

Liquid Biofuels: Fluid Properties to Optimize Feedstock Selection, Processing, Refining/Blending, Storage/Transportation, and Combustion

George Anitescu and Thomas J. Bruno*

Thermophysical Properties Division, National Institute of Standards and Technology, Boulder, Colorado

ABSTRACT: As the availability of petroleum-based liquid fuels is becoming increasingly problematic, alternative renewable biofuels attract growing research and development (R&D) and industry interest. The focus is to produce fuels with desired properties in both technically and economically attractive ways to support sustainability and protect the environment. While abundant, the variety of biomass feedstocks brings a great deal of incompatibility of various biofuels and the combustion engines. A consistent theme is that better knowledge of fuel properties would lead to better designs and shorter development times of everything from fuel production facilities to emission control systems. Thermophysical properties of biofuels are required to efficiently design the processes involved in their production, distribution, and utilization. These properties are also needed to develop and validate physicochemical models, the tools employed in process design, product development, or academic research. To date, the connection between the expertise in fluid properties and an integrating knowledge of where and how these properties are employed has not been adequately developed. Accordingly, the main goal of this review is to unite and set out the potential for synergy between all of the essential steps of fuel production and applications (from feedstock selection to the end use) with the properties of the fuel at each step. An integrating approach on a broad scale is helpful for the increasing number of fuel researchers, process engineers, entrepreneurs, and end users. This review discusses the main driving forces that are likely to encourage further development and move the emerging biofuel technologies from promising ideas to competitive solutions.

■ BACKGROUND

Overview. Considerable efforts are being devoted to extend petroleum-based fuels with renewable and sustainable fuels from biomass (i.e., biofuels) that are ultimately derived from solar energy. While stationary energy production from biomass is more technically and economically convenient, liquid biofuels are required by specific applications. Plant biomass is the only current sustainable source of organic carbon, and biofuels are the only current renewable liquid fuels. These fuels are highly diverse, including commercial ethanol (from sugar/starch) and biodiesel fuels (from oils/fats), mainly mixtures of fatty acid methyl or ethyl esters (FAMEs or FAEEs).^{1–12} Special emphasis in this review is on these fuels. Lignocellulose-based fuels are at a precommercial stage, while liquid biofuel production from algae and some other biological conversion approaches for renewable gasoline, jet, and diesel fuels are at the research and development (R&D) phase. To be a viable extender for petroleum-derived fuels, biofuels should be economically acceptable (absent significant subsidy from governments), should not have negative impacts on environment and food supply, and provide a net energy gain.^{3,4,11,12} Given that these biofuel implications are very complex topics, further comprehensive research is needed in this respect.

Modern engineering design of processing plants relies on sophisticated process simulation packages where fluid-property data are essential (Table 1).^{13–23} Thermodynamic (both physical and chemical/reaction) and transport properties are provided by theoretical and experimental avenues that are part of fundamental science or R&D activities. Models range from empirical correlations of a single property to comprehensive models usually based on equations of state (EOS).^{13–23}

Despite recent progress, there is presently no single comprehensive source of reliable property data for biofuels that can be called upon by industry. An example is representative for the status of this information: “During the design and test phases associated with the development of the portable biodiesel equipment, public domain information on the material properties of supercritical methanol with any lipid was found to be incomplete. Hence, the portable equipment was conservatively designed to account for these uncertainties.”²⁴

While there are still significant needs for information on properties of finished fuels, the most wide-ranging and demanding needs are for properties of feedstocks and process intermediates for biofuel production and combustion. A better knowledge of fuel properties would lead to better designs and shorter development times of everything from production facilities to emission-control systems. To meet these requirements, comprehensive databases are being created or extended.^{13,21,25,26} For example, the DIPPR 801 Database^{21,25} contains information on 2013 compounds and lists values for 49 thermophysical properties. It also contains raw data from the literature and critically evaluated and recommended thermophysical values. Moreover, two standard reference databases are being expanded at NIST to include biofuels.¹³ The ThermoData Engine (TDE) seeks to collect and evaluate all published property data on biofuel components.¹⁹ The NIST comprehensive program containing reference properties (REFPROP) is under continued development to provide

Received: September 14, 2011

Revised: November 20, 2011

Published: November 23, 2011

Table 1. Main Fluid Properties Used for Modeling Fuel Processing and Combustion

property	SI units	type
molecular weight	kg/kmol	constant, thermodynamic
chemical composition	dimensionless	thermodynamic, mixtures
acentric factor	dimensionless	constant, thermodynamic EOS
autoignition temperature	K	constant, thermodynamic
dielectric constant	dimensionless	constant, transport
dipole moment	C·m	constant, transport
octane number	dimensionless	constant, thermodynamic
cetane number	dimensionless	constant, thermodynamic
flash point	K	constant, thermodynamic
Gibbs energy of formation (standard state) ^a	J/kmol	constant, thermodynamic
enthalpy of combustion (standard state) ^a	J/kmol	constant, thermodynamic
enthalpy of fusion at melting point	J/kmol	constant, thermodynamic
enthalpy of formation (standard state) ^a	J/kmol	constant, thermodynamic
heat of vaporization	J/kmol	T-dependent, thermodynamic
heat capacity	J/kmol·K	T-dependent, thermodynamic
density	kmol/m ³ ; kg/m ³	T-dependent, thermodynamic
thermal conductivity	W/m·K	T-dependent, transport
absolute viscosity	Pa·s	T-dependent, transport
melting point (1 atm)	K	constant, thermodynamic
normal boiling point (1 atm)	K	constant, thermodynamic
speed of sound	m/s	T-dependent, EOS development
critical pressure	Pa	constant, thermodynamic
critical temperature	K	constant, thermodynamic
critical volume	m ³ /kmol	constant, thermodynamic
critical density	kmol/m ³ ; kg/m ³	constant, thermodynamic
compressibility factor	dimensionless	constant, T-dependent
thermal diffusivity	m ² /s	T-dependent, transport
refractive index	dimensionless	T-dependent, transport
entropy in standard state ^a	J/kmol·K	constant, thermodynamic
surface tension	N/m	T-dependent, transport
second virial coefficient	m ³ /kmol	T-dependent, thermodynamic
chemical potential (partial molar Gibbs energy)	J/kmol	thermodynamic, mixtures
van der Waals reduced volume	m ³ /kmol	constant, thermodynamic EOS
vapor pressure	Pa	T-dependent, thermodynamic

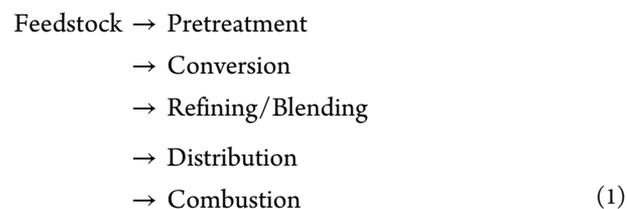
^aStandard state of 298.15 K and 100 000 Pa.

fluid properties of biofuel components and blends based on thermodynamic and transport models.²⁰ These properties are relevant for feedstock processing and engine design. Other specifications such as acidity, oxidative stability, or the allowable

levels of impurities relate to the suitability of a fuel for material compatibility or transportation/storage.

The thermophysical and chemical fluid properties that are needed for both the target fuel and the surrogate components include, but are not necessarily limited to, density, heat capacity, enthalpy, critical properties, thermal conductivity, speed of sound (for EOS development), and viscosity (Table 1). Vapor pressure, the pure-component analog of volatility, is also required. The detailed listing depends, to some extent, on the application intent of the model. For the design of biofuel processing steps,^{6–12,27–29} properties such as chemical composition, miscibility, heat of reaction, and heat content are also required, and some are included in comprehensive process-simulation packages such as AspenPlus and ChemCad.^{22,23} In addition to chemical characterization, specific analytical strategies provide the added potential of linking analytical information with physical property information.^{30–35} This aspect can be used to facilitate EOS development for the complex fluids. Fluid properties have associated uncertainties, arising from the precision and scatter of the underlying experimental data and from the fit of the formulation to those data. Often, the uncertainties vary broadly within the ranges of properties. More information about the uncertainties may be found in the original research papers for the property in question.

Biofuel Supply–End-Use Chain. Research on this topic deals with logistical and life-cycle analyses as well as the chain of technologies required to select, produce, transform, deploy, and use renewable fuels sustainably.^{1–12} The production and combustion of biofuels are only two main links in a multiple-step chain:



The optimization of the farming, collection, and processing of biomass will depend upon the targeted type of fuel, which in turn, will depend upon end uses. Recent R&D efforts have provided potential pathways to make biofuels competitive with petroleum-based fuels.^{1–12,36–41} However, many proposed approaches and technologies exhibit significant deficiencies unless the overall system is optimized or the production is extended to include valuable coproducts.^{1,2,10,36–38} A *green biorefinery* concept envisions a complex and fully integrated system of environment- and resource-protecting technologies for the comprehensive material and energetic use of biomass following the principles of green chemistry.^{2,10,36,38,42–45} A representative diagram of a biomass refinery is shown in Figure 1. It integrates the input of raw biomaterials, processing, and output of the bioproducts. The latter category includes chemical products and fuels. The unifying aspect provided by thermophysical and chemical properties is depicted at the bottom of the figure.

Fuel Processing–Fluid Property Synergy. Integrated information on fuel processing and fuel properties provides the opportunity to drive advancements in both areas. While biofuel research expands the property database, fuel properties contribute to the selection of the appropriate/optimum processing pathways and conditions. There are significant benefits to be

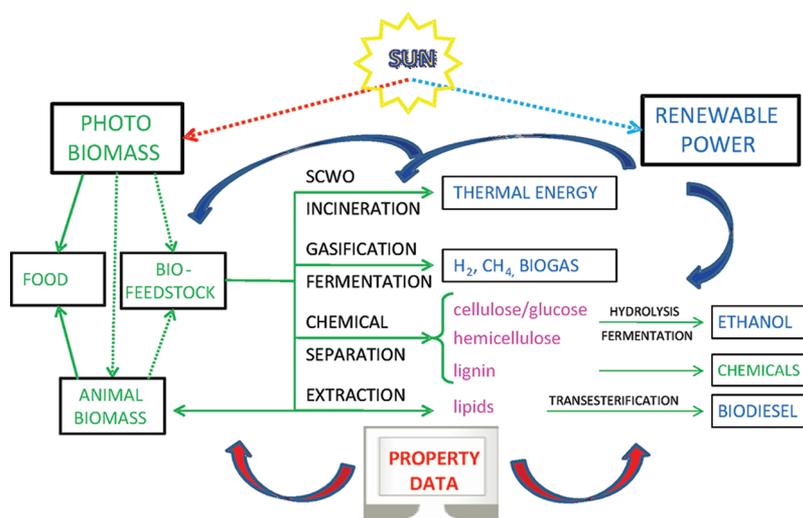


Figure 1. Block diagram of a sustainable biomass refinery. Text: green, main raw materials, feedstocks, and chemical products; blue, main renewable energy/fuels; pink, intermediates. Arrows: green, (pre)processing; red (solid), integrating connections provided by thermophysical property databases; blue (solid), suggested use of the renewable power for biomass processing.

gained from the explicit connection of processing and properties. The optimization (technical and economic) that can result from this philosophy will make possible further integration of sustainability and green chemistry principles.^{2,4,13,36–49}

Molecular Structure–Property Relationships (SPR).

The basic assumption for models based on molecular structure is that similar molecules (or moieties) exhibit similar properties. The group contribution methods to estimate fluid properties such as critical temperature and viscosity are based on this assumption.^{50,51} Frameworks for development of estimation methods have been proposed to predict critical constants for pure compounds⁵² and flash points and cetane numbers for fuels.⁵³ Experimental values of critical constants were critically evaluated using the methods of robust regression, and correlations for these constants were developed based on quantitative SPR methodology. However, careful attention has to be devoted to the SPR paradox: similar molecules do not always have similar properties. There are examples of different structural systems that exhibit similar thermodynamic properties, and this feature is exploited by corresponding state principle applications.⁵⁴

Given the high compositional complexity of biofuels and their blends with petroleum-based fuels, modeling the fuel properties on a practical level can be done with a limited number of fuel components (i.e., surrogates).^{13,55–57} These mixtures must be designed to capture the essential characteristics of a complex fuel. If the properties of the selected surrogate components are available, then the properties of the fuels so generated can often be calculated. If these properties are not available, theoretical approaches based on the corresponding-states principle, group contributions, and the regression of limited or predicted data can sometimes be successfully employed.^{50,54,57} Knowledge of the molecular structures of the components is a prerequisite herein. We emphasize, however, that there is no realistic substitute for measurements on pure components that are used to formulate the surrogate for use in critical predictive applications. It is clear that surrogate mixture models are only as good as the property knowledge base of the (pure component) constituents of the surrogate.

