IOP Conf. Series: Materials Science and Engineering **292** (2018) 012073 doi:10.1088/1757-899X/292/1/012073

Performance characteristics of rubber seed oil biodiesel

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Abstract. The lubricity, ignition quality, oxidative stability, low temperature flow property and elastomeric compatibility of rubber seed oil biodiesel(RSM) were evaluated and compared with conventional petro-diesel. The results indicated that RSM and its blends with petro-diesel possessed outstanding lubricity manifested by sharp decrease in wear scar diameters in the high-frequency reciprocating rig(HFRR) testing. They also provided acceptable flammability and cold flow property,although the cetane numbers (CN) and cold filter plugging points(CFPP) of biodiesel blends slightly decreased with increasing contents of petro-diesel. However, RSM proved to be very susceptible to oxidation at elevated temperatures during prolonged oxidation durations, characterized by increased peroxide values, viscosity, acid values and isooctane insolubles. The oxidation stability of RSM could be significantly improved by antioxidants such as BD100, a phenol antioxidant produced by Ciba corporation. Furthermore, RSM provided poor compatibility with some elastomeric rubbers such as polyacrylate, nitrile-butadiene and chloroprene, but was well compatible with the hydrogenated nitrile-butadiene elastomer.

1. Introduction

The study of biodiesel is not a new topic. Defined as the mono-alkyl esters of long chain fatty acids derived from renewable lipids such as vegetable oils and animal fats, biodiesel has proved to be a competent, environmentally friendly substitute for conventional petro-diesel since it provides very similar properties to those of mineral diesel fuels. In fact, the overall properties of biodiesel are determined predominantly by the sources of feedstocks, or in turn the structural features of the various individual fatty acids, especially chain length, degree of unsaturation, and branching of the chain [1-3]. Although in the past decades, vast amount of studies on the performances of biodiesel have been performed and reported [4-7], it is still important to fully understand how the various fatty acid profiles of different sources can influence biodiesel properties.

Rubber seed oil, a non-edible oil extracted from the seeds of rubber trees and also aco-product of natural rubber industry, with properties similar to linseed and soybean oil, has great potential for supplementing conventional biodiesel feedstocks since, because of reduced food availability, diversion of biodiesel feedstocks from traditional edible oils such as soybean, corn, sunflower, peanut, and rapeseed, to non-edible sources such as palm, castor, rubber seed and cotton seed, has in recent years gained continuously increasing interest [8-12]. But unfortunately, there are until now only a few studies concentrating on performance characteristics of rubber seed oil based biodiesel [13-14]. Further investigations on properties of rubber seed oil biodiesel are as such of important economical and practical significances. In the present investigation, some typical performances characteristics including lubricity, ignition quality, oxidation stability, low-temperature flow property and elastomeric

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compatibility of rubber seed oil biodiesel were evaluated and compared in relation to those of a conventional petro-diesel.

2. Experimental

2.1. Materials

Rubber seed oil biodiesel (RSM): a biodiesel fuel of rubber seed oil origin, provided by Prof. Dr. Yang Ru of Beijing University of Chemical Technology. The mass percentage of the main fatty acid compositions of RSM were 12.3% for palmitic acid, 2.9% for stearic acid, 29.6% for oleic acid, 37.5% for linoleic acid, and 17.1% for linolenic acid, respectively. Some typical physicochemical indices of RSM are presented in table 1.

Table 1. Typical physicochemical indices of RSM and petro-diesel.

parameter	RSM	Petro-diesel
density(20 ^{o}C)/(kg/m^3)	881	835
Kinematic viscosity/(mm^2/s)	4.06(40^{o}C)	4.60(20^{o}C)
flash point(closed cup)/^{o}C	150	65
sulfur / (m/m%)	0	0.119
acid value / (mgKOH/g)	0.22	-
free glycerin/ (m/m %)	0.016	-
total glycerin/ (m/m %)	0.02	-

Petro-diesel: No. 0 commercial petroleum-based diesel fuel obtained from a filling station of Sinopec Group. For comparison purpose, some typical physicochemical properties of the petro-diesel are also listed in table 1.

