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Influence of fatty acid methyl esters from hydroxylated vegetable oils on diesel fuel lubricity

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Abstract

Current and future regulations on the sulfur content of diesel fuel have led to a decrease in lubricity of these fuels. This decreased lubricity poses a significant problem as it may lead to wear and damage of diesel engines, primarily fuel injection systems. Vegetable oil based diesel fuel substitutes (biodiesel) have been shown to be clean and effective and may increase overall lubricity when added to diesel fuel at nominally low levels. Previous studies on castor oil suggest that its uniquely high level of the hydroxy fatty acid ricinoleic acid may impart increased lubricity to the oil and its derivatives as compared to other vegetable oils. Likewise, the developing oilseed *Lesquerella* may also increase diesel lubricity through its unique hydroxy fatty acid composition. This study examines the effect of castor and *Lesquerella* oil esters on the lubricity of diesel fuel using the High-Frequency Reciprocating Rig (HFRR) test and compares these results to those for the commercial vegetable oil derivatives soybean and rapeseed methyl esters.

Keywords: Lubricity; Biodiesel; Castor; *Lesquerella*; Methyl esters; HFRR; Diesel fuel; Soybean oil; Rapeseed oil

1. Introduction

Castor is the only commercial source of vegetable oil containing hydroxylated fatty acids. Also significant, is that fact that one of these fatty acids, ricinoleic acid (C18:0, OH), comprises approximately 88–90% of the oil produced by castor (Da Silva Ramos et al., 1984). Ricinoleic acid is a complex fatty acid which contains both a double bond and a hydroxyl group. Castor oil also contains trace quantities of dihydroxystearic acid (~0.7%) which has two hydroxyl groups. Similarly, the developing crop plant *Lesquerella* also produces hydroxylated fatty acids. The primary fatty acid in *Lesquerella* oil is Lesquerolic acid, a hydroxy arachidonic acid (C20:1, OH). This acid can account for up to 69% of total fatty acid composition in this plant. *Lesquerella* can also produce densipolic acid (C18:2, OH), auricolic acid (C20:2, OH) and even traces of ricinoleic acid (C18:0, OH) (Hayes et al., 1995). Hydroxyl functionality is rare in plant oils and affords these oils some interesting chemical properties. The unique composition of castor oil has long facilitated its use in many different oleochemical applications and makes it and other hydroxyl vegetable oils interesting candidates for other innovative systems. The hydroxyl group is significant because it facilitates plasticization and adhesion of the oil esters, properties which are useful in a variety of applications such as plastics, inks and adhesives. In addition, hydroxyl groups may also afford castor and *Lesquerella* oil esters an increase in lubricity as compared to normal vegetable oil esters (Naughton, 1992). This increase in lubricity would make castor and *Lesquerella* oil esters prime candidates as additives for diesel fuel.

Vegetable oil methyl esters (biodiesel) are already being used as diesel fuel substitutes and extenders. They have been shown to be energy efficient and low emission

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sources of fuel for diesel engines. When added in concentrations of less than 5%, some of these compounds have been shown to provide a significant increase in lubricity to diesel fuels (Van Gerpen et al., 1999). This property is becoming increasingly valuable as recent legislation has mandated further regulation on the composition of diesel fuels including decreases in the sulfur content of diesel fuels. Unfortunately, these cleaner diesel fuels exhibit reduced lubricity as compared to their high sulfur predecessors (Anastopoulos et al., 2001). Although viscosity is not reduced in these new low sulfur fuels, the reduction in lubricity increases the danger of engine wear and damage (Van Gerpen et al., 1999). Finding additives that increase lubricity while not adding to exhaust emissions has become an important goal for the fuels industry. The fact that castor oil may exhibit more effective lubricity than other vegetable oil esters makes it an appealing candidate as a diesel additive. Finding other oil esters that could significantly increase diesel lubricity is also an important objective in this research.