Fluid Properties and Fuel Quality. The properties needed for effective engineering designs include fundamental thermophysical and chemical properties that can be related to fluid theory and can be used for EOS development and more empirical, fit-for-purpose properties that are application specific and required for operation and certification (often embodied in international standards). We note that in some cases such properties overlap. Increasingly, fit-for-purpose properties are being refined and can ultimately become more fundamental and theoretically meaningful. Various specifications that a biofuel must meet are contained in fuel standards, such as ASTM D6751⁵⁸ and EN 14214 for biodiesel fuels.⁵⁹ These specifications include fit-for-purpose properties such as impurity content (via water, sulfur, and ash content), volatility (as boiling temperatures for several volume fractions distilled), reactivity (through cetane numbers), kinematic viscosity, oxidative stability, and cold-flow properties (cloud points). Other properties to consider that are not contained in fuel standards are exhaust emissions from combustion, lubricity, and heat of combustion. The exhaust emissions are addressed by separate legislative and regulatory measures, specifications in standards for conventional petroleum-derived diesel fuel are applied for lubricity, and heat of combustion is contained in the European standard for biodiesel as heating oil.

Impact. The area of liquid biofuels is difficult to review because of the sheer number of the processing routes with various process conditions and fluid properties. An integrating approach on a broad scale is helpful for the increasing number of fuel researchers, process engineers, end-users, and entrepreneurs. Our main goal is to unite and set out the potential for synergy between all of the essential steps of fuel production and applications with the properties of the fuel at each step. Special emphasis is on processes with knowledge gaps (e.g., transesterification, TE) and not on well-known chemical reactions (e.g., fermentation).^{6,10,39} The main driving forces discussed are likely to encourage further development and move the emerging biofuel technologies from promising ideas to competitive solutions. Our goal at this time is not to critically evaluate individual sourcing or the likelihood of deployment of finished fuels or feedstocks. We also do not focus on the

environmental impact of land or aquatic crops and the associated public-policy considerations.

■ FEEDSTOCK SELECTION AND PRETREATMENT

Overview. The expansion of biofuels requires the development of new methods and equipment to collect, store, and preprocess biomass in a manner acceptable to biorefineries.^{8–12} A modern tool to assess feedstock economic feasibility is life-cycle analysis.^{11,46,60–65} This analysis must include some nonprocess inputs that are difficult to quantify accurately.⁶⁶ It is primarily from this issue that scientific debates arise on the sustainability (or not) of important biofuel feedstocks.^{66–69} Although economically and environmentally important, the issues of the land-use competition for food and energy crops⁷⁰ and the agronomic aspects of future energy crops⁷¹ are not included in this review. Feedstock properties (chemical and thermophysical) required in the design step of biofuel production are also needed in feedstock selection and pretreatment steps and will be discussed later. The feedstock composition is the most important property that conveys, in turn, other needed characteristics, such as physical state under ambient conditions, density, reactivity (including thermal stability), and, for liquids, viscosity and component mutual miscibility. These properties are needed in feedstock preprocessing and for the optimum selection of pathways toward biofuel production.

Biomass Resources. Overall, feedstocks for biofuel production include agricultural residues (corn stover, straws and hulls, bagasse, and orchard prunings), forestry products (logging slash, forest thinnings, understory brush, pulping process wastes such as black liquor and tall oil, and southern pine), dedicated energy crops (corn, wheat, sorghum, sugar cane, oil crops, lignocellulosic and herbaceous biomass, and short rotation woody crops such as poplar and willow), and other biowastes (municipal solid wastes, industrial, animal, and yard wastes, and waste oils).^{9,10,42,72}

Triglyceride Feedstocks for Jet/Biodiesel Fuel Production. The most important input in the production of jet/biodiesel fuels is the quality and cost of the triglyceride feedstock. Oil feedstocks for current and potential biofuel production are currently obtained from soybeans, rapeseed/canola, cottonseed, sunflower seeds, groundnut, copra, sesame, linseed, castor seed, corn/maize, palm, coconuts, *Jatropha*, *Cuphea*, *Camelina*, pennycress, etc. Soybeans are a main feedstock in the United States, whereas rapeseed dominates in Europe and Canada, and palm/coconut dominates in Southeast Asia. The major supplies of animal fats and greases for biodiesel fuel production are tallow, turkey and chicken fat, and lard (white grease). The free fatty acid (FFA) content of these feedstocks is usually high (10–30 wt %), making these fats rather unattractive for conventional catalytic TE, which requires less than 0.5 wt % FFA content.^{58,59} Yellow grease is manufactured from spent cooking oil. Municipal sewage sludge is also gaining traction as a lipid feedstock for biodiesel production.⁷³ It is plentiful but difficult to process.

Biodiesel fuel from algae is argued to be a potential substitute for diesel fuels due to its overall performance in the aspects of environment, safety, raw material productivity, and fuel quality.⁴⁶ Microalgae currently stand in the spotlight because of very high lipid content (up to 70% mass/mass), they can be grown in waste, saline, or brackish water, and they require land resources that do not interfere with food crop production.⁷⁴ Despite the tenor of these optimistic evaluations, other analyses

argue far less optimistic projections. Aspects difficult to quantify in a life-cycle analysis from growing algae to final fuel are often questioned.^{61,75} Among the issues cited are (1) the productivities achieved in large-scale commercial microalgae production systems do not surpass those of irrigated tropical crops; (2) cultivating, harvesting, and processing microalgae solely for the production of biofuels is simply too expensive using current or prospective technology; and (3) currently available (limited) data suggest that the energy balance of algal biofuels is very poor. It is, however, suggested that using treated municipal/farm wastewater to offset the nutrient demand may be one promising approach to improve overall economics throughout the life cycle of algae.^{60–62} Liquid biofuel production from algae is currently at the R&D phase; samples of finished fuel from this feedstock are scarce, even for experimentation.

Different compositions between various lipid feedstocks could produce differences in the finished product of biofuel. For example, saturated fats tend to produce biodiesel fuel with slightly inferior cold-flow properties compared to unsaturated oils but with better combustion and storage stability. Combustion tests have also shown animal fats to produce biodiesel fuel with a slightly better engine emission profile.^{12,76}

Cellulosic Biomass for Bioalcohol Production. Economically, lignocellulosic biomass has an advantage over other agriculturally important biofuel feedstocks such as corn starch, sugar cane and soybeans, because it can be produced quickly and at significantly lower cost than food crops. Due to their primary utility as food and feed, the crop-based feedstocks cannot meet the global demand for bioalcohol (ethanol and butanol) production as an alternative transportation fuel.^{10,77} Lignocellulosic biomass is an abundant and renewable raw material, but it is difficult to process.^{10,72,77,78}

Other Resources. In addition to vegetable oils and algae, research has suggested the potential application of cyanobacteria to the generation of bioenergy via converting sunlight into renewable fuels.⁵ The main challenge in this case is the same with that of the algal fuel: the cost of growing, harvesting, and processing these microorganisms for significant quantity of fuel. Although microbial oils are postulated as an alternative to plant oils, not all oleaginous microorganisms have ideal lipid profiles for biodiesel production.⁷⁹ The lipid profiles could be modified by genetic engineering in some oleaginous microorganisms; for example, the biomass from submerged cultures of the oleaginous fungus *M. circinelloides* could have the potential to produce biodiesel fuels.⁷⁹ Some emphasis is also to produce biofuels from intermediates of the preliminary biomass processing, such as glucose, 5-hydroxymethyl furfural, sorbitol, levulinic acid, succinic acid, γ -valerolactone, and glycerol.^{9,10,37,39,42,49}

Feedstock Pretreatment. The main processing step of biofuel feedstocks depends significantly on the feedstock composition that results from the pretreatment steps. There are numerous approaches to optimize various feedstock compositions, based on different upstream and downstream pre- and postprocessing requirements. Biomass feedstocks from cropping natural or cultivated sources are usually not suitable for direct biofuel production. Readily available biomass under catalytic, thermal, and/or biochemical conversion is broken down into different components that can be processed further.^{10,39,72} Raw material pretreatment is also dependent upon the type of biofuel to be obtained. One of the main factors in the biomass preprocessing steps is the widely varying

moisture content. Diminishing this content in order to optimally perform specific processing requires significant energy and time. Accordingly, efforts are directed toward pre-processing biomass feedstocks with high water content, such as algae.^{80,81}

To produce biofuels from microalgae, a multistep process from growing algae to oil TE and ultimately to fuel purification is required. The main issues are the very high water content of the cropped algal biomass and the difficulties of oil extraction and purification. For the latter step, dry algal biomass is preferred but is costly. Alternatively, a two-step process of hydrolysis of biomass followed by esterification of FFAs has been proposed.⁸¹ As another example, typical oilseed pretreatment and oil extraction comprise the following steps:¹² (1) storage of oilseeds; (2) cleaning of the oilseeds; (3) removing the husk or seed coating and separating the seeds from the chaff; (4) heating the seed; (5) extracting oil (e.g., mechanical expression, liquid or supercritical fluid (SC) solvent extraction); (6) oil purification; and (7) storing the purified oil. Animal fats as biodiesel fuel feedstocks are derived from the rendering process by use of animal tissues as the raw material. Yellow/brown grease is manufactured from spent cooking oil. The solids are first filtered out, and the oil is then heated to drive out moisture until the product meets industry specifications for the grease.

Pretreatment of the lignocellulosic biomass is focused on opening/expanding the surface area of the feedstock for the subsequent enzymatic reactions. It includes physical, chemical, and thermal methods to change the biomass structure in order to improve downstream processing. These methods may be divided into (1) those that produce a stream directly for fermentation to ethanol and (2) those that are followed by enzymatic hydrolysis.^{10,39} As a result of pretreatment, the fibrous structure of the feedstock is destroyed.^{10,39} The use of supercritical water and ionic liquids to solubilize polymeric carbohydrates, such as cellulose and starch, to make them accessible to liquid-phase processing has also been explored.^{48,49,82} The carbohydrate compounds of lignocellulosic materials can also be pretreated and partly hydrolyzed by near-critical water.⁸³ CO₂ dissolved in water may be used as catalyst. Pretreatment is one of the most expensive processing steps for the production of sugars from biomass, and more research is needed.

■ FEEDSTOCK PROPERTIES

Properties of Triglyceride Feedstocks and Their Mixtures with Methanol/Ethanol. While for some individual triglycerides and methanol/ethanol the fluid properties needed for TE characterization are available in the literature,^{12,20–26,84} such data are limited for the mixtures. The properties of the triglyceride (lipid) feedstocks are evaluated from two perspectives: the use of feedstock for biofuel production, or directly (without processing) as components in fuel blends. For the former perspective, which is more common, the emphasis is on composition, mutual miscibility with methanol/ethanol, density, volatility, thermal conductivity, heat capacity, critical points, and flow properties (viscosity, diffusivity, and Reynolds number). The most important is the composition, which, in turn, controls other properties.^{12,26} The unrefined oils and fats usually contain FFAs, phospholipids, sterols, water, and other impurities.⁸⁵ Water and FFA contents are important quality parameters that vary significantly with feedstock origin. Of special importance for triglyceride–alcohol mixtures are mutual solubilities and critical P – V – T – X conditions. The latter perspective, far less common, encompasses the properties

needed to combine the feedstock oils directly with, for example, petroleum diesel fuels. The major properties of concern for this application will be discussed later.

Miscibility of Triglycerides with Methanol/Ethanol. The miscibility of triglycerides with methanol/ethanol is essential for the TE process design and operation. The main difference between various TE reaction conditions reported in the literature for near-complete triglyceride conversions largely originates from the reactant mutual miscibility.^{12,40,41,85–93} At similar P – T conditions, this property is strongly dependent on triglyceride composition and alcohol-to-triglyceride ratio. Stoichiometric quantities of liquid triglycerides and methanol are not necessarily well miscible. The TE reactions occur at the interface between the two phases, resulting in a much lower conversion rate than if the reaction mixture was a homogeneous single phase. The TE reactants (methanol/ethanol and triglycerides) and products (FAMES/FAEEs and glycerol) are partially mutually soluble under various P – T – X conditions of TE processes. The alcohol is soluble in glycerol but is not significantly soluble in the feedstock oil. With an increase in the FAME/FAEE yield, the alcohol solubility in the triglyceride–FAME/FAEE phase increases. For example, when FAME content increases to ~70%, the triglyceride–methanol–FAME mixture becomes a homogeneous phase.⁸⁹ Glycerol has a low solubility in both oil and FAMES but has a high affinity for alcohol. The miscibility of a soybean oil–ethanol mixture (1:16 molar ratio) being rapidly heated at constant density from room temperature to 400 °C in a view cell is illustrated in Figure 2.⁸⁶

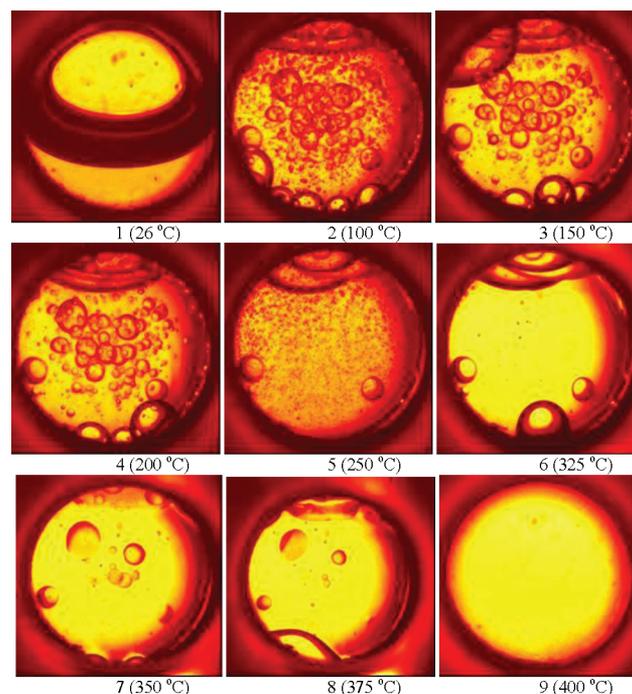


Figure 2. Miscibility of a soybean oil–ethanol mixture (1:16 molar ratio) being rapidly heated from 26 to 400 °C at constant density.⁸⁶ The mixture goes from a two-phase liquid to an SC state. (The view cell volume is ~1 mL.)