Biodiesel-petrodiesel blends: uniform blendings of a proper amount of RSM with petro-diesel on a volume basis, termed B×, where × is a number denoting the volume percent of RSM incorporated in a finished blend, e.g.B20，B50 and B80.

Elastomers: polyacrylate rubber (ACM, 60% of rubber content), hydrogenated nitrile-butadiene rubber (HNBR, 55% ofrubber content), nitrile-butadiene rubber (NBR, 50% of rubber content), chloroprene rubber (CR, 52% of rubber content).

Anti-oxidants：BD50 and BD100were commercially available from Ciba corporation, while1406 (phenol antioxidant) and 1407 (amine antioxidant) and MOA (phenol- amine antioxidant) were provided by Sinopec research institute of petroleum processing.

2.2. Lubricity test

Fuel lubricity affects durability of vehicle components such as fuel injector and fuel pump. The reduced lubricity of a fuel can be damaging to the engine and fuel systems.In this work, the lubricities of biodiesel blends, viz. B0, B20, B40, B60, B80 and B100, were evaluated respectively on a high-frequency reciprocating rig (HFRR) based on the ISO12156-1 method.The HFRR test involved a weighted steel ball and a stationary steel disk which was completely immersed in the test fuel.The ball and disk were heated to 60℃ and brought into contact with each other under the load of 10N and the entire apparatus was vibrated at 50 Hz for 75 min. There after the wear scar diameter (WSD) of the steel ball was measured and reported as the lubricity of the test fuel.

2.3. Ignition quality measurement

Cetane number (CN) is a prime indicator to specify the ignition quality of a diesel fuel, and is thus one of the most significant properties for determination of a fuel performance. Reflecting on the delay durations of ignition, cetane number ensures the readiness of a diesel fuel to autoignite when injected into the combustion chamber of an engine. The CN is generally dependent on the chemical compositions of a fuel. The higher the cetane values of a fuel, the shorter the ignition delay and thus

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better ignition quality. However,a cetane number that is too high or too low can lead to engine problems such as poor startability, high noise level and exhaust emissions. According to the international regulationon ASTM D613, the cetane number of a diesel fuel is commonly determined on a standardized mono-cylinder engine by comparing it to reference fuels of *n*-hexadecane (with an assigned CN=100) and 2,2,4,4,6,8,8-heptamethylnonane (with an assigned CN =15). In this work, the CNs of neat RSM and its blends with No. 0 conventional petro-diesel, namely, B0, B20, B40, B60, B80 and B100, were measured following the procedures of the Chinese method GB/T 386-2010, which well corresponds to the ASTM D613 in the CN determination.

2.4. Low-temperature fluidity test
Cold filter plugging point (CFPP), the temperature at which a fuel jams the filter due to the formation of agglomerates of crystals, is one of the most important indices related to low-temperature operability of diesel fuels. In the present work, CFPPs of various biodiesel blends were determined on a low-temperature flow tester following the Chinese SH/T0248 procedures which well corresponds to EN 116 method.

2.5. Oxidation stability test
Due to polyunsaturated fatty acid content, high oxidative instability of biodiesel is usually a special concern. Oxidation stability is therefore an important quality parameter for biodiesel since oxidation products originated with biodiesel affect storage life and contribute to deposit formation in tanks, fuel systems and filters. In the present study, the oxidation stability of RSM was tested based on the Chinese method SH/T0690, a method equivalent to ASTM D4625which is the most widely accepted method for assessing the storage stability of fuels. Specifically, RSM was oxidized at 43°C over an extended period of time up to 20 weeks. During oxidation experimentation, typical parameters such as peroxide values, kinematic viscosity, acid values and isooctane insolubles, of the aged RSM were determined every four weeks to characterize its oxidation stability.To further understand the oxidation characteristics of RSM, effects of some antioxidants on RSM oxidation stability were also evaluated (by determining peroxide values, kinematic viscosity, acid values and isooctane insoluble) based on the Chinese method SH/T 0175 which well corresponds to the ASTM D2274, and by determining oxidation induction periods based on the Rancimat method EN14112.

