EPOXIDATION - AN IMPORTANT TECHNIQUE FOR ENHANCING THERMAL STABILITY OF BIOLUBRICANTS BASE STOCK

Jaafaru
Mechanical Engineering Department, Kaduna Polytechnic, Kaduna, Nigeria
A. U. Garba
Bio and Agricultural Engineering Department, Kaduna Polytechnic, Kaduna
and
M.N. Danjuma
Chemical Engineering Department Kaduna Polytechnic, Kaduna
Email: aliyujaafar@yahoo.co.uk +2348028433788

Abstract

Crude vegetable oils are thermally unstable due to their inherent weaknesses as a result of multiple double bonds found in their molecular structures. This paper compares between the thermal stabilities of crude jatropha oil (CJO) and epoxidized jatropha oil (EJO). The purpose was to determine the effect of epoxidation on thermal stability of biolubricant base stocks. (CJO) was epoxidized using peracid generated in-situ by the reaction of formic acid and hydrogen peroxide using sulfuric acid as catalyst. Results show that EJO has better thermal stability than CJO with High Temperature High Shear (HTHS) of EJO 2.9 cSt and that of CJO 1.6 cSt.

Keywords: Biolubricant, epoxidation, jatropha and thermal stability.

Introduction

Biolubricants are made from plants such as palm, soy bean, sun flower, karanja, and rapeseed. They can also be made from synthetic esters and petroleum oils that satisfy established biodegradability and toxicity criteria. They are generally considered as lubricants with high biodegradability as well as low human and environmental toxicity (Kumar and Sharma, 2011). The types of feedstock for biolubricant production may differ from country to country and depend on geographical locations. According to Mubarak *et al* (2014), more than 350 oil-bearing plants are known, among which, only palm, soybean, rapeseed, coconut, safflower, cotton-seed, sunflower, and peanut oils are considered as potential alternative biolubricants. Moreover, other non-edible oils such as Jatropha, neem, and Karanja have received worldwide interest (Mofijur *et al,* 2012).

Unmodified vegetable oil such as jatropha oil when used for biolubricant formulation cannot perform satisfactorily due to low thermal stability, poor low temperature performance, low volatility and deposit formation. All these are due to some inherent weaknesses in their molecular structures. Therefore vegetable oils need to be chemically modified before being used for biolubricant production. One of the most effective chemical modifications for vegetable oils is epoxidation of its double bonds (Saurabh *et al*, 2011). Epoxidation is a chemical reaction at the olefinic functionality of the fatty acid chain of a vegetable oil so as to increase its stability.

Epoxidation of fatty acids or vegetable oil can be carried out using peracid generated in-situ or ex-situ by the reaction of carboxylic acid (acetic or formic acid) and hydrogen peroxide in the presence a suitable catalyst (Dinda *et al*, 2008; Salimon and Abdullah 2008).

Thermal stability is the resistance of lubricant to change due to thermal stresses. Lubricant needs to retain its lubricity even at elevated temperatures. If a lubricant lacks thermal stability, it begins to break down when it gets hot, which leads to increased friction. This problem is referred to as Sludging. In extreme cases, sludge can “gum-up” an engine leading to failure and even “seizing” in which the pistons are unable to move against the walls of the cylinders and thus the engine cannot function (Gill, 2013). High temperature, high Shear viscosity is used to determine the thermal stability of lubricant oil at elevated temperatures (Humphrey, 2016).

Materials and Methods

Jatropha oil was purchased at National Research Institute of Chemical Technology, NARICT, Basawa Zaria. Other materials used for the work include: formic acid, hydrogen peroxide, sulfuric acid, magnesium sulfate, anhydrous methanol, Tetraoxosulfate (IV) acid. The Apparatus used include:

Beakers (50-500 mL), Burette (50 mL), Pipette (25 mL), Glass funnel, Measuring Cylinders (5-250 mL), Thermometers (Mercury-in-glass and thermocouples) and retort stand.

Epoxidation of Jatropha oil

The epoxidation of jatropha oil was done by reacting the jatropha oil with performic acid generated in-situ via the reaction of hydrogen peroxide with formic acid using sulfuric acid as catalyst. A jatropha oil sample of mass 500 g, 0.57 mol and 44.5 mL, 1.15 mol of formic acid and of sulfuric acid (6.1 mL, 2% weight of HCOOH and hydrogen peroxide) were weighed at room temperature and poured into a beaker and placed on a magnetic stirrer. The mixture was heated and agitated at a constant rate and the temperature was maintained at 60 ^{0}C. 460 mL, 4.56 mol of H_2O_2 was added into the mixture drop wise and agitation of the mixture continued for further one hour. The mixture was poured into separating funnel allowed to settle. The sulfuric acid and H_20_2 were washed and the settled product dried overnight with magnesium sulphate.

After the production of EJO, physico-chemical properties of the CJO and EJO that have direct link to thermal stability were determined. The test methods employed for the determined properties are presented in table1.

Table 1 : Properties determined and the test methods used

Property	Method
Viscosity Index	ASTM D2270
Flash Point	ASTM D93
Pour Point	ASTM D97
HTHS @ 150 ^{0}C (cSt)	ASTM D 4624

Results and discussions

The results of the various tests conducted for the physico-chemical properties of CJO and EJO are presented in table 2.