Phase Transitions in Triglyceride–Alcohol Mixtures. By observing and recording the P – T – X conditions of phase transitions, as shown in Figure 2, one can construct different binary phase diagrams.^{90,93–96} The global P – T diagrams for

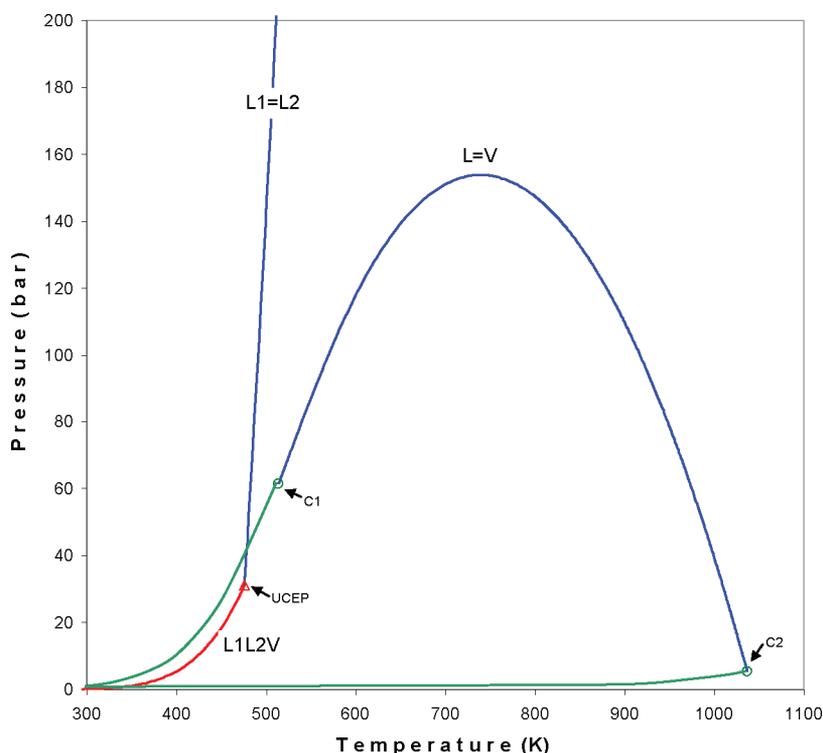


Figure 3. P – T projection of a type II (Scott-van Konynenburg classification) phase diagram for the system ethanol(1) + C_{54} (2).⁹⁵ The green lines are the saturation curves for the pure components.

triglyceride–alcohol binary mixtures are of type II in the Scott–van Konynenburg classification.⁹⁵ These diagrams exhibit two critical lines: one $L = V$ critical line connecting the critical points of pure components C_1 and C_2 , and a liquid–liquid ($L_1 = L_2$) critical line from an upper critical end point (UCEP) to high pressures. Figure 3 shows the projections of such a phase diagram on the P – T plane for the ethanol(1) + C_{54} (2) system (C_{54} as a triglyceride surrogate).⁹⁵ The curves were generated by a Peng–Robinson (PR) EOS with the interaction coefficient $k_{ij} = 0$. For this particular case, the saturation curve of ethanol is very close (nearly overlaps) the L_1L_2V curve up to the UCEP and then continues to C_1 . With this methodology, it will be possible to construct P – T – X phase diagrams for selected binary systems of triglyceride–alcohol solutions.

Critical Conditions of Triglyceride–Alcohol Mixtures. Critical conditions of triglyceride–alcohol mixtures are typically determined by using a view cell and a suitable optical system.^{86,93,94,96} In the experimental cell, however, the reactivity of the triglycerides and alcohol could generate esters that will affect the critical conditions by changing the system composition. This effect will likely be negligible for high heating flux that will lead to short residence time until the desired temperature will be reached. Alternatively, the critical parameters can be calculated by a group-contribution technique, EOS, or other methods.

P – V – T Surface. The P – V – T surface of the reactants and reaction products is an important fluid property for almost any industrial process design, and it is critical to the development of the EOS for a fluid. These data are usually obtained by a measurement of the fluid density under wide ranging temperature and pressure. Instrumentation for performing such measurements include absolute dual sinker densimeters for reference fluid measurements and several automated densimeters that are capable of measurements at atmospheric-pressure

or compressed liquids over industrially relevant temperature ranges (0–200 °C, up to 500 bar, with a typical uncertainty of 0.5 g/mL over the range).^{97–99}

P – V – T data were also measured with a static-type bellows apparatus for various fats and oils at 1–150 MPa and 30–80 °C and compared to those of pure components trilaurin, triolein, and tridecane.¹⁰⁰ The P – V – T behavior for the fats and oils above their melting points was similar and was explained in terms of molecular mass, iodine value, and fatty acid composition. The data were correlated with the Tait, Peng–Robinson, Hederer–Peter–Wenzel, lattice, Flory, and simplified perturbed hard chain theory (SPHCT), but only the Tait, Flory, and SPHCT equations provided satisfactory correlation. SPHCT parameters were generalized in terms of measurable oil properties, saponification value, and iodine value. With the correlated parameters, the P – V – T behavior of the oils was described to within 4.9% average deviation in pressure.

An approach has been proposed to estimate the densities of straight and processed vegetable oils from their fatty acid composition, obviating the need for measured values (particularly for use in process modeling studies).¹⁰¹ The proposed methodology has been validated using the measured densities of 11 different vegetable oils and 13 processed vegetable oils. The predictions are found to agree with the experimental data (~1% uncertainty) at temperatures up to 90 °C.

Speed of Sound. The speed of sound in a fluid is also an important property, because it is related to the isothermal compressibility. Measurements are typically performed on liquids at atmospheric pressure. Some custom-made instruments are available (usually based on spherical resonators) that measure the compressed liquid and gas as well.^{98,99} This property, similar to the P – V – T surface, is critical for EOS development, but it is also a fit-for-purpose property. In many modern aircraft, fuel level indicators function via a speed-of-sound

measurement, thus knowledge of the variability of this property for different finished fuels is critical.

Heat Capacity. The heat capacity of the reactants and reaction products is a fluid property needed when designing heat exchangers, calculating heats of reaction, and heat transfer air–fuel before combustion. While for pure fluids, the divergence of the heat capacity in the vicinity of the critical point is a well-known feature, for the fluid mixtures of interest, the behavior of this property is less striking. There are available data for heat capacities of liquids and liquid mixtures, but these data are scarce near the critical point. In general, the heat capacity for liquid fluids is a linear function of temperature, as shown in Figure 4.¹⁰² Heat capacities at constant pressure (C_p)

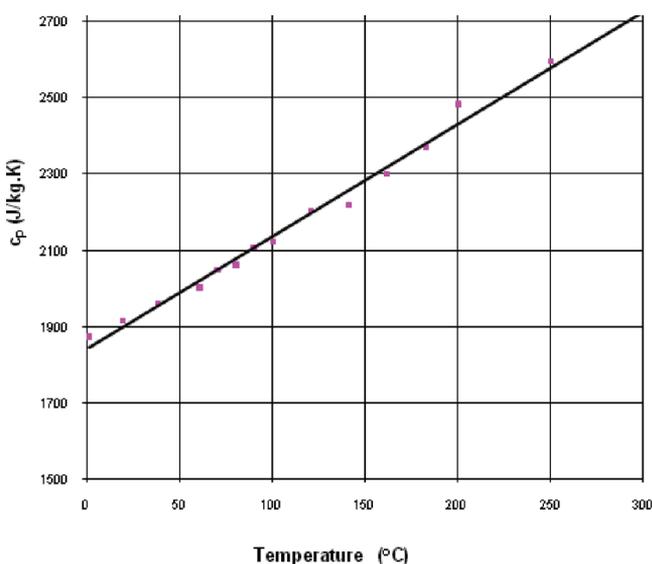


Figure 4. Specific heat capacity of soybean oil–methanol mixture as function of temperature. (Data from ref 102).

of reactants are needed for process design over wide P – T ranges. This property can be determined by using a differential scanning calorimetry (DSC) method, which has been shown to be capable of acquiring C_p data (with 1% uncertainty) up to 350 bar at 300 °C.¹⁰³

Fit-for-Purpose Properties of Triglyceride Feedstocks. The most important fit-for-purpose properties for common oils/fats are given in Table 2.^{76,104} For an easy

comparison, the same properties of typical diesel fuel no. 2 (DF2) are included in the last row. Although most of these properties were determined for the purpose of combusting oils/fats as fuels in diesel engines, these fluids do not exhibit properties suitable for efficient and clean combustion.¹⁰⁵ For example, their viscosity is more than 1 order of magnitude higher than that of petroleum-based diesel fuels, and their volatility is generally too low for good injection and combustion events in a diesel engine. When compared with diesel fuels, the unsuitability of the oil/fats for use in diesel engines is apparent from their relative properties mentioned above.

Triglyceride biofeedstocks exhibit better behavior at low temperatures than many biodiesel fuels. The transition from liquid to solid states is well-defined and occurs at lower temperatures for the oils, while for the fuels, solidification includes a two-phase heterogeneous transition occurring at higher temperatures.^{106,107} This different behavior is due to the homogeneous distribution of the saturated and unsaturated FAs in triglyceride molecules. In biodiesel fuels, the saturated and unsaturated FAMES are separated as temperature is reduced, with the former solidifying first. This characteristic could lead to a more convenient in situ/engine TE of triglyceride feedstocks.¹⁰⁶

Properties of Cellulosic Biomass. The sources of the lignocellulosic ethanol are from the glucose originating from cellulose and from the simple sugars that compose the hemicellulose. The term *cellulosic biomass* refers to potential feedstocks that have cellulose as the primary constituent (40–60%) with hemicelluloses (15–25%), and lignin (15–30%) as secondary components.^{10,108} Cellulose is a linear polymer with glucose groups joined together by β -1,4 chemical bonds. Individual polymer chains are connected by hydrogen bonds forming a microfibril, a three-dimensional (3-D) lattice. Such a network (crystalline cellulose) is very stable against attack by enzymes or acids. Regions with a lesser degree of hydrogen bonding are simply random configurations of glucose polymers (amorphous cellulose). Most natural cellulose is primarily crystalline.^{10,72,108} Hemicellulose is a mixture of linear and branched polymers of xylose and arabinose (5C sugars) and glucose, mannose, and galactose (6C sugars). Hemicellulose is readily dissolved and hydrolyzed to its simple sugars in dilute acids at moderate temperatures (~100–200 °C). Lignin, a complex 3-D matrix of phenolic–propane units, does not participate in the pretreatment or hydrolysis processes, except to decrease the degree of polymerization.

Table 2. Fit-for-Purpose Properties of Various Plant Oils^{76,104}

oil	cetane no.	heat content (MJ/kg)	viscosity ^a (mm ² /s)	cloud point (°C)	pour point (°C)	smoke point ^b (°C)	flash point (°C)
castor		39.50	297		−31.7	200	260
corn	37.6	39.50	34.9	−1.1	−40.0	232	277
cottonseed	41.8	39.47	33.5	1.7	−15.0	216	234
linseed	34.6	39.31	27.2	1.7	−15.0		241
palm	42.0		40.2			235	
peanut	41.8	39.78	39.6	12.8	−6.7	232	271
rapeseed	37.6	39.71	37.0	−3.9	−31.7		246
safflower	41.3	39.52	31.3	18.3	−6.7	266	260
high-oleic safflower	49.1	39.52	41.2	−12.2	−20.6		293
sesame	40.2	39.35	35.5	−3.9	−9.4	232	260
soybean	37.9	39.62	32.6	−3.9	−12.2	238	254
sunflower	37.1	39.58	37.1	−7.2	−15.0	227	274
DF2	47.0	45.34	2.7	−15.0	−33.0		52

^aAt 38 °C and 1 bar, except for palm oil (40 °C and 1 bar). ^bSmoke points from ref 104.