The major objective of this study was to analyze the effectiveness of castor and *Lesqurella* oil esters as lubricity enhancers for diesel fuel and compare their performance to methyl esters of the other oils studied here. The High-Frequency Reciprocating Rig (HFRR) ASTM testing method was used as an analytical tool for this purpose. The HFRR test uses a steel ball to apply force to a rotating disk thereby creating a wear scar on the disk. A series of tests were performed using different concentrations of castor and *Lesquerella* oil esters in mixtures with diesel fuel. The results of these tests are compared to those obtained for soybean and rapeseed oil methyl ester.

Previous studies have shown that castor has improved lubricity over other oils with similar carbon chain-length fatty acids (Drown et al., 2001). The hypothesis was that the hydroxylated fatty acids of ricinoleic acid in castor oil impart it better performance as lubricity enhancer than other common vegetable oil esters. This study tests this theory by including *Lesquerella* oil methyl ester in the study. It is believed that the uniquely high level of hydroxylated fatty acids in *Lesquerella* oil methyl ester would also increase its relative effectiveness as a lubricity enhancer.

2. Methods

2.1. HFRR testing

High-Frequency Reciprocating Rig (HFRR) testing was performed by Williams Laboratory Services (Kansas City, KS) and Southwest Research Institute (San Antonio, TX). The HFRR test (ASTM D6079) used in this study involves a weighted steel ball and a stationary steel disk which is completely submerged in a test fuel. The ball and disk are heated to 60 °C and brought into contact with each other and the entire apparatus is vibrated at 50 Hz for 75 min. The diameter of the wear scar left on the ball is measured under a microscope; this value is reported as the HFRR test result. The International Standards Organization (ISO) and Engine Manufacturers Association (EMA) both agree on a 0.45 mm maximum wear scar limit for diesel used in standard engines (ISO 12156-1; EMA-FQP-1A). Rapeseed oil methyl ester, Castor oil methyl ester and Soybean Oil Methyl Ester were analyzed four times each at 0.10%, 0.25%, 0.50% and 1.00% concentrations in reference diesel fuel and two times each at 3.00% and 5.00% concentrations. Lesquerella oil methyl esters were analyzed two times at 0.10%, 0.25%, 0.50%, 1.00%, 3.00% and 5.00% concentrations.

2.2. Vegetable oil methyl esters

Castor oil methyl ester was provided by CasChem, Inc. (Bayonne, NJ). *Lesquerella fendleri* oil methyl ester was provided by the USDA (Peoria, IL). Soybean oil methyl ester was obtained from Griffin Industries, Inc. (Cold Spring, KY). Rapeseed oil methyl ester was from the laboratory of Dr. Charles Peterson at The University of Idaho (Moscow, ID). Reference Diesel Fuel: All diesel fuel was certified 0.05% sulfur diesel fuel from Chevron-Philips (Borger, TX).

2.3. Fatty acid analysis

Castor oil methyl ester fatty acid profile analysis was provided by Woodson Tenet laboratories (Memphis, TN) using ASTM method D1983-90. Analysis of Soybean and Rapeseed methyl esters was provided by the supplier of each sample using the same method ASTM D1983-90. *Lesquerella fendleri* methyl ester was analyzed by the USDA (Peoria, IL) via gas chromatography using a Supelco (St. Louis, MO) SP-2380 column. Independent analyses conducted on samples drawn from methyl esters used in lubricity analyses.

2.4. Statistical analysis

Standard deviation and standard error for HFRR repetitions were calculated and plotted using Microsoft Excel. Analysis of Variance on HFRR results was performed using the College of St. Benedict's (St. Joseph, MN) online ANOVA applet at http://www.physics.csbsju.edu/stats/anova_NGROUP_NMAX_form.html. As only castor, soybean and rapeseed oil methyl esters were analyzed by HFRR more than twice, ANOVA was performed on these sample sets.

