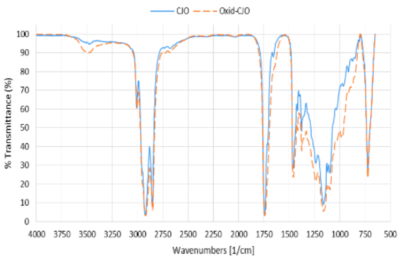
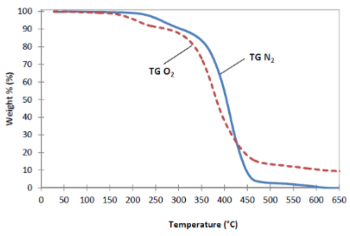
Graphical abstract







Abstract

The application of jatropha oil as alternative lubricant basestock has emerged recently. However, the resistance to oxidation and thermal stability of this oil become a concern to its application as lubricant. In this study, the oxidation and thermal degradation of crude jatropha oil (CJO) have been studied. The oxidation of the CJO was investigated by air bubbling method. The viscosity and functional group changes due to oxidation were studied before and after oxidation test. The thermal stability of CJO was investigated by using Thermogravimetric analysis (TGA) method in O_2 and N_2 gases environment. Jatropha oil was found oxidized by autoxidation mechanism produces high molecular species which capable to increase viscosity of the oil. The TGA results shows that CJO thermally stable in the temperature below 168°C in O_2 gas environment and below 225°C in N_2 gas environment.

Keywords: Jatropha, Lubricant, Oxidation, Thermal Stability

Abstrak

Penggunaan minyak jatropha sebagai alternatif bahan asas pelincir telah muncul baru-baru ini. Walau bagaimanapun, penahanan minyak ini kepada pengoksidaan dan kestabilan haba menjadi satu kebimbangan untuk pemakaiannya sebagai pelincir. Dalam kajian ini, pengoksidaan dan penurunan haba minyak jatropha mentah (CJO) telah pun dikaji. Pengoksidaan CJO telah disiasat dengan kaedah udara menggelegak. Perubahan kelikatan dan kumpulan fungsi disebabkan oleh pengoksidaan dikaji sebelum dan selepas ujian pengoksidaan. Kestabilan haba CJO disiasat dengan menggunakan Termogravimetri analisis (TGA) kaedah di dalam persekitaran gas O_2 dan N_2. Minyak Jatropha ditemui teroksida oleh mekanisme autoxidation yang menghasilkan spesies dengan molekul tinggi yang mampu meningkatkan kelikatan minyak. Keputusan TGA menunjukkan bahawa sifat haba CJO stabil pada suhu di bawah 168 ° C dalam persekitaran gas O_2 dan di bawah 225 °C dalam persekitaran gas N_2

Kata kunci: Jatropha, Pelincir, Pengoksidaan, Kestabilan Haba

1.0 INTRODUCTION

Natural plants seed oils have been used to lubricate parts in motion long time ago before the industrial revolution era. Today, due to environmental issues, the application of these kind oils has emerged again. This related to possibility of mineral based lubricants polluting the environment through spills, leakages, evaporation and disposal of used lubricant. The use of natural plants seed oils as lubricant are influenced by their availability, renewability and environmentally friendly properties.

Jatropha oil (JO) is currently considered as main source for diesel oil substitute. However, it was also found that JO possess good lubrication properties which make it possible to consider as alternative source of lubricant. It has good wear preventive characteristics either used in native oil or as additives in mineral base commercial lubricant oil [1].

Although application of jatropha oil as alternative lubricant has its own advantages, it also has several disadvantages that will limit its function as lubricant. One of the disadvantages is the resistances to oxidation. Capability of lubricant to resist the oxidation process at elevated temperatures in the ordinary air environment is usually known by oxidation stability. Other disadvantage is thermal stability, which is also related to oxidation. Thermal stability of lubricant is the ability of the oil components, both base oil and additive, to resist degradation due to the effects of heat.

It is widely understood that temperature is significantly affect lubricant degradation. Lubricant oil tend to easily oxidized when exposed to air especially in elevated temperatures where the heat will accelerate the oxidation process. Based on Arrhenius rate rule, oxidation will reduce the service life of a lubricant by half for every 10 °C increase in fluid temperature that above 60 °C [2]. Resistance to oxidation and thermal stability is very important for a lubricant since they strongly determine the life of the lubricant. These process are capable to initiate tribo-chemical degrading process due to the heat generated by friction. It is responsible for numerous lubricant problems such as increase of viscosity and acid number (AN), formation of varnish, sludge and sediment, formation of rust and corrosion, etc.