Properties of Intermediate Biofeedstocks. A computational chemistry method was used to predict the gas-phase heats of formation of compounds relevant to the conversion of biomass-derived oxygenated feedstocks into fuels or chemical feedstocks (glucose, 5-hydroxymethyl furfural, sorbitol, levulinic acid, succinic acid, γ -valerolactone, and glycerol).⁴² Heats of formation of the liquid were obtained from calculations of the boiling point combined with the rule of Pictet and Trouton, using modified values for ΔS_{vap} . Densities of levulinic acid, ethyl levulinate, butyl levulinate, furfural, and furfuryl alcohol have been measured using a high-pressure, high-temperature vibrating tube densimeter system over a temperature range from 10 to 68 °C and a pressure range from 0.1 to 60 MPa.¹⁰⁹ From the measured densities, some thermodynamic properties, isobaric thermal expansion and isothermal compressibility, have also been calculated. The properties and performance of levulinate esters as diesel blend components have been also studied in detail.¹¹⁰

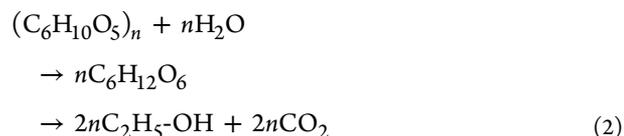
■ FEEDSTOCK PROCESSING AND REFINING TO BIOFUELS

Overview. While the availability of diversified feedstocks is a significant advantage for biofuel production, the variable compositions of these feedstocks render the selection of processing conditions rather difficult. For example, the available lipid feedstocks contain only five main fatty acids: palmitic, stearic, oleic, linoleic, and linolenic. There are, however, 35 triglycerides containing these acids, with different structures and corresponding properties. The sugar-based feedstocks for bioalcohol production are somewhat more limited but, with increasing genetic engineering modifications, these are growing increasingly diversified. Much of the feedstocks contain large molecular compounds (e.g., triglycerides and sugars) or polymers (e.g., lignocellulose and starch) that must be converted into smaller molecules that have acceptable volatility and viscosity, to ensure compatibility with the operation of internal combustion engines. The design of any process involving biofeedstocks requires some degree of knowledge about their thermophysical and chemical properties.

There are a number of implemented technologies and several under development for the production of biofuels. The former include fermentation of sugar substrates to ethanol and TE of natural oils and fats to biodiesel fuels.^{6,10,12,39,72} Lignocellulosic material can be converted into liquid fuels essentially by three primary routes, as shown in Figure 1: (1) syngas by gasification followed by Fischer–Tropsch conversion to alkanes, (2) bio-oil by pyrolysis or liquefaction followed by catalytic upgrading, and (3) hydrolysis of biomass to produce sugar monomer units. Toward implementation of these technologies, special attention could be devoted to the existing processes in petroleum industry that could be applied to biomass refining. Because chemical routes for the transformation of biomass into chemicals are well described in the literature,^{6–10,39,42,72} only a brief presentation is provided here.

Bioethanol. Bioethanol is usually produced from feedstocks with high sugar content by an enzymatic fermentation of six-carbon sugars (mainly glucose).^{6,10,39} When the raw materials are grains, hydrolysis is first used to convert the starches into glucose.^{10,111} The conventional processes use only the germs of the seeds or grains, which represent a small percentage of the total mass of the plant.¹¹² The generated distillers dried grains with solubles is an animal feed with a higher value than the original corn.

Alternatively, ethanol can be produced from lignocellulosic feedstocks through biochemical processes (mainly hydrolysis and fermentation):^{6,10,39}



The hydrolysis is usually catalyzed by acids or cellulase enzymes, and the fermentation is carried out by yeast or bacteria. By-products including 5-hydroxymethylfurfural and levulinic acid are produced by acid-catalyzed degradation of sugars.^{10,42} The presence of lignin and hemicellulose makes the access of cellulase enzymes to cellulose difficult. Factors that affect the enzymatic hydrolysis of cellulose include substrates, cellulase activity and reaction conditions.¹¹³ While bioethanol production from lignocellulosic feedstocks has been improved by the development of new technologies, there are still challenges for a commercial-scale production. These challenges include providing stable performance of fermenting microorganisms, developing more efficient pretreatment technologies for the lignocellulosic biomass, and integrating the optimal components into economic ethanol production systems. Calculations show that up to 0.33 kg of bioethanol, 0.06 kg of furfural, and 0.17 kg of FT-diesel per kg of softwood can be produced and mass, carbon, and energy conversion efficiencies of 56, 70, and 82%, respectively, are achieved.⁴⁵

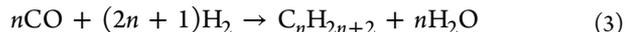
Biobutanol. *n*-Butanol has been manufactured by fermentation of sugars or starch, and the perspective is to use lignocellulosic feedstocks. The process is complex and consists of the anaerobic conversion of carbohydrates by strains of *Clostridium acetobutylicum* into acetone, butanol, and ethanol (ABE fermentation) with a product ratio of 3:6:1.¹¹⁴ When a concentration of 12 g/L is reached, the alcohol will inhibit the bacterial cells.¹¹⁵ Upon completion of the fermentation, there is a relatively small amount of ethanol and acetone in the broth. Recovery and purification of *n*-butanol from the fermented broth is a difficult and costly process. To make this process profitable, in situ product recovery is required by gas stripping, pervaporation, membrane extraction, adsorption, and reverse osmosis.¹¹⁶ There has been some recent progress made, with the final *n*-butanol concentration in the solution reaching about 20 g/L.⁶

Renewable Gasoline, Diesel, and Jet Fuels. The production of these fuels usually involves thermochemical conversion of biomass at higher temperatures and pressures than those of biochemical conversion. The former process allows more flexibility in feedstock choice and a diversity of fuels produced.^{10,72} The process begins with gasification or pyrolysis of a biofeedstock and is generally more capital-intensive. Large-scale production is required for economic benefit, but the final product is a clean finished fuel. Green gasoline can be produced by a combination of hydroprocessing and catalytic cracking to yield alkanes of predetermined chain lengths for the desired range of octane numbers. A common process to produce renewable jet and diesel fuels from vegetable oil utilizes catalytic saturation, hydro-deoxygenation, decarboxylation, and hydro-isomerization reactions.^{10,63,117–119}

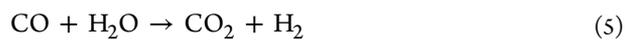
There is a need to reduce the natural oil carbon chain lengths (C_{16} – C_{18}) to the required range for aviation turbine fuel (C_{10} – C_{14}). This need is achieved by catalytic processes of deoxygenation, isomerization, and selective cracking of the

hydrocarbons present in natural oils and fats. The process can be adjusted to produce a specific freeze point of the desired fuel or can be operated to maximize production. Renewable green diesel-type alkanes can be produced by hydrotreating vegetable oils at 270–300 °C with Pt/H-ZSM-5 catalysts.¹¹⁷ The carbon molar yield of C₁₅–C₁₈ *n*-alkanes was ~80% for hydrotreating jatropa oil. The reaction pathway involves hydrogenation of the C=C bonds in triglyceride molecules followed by hydrodeoxygenation with decarbonylation and decarboxylation to form C₁₅–C₁₈ straight chain alkane mixtures. A catalytic hydrothermolysis process aimed at converting triglycerides to nonester biofuels has also been characterized at temperatures ranging from 450 to 475 °C and a pressure of 210 bar.¹¹⁸ The organic phase (biocrude) from the process underwent post-treatment involving decarboxylation and hydrotreating. Other catalysts such as NiMo/Al₂O₃ and CoMo/Al₂O₃ are used for the production of renewable diesel fuel.¹¹⁹ Results derived from plant oils showed that certain biofuel fractions met petroleum distillate specifications.

The liquid biofuels produced from syngas include alkanes by Fischer–Tropsch synthesis:¹⁰



Fischer–Tropsch liquid (FTL) as a renewable fuel is synthesized on Co-, Fe-, or Ru-based catalysts by reacting CO and H₂ produced by steam reforming of a biofeedstock (possibly coupled with the water–gas shift reaction):^{7,10,72,117–122}



The down side of the reaction 3 is the fact that near half of the total hydrogen amount needed goes to water. The FTL is a mixture of mostly straight-chain alkanes (up to ~C₅₀) that can be shipped to a conventional petroleum refinery for processing or refined on site into diesel fuel, jet fuel, or other fractions.^{9,10} Emphasis is on the production of middle distillate fuels with high cetane number and little or no sulfur and aromatics. The analysis indicates that FTL fuels are typically less costly to produce when electricity is cogenerated than when producing mainly liquid fuels.¹²⁰

A numerical simulation of the Fischer–Tropsch (FT) synthesis in a tubular reactor packed with an iron-based catalyst has been conducted to assess the effects of process parameters on product distribution.¹²¹ The study adopted the alkyl and alkenyl mechanisms in predicting the formation of paraffins and olefins. The extent of the variation of the syngas molar–feed ratio, reactor inlet pressure, and reactor length on paraffin and olefin selectivities and mass flow rates has been documented. Also, limiting factors for the heating value output have been discussed, and a study addressed *in situ* H₂O removal by a hydrophilic membrane to maximize carbon efficiency.¹²²

Bio-oils by Feedstock Liquefaction. The energy requirements and costs for dewatering and drying wet biomass (e.g., algae) are very high. Thus, there is a need for processes that convert wet biomass directly into crude bio-oils or biodiesel fuels. Liquefaction of biomass produces a water-insoluble bio-oil by treatments at high pressure (50–200 bar) and relatively low temperature (250–500 °C).^{9,10,72,80,81,123} The hydrothermal and gasification processes investigated offer ways to deliver much of the heating value of the initially wet biomass as fuel-range molecules. The overall objective of biomass

liquefaction is to control the reaction rate and reaction mechanisms, using pressure, gases, and catalysts, to produce a premium liquid oil. During bio-oil production, a large number of reactions occur, including hydrolysis, dehydration, isomerization, dehydrogenation, aromatization, retro-condensation, and coking. The exact composition of the bio-oil is dependent on many factors, such as feedstock composition, heat transfer rate, temperature, and residence time.⁸⁰ The composition of the products can be determined, for example, by solvent fractionation followed by the analysis of various fractions via gas chromatography/mass selective detector (GC/MSD), capillary electrophoresis, NMR, etc.¹²⁴

The pyrolysis of willow wood, corn stalk, rice husk, and sorghum and wheat straw was studied by thermogravimetric analysis (TGA).^{125,126} The experiments yielded dependable kinetic parameters, such as energy of activation and Arrhenius preexponential factor. The resulting models described well the experimental data and may be suitable for predicting kinetic properties. Because of their very complex composition, bio-oils are incompatible with conventional fuels. The most significant problems of bio-oils as fuels are too low volatility, high viscosity, coking, corrosiveness, and cold flow problems.¹⁰ The standard ASTM D7544 specification covers a pyrolysis liquid biofuel produced from biomass intended for use in industrial burners. However, this type of biofuel is not intended for use in residential heaters, small commercial boilers, engines, or marine applications.

Biodiesel Fuels. Methods to reduce the high viscosity of vegetable oils to enable their use in common diesel engines have been extensively investigated and include blending with petroleum-based diesel, pyrolysis, microemulsification (cosolvent blending), and the TE process.¹² The latter is by far the most common method to produce biodiesel fuels. To obtain these fuels on a commercial production scale, the triglyceride feedstock is subjected to a TE process in which the triglycerides are reacted with alkyl alcohols to form fatty acid alkyl esters. The global TE process between triglycerides (TG) of identical fatty acids (e.g., triolein), for example, and methanol can be written as



This overall reaction is, in reality, a sequence of many other competitive or consecutive reactions. Among them, the most significant are



In these reactions, DG and MG are diglycerides and monoglycerides, respectively. Although a molar ratio of 3:1 for methanol to triglyceride is considered to be the stoichiometric ratio, in practice, a large excess of methanol is commonly used. At temperatures >350 °C, glycerol will thermally decompose and react with methanol to produce ethers.^{86–88}

Reaction parameters of a catalyzed TE process include the molar ratio of alcohol to vegetable oil, temperature, reaction time, degree of refinement of the vegetable oil, and the effect of the presence of moisture and FFA.¹² For the maximum TE conversion, the alcohol should be free of moisture (<0.1–0.3% (mass/mass)) and the FFA content of the oil should be <0.5% (mass/mass). The conditions of 60–80 °C, 1 atm,

