A study on improvement of cold flow behaviour and thermal-oxidation stability of *Camellia sinensis* assamica (tea) oil lubricants as industrial lubricant

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Abstract. In recent years, vegetable oil based bio-lubricant has drawn attention due to its inherent eco-friendly characteristics such as non-toxicity and high biodegradability. Low thermal-oxidation stability and pour point temperatures limit large-scale industrial application of vegetable oil based lubricant. The present work studied improvement of pour point temperature and oxidation stability of *Camellia sinensis* assamica (tea) seed oil (CSO) with varying weight percentage of *Camellia sinensis* assamica deoiled cake derived bio-oil. Bio-oil was added with CSO at 5%, 10% and 15% concentration by weight. The results showed improvement of oxidation stability due to presence of alkylated phenols in bio-oil. The oxidation onset temperature was increased from 243.89\degree C to 274.55\degree C. The pour point of CSO also improved from initial temperature -4\degree C to -27\degree C.

Keywords: *Camellia sinensis* assamica, bio-lubricant, pour point, oxidation stability, blend

1. Introduction

Lubricants are used to reduce the friction and wear, heat dissipation, corrosion control, etc. between two moving surfaces in contact. In recent years, due to depletion of petroleum reserve and stringent environment policy for environment protection, vegetable oil based bio-lubricants have drawn attention due to their eco-friendly characteristics. Low thermal-oxidation stability and high pour point temperature limits large-scale industrial application of vegetable based lubricants. Different properties of bio-lubricant depend on the structure of fatty acids \cite{1}. Polyunsaturated fatty acids favour low cold temperature properties while saturated fatty acids are responsible for good oxidation stability \cite{1}. Chemical modification processes such as transesterification, hydrogenation, and epoxidation improve the poor characteristics of bio-lubricants. Addition of suitable pour point depressant and antioxidant additives can also improve oxidation stability and pour point temperature. Addition of phenolic compounds such as butylated hydroxytoluene (BHT), tert-butylhydroquinone (TBHQ), tocopherols, flavonoids etc. inhibits the propagation of radical species generated due to oxidation of lubricants \cite{2}.

Bio-oil is produced through condensation of vapour derived from biomass in pyrolysis process. Bio-oil contains many hindered phenols known to be good antioxidants \cite{3}. In general, antioxidants are phenolic compounds \cite{4}. Some studies have been carried out to explore the utility of bio-oil as antioxidants to retard the oxidation of biodiesel. Garcia et al. \cite{3} blended bio-oil and biodiesel at different concentration (w/w) without the use of co-solvent to study the improvement of oxidation...
stability and cold flow properties. The study showed an increase of oxidation induction temperature from 155 to 225°C. Garcia et al. [1] tested different extraction agents to incorporate bio-oil as an antioxidant to biodiesel. This study showed that the direct addition of a small concentration of bio-oil (less than 4 weight %) with biodiesel significantly increased oxidation stability by 175%. Botella et al. [5] performed hydrotreatment of bio-oil in the temperature range 200-325°C using catalysts Ruthenium on carbon (Ru/C) and blended with biodiesel which results in increase of oxidation stability of biodiesel.

The present work focuses on utilization of bio-oil derived from *Camelia sinesis asamica* seed de-oiled cake by pyrolysis to study its impact on the oxidation stability and cold flow properties of *camellia sinesis asamica* vegetable oil based lubricant derived from the same seeds by the Soxhlet extraction method.

2. Material and methods

2.1 Material

Discarded *Camelia sinesis asamica* (tea) seeds were collected from Lakhi Baruha tea seed supply centre, Tinisukia, Assam, India. Initial the seeds were unshelled and the kernels were sun-dried at an average temperature of 28.6°C (6hrs daily) for three days. The kernels were grounded and sieved to a particle size 0.4mm.

2.2 Production of vegetable oil and bio-oil

Vegetable oil was extracted from grounded kernels (sample weight: 20g) with n-hexane using Soxhlet extraction method. The solvent was removed from the extract with the help of a rotary vacuum evaporator (IKA, RV-3V, Germany). The extracted oil was kept over anhydrous sodium sulphate and filtered to remove the particulate matter (if any) present in it. The filtered oil was weighed. Figure 1 shows the tea seed oil and tea seed cake obtained after Soxhlet extraction.

Figure 2 shows the pyrolysis setup used for the present work. Tea seed cake was oven dried at 105°C and bio-oil was produced by pyrolysis of tea seed cake obtained after Soxhlet extraction. A sample of 10g was pyrolyzed at two different heating rates: 10°C/min and 30°C/min, maintaining N₂ gas (purity 99.99%) flow rate of 100ml/min in a 430mm long and 300mm diameter fixed bed reactor. The reactor was heated to 500°C/min for each run of the experiment. The vapor was passed through a condenser maintained at 4°C. The condensed liquid contained an aqueous phase on top and a densed oily phase (bio-oil) at bottom. The bio-oil was separated out from the aqueous phase in a separating funnel.

