LETTER TO THE EDITOR

Comments on the Use of Fatty Acid Methyl Esters of Linseed and Castor Oil as Biodiesel

Ramasubramania Iyer

Sir,

Literature reports [1, 2] propose that fatty acid methyl esters (FAME) of linseed and castor oil can be used as biodiesel. Three comments have been listed below to point out the pitfalls in using these fatty acid methyl esters as biodiesel.

1. Experimental work on the effect of temperature on neat linseed and castor oil fatty acid esters reported a change of chemical structure and physical properties. The temperatures employed in these studies were lower than temperature conditions in a diesel engine.
2. Cetane number violation and insufficient oxidation stability of linseed oil and castor oil FAME.
3. Rheology of degraded castor oil biodiesel and the importance of viscosity in atomization.

Reported Reactions of FAME of Linseed and Castor Oil at High Temperatures

Linseed oil is dominated by linolenic (three double bonds, 47.4%) linoleic (two double bonds, 24.1%) and oleic (one double bond, 19.0%) fatty acids [3]. Castor oil is predominantly ricinoleic (89.5%) acid with a hydroxyl group at the twelfth carbon and a double bond in the 9,10 position [4]. The study of thermal polymerization of methyl linolenate at 270 °C reported the formation of dimers and trimers with increased time due to the reactive methylene groups and double bonds at the 9,12,15 position [5]. Castor oil is known to form high viscous blown castor oil when heated at 80–130 °C with or without air [6]. In the case of blown castor oil there is the glycerol backbone's viscosity. For methyl ricinoleate, intermolecular polymerization will take place and there being no glycerol backbone, the viscosity of polymerized methyl ricinoleate will be less than that of blown castor oil, but it will be appreciably large enough to lower its performance efficiency as a biodiesel. The role of viscosity is presented in "Rheology of Degraded Castor Oil Biodiesel and the Importance of Viscosity in Atomization" where atomization of liquid fuel is explained.

Conceicao et al. [7] carried out the degradation of castor oil biodiesel (350 mL) by heat-treating at 150 and 210 °C, in a synthetic air atmosphere, in a system as described in [8]. Thermogravimetry (TGA), differential scanning calorimetry of degraded castor oil indicated a change in thermal profile [7]. Infra red spectroscopy on the degraded castor oil biodiesel showed a decrease in intensity of free hydroxyl groups ($3,440$ cm^{-1}) as the period of degradation increased [7]. At 210 °C for a 48-h period, the authors [7] observed the formation of gum, implying that an oxidative polymerization reaction had gone to completion with infrared spectroscopy showing an absence of the hydroxyl group.

In the performing conditions in a diesel engine, where the temperature is about 900 °C [9], there is a distinct possibility of polymerization and oxidation for linseed oil FAME due to the two double bonds between the reactive methylene groups.

One aspect which has not been reported is the pyrolysis at the hydroxyl group of castor oil biodiesel at the temperature of diesel engine operation. The best way to

R. Iyer (✉)
Department of Chemical Engineering,
University of Queensland,
St Lucia, QLD 4072, Australia
e-mail: r.iyer@eng.uq.edu.au

investigate pyrolysis at the diesel engine temperature is to perform laboratory engine tests. A rigorous way to confirm this would be to do wet methods like hydroxyl value, acid value coupled with spectroscopic methods after treating the castor oil fatty acid methyl esters in a laboratory engine test. A drop in the hydroxyl value will indicate dehydration/pyrolysis and a significant increase in acid value due to the formation of fatty acids [4].

Cetane Number Violation and Oxidation Stability of Linseed and Castor Oil FAME

The cetane number (CN) a dimensionless quantity, which denotes the ignition quality of the diesel fuel and describes the ignition time delay a fuel experiences on injection into the combustion chamber. The higher the cetane number, the shorter the ignition delay time and the higher the chances of the fuel igniting [10]. There are two cetane numbers reported for methyl linolenate. McCormick et al. [11] estimated the CN by ASTM D613, and have reported a value of 45.9. Knothe [12] measured the CN by ASTM 6890 and reported a value of 22.7. ASTM D613 uses a single cetane cylinder whereas ASTM D6890 uses the Ignition Quality tester (IQT) which is an automated development of a constant volume combustion apparatus. The author [12] states that IQT is established as an ASTM standard D6890 and is accepted in ASTM biodiesel standard ASTM 6751 as an alternative to ASTM 613. The standard set in United States is a minimum of CN 47 by ASTM D6751 and a CN of 49 by European standards EN 14241. Considering that ASTM D6890 is more accurate, a CN of 22.7 falls far below the US and European standards of 47 and 49, required for biodiesel, implying that methyl linolenate will have a higher ignition delay time. For castor oil FAME, the cetane number is 37.38 [12] which does not meet the minimum EN and ASTM specifications for a performing as a biodiesel.