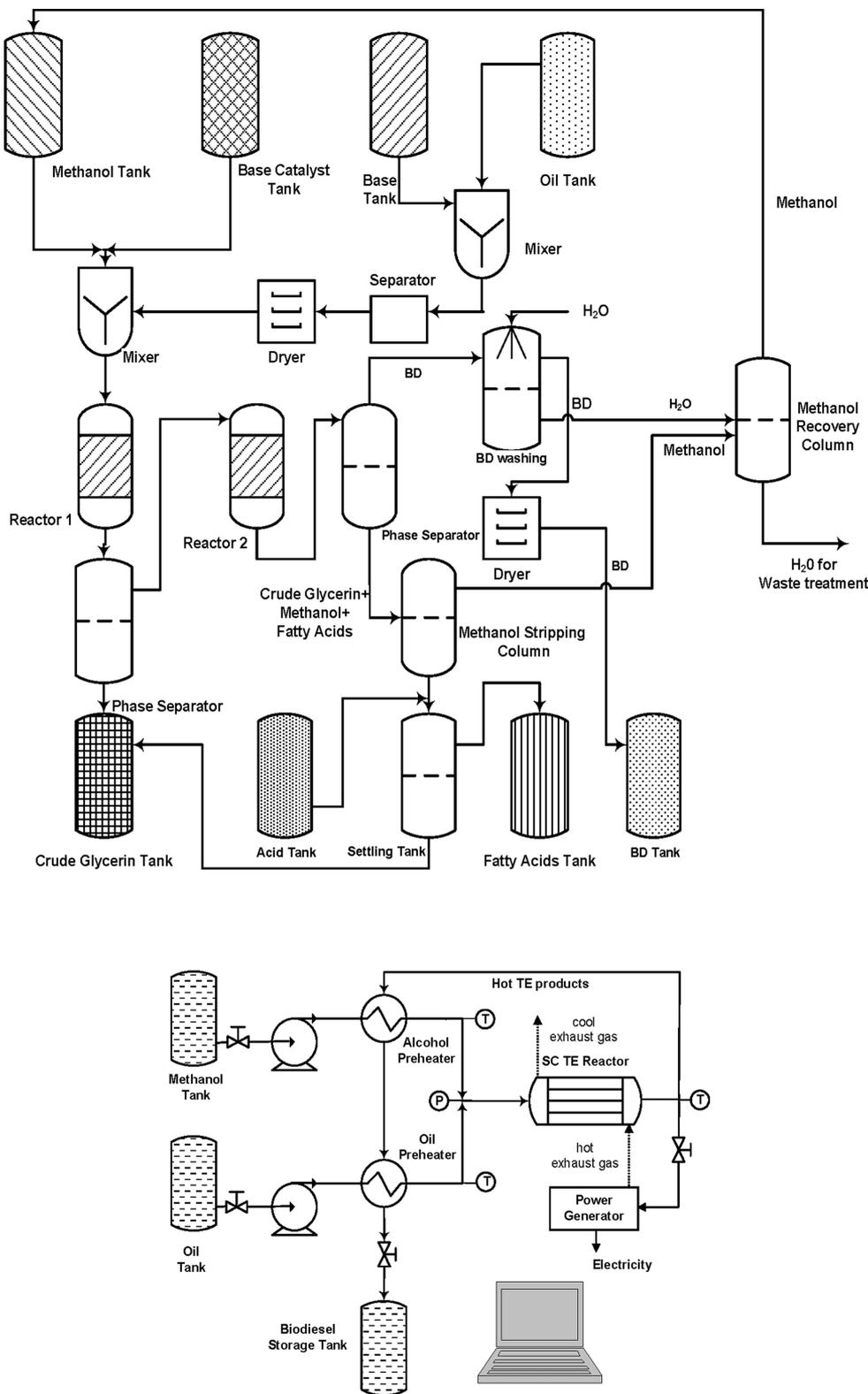


Figure 5. Process diagrams for biodiesel (BD) production by a conventional method (top)¹³⁴ and by SC-TE (bottom).⁸⁶

6:1 methanol/oil molar, 1–3 h reaction time for a conversion of 99% have become standard for conventional TE.¹² However, the complexity of the overall process renders this fuel more expensive than petroleum-derived diesel fuels. The problems reside in the necessity of using highly refined oils and costly separation and purification steps of complex mixtures (residual reactants, catalysts, reaction products, and byproducts).

The effect of the solid-acid and ion-exchange-resin catalysts on TE reactions was studied to enhance the use of lipids with high FA content.^{127–130} Compared with the typical homogeneous catalytic TE reactions, these offer the advantages of simplified product cleanup and a reduction in waste materials. The activity of various catalysts is slightly different, resulting in moderate-to-high TE conversion and product yields. The studies

reported TE temperatures in excess of 200 °C to achieve >90% conversion. Solid catalysts could also play a mixing role for TE reactants, while an improved mixing can occur without a catalytic activity. The kinetics of esterification of fatty acids with alcohols revealed that porosity and surface hydrophobicity of the catalyst are important factors other than acid properties that influence the esterification reaction.^{131,132}

Another nontraditional approach was reported to produce biodiesel fuel through noncatalytic TE of various feedstocks in SC alcohol (e.g., mostly methanol and ethanol).^{40,41,133} New methods related to this technology were reported as simplifying the TE processes. The assessed manufacturing costs are still high, however, as a result of the large excess of alcohol used (molar ratio of ~42:1 vs stoichiometric 3:1) and the necessity to perform glycerol separation. To overcome these issues, a new version of these methods was proposed.^{27,86–88} A comparison between the conventional catalytic¹³⁴ technology and this new SC-TE method⁸⁶ is shown in Figure 5.

The obvious simplicity of the SC-TE method is due to the lower excess of alcohol needed, with cost savings on recycling, glycerol decomposition to valuable fuel components (no need for complex separations), no catalyst to be recovered, and the substitution of batch by continuous flow reactors. These improvements could lead to a manufacturing cost of biodiesel fuel half of that of the conventional catalytic method.^{27,86}

Properties Needed for Transesterification (TE) Reactions. The properties needed to successfully engineer and optimize TE reactions include heats of reaction and kinetic parameters for specific reactants (e.g., fatty acid profile and the nature of alcohol). The main properties needed in the modeling work for the development of a comprehensive TE model are chemical kinetic rate constants, reaction paths, and thermodynamic parameters. Furthermore, the essential properties of biodiesel fuel produced by TE reactions such as glycerol content, ester composition, and volatility (through distillation curves) are also needed in order to have feedback control on feedstock composition and TE conditions. Unfortunately, the science behind biodiesel fuel production is not yet well developed. The heat of the TE reactions, TE reversibility, and catalytic activity (particularly at high temperature) are a few issues that have not yet been convincingly addressed. Often, the role of fluid mixing in increasing TE conversion conferred by a solid bed/mesh is misleadingly assigned to a catalytic activity, and the excess alcohol is erroneously explained as a shifting factor of the reaction equilibrium.

Reaction Reversibility. Theoretically, TE is a reversible reaction, particularly for small molecules. In the production of FAMES in a liquid phase, however, the reverse reaction does not occur or is negligible, simply because the glycerol formed is not miscible with the product (again, a property consideration). Accordingly, the often-claimed involvement of excess methanol as a driving force of the TE equilibrium toward the product side is unsustainable and uneconomical under practical conditions.¹³⁵ Also, for mostly reported SC-TE reactions, a large excess is actually needed for mixing, to bring reactants into one homogeneous phase.⁸⁷

Heat of the Overall TE Reactions. Information regarding the endo- or exothermicity of the overall reactions of the TE process is not yet available. A calculation based on the values of the heat of formation of the TE reactants and products²¹ shows a thermal effect of ~13 kJ/mol. This endothermic effect is in agreement with the increasing triglyceride conversion with increasing TE temperature. DSC or TGA studies of TE

reactions should be performed to acquire reliable data on the thermal behavior of triglyceride–alcohol systems.^{103,136}

The heat of the overall TE reaction ($\Delta_r H(T)$) can be obtained in two ways. First, $\Delta_r H(T)$ can be calculated by the Kirchhoff equation, based on $C_p(T)$ of the reactants and products:¹⁰³

$$\left(\frac{\partial C_{p,\xi}}{\partial \xi}\right)_{T,p} = \left(\frac{\partial \Delta_r H}{\partial T}\right)_{p,\xi} = \sum_i (\nu_i C_{p,i}) \quad (10)$$

$C_{p,\xi}$ is the heat capacity of the system at constant pressure and extent of reaction (ξ), ν_i are the stoichiometric numbers, and $C_{p,i}$ are the partial, molar heat capacities of the reactants and products.

Second, $\Delta_r H(T)$ can be obtained from DSC-measured heat flow rates:

$$\left(\frac{dQ}{dt}\right)_p = C_{p,\xi}(T) \frac{dT}{dt} + \langle \Delta_r H \rangle \frac{d\xi}{dt} \quad (11)$$

where $\langle \Delta_r H \rangle$ is the reaction enthalpy. The reactants are heated as rapidly as possible from room temperature to the reaction temperature, to decrease the effect of the unsteady state. The reaction equilibrium is reached when a constant heat flow rate Φ_{end} is achieved. Because there is no contribution from heat capacity in the isothermal mode, the average reaction enthalpy is

$$\langle \Delta_r H \rangle = \frac{\int_0^t (\Phi_m - \Phi_{\text{end}}) dt}{\int_0^\xi d\xi} \quad (12)$$

Reaction Kinetics. The TE kinetic parameters are dependent on the molar ratio between the triglycerides and the alcohol. For the stoichiometric ratio of 1:3, the overall TE reaction is second order, while for a large excess of alcohol TE is a pseudo-first-order reaction.⁴¹ Kinetic analyses to date have used simple global reaction models with assumed reaction orders, and typically, they have used a single overall reaction.⁴¹ The rate constants for the triglycerides forming diglycerides and then monoglycerides were comparable and temperature dependent, while the last step of monoglyceride conversion to glycerol was much slower. Because diglycerides reach a maximum concentration before monoglycerides (Figure 6),

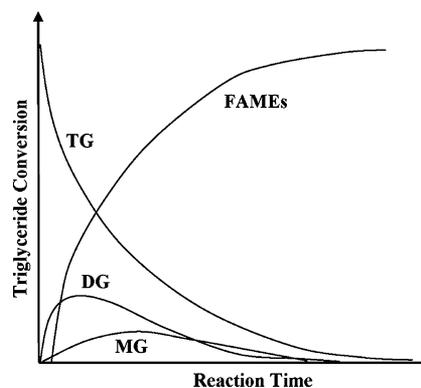


Figure 6. Qualitative dependence of the TE conversion of a triglyceride (TG) to a FAME product on the reaction time. The reaction proceeds through diglyceride (DG) and monoglyceride (MG) steps.

the formation of glycerol from monoglycerides proceeds more rapidly than the formation of monoglycerides from diglycerides.

There are separate linear trends within the subcritical ($T < 239\text{ }^{\circ}\text{C}$) and SC region ($T > 239\text{ }^{\circ}\text{C}$).⁴¹ The existence of these two regions could be linked to the phase behavior. At subcritical conditions, two liquid phases exist, and the rate of interphase mass transfer could limit the observed reaction rate. As the reaction proceeds, the generated FAMES increase methanol solubility in oil, and consequently, the reaction rate increases.

There has been some tendency of separating thermophysical properties and kinetic properties, but we point out that at the present time, efforts are under way to unite the two. For example, there is work in progress on an additional measurement associated with the advanced distillation curve metrology to include ignition delay and sooting properties. These efforts will relate the thermophysical properties of diesel and jet fuels to the kinetics, since detailed kinetic mechanisms are used to predict ignition delay and sooting properties. Also, one cannot measure thermophysical properties without an explicit understanding of kinetics. This is reflected in vapor pressure measurements on FAMES, and on all measurements on finished fuels at high temperatures.

Energy of Activation. Due to the miscibility issues, it is difficult to accurately assess the kinetic parameters of TE reactions. Conflicting results, along with the wide range of activation energies reported in the literature, point to the difficulty of doing TE kinetic studies and separating out transport, mixing, and phase-behavior effects.⁴¹ Another issue is that the kinetic phenomena are sensitive to the specific alcohol and oil used in the TE reactions. Additionally, the experimental data used to determine rate constants and activation energies could be affected by unintended metal-catalyzed reactions. Furthermore, activation energies differ in the subcritical and SC regions in some but not in all of the studies.^{41,137} Separate linear trends were reported within the subcritical ($T < 239\text{ }^{\circ}\text{C}$) and SC region ($T > 239\text{ }^{\circ}\text{C}$) with different values of the activation energy.⁴¹ There is clearly a need for more work on the kinetics of TE reactions, so that the reaction orders, intrinsic rate constants, and activation energies can be determined.

■ BIOFUEL PROPERTIES

Properties of Biodiesel Fuels. Viscosity. Viscosity is one of the most important transport properties for flowing processes, and one of the most sensitive to compositional differences.^{138,139} While most of the biodiesel fuel properties compare favorably with those of petroleum-derived diesel fuels, the higher viscosity of biodiesel fuel can affect fuel injection parameters. Although it meets the specifications in the ASTM standards, the viscosity of commercially produced biodiesel fuel is outside the allowed range by ASTM standard D975 for petrodiesel fuels (4.2–4.6 vs 2.5–3.2 mm^2/s at 40 $^{\circ}\text{C}$).¹³⁸ Biodiesel fuels from soybean oil usually display viscosity slightly below 4.2 mm^2/s .

The standard test method ASTM D445¹⁴⁰ is commonly used to measure the viscosity of liquid petroleum products. The kinematic viscosity is determined by measuring the time for a known volume of liquid flowing through a calibrated glass capillary viscometer tube. The manufacturers of the viscometer tubes provide calibration constants at two temperatures, usually at 40 and 100 $^{\circ}\text{C}$. According to the ASTM standard, in order to accept a viscosity measurement, the measurement should be conducted twice, and the first and second measurements should agree within 0.02 mm^2/s .

