COCONUT OIL AS BIO LUBRICANT- STUDY OF THE ANTI-WEAR PROPERTIES USING QUANTUM CHEMICAL CALCULATIONS AND TRIBOLOGICAL TESTS

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ABSTRACT
In this paper Spartan 02, a molecular dynamics software is used to analyze and predict the tribological properties of coconut oil in a qualitative manner on the basis of carbon chain length of the constituent fatty acids, their polarity (Net electrostatic charge, \( Q_r \)) and the energies of the molecular orbitals \( E_{\text{HOMO}} \) (Energy of the Highest Occupied Molecular Orbital) and \( E_{\text{LUMO}} \) (Energy of the Lowest Unoccupied Molecular Orbital) and the enthalpies of formations (\( H_{\text{form}} \)) of the iron soaps of respective fatty acids. Tribological properties of the constituent fatty acids of coconut oil were evaluated using a four-ball tester as per ASTM D4172 method. The experimental results showed good correlation to the selected quantum chemical descriptors. The influence of an anti-wear additive on the tribological performance of coconut oil and the optimum additive concentration were also evaluated experimentally.

INTRODUCTION
A major fatty acid constituent of coconut oil is lauric acid (C12) whereas oleic acid (C18:1) is the major fatty acid constituent of vegetable oils like rape seed oil and olive oil which were widely used as lubricants [1]. The anti-wear characteristics of vegetable oils depend on three phenomena namely physical adsorption, chemical adsorption and surface chemical reaction. The adsorption mechanisms and surface chemical reactions result from the interaction of the polar group (-COOH) of the constituent fatty acids of the respective vegetable oils with the metallic surface [2] resulting in a surface film believed to inhibit metal to metal contact. Strength of adsorption of lubricants on metallic surfaces depend on the nature of adsorption viz. physical adsorption and chemical adsorption which in turn depend on the electrostatic attraction of the polar head of the vegetable oil molecules and the metal atoms and the electron sharing between vegetable oil molecules and metal atoms. In this paper the electrostatic attraction and the tendency of adhesion of lubricant on the metal surface due to electron sharing are studied in a qualitative manner using the popular quantum chemical descriptors namely \( Q_r \) - net electro static charge and \( \Delta E \) - orbital energy gap between HOMO and LUMO. At high temperatures formation of iron soaps of fatty acids due to surface chemical reaction influence the tribological behavior of vegetable oils [3].

EXPERIMENT DETAILS
Quantum chemical calculations
All quantum chemical calculations were carried out using the molecular dynamics simulation package SPARTAN '02, Wavefunction Inc., USA. Since iron possesses the body centered cubic lattice structure, their surface plane will be (110), and a five-atom cluster is enough to show the local information of the metal surface [2]. So we chose a calculation model of Fe (110) faces formed by five atoms. The constituent fatty acids of coconut oil (Table 1) have been modeled with SPARTAN '02. Quantum chemical calculation are performed using ab initio method (Hartree- Fock approximation), with 6-31G as basis set to determine

1. \( Q_r \) : net atomic charge as fraction of unit electronic charge on the -COOH polar group.
2. \( \Delta E \) : orbital energy gap between LUMO of iron and HOMO of constituent fatty acids

PM3 (t-m) semi empirical method was used to calculate the enthalpy of formations (\( H_{\text{form}} \)) of iron soaps of different fatty acids in Kcal/mol.

Tribological tests on four-ball tester
Wear tests on constituent fatty acids (C10 to C18:1) of coconut oil were conducted using a four ball tester TR 30L, DUCOM, Bangalore, India as per ASTM D4172. To improve the tribological properties of coconut oil an anti-wear/ extreme pressure additive Zinc-Dialkyl-Dithio-Phosphate (ZDDP) was added to coconut oil. To determine the optimum additive concentration the wear tests were conducted at different
additive concentrations. The wear tests with lauric acid, oleic acid, coconut oil and additivated coconut oil were conducted at different temperatures to find out the transition temperature in to high wear regime.

RESULTS AND DISCUSSION

Though the net atomic charge ($Q_r$) on different fatty acid molecules do not show significant difference $\Delta E$ values for different carbon chain lengths show a decreasing trend from C12 to C18:2 as shown in Figure 1. Tenacity of physisorbed lubricant film has a direct relationship to the electrostatic attraction of oxygenated anion to metallic cation. The lower the values of $\Delta E$, the stronger are the chemisorbed lubricant films and hence better tribological properties [2]. Wear test results in Figure 2 show a decreasing trend in coefficient of friction ($\mu$) and wear scar diameter (WSD) with increasing carbon chain length as predicted. Since iron soaps are low shear strength materials their continuous formation and removal due to sliding action result in high wear rate at high temperatures. The higher the enthalpy of formation (Figure 1) of the iron soap of a fatty acid, the higher is the onset temperature of high wear regime (Figure 3). The optimum concentration of ZDDP is 2% (app) by weight as obtained from Figure 4 corresponding to the lowest values of $\mu$ and WSD. At high temperatures tenacious sulfide and phosphide films are formed in the presence of ZDDP drastically reducing wear [4].

CONCLUSION

Since the major fatty acid constituent of coconut oil is lauric acid it has slightly inferior tribologuical properties compared to high oleic vegetable oils. Tribological properties of coconut oil can be dramatically improved by the addition of AW/EP additives. Quantum chemical calculations can be effectively used as a tool to evaluate tribological properties of lubricants based on their chemical structure

Table 1: Fatty acid constitution of coconut oil

<table>
<thead>
<tr>
<th>Component</th>
<th>C12:0</th>
<th>C14:0</th>
<th>C8:0</th>
<th>C16:0</th>
<th>C18:1</th>
<th>C18:0</th>
<th>C18:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction (%)</td>
<td>51.0</td>
<td>18.5</td>
<td>9.5</td>
<td>7.5</td>
<td>5.0</td>
<td>3.0</td>
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REFERENCES