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Research

Research in my laboratory is primarily focused on the synthesis and evaluation of lipid-derived additives to address one or more technical deficiencies of biodiesel, such as low temperature fluidity or oxidative stability. Principles of green chemistry and economic efficiency when designing synthetic strategies are emphasized. Other areas of related research include evaluation of alternative feedstocks for biodiesel use, correlation of structure and composition to fuel properties of biodiesel, and elucidation of the effects of blending biodiesel ultra low sulfur diesel fuel (ULSD, < 15 ppm S).

Synthesis and evaluation of oleochemicals as additives for biodiesel

Although biodiesel, defined as the monoalkyl esters of vegetable oils or animals fats, enjoys many advantages over conventional petrodiesel, such as derivation from a renewable domestic resource, improved lubricity and biodegradability, higher flash point, lower toxicity, and reduction of most exhaust emissions, there are important areas where biodiesel fuel remains inferior to petrodiesel, which include storage stability, cold weather operability, and NO_x exhaust emissions. The additive approach to address one or more of the deficiencies of biodiesel is undertaken in this study whereby a number of novel lipid-derived branched-chain ethers were synthesized and subsequently evaluated, both neat and at additive levels in biodiesel fuel. The branched-chain ethers produced in this series of studies showed enhanced low temperature operability over soybean oil methyl esters (SME), which is presumably due to the alkoxy branching moiety introduced into the lipid backbone. Furthermore, the branched-chain ethers showed improved oxidation stability over that of SME, which is due to the elimination of unsaturation from the lipid backbone. Thus far at additive levels in SME the branched-chain ethers show little to no improvement in the low temperature operability of the fuel and have, as expected, no anti-oxidant effect. Further investigation whereby additional branching is introduced into the fatty acid backbone of lipid-derived materials is currently underway. *For more information, please see publications 4, 9, and 11 from the list below.*

Evaluation of partially hydrogenated soybean oil methyl esters as biodiesel
Standards mandating biodiesel quality, such as EN 14214 and ASTM D6751, can limit feedstock choice in the production of biodiesel fuel. For instance, EN 14214 contains a specification for iodine value (IV < 120) that eliminates soybean oil as a potential feedstock, as it generally has an IV > 120. Therefore, partially hydrogenated soybean oil methyl esters (PHSME, IV = 116) were evaluated as biodiesel by measuring a number of fuel properties, such as oxidative stability, low temperature performance, lubricity, kinematic viscosity, and specific gravity. Compared to SME, PHSME has superior oxidative stability, similar specific gravity, but inferior low temperature performance, kinematic viscosity, and lubricity. The kinematic viscosity and lubricity of PHSME however were within US and European specifications. There is no set value for low temperature performance in biodiesel specifications, but PHSME has superior cold flow behavior when compared to other alternative feedstock fuels, such as palm oil, tallow and grease methyl esters. The production of PHSME from refined soybean oil would increase biodiesel production costs by US$0.15/gal in comparison to SME. In summary, PHSME is within both the European and American standards for all properties measured in this study and deserves consideration as a potential biodiesel fuel. *For more information, please see publication 10 from the list below.*

Soy-based fluids as lubricants and additives
Several diesters were prepared from commercially available oleic acid and common organic acids. The key step in the three step synthesis of oleochemical diesters entails a ring opening esterification of alkyl 9,10-epoxyoctadecanoates (alkyl: propyl, isopropyl, octyl, 2-ethylhexyl) using propionic and octanoic acids without the need for either solvent or catalyst. Each synthetic diester was evaluated for both low temperature operability and oxidation stability through measurement of cloud point, pour point, oxidation onset temperature, and signal maximum temperature. It was discovered that increasing chain length of the mid-chain ester and branching in the end-chain ester had a positive influence on the low temperature properties of diesters. Improved oxidation stability is achieved when the chain length of the mid-chain ester is decreased. Additionally, the mid-chain ester plays a larger role in oxidation stability than the end—chain ester. These products may prove useful in the search for bio-based industrial materials, such as lubricants, surfactants, and fuel additives. *For more information, please see publications 7, 8, and 12 from the list below.*