The oxidation stability of biodiesel depends on the presence and number of double bonds [13]. Knothe [13] quotes Frankel's [14] relative rates of oxidation as 1 for oleates, 41 for linoleates and 98 for linolenates. European standards EN 14214 restricts the content of methyl linolenate to 12% considering its susceptibility to oxidation if methyl linolenate is greater than 12% in a mixture of fatty acid methyl esters. The FAME of linseed oil have a methyl linolenate content of about 45–47%, which is way over the European standards limit and will be prone to oxidation. According to Knothe [12], the oxidation stability of methyl ricinoleate is four times less than methyl oleate, which would add to oxidative polymerization build up.

Rheology of Degraded Castor Oil Biodiesel and the Importance of Viscosity in Atomization

It has been shown by the High-Frequency Reciprocating Rig (HFRR) test that castor oil methyl ester performs very well as a lubricity enhancer due to the hydroxyl group in methyl ricinoleate at concentrations of less than 1.0%.[15]. The viscosity measurements of Conceicao et al. [16] using a Brookfield model viscometer LV-DVII, found that castor oil had a higher viscosity than type D diesel oil, whereas the castor oil biodiesel had a lower viscosity than castor oil, but higher than type D diesel oil. This prompted them to blend castor oil biodiesel (FAME) with diesel oil. Blends of castor oil biodiesel to diesel oil were made in 5, 10, 15, 20, and 25% (v/v) of castor oil biodiesel to diesel oil. These blends on prolonged shear showed an increase in viscosity and return to its original viscosity once the shear is suspended. There was an increase in viscosity with a volume concentration increase of castor oil biodiesel in diesel oil.

Rheological studies [16] showed an increase in viscosity when the degradation of castor oil biodiesel was done over a period 1, 6, 12, 24, 36, 48 h at 150 °C and at 1,6,12, and 24 h at 210 °C. The viscosity of the 24 h sample run at 210 °C, showed an increase of viscosity by a factor of 6.8, compared to the 24 h run at 150 °C. There exists a problem of translating the shear rate from a viscometer to strokes in a diesel engine for thorough interpretation. Laboratory diesel engine tests and viscosity measured on both the neat and stroked fatty acid methyl esters would indicate the changes in viscosity leading to a correlation between strokes and viscosity to give insights into the atomization characteristics of biodiesel and its blends.

Ejim et al. [17] quote Lefebvre [18] in their study on atomization of biodiesels and their blends in an injector, that for significant atomization of a fuel, the values of viscosity, surface tension and density of the fuel should be well balanced. The function of atomization is to prepare the less volatile liquid fuels for progressive vaporization in suspension in turbulent air [19]. Atomization produces smaller droplets, large surface area and, in effect, easier progressive vaporization. Ejim et al. [17] studied atomization characteristics of 7 biodiesels and 17 binary and ternary blends with D1 and D2 diesel engines at 80 °C using a direct injector. They concluded that the most effective physical property for atomization was the contribution of viscosity of fuel being investigated. The appropriate drop size for atomization of fuel is the Sauter Mean Diameter (SMD) and is defined as the diameter of the drop whose ratio of volume to surface area is equal to that of the spray [18]. Ejim et al. [17] used the dimensionless correlation of Elkotb [20] to calculate SMD and found that a change in viscosity of the fuel has the maximum change ($\sim$90%) on SMD. It is beyond the scope of

this letter to present the quantitative details of SMD's correlation with viscosity, surface tension and density. Readers interested in this correlation should refer to Elkotb [20] and Ejim et al. [17] for application of SMD to biodiesel and its blends. The increase in viscosity of castor oil biodiesel/diesel oil blends [16] and oxidative polymerization of degraded castor oil biodiesel [7] will have a direct bearing on atomization as presented by [17].

