Full Length Research

Synthesis and characterization of bio lubricants from tobacco seed oil

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Vegetable oils are noticed to be potential alternatives to mineral oils for lubricant base stocks because of certain inherent properties viz. high viscosity, high boiling range and biodegradability. Fatty acids present in oil can be chemically modified to form high molecular weight esters, which can substitute conventional mineral oil-based lubricants. This paper mainly reveals about structural modification namely esterification of fatty acids present in tobacco oil. The esterified products were thus examined by GC-MS for confirming the desired structure of fatty acid esters. Tribological study of the esterified products was done using pin on disc tribometer. The bio based grease had excellent co-efficient of friction compared to Hindustan Petroleum all-purpose grease NLGI grade 3 which proves it as potential base stock for biolubricant. Thermogravimetry analysis results shows that fatty acid esters had far more thermal stability Hindustan Petroleum all-purpose grease NLGI grade 3.

Key words: Base-stock for grease, tobacco oil, esterification, GC-MS, thermal stability.

INTRODUCTION

Pollution has become a matter of discussion throughout the globe and it affects the normal working of environment, causing various types of harmful effects on the living beings and their functioning. The term pollution is described as “The presence of harmful or poisonous stuff, which causes adverse effect on the environment and its functioning” (Jain and Suhane, 2013). One of the major cause of pollution is because of the spillage and loss of petroleum based lubricants in environment. “The National Oceanic and Atmospheric Administration (NOAA) estimates that over 700 million gallons of petroleum enter the environment each year. Only half of it is the result of irresponsible and illicit disposal. Industry experts estimate that 70% to 80% of hydraulic fluids leave through leaks, spills, line breakage and fitting failure, and about 40% of that ends in the environment” (Jean Van Rensselar, 2013). Lubricating oils, greases comprises of base fluid, additives, thickening agents, among which base fluid is mainly a petroleum oils and rest is additives to give desirable properties. These petroleum oil based lubricants are poorly biodegradable shows high toxic effect. Over brim of these types of lubricants from the working area to the surrounding water or in soil causes ill effect to the ecological system, which is unacceptable because of rise in environmental concerns (Jain and Suhane, 2013). Also the petroleum feedstock’s are definite, so depending on such finite resources could lead to a misery (Table 1).

The problems must be solved permanently by either decreasing the use of lubricant, which is practically not possible, or by developing a bio based greasing base-stock.

Insisting on bio based lubricants is largely because of the rapid depletion of world fossil fuel reserves and increasing concern for environmental pollution from excessive mineral oil use. Non edible vegetable oil have enough potential and can be good alternative for producing these types of lubricants. Vegetable oils as lubricants are preferred because they are biodegradable and nontoxic, unlike conventional mineral-based oils.
Table 1. Comparison of petroleum based lubricants with lubricants from alternative Resources Environmental Pollution Control.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Petroleum based lubricants</th>
<th>Bio based lubricants</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bio degradable</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>Toxic</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>Pollutes environment</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>Economic gain to farmers</td>
<td>Yes</td>
</tr>
<tr>
<td>5</td>
<td>Harmful byproduct emission</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td>Alternative resource</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Industrially, most fatty acids are obtained from animal or vegetable sources. It is possible to produce several industrial products from vegetable oils and fats. Vegetable oils as lubricants are preferred because they are biodegradable and nontoxic, unlike conventional mineral-based oils. They have low volatility because of the high molecular weight of the triglyceride molecule and have a narrow range of viscosity changes with temperature. Numbers of researchers have contributed to make vegetable oil based bio lubricants by chemical modifications of the natural oil or fats. These modifications involves trans esterification (Erhan and Sharma, no date) epoxidation (Salimon and Salih, 2010), enzyme catalyzed esterification (Chauhan and Chibber, 2013) and estolide formation (Randles and Wright, 1992). Traditional method which uses thickeners is also reported by number of authors in which mineral oils are replaced by vegetable oils and fats (Dinda et al., 2008). But use of thickeners will leach heavy metals into water resources after disposing the lubricants. In the present work the attempt has been done to produce a base stock for lubricating grease by chemical modification of Tobacco oil. Tobacco oil was converted into its methyl ester which was then further modified by trans esterification with different alcohols viz. Hexanol, Octanol and NPG. The trans esterified products were confirmed by GC-MS and the base stocks thus produced were characterized by thermogravimetric analysis (TGA), Coefficient of friction, kinematic viscosity and viscosity indices. All-purpose grease of M/s Hindustan petroleum limited was used as a standard to compare various properties of biolubricants.