Biodiesel fuel viscosities were found to increase exponentially with both rising pressure and reducing temperature.¹⁴¹ The regression equation for isobaric viscosity data that is commonly recommended in the literature is¹³⁸

$$\ln \eta = A + B/T + C/T^2 \quad (13)$$

In this equation, η is the kinematic viscosity in mm^2/s (cSt), A , B , and C are constants for the fluid, and T is the absolute temperature. The empirical values of A , B , and C can be found using common polynomial curve-fitting software. If individual viscosity data for biofuel components are available in the literature, viscosity for the bulk fuel of composition x_i can be calculated using the simplified Grunberg–Nissan equation:

$$\ln \eta_{\text{mix}} = \sum x_i \ln \eta_i \quad (14)$$

A group-contribution method has also been proposed for the estimation of the viscosity of fatty compounds and biodiesel esters as a function of temperature.^{51,142}

The viscosity of some of biodiesel fuels was reported to increase linearly with pressure until ~ 35 MPa, followed by a higher order response to pressure.¹⁴³ Except for biodiesel from coconut oil, the biodiesel samples have viscosities that are greater than petroleum-derived diesel at both ambient and elevated pressures. The viscosity of biodiesel fuels with pressure can increase nearly 300% over their respective ambient-pressure viscosity, while diesel fuel no. 2 increases up to $\sim 400\%$ over similar pressures. The biodiesel samples at 10 $^{\circ}\text{C}$ were found to experience pressure-induced cloud points (solid–liquid equilibrium) from 70 to 100 MPa, which significantly increases their viscosity. The Tait–Litovitz equation was found to correlate the data well over the large range of both temperature and pressure.¹⁴³ The viscosity was also measured for the algal methyl ester formulations.¹⁴⁴

Volatility. Volatility is a crucial fluid property for fuel replacement and enhancement, and for proper engine operation. Volatility information for the main FAME compounds in natural lipid feedstocks is provided in Table 3 as boiling points. Volatility of complex fuels is very sensitive (if not the most sensitive property) to compositional variability and can be determined by the advanced distillation curve (ADC) technique, method developed at NIST.^{30–35,145–148} The distillation curve for multicomponent fuels, usually presented graphically as boiling temperature against volume fraction distilled, is often cited as a primary criterion for design and testing of liquid fuels. While the standard test method, ASTM D-86, provides the usual approach to measurement, it has no basis in theory.¹⁴⁹ The advanced distillation curve gives a thermodynamically consistent measure of fuel volatility fraction by fraction.^{30–35,145–148} For this reason, the ADC data can be used for fluid modeling. There are numerous engineering and application-specific parameters that can be related to a distillation curve. When applied to liquid fuels, for example, one can estimate engine starting ability, fuel-system icing and vapor lock, fuel-injector timing, fuel autoignition, etc.

The fuel composition, the most important parameter that governs distillation curve shape, has been determined for a variety of fuels, including biodiesel fuels.^{13,17,34,35,147,148} The distillation curves can be easily compared with those of selected fuels that are considered typical (e.g., DF2 and commercial soybean biodiesel fuel) as shown in Figure 7.¹⁵⁰ Also, equations based on experimental data were proposed for the normal boiling temperature of FAMES, T_{nb} , as a function of the number

Table 3. Property Information for the Main FAME Compounds in Natural Lipid Feedstocks

FAME	molecular structure	CAS number	RMM ^a	bp ¹⁴⁸ (°C) ^b	mp ²¹² (°C) ^c
methyl caprylate	C8:0	111-11-5	158.24	193.0 (0.35) ^d	-37.43 (0.26)
methyl caprate	C10:0	110-42-9	186.29	224.1 (1.00)	-13.48 (0.52)
methyl laurate	C12:0	111-82-0	214.34	266.9 (13.3)	4.30 (0.54)
methyl myristate	C14:0	124-10-7	242.40	323.1 (2.00)	18.09 (0.42)
methyl palmitate	C16:0	112-39-0	270.45	331.9 (3.30)	28.48 (0.44)
methyl stearate	C18:0	112-61-8	298.50	360.9 (18.0)	37.66 (0.25)
methyl oleate	C18:1	112-62-9	296.49	343.9 (34.4)	-20.21 (0.51)
methyl linoleate	C18:2	112-63-0	294.47	346.0 (10.4)	-43.09 (0.71)
methyl linolenate	C18:3	301-00-8	292.46	347.0 (10.4)	-57.00 (0.57)

^aRMM is the relative molecular mass of the compound. ^bbp is the normal boiling point. ^cmp is the normal melting point. ^dThe uncertainties are provided in parentheses.

of the carbon atoms, N_C . An example is the following:¹⁵¹

$$T_{nb}(K) = 218.49 \ln N_C - 6.933 \quad (15)$$

The equation was obtained from the data of C₁₀–C₁₈ and was applied up to C₂₄ with a maximum prediction error less than 1.5 °C.

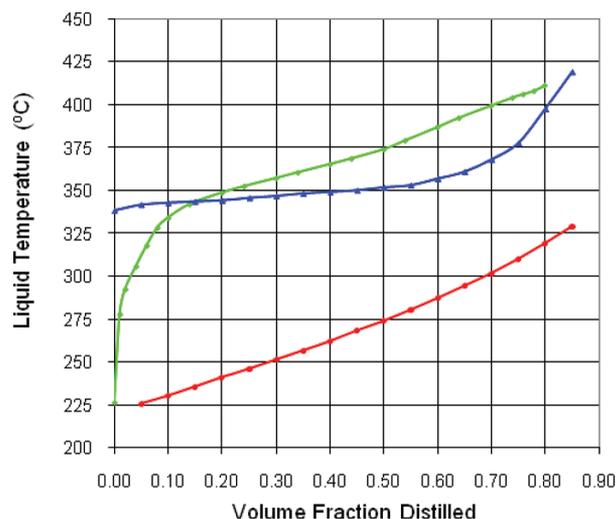


Figure 7. Distillation curve for biodiesel fuel obtained under SC-TE conditions from soybean oil (green) compared to those of commercial biodiesel fuel (blue) and diesel fuel DF2 (red).¹⁵⁰

The experimental results show that renewable biodiesel fuel samples obtained from SC fluid processing exhibit higher volatility compared to commercial biodiesel fuels produced by a conventional catalytic method.¹⁵⁰ This volatility is very close to that of the DF2 at the start of vaporization, while commercial biodiesel fuel starts boiling at a temperature higher by more than 100 °C. At the end of the distillation curves, biodiesel fuel samples obtained at 400 °C by SC-TE showed no significant thermal decomposition.¹⁵⁰ The distillation curve of the commercial biodiesel fuel exhibits a sharp increase in temperature at volumetric fractions higher than ~70% as a result of significant thermal decomposition.¹⁵⁰ Thermodynamic models have also been developed to represent the volatility and other thermophysical properties such as density, speed of sound, heat capacity, viscosity, etc.^{51,99,101,142} Fuel volatility provides a basis of comparison among fuels in terms of the fundamental thermophysical properties. This comparison is critical in determining the applicability and suitability of feedstocks designed

for the production and manufacturing of biodiesel fuel to enhance/extend current petroleum-derived diesel fuels. Alternatively, simulated distillation has been used to classify novel biofuels regarding boiling characteristics and quality.¹⁵²

Thermal Conductivity. Thermal conductivity is a fuel property mainly involved in the combustion process when heat from the SC air is transferred to the fuel droplets to vaporize. It is also needed in the design of heat exchangers when the processing step involves heating of the fluids. Experimental data on the thermal conductivities of the methyl oleate and methyl linoleate in the liquid phase have been reported.¹⁵³ These data, covering the temperature range 29–235 °C at 1–420 bar, were used to develop correlations for the thermal conductivity. The experimental data reported have an uncertainty of less than 1%, while the thermal conductivity correlations are estimated to have a relative uncertainty of about 2.5% at a 95% confidence level.

Density and Speed of Sound. Density is one of the most important biodiesel properties, because engine injection systems must deliver an amount of fuel precisely adjusted to provide efficient and clean combustion. The pressure effect on fuel density has become particularly important with the increased use of modern common rail systems, where pressures can be >2000 bar. Experimental measurements, from 10 to 60 °C and from atmospheric pressure to 450 bar, were performed for methyl laurate, methyl myristate, and methyl oleate, for methyl biodiesels from palm, soybean, and rapeseed oils, and for three binary and one ternary mixtures of these oils.¹⁵⁴ The cubic-plus-association EOS was shown to be an appropriate model to be applied to production and purification processes of these biodiesel fuels. The high-pressure experimental data reported were predicted with a maximum uncertainty of 2.5%. The density and speed of sound were also measured for five FAMES (at 83 kPa, 5–65 °C)⁹⁹ and for the algal FAMES.¹⁴⁴

Fit-for-Purpose Properties. A FAME mixture as a fuel is regulated under ASTM D6751⁵⁸ or EN 14214.⁵⁹ Several properties of representative FAMES and FAEs (cetane number, heat content, viscosity and cold properties) are compared to those of DF2 in Table 4. While the cetane numbers of biodiesel fuels are larger than those of diesel fuels, others properties, such as viscosity and cold-flow properties, are inferior. Additionally, common properties of ethanol and an average biodiesel fuel are presented in Table 5.¹⁵⁵ For comparison, the table also includes properties of gasoline and petrodiesel fuel DF2. Although the flash point of a biodiesel fuel is difficult to predict because it is strongly dependent on alcohol content, QSPR models were used to predict flash points

Table 4. Selected Fit-for-Purpose Properties of the Main Esters Produced from Oils and Fats⁷⁶

ester source	CN ^a	heat content (MJ/kg)	viscosity ^b (mm ² /s)	CP (°C) ^c	PP (°C) ^d
Methyl					
rapeseed	54.4	40.45	6.7	-2	-9
soybean	46.2	39.80	4.1	2	-1
sunflower	46.6	39.80	4.2	0	-4
tallow		39.95	4.1	12	9
Ethyl					
palm	56.2	39.07	4.5	8	6
soybean	48.2	40.00	4.4	1	-4
DF2	47.0	45.34	2.7	-15	-33

^aCN = cetane number. ^b at 40 °C. ^cCP = cloud point. ^dPP = pour point.

and cetane numbers of fuels with no experimental data in the literature. Using available information from other similar fuels, evolutions of properties with the number of carbon atoms in families of compounds, such as hydrocarbons, alcohols, and esters, have been studied.⁵³

Cold-flow properties are the Achilles' heel of biodiesel fuels in cold climates. To investigate precipitation above the cloud point (CP) in biodiesel fuels, three saturated monoglycerides (SMGs) (monomyristin, -palmitin, and -stearin) were spiked into B100.¹⁰⁷ It was shown that above the eutectic concentration, the SMGs significantly raise the CP of B100. SMGs have an even greater impact on the final melting temperature (FMT) at concentrations above the eutectic point. FMT is highly dependent on the heating rate. When the results were compared to a thermodynamic model for an ideal solution, the model was able to provide reasonable prediction of the eutectic point but was less successful at predicting CP and FMT above the eutectic. Also, the liquid- and solid-phase compositions and fractions at temperatures below CP (-13 to 2 °C) were studied for commercial biodiesel fuels.¹⁵⁶ A thermodynamic model able to describe these multiphase systems was developed based on the predictive UNIQUAC model. To improve the cold-flow properties of biodiesel fuels, it

has been suggested that the FA profile of oils be altered before the TE processing.¹⁵⁷

Properties of Bioalcohols. Because the chemical structures of bioalcohols do not differ from those of the common alcohols, their properties are well-known and, consequently, will not be discussed here in detail. Comparatively, bioalcohols exhibit high polarity, while biodiesel fuels are slightly polar and petroleum-derived fuels are practically nonpolar. The real problem comes in modeling the thermophysical properties of such polar molecules; this is still in the early stages. Thus, the real problem is not always in property measurements and availability. Compared to ethanol, butanols have more carbon-hydrogen bonds and thus higher molar energy content. The butanols are significantly less volatile than ethanol, and they appear to lower NO_x combustion emissions in mixtures compared to gasoline.¹⁵⁸ Butanol blends do not have the phase-separation problems seen with ethanol, and they are also much more compatible with the materials found in typical engines. These blends have a much lower antiknock index than blends with ethanol, however. Currently, refiners make a hydrocarbon blending stock that does not meet the minimum requirements for antiknock index until ethanol is added; this is known as a blendstock for oxygenate blending, or BOB. Both conventional and reformulated BOB are mainly manufactured as suboctane materials intended for ethanol blending. This is a significant issue for the market introduction of butanol, and octane number is a major fit-for-purpose property.