Discussion

Thermal polymerization of methyl linolenate at 270 °C and the formation of gum for castor oil biodiesel at 210 °C, indicates that deleterious effects could be more pronounced at the diesel engine operating temperature of 900 °C. The changes in chemical structure due to thermal polymerization and oxidation of methyl linolenate, due to the three double bonds and reactive methylene groups in between the double bonds would alter the physical properties of linseed oil fatty acid methyl esters. In both the FAME there will be changes in viscosity affecting atomization. The use of methyl ricinoleate as a lubricity additive to diesel oil or a FAME is a better option than being used as a complete biodiesel [15].

The cetane number of linseed and castor oil FAME is not within the prescribed specifications of American and European biodiesel standards. This would result in ignition delays.

It would be prudent to study the oleochemistry of fatty acid methyl esters, by referring to published literature on neat fatty acid methyl esters with respect to temperature, pressure and flow properties. A rigorous way would be to perform laboratory engine tests before claiming that a single or blend of fatty acid methyl esters could be used as a complete biodiesel.

References

1. Varma N, Madras G (2007) Synthesis of biodiesel from castor oil and linseed oil in supercritical fluids. Ind Eng Res 46:1–6
2. Demirbas A (2009) Production of biodiesel fuels from linseed oil using methanol and ethanol in non-catalytic SCF conditions. Biomass Bioenergy 33(1):113–118
3. Turner J (1987) Linseed law. A handbook for growers and advisors, 2nd edn. BASF, UK
4. Kudchadkar A (1978) Castor oil cracking products. In: Mcketta JJ, Cunningham WA (eds) Encyclopaedia of chemical processing and design. Marcel Dekker, New York, pp 401–420
5. Paschke F, Wheeler DH (1955) Thermal polymerization of methyl linolenate, alpha- and beta-eleostearates. J Am Oil Chem Society. 32(9):469–473
6. Kirk Othmer (1979) Encyclopaedia of chemical technology, vol 5. Wiley, New York
7. Conceicao MM, Fernandes VJ, Araujo AS, Farias MF, Santos IMG, Souza AG (2007) Thermal and oxidative degradation of castor oil biodiesel. Energy Fuels 21:1522–1527
8. Santos JC, Souza AG, Santos IMG, Sobrinho EV, Fernandes VJ Jr, Silva AJN (2004) Thermoanalytical and rheological characterization of automotive mineral lubricants after thermal degradation. Fuel 83:2393
9. Bosch R (2004) Diesel engine management, 3rd edn. Professional Engineering Publishing Ltd, UK
10. Knothe G (2006) Analysing biodiesel: standards and other methods. J Am Oil Chem Soc 83(10):823–833
11. McCormick RL, Graboski MS, Alleman TL, Herring AM (2001) Impact of biodiesel source material and chemical structure on emissions of criteria pollutants from a heavy duty engine. Environ Sci Technol 35:1742–1747
12. Knothe G (2008) Designer biodiesel: optimizing fatty ester composition to improve fuel properties. Energy Fuels 22:1358–1364
13. Knothe G (2006) Biodiesel and vegetable oils: then and now. Intern News Fats Oils Relat Mater (INFORM) 17(11):729–731
14. Frankel EN (2005) Lipid oxidation, 2nd edn. Oily Press an imprint of PJ Barnes & Associates, England
15. Goodrum JW, Geller DP (2005) Influence of fatty acid methyl esters from hydroxylated vegetable oils on diesel fuel lubricity. Bioresour Technol 96:851–855
16. Conceicao MM, Candeia RA, Dantas HJ, Soledade LEB, Fernandez VJ, Souza GA (2005) Rheological behaviour of castor oil biodiesel. Energy Fuels 19:2185–2188
17. Ejim CE, Fleck BA, Amirfazli A (2005) Analytical study for atomization of biodiesels and their blends in a typical injector: surface tension and viscosity effects. Fuel 86:1534–1544
18. Lefebvre H (1989) Atomization and sprays. Hemisphere Publishing Corporation, New York
19. Joyce JR (1949) The atomization of liquid fuels for combustion. J Inst Fuel 22(124):150–156
20. Elkotb MM (1982) Fuel atomization for spray modelling. Prog Energy Combust Sci 8:61–91