2.6. Elastomeric compatibility test
Some rubber elements in engines such as gaskets and seals can be exposed to oil and fuel. The physical, chemical and mechanical properties of the elastomeric materials can deteriorate during exposure to these fluids. The use of biodiesel as the diet of diesel engines may create unforeseenable problems with some elastomeric components,and resistant plastic materials are required.For this reason, the compatibility of different RSM biodiesel blends with four elastomeric elements which have been commonly used in diesel engines was tested in this study. The laboratory trials were conducted by immersing the elastomers with RSM biodiesel blends under atmospheric temperatures for 72 h. Thereafter, the changes in mass, volume and hardness of the elastomers before and after testing were determined to characterize the elastomeric compatibility of RSM.

3. Results and Discussion

3.1. Lubricity
Figure 1 shows the HFRR wear scar diameters tested with B0, B20, B40, B60, B80 and B100, respectively.

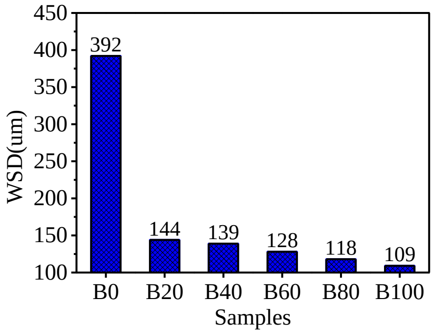


Figure 1. Wear scar diameters tested with biodiesel blends.

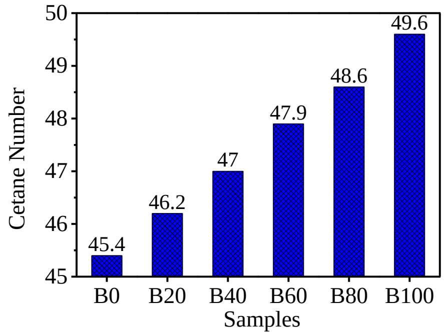


Figure 2. Cetane numbers of biodiesel blends.

It is clear from figure.1 that neat RSM and its blends with proper amount of petro-diesel provided outstanding lubricity with respect to neat petro-diesel. The lubricity of RSM biodiesel decreased with increasing contents of petro-diesel in a blend, indicating that petro-diesel to some extent impaired the lubricity of RSM. From practical point of view, excellent lubricity of RSM is very important to reduce engine wear and to protect the injection system. It can also be drawn from figure 1 that incorporation of RSM into petro-diesel markedly improved the lubricity of petro-diesel, manifested by sharp decrease in WSD. The excellent lubricity of RSM may be attributed to its unique FAME (fatty acid methyl esters) molecules, which adsorbed on or tribo-reacted with the friction surfaces to form a lubricious boundary protection film [15-16].

3.2. Ignition quality

Shown in figure 2 are the cetane numbers of B0, B20, B40, B60, B80 and B100, respectively. It can be found from figure 2 that the CN of neat RSM (B100) is higher than that of neat petro-diesel(B0), demonstrating that the flammability of RSM biodiesel is better than that of conventional No. 0 petro-diesel. The CNs of biodiesel blends from B80 to B20 slightly decreased with the increase of petro-diesel contents. According to the ASTM D6751 biodiesel standard, which prescribes a minimum of 47 for biodiesel cetane numbers in the United States, the cetane numbers of the RSM biodiesel blends are all acceptable, although in some European countries,higher cetane values of biodiesel are usually required.

3.3. Low-temperature Flow Property

The CFPPs of different RSM biodiesel blends, viz. B0, B20, B40, B60, B80 and B100, are listed in figure 3.