![Figure 1. (a) Tea seed oil (b) tea seed cake](image)

![Figure 2. Pyrolysis setup](image)

2.3 Preparation of bio-oil/ bio-lubricant blends

Bio-oil/bio-lubricant blends were prepared by direct addition of bio-oil at a concentration of 5, 10 and 15 weight % into vegetable oil. The samples were labelled as: B1(95 wt% bio-lubricant, 5 wt% bio-oil); B2(90 wt% bio-lubricant, 10 wt% bio-oil) and B3(85 wt% bio-lubricant, 15 wt% bio-oil).
Initially the bio-oil was taken in the container followed by the addition of vegetable oil. All the blends were prepared at room temperature 25°C. After 48h of preparation, no visible layer was noticed in each blend. Figure 3 gives evidence all samples are homogeneous. The samples were characterized after 48h of preparation.

2.4 Accelerated stability test

The long term stability of the blends was estimated following the methodology adopted by Alcala and Bridgwater [6]. The samples were heated continuously for 24hrs at 80°C. This method involves measuring variation in viscosity or water content before and after heat treatment. The variation was calculated using the Equation (1) [6]:

\[
\text{Variation in property (\%)} = \left( \frac{\text{value of property after Heat treatment} - \text{initial value of property}}{\text{initial value of property}} \right) \times 100
\]  \hspace{1cm} (1)

In the present work, viscosity was measured before and after the heat treatment using rotational viscometer (Make: IKA, Model: Rotavisc Lo-Vi).

2.5 Determination of cold flow properties

A Cleveland open cup apparatus (Model: HAMCO 19C) was used for the measurement of flash point as per ASTM D92. The pour point (PP) was measured to an accuracy of ±3°C adhering to the ASTM D97-15 method using a cloud and pour point apparatus (Make- Hindustan Apparatus, Model HAMCO 9B).

2.6 Oxidation stability analysis

Oxidation stability analysis was performed in Mettler Toledo thermal gravimetric analyzer (TGA) instrument (model- TGA2) in a temperature range of 25–600°Cat a heating rate of 30°C/min under O₂ (purity-99.995%) atmosphere with each sample of 10 ± 5 mg. The oxidation onset temperature was determined as parameter to investigate oxidation stability of samples.
2.7 Identification of compound present in Bio-oil

GC–MS analysis of bio-oil was carried out using Perkin Elmer Clarus680 GC/600C MS, equipped with flame ionization and mass spectrometry detection (GC–FID–MS) was used. A capillary column coated with a film of DB-5 with a length of 60 m and diameter 0.25 mm was used. The GC was equipped with a split injector at 200°C with a split ratio of 1:10. Helium gas of 99.995 % purity was used as the carrier gas at a flow rate of 1.51 ml/min. The oven initial temperature was set to 40°C for 2 min and then increase to 140°C at a rate of 10°C/min and hold for 2 min. Finally, temperature was increased to 290°C at a rate of 7°C/min and maintained for 5 min. All the compounds were identified by means of the NIST library (NIST 14 version 2.4). Mass spectrometer was operated at an interface temperature of 200°C with ion source temperature of 180°Cof range 40–1000 m/z.

3. Results and discussion

3.1 Bio-oil production and Characterization of Bio-oil and bio-lubricant

The yield of products obtained by pyrolysis of *Camelia sinesis asamica* deoiled cake (CSDC) is presented in Table 1. The maximum yield of bio-oil obtained at final temperature 500°C with a heating rate of 30°C/min under constant flow rate of N₂ was 31.02 ± 0.07 wt %. The phenolic compounds identified in the bio-oil are shown in Table 2. Fatty acid composition of vegetable oil based bio-lubricant derived from tea seed can be found elsewhere [7]. Oleic acid (56%), linoleic acid (22%) and linolenic acid (0.3%) are the major constituents of fatty acid composition of tea seed oil. Low polyunsaturated fatty acid (PUFA) content indicates poor cold temperature of biolubricant derived from tea seeds.

### Table 1. Yield of pyrolysis products at final temperature 500°C

| Condition of experiment | Biochar (wt %) | Bio-oil (wt %) | Aqueous phase (wt %) | Gas (wt %) |
|-------------------------|----------------|----------------|---------------------|------------|
| N₂ Flow rate 100ml/min  |                |                |                     |            |
| Heating rate 10°C/min   | 26.41 ± 0.24   | 30.11 ± 0.15   | 29.12 ± 0.11        | 14.36 ± 0.12 |
| Heating rate 30°C/min   | 24.76 ± 0.03   | 31.02 ± 0.07   | 29.22 ± 0.04        | 15.00 ± 0.02 |
| N₂ Flow rate 100ml/min  |                |                |                     |            |