3. Results and discussion

The results of HFRR testing on mixtures of diesel fuel with castor, *Lesquerella*, rapeseed and soybean oil esters are shown in Fig. 1. The esters were mixed with reference diesel fuel at the following concentrations: 0.10%, 0.25%, 0.50%, and 1.00% on a mass basis. The properties of this reference fuel are shown in Table 1. To examine the effects of additive concentrations beyond 1.00%, the analysis was repeated with higher mass concentrations of methyl esters; 0.5%, 3.0% and 5.0% as shown in Fig. 2. The 100% reference diesel was tested in each analysis and the value is given in the respective figures. In this test, the smaller the wear scar, the better performance of the lubricant. The measured HFRR wear scar values were within 4% of each other for 0.50% concentrations in each set of tests, suggesting these analyses were comparable but not identical; therefore the data from each set of tests is reported separately and analyzed relative to the reference diesel sample examined in each test. Analysis of variance on the data verified that the results shown are legitimately due to the variation in additive concentration as the probability of the observed results assuming the null hypothesis was less than 0.003. Standard error bars are included in both figures as further illustration of the statistical validity of the data.

It was found that castor oil methyl esters enhanced lubricity most effectively at all concentrations. It can also be noted that *Lesquerella* oil methyl ester exhibits very similar lubricity behavior. Both show improvement consistent with the recommended 0.45 mm wear scar limit at concentrations as low as 0.25%. Observations in Figs. 1 and 2, suggest that at a concentration slightly higher than 1.0%, castor and *Lesquerella* oil methyl ester lubricity enhancement begins to level off. That is, as the additive concentration is increased, a dramatic increase in lubricity is no longer seen. Interestingly, almost identical behavior of soybean and rapeseed oil methyl ester at the lower concentrations is apparent in data from the plots in Fig. 1. At 1.0% it can be noted that soybean methyl ester begins to show a marked improvement over rapeseed methyl ester. A dramatic increase in soybean oil methyl ester performance is observed as the concentration is increased beyond 1.0%. This is consistent with the jump in performance that is observed for soybean oil methyl ester in Fig. 1 as the concentration approaches 1.0%. However the same dramatic increase in lubricity is not observed with rapeseed oil methyl ester, suggesting it may require higher concentration before significantly increasing diesel fuel lubricity.

Variation in lubricity enhancement properties is evident between the uniquely composed castor and *Lesquerella* oils and the major agronomic oils from soy and rapeseed. The fatty acid composition of each of the oils studied here is shown in Table 2. Rapeseed and soy oils have relatively similar compositions. This is especially obvious when one looks at the concentrations of unsaturated compounds such as oleic acid. In contrast to this, castor and *Lesquerella* oils are significantly different due to the presence of hydroxyl fatty acids such as ricinoleic acid and dihydroxystearic acid in castor oil and lesquerolic acid in *Lesquerella* oil. Not only is ricinoleic acid

Table 1
Properties of 0.05% sulfur diesel type 2 (Chevron Phillips, 2004)

Tests	Results	Specifications	Method
Specific gravity, 60/60	0.8440	0.8398–0.8659	ASTM D-4052
API gravity	36.15	32–37	ASTM-D1298
Sulfur, Wt%	0.0317	0.03–0.05	ASTM-D2622
Viscosity, cs 40 °C	2.61	2.0–3.2	ASTM-D-455
Cetane number	47.3	46–48	ASTM D-613
Distillation			ASTM D-86
IBP	368.7 °F	340–400 °F	
5%	410.2 °F		
10%	424.8 °F	400–460 °F	
15%	437.3 °F		
20%	449.5 °F		
30%	469.5 °F		
40%	484.4 °F		
50%	497.8 °F	470–540 °F	
60%	511.5 °F		
70%	527.7 °F		
80%	550.3 °F		
90%	586.1 °F	560–630 °F	
95%	620.6 °F		
EP	654.0 °F	610–690 °F	
Loss	0.7%		
Residue	1.0%		
Hydrocarbon type	Vol. %		ASTM D-1319
Aromatics	29.0%	28–32%	
Olefins	1.1%		
Saturates	69.0%		