Derivatives of castor and lesquerella oils as fuel additives

The use of petroleum-derived additives is ubiquitous in fuels production, including biodiesel (BD) and ultra-low sulfur diesel (ULSD) fuels. Development and employment of domestically derived, biodegradable, renewable, and non-toxic additives is an attractive goal. As such, estolides and 2-ethylhexyl esters derived from castor and lesquerella oils, due to their excellent low temperature, lubrication, and oxidation stability properties, were investigated as potential fuel additives in soybean oil methyl esters (SME), palm oil methyl esters (PME), and ULSD. With respect to SME and PME, low temperature operability improvement utilizing these materials at low blend ratios (≤ 5 wt %) was of interest. Although cloud point (CP) and pour point (PP) of SME were unaffected, PP of PME was improved by 3 ^{o}C, indicating that these materials may be useful as pour point depressants for PME in moderate temperature climates. With respect to ULSD, improvement of lubricity was of interest. All materials imparted significantly improved lubricity to ULSD at low blend ratios (≤ 2 wt %). In fact, the 2-ethylhexyl esters were superior to SME and PME as lubricity enhancers in ULSD. The estolides imparted superior lubricity to ULSD when compared to PME. These results indicate that all of these materials would be as or more effective lubricity enhancers in ULSD than SME and PME. Kinematic viscosity of blends of these materials in SME, PME, and ULSD tended to increase with increasing level of additive, but all values were within prescribed relevant kinematic viscosity fuel specifications. In summary, bio-based materials, such as estolides and 2-ethylhexyl esters derived from castor and lesquerella oils**,** have potential as fuel additives in BD and ULSD. *For more information, please see publication 5 from the list below.*

Alternative feedstocks for biodiesel production

Biodiesel is an alternative to petroleum-based conventional diesel fuel and is defined as the mono-alkyl esters of vegetable oils and animal fats. Biodiesel has been prepared from numerous vegetable oils, such as canola (rapeseed), cottonseed, palm, peanut, soybean and sunflower oils as well as a variety of less common oils. In this work, *Moringa oleifera* is reported for the first time as potential feedstock for biodiesel. After acid-pretreatment to reduce the acid value of *M. oleifera* oil, biodiesel was obtained by a standard transesterification procedure with methanol and an alkali catalyst at 60^{o}C and alcohol/oil ratio of 6:1. *M. oleifera* oil has a high content of oleic acid (> 70%) with saturated fatty acids comprising most of the remaining fatty acid profile. As a result, the methyl esters obtained from this oil exhibit a high cetane number of approximately 67, one of the highest found for a biodiesel fuel. Other fuel properties of biodiesel derived from *M. oleifera* such as cloud point, kinematic viscosity and oxidative stability were also determined and are discussed in light of biodiesel standards such as ASTM D 6751 and EN 14214. The ^{1}H-NMR spectrum of *M. oleifera* methyl esters is reported. Overall, *M. oleifera* appears to be an acceptable feedstock for biodiesel. *For more information, please see publications 2, 3, and 17 from the list below.*

Oxidative stability of biodiesel

A natural antioxidant which is found in many fruits, vegetables, and other plants, myricetin (a flavonol) was evaluated as a potential antioxidant additive for SME. A comparison of the efficacy of myricetin with common natural (α-tocopherol) and synthetic (TBHQ) antioxidants was also performed. Myricetin was found to be superior to the natural antioxidant, and was nearly as effective as the synthetic antioxidant. Furthermore, the oxidative stability, as determined by Rancimat (EN 14112), pressurized differential scanning calorimetry (PDSC), and thermogravimetric (TGA) accelerated methods, of individual components of biodiesel is currently under investigation. Of interest is the effect of double bond orientation (*cis* versus *trans* configurations), fatty acid chain length, and number and location of double bonds on the oxidative stability of biodiesel. *For more information, please see publication 18 from the list below.*