Properties of Renewable Gasoline, Jet, and Diesel Fuels. The properties of renewable gasoline are similar to those of petroleum-based gasoline and thus, well established. For the renewable gasoline and jet/diesel fuels, the modeling is also well in hand. Density, speed of sound, thermal conductivity, and VLE can be predicted or modeled within experimental uncertainty. Viscosity is more of a problem. These fuels are compatible for blending with standard petroleum-derived fuels. In contrast to FAMES, where fuel properties depend on feed origin and process configuration, the renewable jet and diesel fuels are largely independent of feedstock origin, and the fully deoxygenated biofuel is readily blended with a conventional petroleum-derived fuel. A life-cycle analysis of

Table 5. Fit-for-Purpose Properties of Ethanol, Biodiesel B100, and Blend B20 Compared to Gasoline and Diesel Fuel No. 2 (DF2)¹⁵⁵

property	ethanol	gasoline ^a	B100 ^a	B20 ^a	DF2 ^a
chemical formula	C ₂ H ₅ OH	C ₈ H ₁₅	C ₁₉ H ₃₆ O ₂	C _{15.4} H ₃₀ O _{0.3}	C ₁₄ H ₂₇
molecular weight	46	111	296	220	200
carbon (mass/mass %)	52	86	77	84	86
hydrogen (mass/mass %)	13	14	12	13.6	14
oxygen (mass/mass %)	35	~0	11	2.4	~0
specific gravity	0.79	0.75	0.88	0.86	0.85
boiling temp. (°C)	78.5	37-225 ^b	340-440 ^b	218-390 ^b	216-343 ^b
octane no.	107	87-98			
cetane no.			46-65	46	40-55
freezing point (°C)	-114	-40	(-9)-9		-30
viscosity (mm ² /s) at 20 °C	1.5	0.5-0.6	4.1-6.3	2.92	2.6-4.1
autoignition temp. (°C)	423	257			315
flash point (°C)	13		>93/130		52
lower heating value (MJ/L)	21	32	36	38	39
specific heat (kJ/kg °C)	2.5	2.4	2.0	2.0-2.2	2.2
critical temp. (°C)	249	296-308	448-492	458	439-467
critical pressure (MPa)	6.3	2.5	1.3	1.3-1.4	1.4

^aApproximate molecular formula and property values are given, because the compositions of these fuels are widely variable. ^b90% (v/v) distilled.

new biofuel production technologies quantified the intrinsic benefits of the fit-for-purpose properties of renewable jet/diesel fuel production over the current practice of converting various forms of lipids to FAMES.⁶³

Biofuel Purification/Refining and Blending. *Product Purification/Refining.* Products of biofuel processing include not only the biofuel but also some other by-products. For example, TE products contain, along with FAMES, several by-products in different phases such as soap, glycerin, excess alcohol, catalyst, and various amounts of water. For a biofuel to meet the standard specifications, all of these by-products must be removed, although the order of removal is process-dependent. Because the glycerin-rich phase is denser than that of biodiesel fuel, it settles out and can be removed from the bottom of the product vessel. Once separated from the glycerin, the residual biodiesel phase goes through a cleanup or purification process to remove excess alcohol, catalyst, and soaps. Residual methanol is typically removed through distillation and reused, though it can be washed out with water as aqueous waste. Soaps can be removed by one or more washings with clean water. The fuel is then dried and sent to storage. Residual water must be removed from the fuel to <0.05 vol %. The biodiesel phase can also go through an additional distillation step to produce a colorless, odorless, zero-sulfur biodiesel fuel.

Bioethanol aqueous solutions obtained by feedstock fermentation require both time- and energy-consuming steps to yield an acceptable fuel. These issues are due to the fact that ethanol forms an azeotropic solution with water at 96% (v/v) ethanol concentration. To break the azeotrope, significant energy is required. Distillation, followed by molecular sieve separation for anhydrous ethanol, is the method of choice for the recovery of ethanol from fermentation broth at an industrial scale.^{72,78} Distillation is an energy-intensive process, and the ethanol concentration that can be obtained in the fermentation broth is limited by ethanol inhibition of the fermenting strains. To overcome this problem, in situ ethanol separation can be used by integrating the reaction-separation processes.^{159,160} Ethanol removal by vacuum has reportedly increased the ethanol productivity 12-fold, as compared to conventional systems.^{161,162} Other methods of ethanol removal include gas stripping by CO₂ (generated during fermentation), pervaporation, solvent extraction, membrane distillation, the use of hollow fiber fermentors and membrane bioreactors, etc.^{9,10,78}

As was said in a previous section, the properties that most negatively affect bio-oil fuel quality are low heating value, incompatibility with conventional fuels, solid content, high viscosity and acidity, low volatility, and chemical instability.^{10,163,164} Bio-oils can be upgraded into a liquid transportation fuel by three different routes: (1) hydrodeoxygenation with typical hydrotreating catalysts (sulfided CoMo or NiMo), (2) zeolite upgrading, or (3) forming emulsions with the diesel fuel.¹⁰

Blends of Petroleum-Derived Fuels with Biofuels. Biodiesel fuel compositions vary significantly due to the various feedstocks used in fuel production. Many of these compositions render fuels unsuitable for specific applications. However, if these fuels of different origins are blended together and/or with petroleum-derived diesel fuels, their properties can be improved to meet specific fit-for-purpose requirements (Table 6).^{58,165} Oil companies and vehicle manufacturers are actively working with biofuel extender producers to have agreed standards for biodiesel fuels suitable for blending with conventional diesel

Table 6. Main ASTM Properties of Biodiesel (B100)⁵⁸ and a B20 Blend¹⁶⁵ Compared to DF2

property	DF2 ASTM D975	B20 ^a ASTM D7467	B100 ASTM 6751
flash point, minimum (°C)	52	52	93
cetane no., minimum	40	46	47
viscosity (mm ² /s at 40 °C)	2.6–4.1	1.9–4.1	1.9–6.0
cloud point (°C)	–17	–14	report
distillation, T90 (°C)	<343	<343	<360
acid no. (mg KOH/g)	<0.005	<0.3	<0.50
free glycerin (% mass)			<0.020
total glycerin (% mass)			<0.240
methanol (% vol)			<0.2
water and sediment (% vol)	<0.05	<0.05	<0.05
sulfur (ppm)	<15	<15	<15
phosphorus (% mass)			<0.001
oxidation stability (h)		>6.0	>3.0

^aDF2 and B100 in this blend have to meet the specifications of neat fuels.

fuels to ensure that the product meets the technical requirements of modern diesel engines. The minimum test requirements for biodiesel blend extenders are specified in ASTM D6751⁵⁸ in the United States and EN 14214⁵⁹ in Europe.

EN 590¹⁶⁶ and ASTM D975¹⁶⁷ fuel specifications for petroleum-based diesel fuels currently permit a biofuel extender content of up to 5 and 20% (v/v), respectively. Biodiesel fuel is usually blended with petroleum diesel to form a B20 blend, although other blends can be used up to B100. B20 fuel blend can be used in existing engines and fuel injection equipment with little impact on operating performance. In a NREL nationwide survey of the quality of B20 samples (mainly from soybean- and fat-derived B100), the B20 samples were tested against multiple properties.¹⁶⁸ 25% of the samples were below the 6-h proposed limit for the induction period, while the average of 8.4 h was well above the 6-h limit. Every sample except one met the proposed acid-value specification of 0.3 mgKOH/g. The average cloud point was –12.6 °C, and all the samples met the flash point minimum of 38 °C. The range of cetane number for the blends was 46 to 52. As expected by its higher polarity, the average Karl Fisher water content of the B20 samples was about 30% higher than that of conventional diesel fuel. The metal content of the blends was low. Moreover, B20 has a heat content that falls in the range between those of no. 1 and no. 2 diesel fuels. The parent B100 stock was typically on-specification for glycerin.

Ethanol contains only ~67% (v/v) of the energy of gasoline, but it has a higher antiknock index. Ethanol is typically blended with gasoline to form an E10 blend (5–10% (v/v) ethanol), but it can be combined with gasoline in higher concentrations within modified spark-ignition engines (so-called flexi-fuel vehicles). There has been some testing of the volatility (Reid vapor pressure and distillation curves) of alcohol-gasoline blends containing 5–85% (v/v) of methanol, ethanol, propanol, and butanol.^{169–171} E85 is nominally 85% (v/v) ethanol in gasoline, although the ethanol content is <83% (v/v) by the specification (ASTM D5798¹⁷²). E85 properties, such as ethanol concentration, water content, sulfur, vapor pressure, acidity, pH, inorganic chloride, and sulfate, vary with time of year, geography, and ambient temperature. Results showed

significant problems with the ethanol content and volatility.¹⁷¹ Selected samples were also tested for stability, octane, peroxides, and silver corrosion.¹⁷¹ Most alcohols form near-azeotropic mixtures with hydrocarbons in gasoline that affect the vapor pressure and distillation curves of the blends.

Both bioethanol and biodiesel fuels are used as oxygenate additives to improve combustion characteristics of gasoline and diesel fuels, respectively. When blended together, the fit-for-purpose physicochemical properties of ethanol–biodiesel blends could significantly influence the fuel injection and combustion characteristics, and subsequently, the exhaust emissions. In this context, the following properties have been investigated experimentally: fuel stability, density, viscosity, cold filter plugging point (CFPP), cloud point (CP), pour point (PP), flash point, filter plugging tendency (FPT), corrosiveness, lubricity, Fourier transformation infrared (FTIR) analysis, C–H–N composition, and water content.¹⁷³ The tested fuels were pure biodiesel (B100) and 5, 10, and 15% (v/v) ethanol–biodiesel blends. In general, the results showed that ethanol in biodiesel influences beneficially the most important fuel properties of the blended fuel. Biodiesel fuels could also contain glycerol ethers from *in situ* etherification during SC-TE^{86–88} or catalytic reactions of glycerol with alcohols.^{43,174}

As we have mentioned earlier, the most important application of high precision thermophysical property measurements is for the development of reliable predictive models. We have also noted that the models are only as good as the data that are used in the formulation of those models. We caution the reader further to avoid the use of predictive results that are far outside the temperature and pressure range of available measurements. It is clear that models based on measurements performed at atmospheric pressure have limited utility when tasked with predictions at elevated pressure. There are two aspects to this limitation. Surrogate mixture models require measurements not only of the target fuel (for example, a biodiesel fuel) but also of the pure components that compose the surrogate slate. Thus, a model developed for a fuel might include measurements in the compressed liquid state for the fuel itself, but the pure components used in the surrogate might have limited data. The conclusion here is that progress will only be possible if measurements on pure components are performed along with measurements on the finished fuels.

A blend of a biofuel with gasoline or diesel fuels involves hundreds of chemical components, mostly hydrocarbons and oxygenated compounds. The bioalcohols and biodiesel fuels have fundamentally different chemical characteristics compared to petroleum-derived hydrocarbons. Biofuel molecules (alcohols, esters, and/or carboxylic acids) are all polar and associating. This is a great challenge for property science, which is currently focused on pure fluids and simple mixtures. The successful implementation of biofuels demands accurate property data for mixtures with hundreds of components, which may chemically be very dissimilar. Meeting this challenge requires new approaches to modeling and measurements. Rapid experimental methods are needed to characterize the multitude of molecular interactions present in complex mixtures. Measurements have to be performed over wide ranges of thermodynamic conditions that are required for a successful model development. Modeling approaches must be expandable to many components and to the various types of molecular interactions.

■ STABILITY OF BIOFUELS DURING TRANSPORT AND STORAGE

Overview. Once a fuel is produced, it must be transported from the refining/blending site to the storage facilities, either locally or remotely. Liquid-fuel systems can integrate biofuels for transport applications or for other applications. Pure (100%) biofuels, or more usually those blended with petroleum-based fuels, must meet technical standards consistent with vehicle-engine fuel specifications. It is likely that distribution of neat or blended biofuels can be accommodated with the existing fuel infrastructure, including pipeline transport.

Because biofuels come from biofeedstocks, they are more prone to oxidation than fossil fuels. Aging in air can produce insoluble gums and acids that may plug and corrode engine components. The storage stability of fuels based on FAMES is a critical issue. Practical methods to define minimum stability requirements and assess biodiesel fuel shelf life are needed.¹⁷⁵ Standardized chemical analysis indicates that pure biodiesel fuels obtained from different sources range widely in shelf life from 4 weeks to 4 months. Replacing natural antioxidants removed in refining extended shelf life by mitigating formation of insoluble materials and acids.^{175,176}

Thermal and Oxidative Stability of Biofuels. The thermal/oxidative stability of finished biofuels depends upon the feedstocks used for production. For example, the stability is much greater for biodiesel fuels with high saturated fatty acid content and decreases with the degree of fatty-acid unsaturation. FAMES containing fatty acids with no C=C bonds and with multiple C=C bonds will have stability in the sequence: palmitic (0) > oleic (1) > linoleic (2) > linolenic (3). A review of current technology regarding the oxidation stability of biodiesel fuels is available in the literature.^{144,177,178} Long-term thermal and oxidative stability of biodiesel fuel becomes significant particularly when the fuel is exposed to air, heat, light, or trace metallic species.¹⁷⁹ As a result, different polymers, oligomers, acids, aldehydes, etc. are formed with negative consequences on fuel pump components, combustion profile, and overall engine performance. Accordingly, the long-term oxidative stability of biodiesel fuel in the presence of stabilizers has been evaluated.^{176,180}

Various analytical and instrumental techniques to assess biodiesel fuel quality under normal and stressed conditions have been investigated. The properties measured include peroxide values (ASTM D-3307), induction period Rancimat (EN 14112), level of insolubles and gum formation (ASTM D-2274), acid value (ASTM D-664), viscosity (ASTM D-445), etc.¹⁸⁰ Using DSC to study the stability to oxidation of samples generally requires an airtight sample chamber. Usually, such tests are done isothermally (at constant temperature) by changing the atmosphere of the sample. First, the sample is brought to the desired test temperature under an inert atmosphere, usually nitrogen. Then, oxygen is added to the system. Any oxidation that occurs is observed as a deviation in the baseline. Such analysis can be used to determine the stability and optimum storage conditions for a biofuel. Other methods quantify the oxidative stability of biodiesel fuels by measuring the level of insolubles, polymerized postoxidation gum, or sediment.¹⁸¹ Wet-chemistry methods are currently used to determine the peroxide and acid values of the fuels. However, oxidative stability measurements cannot always predict the formation of insolubles that plug filters. It was

observed that the induction period, peroxide value, viscosity, and acid value all were affected by this phenomenon. Research on this topic led to relatively good results on product stability versus time.¹⁷⁶

Because the oxidative stability of biodiesel fuels has a major impact on fuel quality, this issue has been addressed by various international standardization bodies such as the American Society for Testing and Materials (ASTM) and the European Committee for Standardization (CEN). Specifications have been established and included in the ASTM D-6751 as well as the EN 14214. Currently, the European standard EN 14214 prescribes the use of EN 14112 with 6 h minimum determined by this method. On the other hand, the ASTM biodiesel fuel standard D-6751 requires a minimum 3 h. Both organizations are considering raising the minimum oxidative stability requirements to address longer storage time and handling for biodiesel fuels.

