Available online at www.sciencedirect.com

SCIENCE DIRECT®

Bioresource Technology 96 (2005) 851–855

BIORESOURCE TECHNOLOGY

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

John W. Goodrum *, Daniel P. Geller

Department of Biological and Agricultural Engineering, University of Georgia, Athens, GA 30602, USA

Received 29 March 2004; received in revised form 6 July 2004; accepted 6 July 2004
Available online 16 September 2004

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

* Corresponding author. Tel.: +1 706 542 0867; fax: +1 706 542 8806.
E-mail address: jgoodrum@engr.uga.edu (J.W. Goodrum).

0960-8524/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2004.07.006

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.