MATERIALS AND METHODS

All the chemicals procured from SD Fine chemical Baroda are of laboratory reagent grade and were used without any further purification. Tobacco oil was procured from Anand Agriculture University. It was evaluated for Iodine value, Saponification value and Peroxide value as per ASTM D5554, ASTM D5558 and ISO 3960 respectively. Fatty acid profile was evaluated by Gas Chromatography.

Gas chromatography analysis

Gas chromatography of Tobacco oil was carried out using Perkin Elmer Auto System XL. The column used was BP-225, having 25 meters length and 250 mm diameter.

The operating conditions of GC for Tobacco oil are as follows:

- Injector Temperature: 250°C Celsius
- Detector Temperature: 250°C Celsius
- Oven Temperature: 60°C for 5 minutes the rate of increase in temperature was 10°C per minute and the sample was held at 220°C for 10 minutes
- Carrier Gas: Nitrogen
- Injector Volume: 1 microliter
- Carrier flow: 6 psi

Synthesis of tobacco oil methyl esters

Esterification of tobacco seed oil was done using methanol to form fatty acid methyl esters (FAME). Catalyst used in this process was NaOH, 1%w/v of oil. Alcohol to Oil ratio was 6:1. Temperature of the reaction mass was maintained at 60-65°C for 90 min (Bokade and Yadav, 2007). After the completion of reaction the mixture of methyl esters and glycerol was separated in a separating funnel. The upper layer of methyl esters was washed with distilled water to remove excess methanol and catalyst until the fatty acid methyl esters became completely translucent. The methyl esters were further trans esterified with alcohols to form high molecular weight esters.

Synthesis of lubricating grease base stock-Trans esterification of Tobacco oil methyl esters

The methyl esters were further trans esterified with various alcohols such as Octanol and Neo-pentyl glycol to form various high molecular weight esters- lubricating grease base stock. The reaction was carried out at desired temperature and pressure conditions using 3% sodium methoxide as catalyst. Entire reaction was
conducted under vacuum which simultaneously removed methanol as byproduct. The product obtained was characterized by GC-MS and its temperature stability was checked by TGA. It was evaluated for viscosity, viscosity index and Co-efficient of friction.

Gas chromatography-mass spectroscopy analysis

GC-MS analysis of Tobacco oil esters was carried out on Perkin Elmer Auto system XL with turbo mass. The column used was PE-5MS. The operating conditions of GC-MS for the Tobacco oil esters are as follows:

- Column: PE-5MS
- Column Length: 30 meters
- Injector Temperature: 250°C Celsius
- Oven Temperature: 80°C for 5 min, the rate of increase in temperature was of 10°C per min and the sample was held at 290°C for 10 min
- Flow Rate: 1ml per min
- E.I Source Temperature: 220°C per min
- Transfer line temperature: 250°C per min
- Mass range: 20 to 620 AMU
- Split ratio: 1:70

TGA analysis

Heat stability is an important characteristic for any lubricant. For this purpose, thermo-gravimetric analysis (TGA) of the Tobacco oil ester was done using a Pyris-1 Thermogravimetry analyzer of Perkin Elmer. Around 10-20 milligrams of sample was taken and heated up to a final temperature of 600°C and a residence time of 1 min at 600°C was allowed. TGA was performed in air atmospheres at a heating rate of 10°C/Min. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which the sample has maximum thermal stability and minimum weight loss.

Viscosity measurement and viscosity index

Viscosity measurement of all the Tobacco oil esters was carried out on Brookfield viscometer at 40°C and 100°C using constant temperature water bath. The absolute viscosities were converted into kinematic viscosity by using the density of the ester samples.

Brookfield Viscometer Operating Conditions:

- Spindle number: 07
- Rotations Per Minute: 20
- Factor: 2000
- Absolute Viscosity (Centipoise) = Dial Reading x Factor
- Kinematic Viscosity (Centistoke) = \frac{\text{Absolute Viscosity}}{\text{Density}}

Co-efficient of friction

Co-efficient of friction for all the Tobacco oil esters was measured by using Ducom Wear and Friction Monitor pin on disc equipment. A baseline was run without any lubricant sample to check the actual friction generated between pin and disc. Then, after a thin coat of sample was applied on disc and then it was allowed to rotate against pin for 1000 seconds at 500 rpm speed. The friction factor was obtained for all the samples using the same procedure. All-purpose grease of Hindustan Petroleum Ltd. NLGI grade 3 was used as a standard sample for this test.