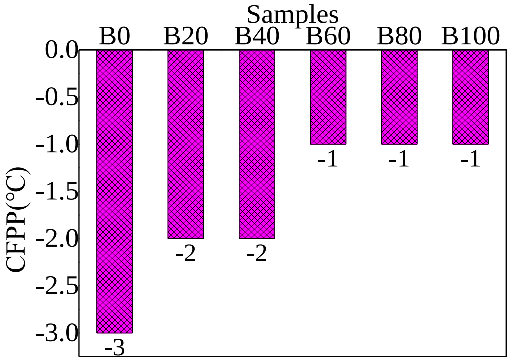
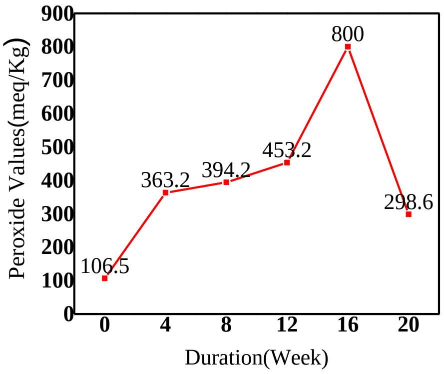


Figure 3. CFPPs of biodiesel blends.

We can see from figure 3 that CFPPs of the biodiesel blends, all below 0℃, were slightly different, although CFPPs increased with increasing contents of RSM in the blends. Virtually, CFPP of neat RSM was only 2℃ higher than that of conventional petro-diesel. The results demonstrated that RSM and its blends with petro-diesel provided acceptable cold flow property.

3.4. Oxidation Stability of RSM

Shown in figure 4, figure 5, figure 6, and figure 7 are peroxide values, viscosity, acid values and isooctane insolubles against oxidation durations for neat RSM, respectively.



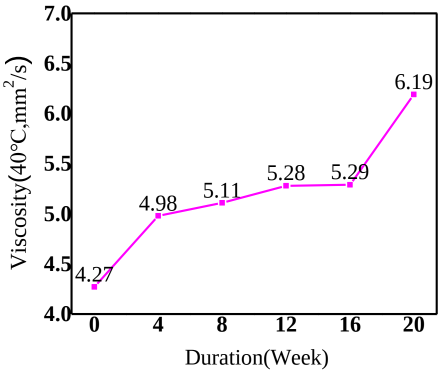
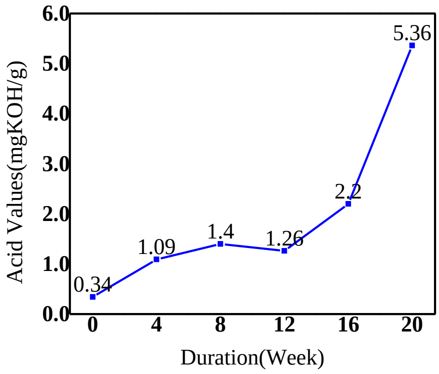


Figure 4. Peroxide values *vs*. test durations. **Figure 5.** Viscosity *vs.*test durations.



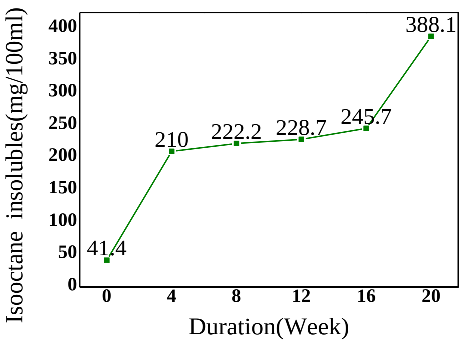


Figure 6. Acid values *vs.*test durations. **Figure 7.** Isooctane insoluble *vs.*test durations.

From figure 4 it can be clearly observed that, from the beginning of oxidation test onwards, the peroxide values of RSM increased with increasing test durations, followed by a sharp decrease after 16 weeks. The sharp decrease of peroxide values after 16 weeks may be ascribed to dramatic elimination of peroxides due to transformation to secondary oxidizers [17-18]. In figure 5, the viscosity of neat RSM increased gradually as the oxidation time increased because of oxidation polymerization and thus formation of viscous high molecular polymers [19]. In figure 6 shows that the acid values of RSM increased mildly from the beginning of the oxidation test up to 16 weeks, but markedly increased at 20 weeks. This well coincided with the sharp increase of peroxide values at 16 weeks shown in figure 4, and may be attributed to the substantial production of acidic oxidation products [20]. Concurrently, characterized by an all-along increase towards oxidation, the variation of isooctane insoluble with oxidation durations shown in figure 7 exhibited a very similar trend to those of peroxide values, viscosity and acid values. This well corresponded to continual oxidation polymerization and thus formation of polar polymeric materials as a result.