The resistance of typical natural plant oils to oxidation and thermal degradation is considered affected by the fatty acid contained in the oil. It is known that the fatty acid alkyl chain contained in most plant seed oil is susceptible to oxidation both at double bonds and adjacent allylic carbons [3]. Jatropha oil is found to have about of 29-44.2% of linoleic acid (C18:2) [4, 5]. The presences of high content this polyunsaturated fatty acid is believed will influence the oxidative stability of jatropha oil when used as lubricant due to heat generated during frictional contact between two surfaces. In this study, oxidation and thermal degradation of crude jatropha oil were investigated.

2.0 EXPERIMENTAL METHOD

2.1 Materials

Crude jatropha oil (CJO) is used as main lubricant in this research. The oil was obtained from local market, used as sample without any treatment

2.2 Thermal Degradation Test

In order to analyze thermal stability of the sample oil, thermos gravimetric analysis (TGA) was employed. Thermo gravimetric analysis is a common method useful in comparing the degradation of lubricants under thermal and oxidative conditions. If the lubricant is thermally stable, there will be no observed mass change in the TGA curve. The TGA method can also be used to show volatility of the lubricant [6]. In general, thermal degradation of the oil takes place at much higher temperatures than the oxidation. Thus the maximum temperature where oil still can be used is determined by its thermal stability [7].

Thermal degradation of the samples were analyzed with Perkin-Elmer Pyris-1 Thermo Gravimetric Analyzer. To simulate inert and oxidized environment, the samples were analyzed in nitrogen and oxygen gases environment. The gas flow was set to 20 mL/min and heating rate was 10°C/min in the temperature range of 30 – 650°C.

2.3 Oxidation Test

The oxidation test was carried out by air bubbling method. The test was carried out in a 500 mL round bottom flask consist of condenser and a Dreschel bottle head connected to an air pump to supply air to the test oil as shown in Figure 1.

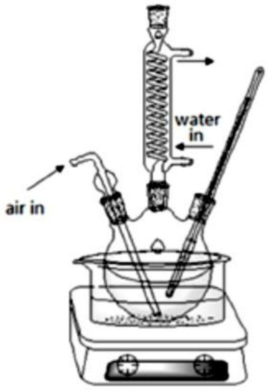


Figure 1 Schematic experimental set up of air bubbling oxidation method

The air delivery tubes was set so that the lower end of the tubes was within 6 mm to the bottoms of the flask and then connected to air supply through a flow meter. The test oil (100 mL) was heated up to 95±3°C in the flask for 72 hours with 10±0.5 L/h air was flown into the oil. A copper strip with size of 15 mm × 15 mm × 3 mm was used a catalyst and drawn into the oil. Temperature of the oil samples and the rate of air flow were checked periodically to maintain them to be constant. Oil sample was cooled to room temperature to measure its viscosity after the test. Oxidative behavior of the oil samples was determined from oil viscosity changes.

2.4 Viscosity

Viscosity of oil samples were measured at 40°C using capillary viscometer according to ASTM D-445-04 standard method (Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity). This method is using time for a fixed volume of oil sample to flow under gravity through the capillary of a calibrated viscometer tube under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity is the product of the measured flow time and calibration constant of the viscometer.

2.5 Functional Group

Fourier transform infrared spectroscopy (FTIR) analysis was applied to examine functional groups of the oil sample before and after oxidized. A Shimadzu FTIR-8400S analyzer within scanning range of 600 – 4000 cm-1 was employed. This method has found as a very useful method to study oxidation of lubricant [8].

3.0 RESULTS AND DISCUSSION

In the frictional system, the heat generated during process of friction could accelerate the oxidation. The oxidation process will result in the increase on oil viscosity, reduction of the oil polarity, formation of sludge and varnish, corrosion of the metal surfaces, etc [9]. These oxidation effects will significantly reduce friction and wear prevention properties of the oil. Figure 2 shows the viscosity changes due to prolong heating on the jatropha oil. It can be seen that the prolong heating process has increased the oil viscosity up to 68.2 % from the initial value (32.9 cSt) after heated for 72 hours.

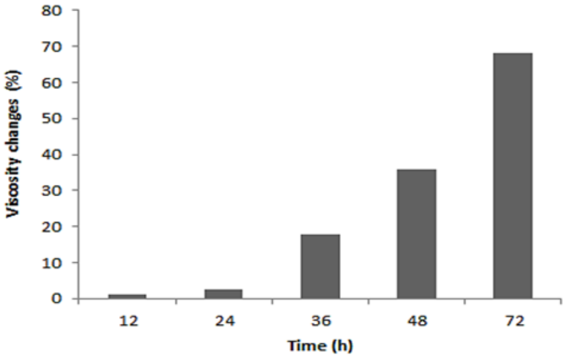


Figure 2 Effect of oxidation to jatropha oil viscosity

Figure 3 shows the FTIR spectra of jatropha oil oxidized by prolong heating. Most of the peaks were similar before and after the heating at except three regions. The unsaturated (double carbon) bonds contained in most vegetable oil are known prone to oxidation [6]. The oxidation of unsaturated fatty acids contained in the oil taken place by auto-catalytic (autoxidation) process which once started, the reaction is self-propagating and self-accelerating although also can be accelerated by presence of catalysts such as metal, heat and light [3].