Blend studies of biodiesel in ultra-low sulfur diesel fuel

Currently the primary use for biodiesel in on-road applications is as a blend with ultra-low sulfur diesel fuel (ULSD). Generally, depending on state tax laws, the blend ratio of biodiesel may range from 1 to 20% (B1 – B20). However, the effect of biodiesel at these levels on the physical and chemical properties of ULSD is poorly understood. Furthermore, often the actual blend ratio of biodiesel to ULSD in a commercial setting does not match what is reported. Therefore, the objectives of the current study are to measure a number of physical and chemical properties of biodiesel-ULSD blends to learn more about how blending affects bulk fuel properties. Additionally, correlation of physical and chemical properties with blend ratio is also of interest as a means to develop quick and reliable test methods for biodiesel blend ratios in ULSD. *For more information, please see come back later, as this work is currently in preparation for future publication.*

Effects of blending biodiesel from different feedstocks on fuel properties

Single, binary, ternary, and quaternary mixtures of canola (low erucic acid rapeseed), palm, soybean, and sunflower (high oleic acid) oil methyl esters (CME, PME, SME, and SFME, respectively) were prepared and important fuel properties measured, such as oil stability index (OSI), cold filter plugging point (CFPP), cloud point (CP), pour point (PP), kinematic viscosity (40 ^{o}C), lubricity, acid value (AV) and iodine value (IV). The fuel properties of SME were improved through blending with CME, PME, and SFME to satisfy the IV (< 120) and OSI (> 6 h) specifications contained within EN 14214, the biodiesel standard from the European Committee for Standardization. SME was satisfactory according to ASTM D6751, the American biodiesel standard, with regard to OSI (> 3 h). The CFPP of PME was improved by up to 15 ^{o}C through blending with CME. Statistically significant relationships were elucidated between OSI and IV, OSI and saturated fatty acid methyl ester (SFAME) content, OSI and CFPP, CFPP and IV, and CFPP and SFAME content. However, the only relationship of practical significance was that of CFPP versus SFAME content when SFAME content was greater than 12 weight percent. *For more information, please see publication 19 from the list below.*

Synthesis of anticancer natural products

In graduate school, the focus of my research under the direction of Dr. George Robert Pettit of the Arizona State University Cancer Research Institute was the synthesis of anticancer natural products and their derivatives. Specifically, the total synthesis of the potent antineoplastic agent combretastatin A-2 was accomplished, along with a number of water-soluble prodrug derivatives. Additionally, synthesis of analogues of the extremely potent anticancer compound, cephalostatin 1, was accomplished. *For more information, please see publications 1, 6, 13, 14, and 15 from the list below.*

PUBLICATIONS

1. G.R. Pettit. A.J. Thornhill, **B.R. Moser**, F. Hogan, Antineoplastic Agents 552. Oxidation of Combretastatin A-1: Trapping the *o*-Quinone Intermediate Considered the Metabolic Product of the Corresponding Phosphate Prodrug. *J. Nat. Prod.* (accepted)

2. U. Rashid, F. Anwar, **B.R. Moser**, Optimization and Characterization of Alkali-Catalyzed Methanolysis of Sunflower Oil. *Biomass and Bioenergy* (in press) doi:10.1016/j.biombioe.2008.03.001.

3. U. Rashid, F. Anwar, **B.R. Moser**, G. Knothe, *Moringa oleifera* Oil: A Possible Source of Biodiesel. *Bioresource Technology* (in press) doi:10.1016/j/biortech.2008.03.066.

4. **B.R. Moser**, S.Z. Erhan, α-Hydroxy Ether Derivatives of Alkyl Oleates: Tribological, Rheological, Oxidation, and Low Temperature Properties. *Fuel* **2008**, *87*, 2253-2257.

5. **B.R. Moser**, S.R. Cermak, T.A. Isbell, Evaluation of Castor and Lesquerella Oil Derivatives as Additives in Biodiesel and Ultra Low Sulfur Diesel Fuels. *Energy & Fuels* **2008**, *22*, 1349-1352.