Table 2 gives the oxidation test results for RSM and its formulations with 1.0 wt.% of different antioxidants, in which the peroxide values, viscosity, acid values and isooctane insolubles were determined based on SH/T0175, while the induction periods determined based on EN14112.The results presented in table 2 show that the oxidation stability of RSM was significantly improved by the antioxidants, manifested by markedly increased induction periods and decreased peroxide values, viscosity, acid values, as well as insolubles.It can also be observed from table 2 that BD100 was the most effective antioxidizer. The mechanisms of antioxidants in inhibiting oxidation of RSM need further investigation.

Table 2. Oxidation results of RSM doped with oxidation inhibitors.

Test sample	Acid value (mgKOH/g)	Peroxide value (mg/kg)	Viscosity (40℃, mm^2/s)	Iso-octane insoluble (mg/100ml)	Induction period (*h*)
RSM	7.18	750.6	7.91	349.5	0.6
RSM+BD50	3.45	360.4	4.46	135.3	5.0
RSM+BD100	3.12	300.3	4.38	78.9	6.2
RSM+1407	4.09	561.5	6.57	304.2	3.1
RSM+1406	4.88	603.7	7.10	311.1	2.2
RSM+MOA	3.06	393.1	4.85	227.2	4.8

3.5. Elastomeric compatibility

Figure 8 and figure 9 show the changes in mass, volume and hardness of four elastomers ACM, CR, NBR and HNBR before and after immersion with RSM, respectively.

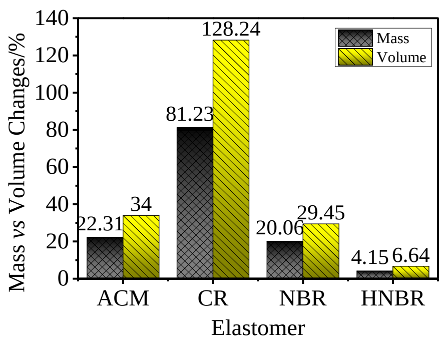


Figure 8. Mass *vs* Volume changes of elastomers after immersion with RSM.

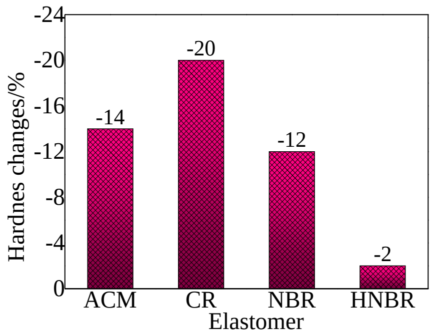


Figure 9. Hardness changes of elastomers after immersion with RSM.

It can be observed from figure 8 and figure 9 that, characterized by dramatic increases in mass, volume and hardness, the elastomers ACM, NBR and CR were to great extent degraded by RSM biodiesel blends, emonstrating that they were poorly compatible with RSM. Furthermore, it is also clear from figure 8 and figure 9 that ACM, NBR and CR were more severely deteriorated with increasing contents of RSM in the blends. Otherwise, the mechanical properties of HNBR were almost un-affected by RSM blends at whatever concentrations of RSM. This indicated that HNBR seemed to be an excellent RSM-resistant material, and is probably a promising elastomeric candidate for RSM-fueled engines.