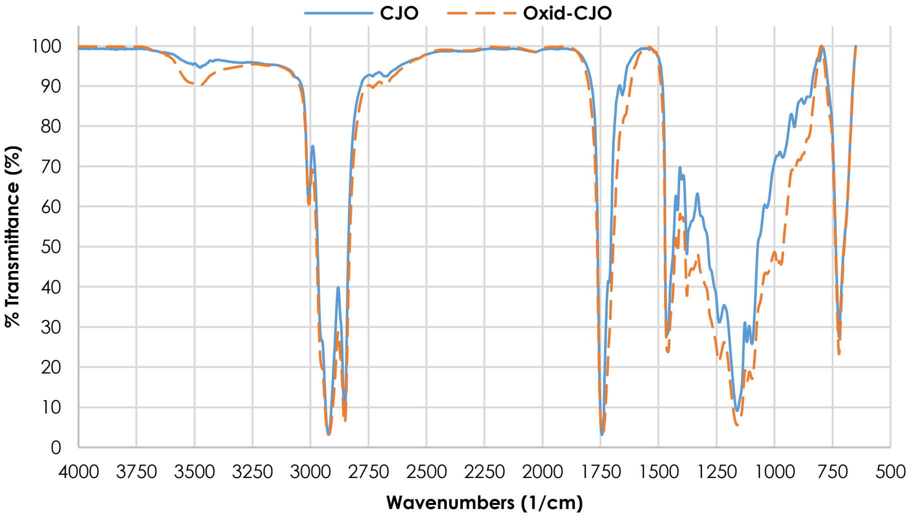


Figure 3 FTIR spectra of crude and oxidized jatropha oil

The autoxidation of fatty acid is typically consisting of initiation, propagation, and termination process [7]. In initiation process, a-methylenic H atom is abstracted from the unsaturated molecule to form an alkyl radical which generates free radicals (RH → R• + H•). Since the free radical (R•) is highly reactive, it can react with atmospheric oxygen, thus a simple reaction resulting from the radical nature of the oxygen molecule produces a peroxy radical (R• + O2 → ROO•). Disappearance of peaks at 1658 and 1710 cm-1 band, which typically show C=C bond vibration, is believed to be associated with oxidation attack to the double bond (-HC=CH-) at the unsaturated site. In the propagation reactions, the peroxy radical reacts with another unsaturated molecule (RH) to form a hydroperoxide (ROOH) and a new unstable methyl radical (R•). A spectra change was observed at the range of 3700 – 3500 cm^{-1} band which is typically associates with hydroxyl functional group. This indicates the formation of hydroperoxide in the oxidized jatropha oil (ROOH). These hydroperoxide produced are unstable and may degrade to radicals that accelerate propagation of the reactions (ROOH → RO• + •OH). As a new free radical is generated, more oxygen is incorporated into the system and the newly propagated radical then reacted with oxygen again to produce another peroxy radical (RO• + RH + O2 → ROH + ROO• and OH• + RH + O2 → ROO• + H2O) . These reactions are known as branching steps of the fatty acid autoxidation process and could produce other secondary products such as aldehydes (RCHO) and ketones (RCOR) Appearance of two new spectra peaks at 990 and 970 cm^{-1} band along with disappearance of peaks at 905 and 865 cm^{-1} band is related to formation of dimer carboxylic acid in the oil. The occurrence of this acid is evidently showed that the oxidation proceeds to formed aldehyde and ketone after the branching process. The aldehyde and ketone then undergo further reactions to form carboxylic acids as well as other high-molecular-weight species that thicken the oil thus increase viscosity.

Non isothermal thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis of crude jatropha oil under nitrogen (N_2) and oxygen (O_2) environment are shown in Figure 4 and Figure 5. In Figure 4, the thermal degradation of jatropha oil takes place by three steps under the N_2 environment. The first step onset point observed at 225°C, where about 1 wt.% of oil already lost at this point. The first step ended at offset point of 294°C with 9.3 wt.% of the oil lost at this point. The second step onset observed at 374°C with 16.2 wt.% of the oil already lost at this point. The second step was ended at an offset at 457°C and about 96 wt.% of the oil lost at this point. The third step onset observed at 550°C and about 98 wt.% of the oil already lost at this point. The third step was ended at 650°C with no residue left. Two significant degradation rate peaks are observed at 268°C and 410°C and a broad peak observed at 605°C from DTG curve under N_2 environment (Figure 5).