6. **B.R. Moser**, Review of Cytotoxic Cephalostatins and Ritterazines: Isolation and Synthesis. *J. Nat. Prod.* **2008**, *71*, 487-491.

7. K.M. Doll, **B.R. Moser**, B.K. Sharma, S.Z. Erhan, Surface tension studies of methyl esters and epoxidized methyl esters relevant to oleochemical based fuel additives. *Energy & Fuels* **2007**, *21*, 3044-3048.

8. **B.R. Moser**, B.K. Sharma, K.M. Doll, S.Z. Erhan, Diesters From Oleic Acid: Synthesis, Low Temperature Properties, and Oxidation Stability. *J. Am. Oil Chem. Soc.* **2007**, *84*, 675-680.

9. **B.R. Moser**, S.Z. Erhan, Preparation and Evaluation of a Series of α-Hydroxy Ethers from 9,10-Epoxy-stearates. *Eur. J. Lipid Sci. Technol.* **2007**, *109*, 206-213.

10. **B.R. Moser**, M.J. Haas, J.K. Winkler, M.A. Jackson, S.Z. Erhan, G.R. List, Evaluation of Partially Hydrogenated Soybean Oil Methyl Esters as Biodiesel. *Eur. J. Lipid Sci. Technol.* **2007**, *109*, 17-24.

11. **B.R. Moser**, S.Z. Erhan, Synthesis and Evaluation of a Series of α-Hydroxy Ethers Derived from Isopropyl Oleate. *J. Am. Oil Chem. Soc.* **2006**, *83*, 959-963.

12. K.M. Doll, **B.R. Moser**, B.K. Sharma, S.Z. Erhan. Current Uses of Vegetable Oil in the Surfactant, Fuel, and Lubrication Industries. *Chimica Oggi/Chem. Today* **2006**, *24*, 41-44.

13. G.R. Pettit, **B.R. Moser**, Preparation of Combretatatin A-2 Prodrugs as Antitumor and Antimicrobial Agents. U.S. Patent WO 7,105,695. **2006** (Sept. 15).

14. **B.R. Moser**, Synthesis of Combretastatin A-2 Prodrugs and Cephalostatin 1 Structural Analogues, Ph.D. dissertation, **2004**, Arizona State University, Tempe, AZ.

15. G.R. Pettit, **B.R. Moser**, M.R. Boyd, J.M. Schmidt, R.K. Pettit, J.C. Chapuis, Antineoplastic Agents 460. Synthesis of Combretastatin A-2 Prodrugs. *Anti-Cancer Drug Design* **2001**, *16*, 185-193.

16. P. Suarez, **B.R. Moser**, B.K. Sharma, S.Z. Erhan, Comparing the Lubricity of Biofuels Obtained from Pyrolysis and Alcoholysis of Soybean Oil and their Blends with Petroleum Diesel. *Fuel* (submitted).

17. H.C. Joshi, J. Toler, **B.R. Moser**, T. Walker, Biodiesel from Canola Oil Using an Equimolar Mixture of Ethanol and Methanol. *Eur. J. Lipid Sci. Technol.* (submitted).

18. **B.R. Moser**, Efficacy of Myricetin as an Antioxidant in Methyl Esters of Soybean Oil. *Eur. J. Lipid Sci. Technol.* (submitted).

19. **B.R. Moser**, Influence of Blending Canola, Palm, Soybean, and Sunflower Oil Methyl Esters on Fuel Properties of Biodiesel. *Energy & Fuels* (submitted).

20. R.O. Dunn, S.Z. Erhan, G. Knothe, **B.R. Moser**, Fuel Properties and Performance of Biodiesel, in *Biocatalysis and Bioenergy*, John Wiley & Sons, Company: New York (book chapter - accepted).

21. R.O. Dunn, **B.R. Moser**, Low Temperature Operability of Biodiesel, in *The Biodiesel Handbook, 2nd Ed.*, AOCS Press: Champaign, IL (book chapter – in preparation).

Last Updated 6/24/08