4. Conclusions

The results of the present study revealed that rubber seed oil biodiesel and its blends with petro-diesel provided excellent lubricity, acceptable flammability and cold flow property, with respect to neat petro-diesel. However, RSM were prone to oxidation although the oxidation stability of RSM could be markedly enhanced by specific antioxidants such as BD100. Furthermore, RSM exhibited poor compatibility with many elastomers with the exception of hydrogenated nitrile-butadiene, which might be potential as a perspective elastomeric material for RSM-powered engines. The experimental results also provided the basis for future work regarding the performances and applicability of RSM/petro-diesel blends.

Acknowledgement

The authors gratefully acknowledge financial support of National Natural Science Foundation of China (project1 No. 51375491; project2 No. cstc2017jcyjAX0058)

References

[1] Gerhard K 2005 Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters *Fuel Processing Technology* **86** 1059-1070
[2] C A W Allen, K C Watts and R G Ackman 1999 Predicting the viscosity of biodiesel fuels from their fatty acid ester composition *Fuel* **78** 1319-1326
[3] Daniel P G and John W G 2004 Effects of specific fatty acid methyl esters on diesel fuel lubricity *Fuel* **83** 2351-2356
[4] Laforgia D and Ardito V 1995 Biodiesel fueled IDI engines: Performances, emissions and heat release investigation *Bio resource Technology* **51**(1) 53-59
[5] A E Atabani, A S Silitonga and I A Badruddin 2012 A comprehensive review on biodiesel as an alternative energy resource andits characteristics *Renewable and Sustainable Energy Reviews* **16** 2070-2093
[6] S K Hoekman, Amber B and Curtis Robbins 2012 Review of biodiesel composition, properties, and specifications *Renewable and Sustainable Energy Reviews* **16** 143-169
[7] Mustafa C, Ahmet E and Erol A 2006 Performance and exhaust emissions of a biodiesel engine

Applied Energy **83** 594–605
[8] H Sharon,K Karuppasamy and D R Soban Kumar 2012 A test on DI diesel engine fueled with methyl esters of used palm oil *Renewable Energy* **47** 160-166
[9] Masjuki Hj Hassan, Md Abul Kalam 2013 An overview of biofuel as a renewable energy source: development and challenges *Procedia Engineering* **56** 39-53
[10] D Huang,H Zhou and L Lin 2012 Biodiesel an Alternative to Conventional Fuel *Energy Procedia* **16** 1874-1885
[11] L Ranganathan, G Lakshmi Narayana Rao and S Sampath **2011** Experimental Investigation of a Diesel Engine Fuelled With Optimum Biodiesel Produced From Cotton Seed Oil *European Journal of Scientific Research* **62(1)** 101-115
[12] M A Fazal, A S M A Haseeb, H H Masjuki **2010** Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials *Fuel Processing Technology* **(91)** 1308-1315
[13] WW Liu etc, 2005 Preparation of biodiesel fuel with rubber seed oil rubber seed oil *China oils and fats* **30(10)** 63-66
[14] Ramadhas etc, 2005 Performance and emission evaluation of a diesel engine fueled with methyl esters of rubber seed oil *Renewable Energy* **30** 1789-1800
[15] Gerhard K and K R Steidley 2005 Lubricity of Components of Biodiesel and Petrodiesel.--The Origin of Biodiesel Lubricity *Energy & Fuels* **19** 1192-1200
[16] D P Geller and J W Goodrum 2004 Effects of specific fatty acid methyl esters on diesel fuel lubricity *Fuel* **83** 2351-2356
[17] N Kapilan, T P Ashok Babu and R P Reddy 2009 Technical Aspects of Biodiesel and its Oxidation Stability *International Journal of ChemTech Research* **1(2)** 278-282
[18] A Bouaid, M Martinez and J Aracil 2007 Long storage stability of biodiesel from vegetable and used frying oils J *Fuel* **86(16)** 2596-2602
[19] Knothe G 2007 Some aspects of biodiesel oxidative stability *Fuel Processing Technology* **88(7)** 669-77
[20] M C RL,Ratcliff M, Moens L and Lawrence R 2007 Several factors affecting the stability of biodiesel in standard accelerated tests *Fuel Processing Technology* **88(7)** 651-7