Table 2 physico-chemical parameters of CJO and EJO

Property	CJO	EJO
Viscosity Index	197	112
Flash Point (^{0}C)	192	249
Pour Point (^{0}C)	2	-5
HTHS @ 150 ^{0}C (cSt)	1.6	2.9

Viscosity / viscosity index

The viscosities of CJO at 40 ^{0}C and 100 ^{0}C were determined to be 34.06 cSt and 7.5 cSt. Whereas for EJO, 170.63 cSt and 17.6 cSt respectively. Wu *et al,* (2000) and Sammaiah *et al,* (2014), ascribed viscosity and density increase of epoxides due to increase in molecular weight of the epoxides and more polar structure and stronger interactions between molecules of the epoxides than the virgin oil. This means that at both low and high temperatures EJO will be much thicker than CJO. As lubricant base stock, EJO will offer better protection to engines parts. However the VI of CJO (197) is much higher than that of EJO (112). This implies that the rate of viscosity change with temperature is higher for EJO than CJO. Viscosity decrease with temperature is not desirable due to risk of mechanical failure at elevated temperatures, though it offers better fuel economy, Humphrey (2016). According to API Viscosity Index classification, the

CJO viscosity (197), falls within Super High range (160-200). However VI of 112 for EJO, falls within very high range (110-125). Thus EJO has excellent VI and can therefore be an excellent candidate for high temperature applications.

Flash point

The flash points for the CJO and EJO were found to be 192 ^{0}C and 249 ^{0}C respectively. The results agree with that of Sammaiah *et al,* (2014), who got Flash point for Jatropha oil to be 186 ^{0}C and for epoxidized Jatropha oil 288 ^{0}C. This means that EJO is much less volatile and fire resistant than CJO.

Pour point

This was found to be -2 ^{0}C for CJO and -5 ^{0}C for EJO. The improvement in pour point of the EJO was due to conversion of carbon-carbon double bonds to saturated epoxy group (Sammaiah *et al*, 2014). The lower the pour point, the better the lubricant's protection to engine parts at low temperature services. A rule of thumb commonly used in lubricant selection is to ensure that the lubricant has a pour point at least 10 ^{0}C below the lowest anticipated temperature of the use location (Muhammed 2015). Therefore pour point of -5 ^{0}C will ensure safe cold cranking.

HTHS viscosity

The High Temperature High Shear (HTHS) Viscosity of EJO was determined to be 2.9 cSt, whereas CJO was 1.6 cSt. This implies that EJO will offer better protection to engine parts at elevated temperature and shears than CJO. However CJO will offer more fuel economy at high temperature and shear due to decrease in flow resistance. Sufficient HTHS viscosity creates enough protective oil film between engines. This is critical for prevention of wear at ring/liner interface (Humphrey, 2016).

Conclusion

It can be concluded that epoxidation has positive effect on thermal stability of vegetable oils. The thermal stability of EJO was found to be almost twice that of CJO.

References

API Engine oil Classification (2015), "Service Fill Oil For Gasoline Engines, Light-duty Diesel Engines". Retrieved on September 23rd 2017 from www.infineum.com.

Dinda S., Patwardhan A.V., Groud, V.V., and Pradhan, N.C., (2008), " Epoxidation of cotton seed oil by aqueous hydrogen peroxide catalyzed by liquid inorganic acids." *Bioresource Technology*, Volume 99 number 9, pp. 3737-3744.

Gill, P.S., (2013), "*Automobile Engineering- I*", S.K. Kataria & Sons. New Delhi-110002.

Humphrey B. (2016) Using Engine Oil to Improve Fuel Economy. OEM Technical Laison-HD Driveline, *Petro-Canada Lubricants*. LUB 3431E.

Mofijur, M., Masjuki, H.H., Kalam, M.A., Hazrat, M.A., Liaquat, A.M. and Shahabuddin M., (2012), "Prospects of Biodiesel from Jatropha in Malaysia." *Renew Sustain Energy Rev. Volume 16*, pp. 5007–20.

Mohammed, N., (2015), "Synthesis of Biolubricant from Vegetable oils." Msc Thesis. Department of Chemical Engineering, Ahmadu Bello University, Zaria.

Mubarak, H.M., Mohammed, N. E., Masjuki, H.H., Kalam, M.A. and Al Mahmud, K.A.H., (2014), "the prospects of biolubricants as alternatives in automobile applications." pp. 34-43

Salimon, J. and Abdullahi, R. (2008) Physico-chemical Properties of Malaysian Jatropha curcas Seed Oil. *Sians Malaysiana.* Volume 37 number 4, pp. 379-382

Sammaiah A., Korlipara V. P. and Rachapudi B. N. P. (2014) Synthesis of Epoxy Jatropha Oil and its Evaluation for Lubricant Propperties. *Journal of Oleo Science*, Japan oil Chemist's Society. J-STAGE Advance Publication. ISSN 1347-3352.

Saurabh T., Patnaik M., Bhagt S.L., Rang V.C. (2011) Epoxidation of Vegetable Oils : a Review. International *Journal of Advanced Engineering Technology*, Volume 2 number 4, pp 491-501.

Wu, X.; Zhang, X.;Yang ,S.; Chen, H.; and Wang, D.; (2000) The Study of epoxidized rapeseed oil used as a potential biodegradable lubricant. *J. Am. Oil Chem. Soc.* Volume 77, pp. 561-563.