Operating Conditions were as follows:

- Name of equipment: Ducom Wear & Friction Monitor
- Model no: TR-20LE-PHM-200
- Operating time: 1000 sec.
- Operating Temperature: Room Temperature (29°C)
- Operating Speed: 500 RPM
- Track Diameter: 10mm
- Pin Diameter: 3mm
- Material of pin: Aluminum
- Material of Disc: EN31

RESULTS AND DISCUSSION

Physicochemical properties

Physicochemical properties of Tobacco oil viz. Saponification value, Iodine value and Peroxide value were calculated which are tabulated in Table 2.

Fatty acid profile

Fatty acid profile of Tobacco oil was done by Gas Chromatography. The results of fatty acid profile shows the presence of Linoleic acid upto 73.43%, other fatty acids are also present which are tabulated in Table 3.

Figure 1 is the gas chromatogram of Tobacco oil in which peak at retention time 19.68 minute is of linoleic acid, having the highest concentration amongst other fatty acids. Percentage of fatty acids in Tobacco oil are tabulated in Table 3.
Table 2. Physicochemical properties of Tobacco oil.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saponification Value</td>
<td>160</td>
</tr>
<tr>
<td>Iodine value</td>
<td>138.52</td>
</tr>
<tr>
<td>Peroxide value</td>
<td>06.06</td>
</tr>
</tbody>
</table>

Table 3. Fatty acid composition in percentage.

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic Acid</td>
<td>09.57</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>3.95</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>11.92</td>
</tr>
<tr>
<td>Linoleic Acid</td>
<td>73.43</td>
</tr>
<tr>
<td>Linolinic Acid</td>
<td>0.83</td>
</tr>
<tr>
<td>Unknown Fatty Acids</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Figure 1. Gas chromatogram of Tobacco oil.
Gas chromatography–mass spectrometry analysis

Gas Chromatography–mass spectrometry was carried out of various Tobacco oil esters, which are our desired product and can replace mineral oil based lubricants. The chromatograms of Octyl and Neo-pentyl glycol esters of Tobacco oil are shown as Figures 2 and 3.

Significant amount of peaks were obtained between retention time of 20 to 25 minutes which indicates the formation of fatty acid esters. The peak at retention time 24.82 min is due to octyl ester, which confirms the trans esterification of Tobacco oil methyl ester using Octanol.

Significant amount of peaks were obtained confirming the formation of esters, out of which the peak at retention time 26.20 min is due to fatty acid ester formed by esterification of neo pentyl glycol and fatty acid methyl esters, which confirms the trans esterification of Tobacco oil methyl ester using neo pentyl glycol.

Thermogravimetry analysis

Thermo gravimetric analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature. TGA is helpful in determining the range of temperature under which the moisture and the volatile content of the substance is driven out. It also helps to study the decomposition of the material with increase in temperature and hence, to know about the thermal stability of a material. The Figures 4, 5 and 6 represents the thermograms of Octanol and Neo Pentyl Glycol esters of Tobacco oil and HP all-purpose grease respectively. The thermograms shows that all the three esters have sufficient thermal stability. The hexyl and octyl esters are comparatively more stable than the neo-pentyl glycol esters. While the HP all-purpose grease was least stable in comparison to the all three bio-based lubricants. The percentage weight retained at 50°, 100°, 150° and 200° Celsius are tabulated in Table 4.

From the thermogram of Octanol ester of Tobacco oil, in Figure 4, it was observed that 74.979% of product is stable at 200°C.

From the thermogram of Neo Pentyl Glycol ester of Tobacco oil, in Figure 5, it was observed that 72.194% of product is stable at 200°C.

From the thermogram in Figure 6, it was observed that 54.372% of product is stable at 200°C.
Co-efficient of friction analysis

The coefficient of friction, often symbolized by the Greek letter \( \mu \), is a dimensionless scalar value which describes the ratio of the force of friction between two bodies and the force pressing them together. The
Figures 7 and 8 represent the graphs of time vs coefficient of friction of Hexanol, Octanol, NPG esters of Tobacco oil respectively. These are comparative graphs showing the data of coefficient of friction for dry and clean condition, HP all-purpose grease and esters of Tobacco oil. The NPG ester has the least coefficient of friction indicating its highest lubricating tendency. The results of graph are tabulated in Table 5.