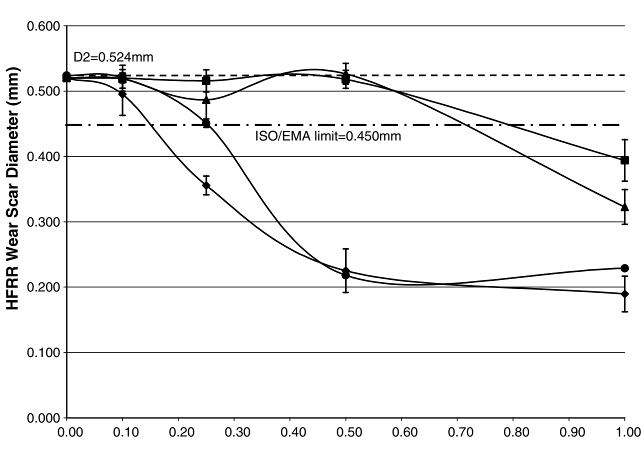

Fig. 1. HFRR lubricity evaluation for Castor (-♦-), *Lesquerella* (-●-), Soybean (-▲-) and Rapeseed (-■-). Methyl esters at low concentrations in diesel fuel. Vertical bars represent standard error for 4 repetitions except for *Lesquerella* which was based on 2 repetitions.

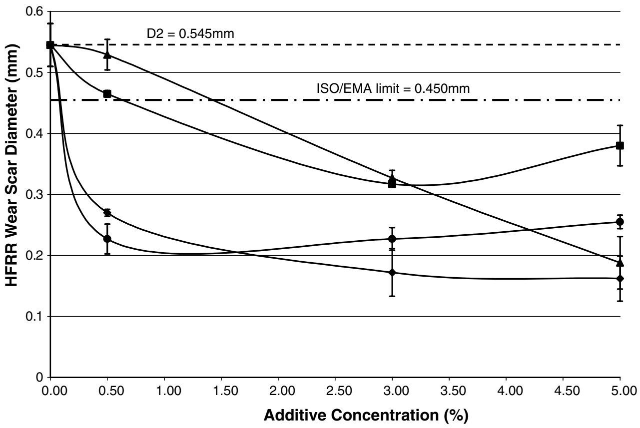

Fig. 2. HFRR lubricity evaluation for Castor (-♦-), *Lesquerella* (-●-), Soybean (-▲-) and Rapeseed (-■-). Methyl esters at elevated concentrations in diesel fuel (average of two repetitions). Vertical bars represent standard error for 2 repetitions.

unique to castor oil, but it comprises nearly all of the oil. Likewise, lesquerolic acid comprises over half of *Lesquerella* oil composition. In addition both of these major components are unsaturated as well as hydroxylated. This variation in composition likely had a significant effect on the lubricating properties of these esters (Drown et al., 2001). HFRR values for castor and *Lesquerella* oil ester enhanced diesel fuel were consistently lower than those for fuel with soy and rapeseed ester additives indicating these oils are performing better as lubricity enhancers. Also it should be noted that at low concentrations (0.1–1.0%), soy and rapeseed additives displayed nearly identical behavior which was expected due to their similar fatty acid methyl ester profiles. *Lesquerella* oil based additive followed castor behavior closely showing dramatic increases in diesel fuel lubricity at low additive concentration.

Previous studies have examined the lubricity enhancing qualities of rapeseed, soybean and castor oil methyl esters (Drown et al., 2001; Van Gerpen et al., 1999). However, this property has not been previously reported for *Lesquerella* oil methyl ester. Drown et al. (2001) reported results similar to those presented here for the aforementioned, previously studied esters. Despite the fact that the JP-8 reference fuel used in their study was of different origin and had a higher baseline HFRR score of 0.740 mm; their reported HFRR results for all three additives at concentrations of 0.50% and 1.00% were within 10% of the results reported here. At lower concentration (0.10%), the HFRR scores from these two independent studies show great disparity, on the order of 35–50%. This data correlation is significant as it is consistent for three of the vegetable based additives studied here. This pattern suggests that at lower additive concentrations, the lubricity of the mixture is controlled by the lubricity of the fuel itself. However, it may be possible that there is a threshold concentration after which the additive itself has a greater influence on the overall lubricity of the mixture. Such a concept would explain the consistency of data at higher additive concentrations between the two studies which used reference fuels of significantly different baseline lubricity.

