RU: Food and Industrial Oil Research, National Center for Agricultural Utilization Research, Peoria, IL

Current research project:
Improving the Performance of Alternative Fuels and Co-products from Vegetable Oils.

Objective:
Biodiesel is an alternative diesel fuel derived from vegetable oils, animal fats or used oils. While it is competitive with (in some aspects even technically superior to) conventional, petroleum derived diesel fuel, its use is still affected by several technical issues that hinder more widespread commercialization. Therefore, this project proposes to improve the combustion characteristics and fuel properties of vegetable oils (emphasizing soybean oil) and their derivatives as alternative diesel fuels, extenders, and additives in the operation of compression ignition (diesel) engines for on road and off road applications. Fatty derivatives will be utilized for performance enhancement and exhaust emission reduction (e.g. nitrogen oxides). Specific objectives for this project include: 1) improved cold weather start up and operability performance, 2) novel fuel formulations that reduce regulated exhaust emissions such as nitrogen oxides, 3) improvement of fuel quality through enhanced oxidative stability and development of new, rapid analytical methods for assessing biodiesel fuel quality, and 4) development of specialty chemicals from biodiesel co-products.

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Key accomplishments:
- Developed thermodynamic model using freezing point depression theory to predict cloud points of biodiesel. Experimental parameters determined by differential scanning calorimetry (DSC).
- Determined effects of small concentrations of contaminants on cold flow properties of biodiesel from soybean oil. Long-term storage of biodiesel in cold weather raised concerns with respect to precipitation of such contaminants left over from the conversion process. Methods were developed to solids collected in biodiesel storage tanks operated by a local fuel distributor.
- Developed biodiesel admixtures with improved cold flow properties by mixing soybean oil methyl esters with soybean alkyl esters derived from medium-chain branched alcohols.
- Developed automated analytical instrument techniques to measure cloud point and other cold flow properties of biodiesel and its blends with petrodiesel. Two user-friendly methods (light scattering, DSC) may be used to monitor cold flow properties of biodiesel than more common manual methods.
- Developed new index pertaining to oxidative stability of fatty compounds more specific than the iodine value which is still used in oleochemistry and often applied to biodiesel.

- Determined the effect of compound structure and presence of metals on biodiesel oxidation using the oil stability index method, which is nearly identical to the Rancimat method in biodiesel standards.
- Developed two models for predicting temperature effects on oxidation of biodiesel as analyzed by oil stability index (OSI). Although both models predicted OSI behavior, only one model was useful for deriving the activation energy for biodiesel oxidation. This questions the validity of high-temperature OSI analyses and using results to predict behavior at lower temperatures.
- Developed kinetic model to describe reaction kinetics and predict oxidative stability behavior of biodiesel exposed to air. Analysis by non-isothermal pressurized-differential scanning calorimetry (P-DSC) gave kinetic parameters such as activation energies and rate constants. P-DSC is effective for rapidly monitoring oxidative degradation of biodiesel during storage.
- Determined effects of storage and handling conditions on efficacy of various antioxidants and their mixtures in biodiesel. Developed basic storage and handling procedures for antioxidants.
- Determined cetane numbers of various fatty esters in an Ignition Quality Tester, an alternative to the method in biodiesel standards. Cetane number is a diesel fuel quality index related to ignition and combustion, with biodiesel and its components performing well. The new data help establish which fatty esters should be enriched in biodiesel fuels with enhanced fuel properties.
- Exhaust emissions of biodiesel and components thereof as well as petrodiesel and components thereof were determined in a newer technology heavy-duty engine (2003 model year, EGR, turbocharging). Biodiesel and its components almost met 2007 regulations regarding particulate matter exhaust emissions without any further exhaust aftertreatment technologies being used.
- The influence of compound structure of biodiesel components on viscosity was determined. The kinematic viscosity of several biodiesel components was determined down to -10EC. A new index for assessing low-temperature viscosity behavior was developed. The results aid in developing a biodiesel fuel with composition modified for optimizing fuel properties.
- The effects of compound structure and minor components of biodiesel on its lubricity were determined. Minor components of biodiesel (monoglycerides, free fatty acids) play a major role in enhancing the lubricity of low-level blends (for example, B2) of biodiesel with petrodiesel.
- Determined effects of blend ratio (biodiesel volume percent) on cloud point, density, viscosity and other fuel properties of biodiesel derived from various feedstocks blended with ULSD. This work was in response to terminal operators and consumers seeking data for blends with ULSD. Subject to available accurate data for “pre-blended” biodiesel / ULSD, blend ratios can be rapidly and inexpensively determined.
- Several fatty derivatives with bulky moieties were synthesized from oleic acid by treatment of various alkyl oleates with different alcohols to yield hydroxy ethers which were analyzed for low temperature behavior. 2-Ethylhexoxy ethers of oleates containing bulky head groups showed the best performance. Thus agricultural-based materials are potential biodiesel cold flow additives.

- Obtained biodegradable polyesters by condensation of glycerol with adipic, azelaic, suberic, and sebacic acids. They show promise as weed barriers or mats and can serve as controlled release materials to deliver fertilizer or pesticides. Glycerol polyesters could replace petrochemical polymers (polyethylene, polypropylene), providing an outlet for surplus glycerol.
- Esterification of glycerol with cinnamic acid and related ultraviolet absorbing compounds was investigated to determine conversion rates for potential commercialization. These materials are not absorbed into the skin from a topical formulation and do not present the health risks associated with sunscreen components made from fatty or oil compounds.