Figure 7 shows the time vs coefficient of friction graph of Octyl ester of Tobacco oil. This is a comparative graph of base stock for bio-based lubricants, i.e Octyl ester of tobacco oil and HP all-purpose grese NLGI grade 3. The coefficient of friction obtained using tobacco oil ester on pin on disc apparatus was 0.039, which is better than HP all-purpose grease (0.102) under same operating conditions. The friction factor for the dry condition (without
Table 4. Comparative data of TGA at 50\(^\circ\), 100\(^\circ\), 150\(^\circ\) and 200\(^\circ\) Celsius respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>50 (^\circ)</th>
<th>100 (^\circ)</th>
<th>150 (^\circ)</th>
<th>200 (^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octyl Ester of Tobacco Oil</td>
<td>99.908%</td>
<td>98.078%</td>
<td>94.545%</td>
<td>84.015%</td>
</tr>
<tr>
<td>Neo-pentyl Ester of Tobacco Oil</td>
<td>99.738%</td>
<td>93.298%</td>
<td>81.229%</td>
<td>72.194%</td>
</tr>
<tr>
<td>HP all-purpose grease</td>
<td>99.904%</td>
<td>90.983%</td>
<td>72.953%</td>
<td>54.372%</td>
</tr>
</tbody>
</table>

Figure 7. Time v/s co-efficient of friction graph of octyl ester of tobacco oil.

Figure 8. Time v/s co-efficient of friction graph of Neo pentyl glycol ester of tobacco oil.

any type of grease) was 0.385.

Figure 8 shows the time v/s co-efficient of friction graph of Neo pentyl glycol ester of tobacco oil. This is a comparative graph of base stock for bio-based lubricants, i.e. Neo pentyl glycol ester of tobacco oil and HP all-purpose grease NLGI grade 3. The co-efficient of friction
Table 5. Comparative data of co-efficient of friction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co-efficient of friction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry condition</td>
<td>0.385</td>
</tr>
<tr>
<td>Tobacco Octanol</td>
<td>0.039</td>
</tr>
<tr>
<td>Tobacco NPG</td>
<td>0.098</td>
</tr>
<tr>
<td>All-purpose grease</td>
<td>0.102</td>
</tr>
</tbody>
</table>

Table 6. Absolute viscosity, kinematic viscosity and viscosity index.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absolute Viscosity @ 40 degree Celsius</th>
<th>Absolute Viscosity @ 100 degree Celsius</th>
<th>Kinematic Viscosity @ 40 degree Celsius</th>
<th>Kinematic Viscosity @ 100 degree Celsius</th>
<th>Viscosity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tobacco Octanol</td>
<td>15,000</td>
<td>4000</td>
<td>17647.05</td>
<td>4705.88</td>
<td>563.39</td>
</tr>
<tr>
<td>Tobacco NPG</td>
<td>6000</td>
<td>5000</td>
<td>7058.82</td>
<td>5882.35</td>
<td>793.48</td>
</tr>
<tr>
<td>HP grease</td>
<td>1,10,000</td>
<td>21,000</td>
<td>129411.76</td>
<td>24705.88</td>
<td>600.09</td>
</tr>
</tbody>
</table>

obtained after applying Tobacco oil ester on pin on disc apparatus was 0.098, which is better than that of HP all-purpose grease 0.102 under same operating conditions. The friction factor for the dry condition (without any type of grease) was 0.385 (Table 5).

**Viscosity analysis**

Viscosity is a measure of resistance to flow. It decreases (thins) with increasing temperature and increases (or thickens) with decreased temperature. Viscosity of lubricants is measured most commonly by kinematic viscosity and reported in a unit called the centistoke (cSt). Kinematic viscosity, viscosity index and shear stress/shear rate are all factors that should be taken into account during manufacture of lubricant (Table 6). Table 6 shows the data of absolute viscosity at 40° and 100°C, Kinematic viscosity at 40° and 100°C and viscosity index of Octyl, Neo-pentyl glycol esters of Tobacco oil and HP all-purpose grease. Amongst the bio-based basestocks for grease, absolute and kinematic viscosity of Tobacco oil octyl ester was the highest. While the absolute and kinematic viscosity of HP all-purpose grease was higher than all the three bio-based basestocks for grease.

**Conclusion**

Tobacco oil methyl esters were successfully trans esterified using various alcohols viz. Hexanol, Octanol and Neo-Pentyl Glycol. These esters have superior performance properties against standard and reputed product obtained in the market (All-purpose grease of M/s Hindustan Petroleum Limited NLGI grade 3). Thus these esters derived from Tobacco oil- a renewable source, can be used as base stock to formulate lubricating grease. Use of such natural materials for deriving a value added product like lubricants can eliminate various problems related to environment and depletion of finite resources; which are still in search of a legitimate solution.

**REFERENCES**


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