To be an effective diesel additive, optimum lubricity improvement should be achieved at a concentration less than 1.0%. A value similar to acceptable concentrations frequently used for additives to increase cetane, reduce moisture content, and other components. That is the point at which addition of more additive does not significantly increase lubricity, should be less than 1.0%. The trends seen here suggest that castor and *Lesquerella* oil

Table 2
Fatty acid profile of vegetable oil methyl esters

Triglyceride	Name	Castor	*Lesquerella*	Rapeseed	Soybean
C14:0	Myristic	*	*	*	0.56
C14:1	Myristoleic	*	*	*	0.18
C16:0	Palmitic	0.86	1.00	2.70	14.17
C16:1	Palmitoleic	*	0.60	*	1.27
C16:2	Hexadecanoic	*	*	*	0.24
C18:0	Stearic	1.01	1.70	0.90	5.19
C18:0, 2OH	Densipolic	0.70		*	*
C18:1	Oleic	2.63	16.70	12.60	48.20
C18:1, OH	Ricinoleic	89.54	0.50	*	*
C18:2	Linoleic	4.10	6.80	12.10	22.19
C18:3	Linolenic	0.36	11.40	8.00	1.45
C18:4	Octadecatetraenoic	0.29		*	*
C20:0	Arachidic	0.16	0.80	*	0.28
C20:1	Eicosenoic	0.35		7.40	*
C20:1, OH	Lesquerolic	*	56.30	*	*
C20:2, OH	Auricolic	*	3.50	*	*
C22:0	Behenic	*	*	0.70	*
C22:1	Erucic	*	*	49.80	*

* Component not detected in methyl ester.

methyl esters are functioning as effective lubricity enhancers. It is important to note that wear scar diameters were reduced to acceptable levels for these hydroxylated additives at 0.25% or less. Soybean oil methyl ester did not show a dramatic increase in performance until concentrations were at or above 1.0%. Rapeseed oil methyl ester never showed as dramatic an improvement, even at concentrations as high as 5.0%.

4. Conclusions

Lubricity analysis by HFRR shows that castor oil methyl ester performs quite well as a lubricity enhancer for diesel fuel at concentrations less than 1.0%, giving our reference diesel fuel an acceptable level of lubricity at 0.20% concentration. Likewise, HFRR data confirmed that similarly composed *Lesquerella* oil methyl ester also enhanced lubricity to acceptable levels at concentrations as low as 0.25%. Soybean and rapeseed methyl esters do not show such dramatic improvement in diesel lubricity at concentrations less than 1.0%. It is not until higher levels of these non-hydroxylated methyl esters are added that a significant improvement in lubricity can be observed. It is believed that the high concentration of the unique fatty acid methyl ester, methyl ricinolate could be responsible for the lubricity enhancing properties of castor oil methyl ester. Similarly, the hydroxy fatty acids lesquerolic acid and auricolic acid may influence the lubricity enhancing effects of *Lesquerella* oil methyl esters. Another significant observation is that the major fatty acid components of castor (ricinoleic acid, 89.54%) and *Lesquerella* (lesquerolic acid, 56.30%) are not only both hydroxylated, they are both unsaturated, each having one double bond. It is suggested that this unique fatty acid profile may impart castor and *Lesquerella* oil methyl esters with exceptional value as diesel fuel additives. This is in general agreement with the preliminary castor fatty acid methyl ester results of Drown et al. (2001).

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