![Figure 4. GC-MS of bio-oil obtained from CSDC](IC-1_25-6-2013)
| Sl.No. | \(T_R\) (min) | Area (%) | Tentative Phenolic compounds | Empirical formula |
|-------|----------------|----------|-------------------------------|------------------|
| 1     | 12.49          | 5.149    | Phenol                        | \(C_6H_6O\)      |
| 2     | 13.93          | 1.527    | Phenol, 2-methyl              | \(C_7H_8O\)      |
| 3     | 14.26          | 2.287    | Phenol, 2-methoxy-            | \(C_7H_8O_2\)    |
| 4     | 14.73          | 3.869    | Phenol, 4-ethyl-              | \(C_8H_10O\)     |
| 5     | 15.84          | 1.422    | Phenol, 2,6-dimethoxy         | \(C_9H_12O_2\)   |
| 6     | 17.37          | 3.571    | Hydroquinone                  | \(C_6H_12O_2\)   |
| 7     | 18.73          | 4.107    | Phenol, 2,6-dimethoxy-4-(1-propenyl)-, (E)- | \(C_{11}H_{16}O_3\) |
| 8     | 20.20          | 1.876    | Phenol, 2,6-dimethoxy-4-(2-propenyl)- | \(C_{11}H_{16}O_3\) |
| 9     | 23.17          | 2.706    | Phenol, 2,6-dimethoxy-4-(2-propenyl)- | \(C_{11}H_{16}O_3\) |

**Table 3. Properties of Bio-lubricant derived from tea seeds and prepared blends**

| Properties                  | CSO     | B1     | B2     | B3     |
|-----------------------------|---------|--------|--------|--------|
| Pour point temperature (℃)  | -4 ± 0.02 | -20 ± 0.15 | -24 ± 0.27 | -27 ± 0.13 |
| Viscosity (mm²/sec) at 40℃  | 39.36   | 47.89  | 55.57  | 80.12  |
| Viscosity (mm²/sec) at 80℃  | 14.42   | 14.91  | 15.37  | 16.04  |

Figure 4 represents GCMS of CSDC bio-oil and Table 3 represents the pour point temperature and viscosity of bio-lubricant and all the blends prepared in the present study. The results show that the addition of bio-oil improves pour point temperature of bio-lubricant due to potential interactions between the soluble fraction of bio-oil and unsaturated fatty acid methyl esters which contribute to lower the gel formation temperature [3]. The viscosity of bio-lubricant increased may be due to solubilisation of lignin derived oligomers present in bio-oil [3].

### 3.2 Oxidation stability

![Oxidation stability graph](a)
Table 4 represents the oxidation onset temperature of CSO and blends whereas Figure 5 represents the TGA and derivative thermogravimetric (DTG) curves of the same. Table 4 and Figure 5 evidence that addition of bio-oil improved the oxidation stability of bio-lubricant. This may be due to extraction of phenols from bio-oil which led to the formation of sterically phenoxyl radicals and prevented further polymerization [3]. The oxidation onset temperature of bio-lubricant increased with increasing concentration of bio-oil from 5% to 15%.

### 3.3 Accelerated stability test

Table 5 shows the results of accelerated stability test. The results evidence that weight loss of the blends is less than 0.1% and the change in viscosity of the blends is less than 0.3% which can be described as remarkably good stability of the blends.

### Table 5. Accelerated stability test results

| Blend | Value before heat treatment | Value after heat treatment | Variation (%) |
|-------|-----------------------------|----------------------------|---------------|
| B1    | 10.3648                     | 10.3648                    | 0.000         |
|       | 14.91                       | 14.91                      | 0.000         |
| B2    | 10.3633                     | 10.3589                    | -0.042        |
|       | 15.37                       | 15.34                      | -0.215        |
| B3    | 10.3658                     | 10.3549                    | -0.105        |
|       | 16.04                       | 16.02                      | -0.116        |
4. Conclusion

The present work is a systematic approach to improve oxidation stability and pour point temperature of vegetable oil based bio-lubricant derived from discarded Camellia sinensis assamica (tea) seed by addition of bio-oil derived from Camellia sinensis assamica (tea) seed cake through pyrolysis. The pour point temperature of bio-lubricant decreased from -4°C to -27°C by addition of bio-oil at concentrations of 5, 10 and 15wt%.

The oxidation stability was determined by measuring the oxidation onset temperature. The oxidation stability is improved by the addition of bio-oil. The oxidation onset temperature increased with increase in concentration of bio-oil. The maximum oxidation onset temperature was recorded as 274.55°C at 15% concentration of bio-oil in bio-lubricant.

Accelerated stability tests showed less than 0.3% change in viscosity of prepared blends which indicates that they will remain stable and homogenous for a long period of time.

Nomenclature

CSO- Camellia sinensis assamica (tea) oil
TGA- Thermogravimetric analysis
DTG- Derivative thermogravimetric analysis
PP- Pour point

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