Similar to thermal degradation under nitrogen gas, thermal degradation of jatropha oil under oxidized environment (O_2 gas) shows three degradation steps as well (Figure 4). The effect of oxygen was observed to first and second step of jatropha oil degradation, which was found lower than the nitrogen gas. The first step's onset point was observed at 168°C where about 1 wt.% lost at this point. The first step ended at an offset point of 232.5 and 8.2 wt.% of the oil was lost. The second onset point observed at 334°C and about 13.8 wt.% of oil lost at this point. The step ended at offset point of 423°C with around 84 wt.% of oil already lost. The last degradation observed at onset point of 548°C with around 88 wt.% of the oil already lost. At the final testing temperature (650°C), the oil has residue of around 9.1 wt.% in the pan. From the DTG curve, two distinct degradation rate peaks observed at 210°C and 378°C and a broad peak observed at 588°C.

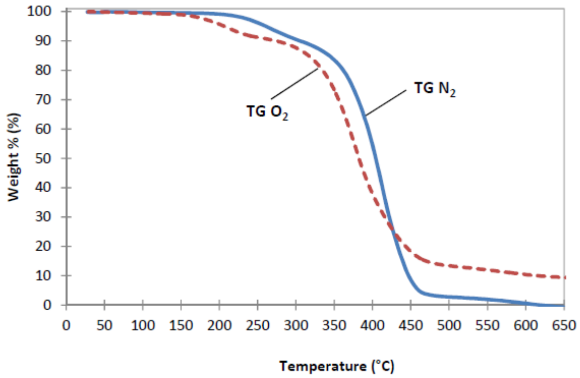


Figure 4 TG curve of jatropha oil in N_2 and O_2 gases environment

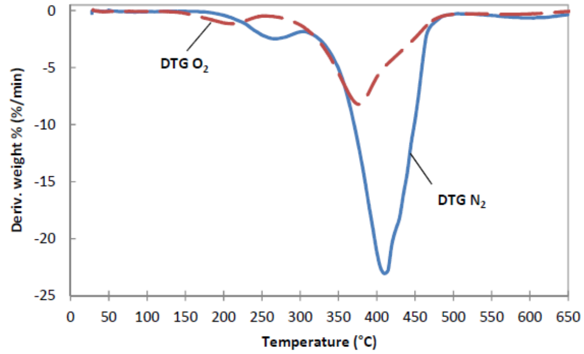


Figure 5 DTG curve of jatropha oil in N_2 and O_2 gases environment

Jatropha oil is generally contained three main hydrocarbon components, *i.e.* polyunsaturated, monounsaturated and saturated fatty acids, respectively. The occurrence of three degradation steps is believed related to degradation of these main component during heating, especially under oxidative environment (O_2 gas) [10, 11]. During the heating process, the first degradation step is believe due to the breakdown of polyunsaturated fatty acids contained in the oil [10, 12]. Under oxidative environment, the first onset point can be considered as the point where mass loss of polyunsaturated fatty acids is begin. Therefore, this point can be used to show thermo-oxidative degradation of the oil. Polyunsaturated fatty acids, such as linoleic and linolenic acids contained in jatropha oil were decomposed at the first degradation step in the range of 168−232.5 °C under O_2 and 225−294°C under N_2 environment. At this step, the oil could produce volatile compounds which were constantly removed by vapor generated during heating [10]. In this process, the dimers, trimers, and polymers, were formed principally by thermal reactions of the polyunsaturated fatty acids which also found in the oxidation test results.

The second step in the thermal degradation of jatropha oil under O_2 and N_2 gas was corresponding to decomposition of the monounsaturated fatty acids, i.e. oleic acid. At this step, large component of the oil was thermally degraded in both test environments. This possibly related to high content of oleic acid in jatropha oil and also loss of remaining polyunsaturated fatty acid. This tendency is also in accordance to high degradation rate shown at the DTG curve due to high content of monounsaturated (oleic acid) in jatropha oil. The third step is corresponding to degradation of saturated fatty acid, *i.e.* palmitic and myristic acids, which show relatively low mass loss during this step. This also can be observed from broad peak with low degradation rate shown in DTG curve. Degradation products from polyunsaturated content in previous step also took part in this step. Where the unsaturated carbon chain changed to saturated due to the continuous heating [10].

4.0 CONCLUSION

Crude jatropha oil (CJO) is concluded to be oxidized by autoxidation mechanism. This process typically attack the double bond site of the CJO's fatty acid to produce hydroperoxide, aldehyde and ketone which increase viscosity of the oil.

Based on TGA result, it is conclude that CJO is thermally stable in the temperature below 225°C in the N_2 gas environment and below 168°C in the O_2 gas environment. The oil was totally decomposed at the temperature of 650°C in N_2 gas. However, residue still found when the oil was heated to 650°C in O_2 gas environment

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