Another chemical property of the biodiesel fuel that can be used to predict the oxidative stability is the iodine value. This property is a quantification of the number of double bonds of the fatty acids in FAME. The EN 14111 specifies a value of 120, which is reflective of canola or rapeseed-based biodiesel fuel, while for soybean-based biodiesel fuel the iodine value is about 130. The ASTM D-6751 does not include the iodine-value specifications. Unlike the Rancimat or peroxide value, the iodine value does not discriminate between the sources of double bonds. There are several approaches to improve the oxidative stability of biodiesel fuels that can be applied. One of them is to avoid contact of the biofuel with oxygen (air). Another is to prevent contact with materials and substances that promote or catalyze the reaction of oxidation such as pro-oxidants, trace metals, higher temperature, light, etc. These are mostly preventative measures, but they may not be fully applicable to the real transport/storage environment. Thus, the use of antioxidants becomes indispensable. From a functional stand point, antioxidants decelerate the kinetics of the autoxidation reaction initiated by free radicals. Therefore, the induction period (Rancimat) is extended by the addition of antioxidants until they are totally consumed by the reaction. The overwhelming majority of antioxidants used by the biodiesel fuel industry are synthetic antioxidants known for their robustness, superior chemical and thermal stability, and cost-effectiveness.^{144,176,182,183}

Bacterial Degradation of Biofuels. Biodiesel fuel is subjected to facile both aerobic and anaerobic biodegradation by wild-type bacteria commonly present in natural environments.^{184,185} This result should lessen any environmental concern for its use as alternative fuel, solvent or lubricant. However, when this degradation occurs during fuel storage, it is obviously detrimental to fuel quality. The susceptibility of biodiesel fuel to biodegradation and its propensity to stimulate biocorrosion via hydrolysis of FFA suggest caution when integrating this fuel with the existing infrastructure.¹⁸⁵ Biodiesel fuel must have a low moisture content resulting in less biological growth and fuel-filter plugging. This requirement is among listed ASTM specifications for biodiesel fuel and is imposed at less than 0.05 vol %.

Sustained efforts have been dedicated to the methods being utilized to study oxidation and bacterial stability of biodiesel fuels.^{177,181,185} These methods have directed to improve the long-term storage of biodiesel fuels. As the biodiesel industry continues to develop, the need for better testing equipment will steadily increase. The next generation of testing instruments

will need to be far more accurate and faster than instruments currently available. For this reason, the photochemiluminescence method appears to be a promising way forward, but more research is required.¹⁷⁷

■ COMBUSTION QUALITY AND FUEL PROPERTIES

Overview. This section deals with the practicality of using biomass-derived fuels in current-day engines. Fuel combustion is the central process of engines and the ultimate use of the energy that a fuel contains. Along with hardware improvements, the analysis of engine performance also demands reliable fuel-property data. The thermodynamic and transport properties of the fuel are relevant for the design of engines involving injection timing, duration, spray characteristics, and combustion quality. The differences in the fuel ignition/combustion are due to significant differences in chemical composition and physical properties of the fuels. The majority of the reported data and models on fuel combustion refer to phenomena associated with fuel-droplet vaporization (e.g., volatility), fuel–air diffusion, flame propagation, and emission formation.^{56,186–199} However, due to the potential benefits of combustion based on homogeneous charge compression ignition (HCCI), studies have been focused on SC combustion (the fuel–air mixtures are in SC states at the time of ignition).^{200–203} While HCCI offers a potential path toward high fuel efficiency and low emissions, but requires careful attention to the nature of the fuel and the unsolved issue of the ignition control, SC combustion eliminates fuel vaporization, diffusion, and flame propagation. Consequently, the reaction kinetics of the combustion process is the main player in these methods, though one not easy to control.^{57,199–207}

For conventional combustion, the subsystem of modeling transport phenomena must be coupled with chemical kinetics mechanisms. Direct integration of computational fluid dynamics (CFD) with a detailed chemistry autoignition model (KIVA-CHEMKIN) performs reasonably well for predicting ignition delay, combustion, emissions, and flame structure for engine operations.^{198,203} To extend the range of the existing models, a hybrid model (KIVA-CHEMKIN-G) was proposed, validated and applied for both a stratified diesel engine and partially premixed dual-fuel engine operation.²⁰³ Difficulties of the detailed combustion studies based on reaction kinetic, pathways, and mechanisms arise from the high diesel-fuel reactivity under engine conditions, particularly from very high temperatures.^{57,198,202–207} At these conditions, no significant amounts of combustion intermediate products are available for the current analytical methods. Despite these difficulties, in the presence of reaction moderators such as CO₂, H₂O, or exhaust gas recycled (EGR) and under lower temperatures, useful information can be acquired under common experimental conditions for oxidation reactions.⁹⁶

The differences between modern diesel and gasoline engine configurations are now becoming smaller and smaller.^{186,196,200} The trend in engine design is toward high compression ratios and complex direct injection strategies. The HCCI/SC combustion mode is likely to lead to the merging of gasoline and diesel engine technologies to handle the challenges they are facing, offering a number of opportunities for the development of the fuels and engine control.^{196,200,201}

Renewable Gasoline and Bioalcohols. These fuels are less reactive than fuels with higher molecular mass components such as jet and diesel fuels. Accordingly, a spark is required to trigger their timing-controlled ignition in a combustion

chamber. This mode of ignition leads to flames with high temperature at the propagation front, thus generating NO_x pollutants. On the other hand, the chemical stability of gasoline and alcohols is not high enough to prevent uncontrolled autoignition at higher compression ratios associated with knocking. To avoid this problem, gasoline engines are built with low compression ratios, and hence, they are less efficient than diesel engines. The heat needed to vaporize ethanol is higher than that of gasoline, and its low vapor pressure and high boiling point generally cause poor performance in cold conditions. More specifically, the heating value and stoichiometric air–fuel ratio of ethanol are relatively lower compared to those of gasoline. To achieve the same power or torque as gasoline, a larger amount of ethanol fuel must be supplied to the combustion chamber, resulting in a higher fuel consumption rate.

Lean combustion and exhaust emission characteristics in a spark-ignition engine with variation of the bioethanol–gasoline blending ratio and the excess–air ratio were recently investigated.¹⁸⁷ The results showed that the peak combustion pressures and the rate of heat release linearly decreased as the excess–air ratio increased. Compared to gasoline at each given excess–air ratio, there were slight improvements in combustion pressure for bioethanol–blended fuels. All of the ethanol blends emitted slightly less NO_x compared to gasoline.

Renewable Jet and Diesel Fuels. As shown earlier, the chemical composition of these biofuels can be closely tailored to mimic that of petroleum jet and diesel fuels. Thus, the properties involved in combustion processes of these fuels are similar to those of the petroleum-derived fuels, which are well studied. Accordingly, no further discussion on the combustion of these fuels is provided here.

Bio-oils. The main concerns for burning bio-oils in diesel engines have to do with difficult ignition (due to low heating value and high water content), corrosiveness (acids), and coking (thermally unstable components). Bio-oils must be upgraded or blended to be used in diesel engines.^{10,208} The effect of swirl, atomization quality, ignition source energy, air/fuel preheat, and equivalence ratio on the particulate matter emissions of bio-oil spray flames was investigated in a swirl burner.¹⁹⁰

Biodiesel Fuels. As we have discussed, there are significant differences in petroleum-derived and biodiesel fuel combustion, related to the different properties. In general, a biodiesel fuel has higher viscosity, lower volatility, higher cetane number, higher cloud/pour points, etc. While exhaust emissions from biodiesel fuels contain less smoke/PM, as a result of a higher combustion temperature, this same effect leads to higher NO_x content of the exhaust gases. Particular compositions of biodiesel fuels when higher in saturated FAMES confer poor behavior of these fuels in cold-weather conditions. The corrosive/solvent properties also require engine gasket/seal replacements for fuel blends with higher biodiesel content.¹⁷⁹ In addition to ignition quality as expressed by the cetane number,^{209–211} several other properties are important for determining the suitability of biodiesel as a fuel: heat of combustion, pour/cloud point, viscosity, oxidative stability, and lubricity.^{12,210–212} Modeling FAME combustion requires enthalpies of formation, entropies, and specific heats of the species involved in the free-radical reactions.⁵⁷

Biodiesel fuels derived from different feedstocks may have significantly different fatty acid profiles and physicochemical properties. To gain further insight into the effect of the

biodiesel chemical structure, specifically its degree of unsaturation, on engine performance, combustion characteristics, and emissions, experimental investigation have been conducted with diesel engines fueled with mixtures of fatty acid methyl esters.^{178,191–194,197} The effect of the degree of unsaturation of the tested biodiesel fuels was isolated.¹⁷⁸ This allowed for the maximization of the effect of the cetane number, while the other properties, such as the chain length, oxygen content, density, viscosity, and volatility, varied within a small range. Results indicated that the degree of unsaturation of biodiesel fuels did not significantly affect engine performance and the start of injection, but it had a noticeable influence on combustion characteristics and emissions, via its effect on the cetane number. A higher degree of unsaturation of biodiesel fuels led to a longer ignition delay and, consequently, a more retarded start of combustion. The premixed portion of combustion, peak heat release rate, maximum pressure gradient, peak in-cylinder bulk-gas-averaged temperature, total hydrocarbon (THC) emissions, smoke opacity, and NO_x emissions increased with the degree of unsaturation.¹⁷⁸

Spray/Jet Quality and Fuel Properties. High thermodynamic cycle efficiency for diesel engines requires the fuel injection event to be near top dead center (TDC) for the heat release to take place shortly after TDC of the engine power stroke.¹⁸⁶ In order to achieve these events, the injection must be followed by rapid air–fuel mixing with a short ignition delay. The spray/jet quality of fuels injected into a combustion chamber is the main factor affecting combustion phenomena and, hence, the engine efficiency and emission cleanliness. The main issue with fuel sprays and jets is their level of mixing with air under tight engine conditions (i.e., thermodynamic cycles of a few milliseconds). Obviously, in the case of sprays, the level of mixing is much lower compared to that in jets. From injection to ignition/combustion, the fuel is subjected to a sequence of complex events such as fuel atomization, heating, vaporization, and diffusion within the air charge.

The different properties of biodiesel fuel compared to those of petrodiesel fuels lead to different injection characteristics and, consequently, to different fuel spray geometries. The biodiesel fuel spray angle is narrower and the penetration length is larger.^{192,213} Some of the most important reasons for these characteristics are low fuel vaporization, worse atomization, and higher injection pressure of biodiesel fuel. Worse atomization is a consequence of high surface tension and viscosity, which lead to deeper spray-tip penetration and to larger mean droplet size. Higher injection pressure causes a higher injection rate, resulting in higher spray velocities as well as narrower and longer sprays. Liquid lengths are always longer for biodiesel fuel because of its higher heat of vaporization. Ambient air entrainment is also lower for biodiesel mainly because of slower atomization and breakup.¹⁸⁹ For this reason, recent research is devoted to replacing fuel sprays with homogeneous fuel–air mixtures such as those in the HCCI and SC methods.^{199–207} Superior ignition–combustion characteristics can be achieved by injecting the fuel in the form of a SC fluid.^{200,201}

Figure 8 shows shadowgraph images of ethanol injected in open space from 105 bar and various temperatures, taken with a high-speed digital camera (at 1000 frames/s).²¹⁴ The temperature effect on sprays/jets shape and size is significant and can be exploited for combustion of better quality. Fuel injected under SC conditions can achieve the highest level of mixing with air upon injection. On the basis of the above observations,

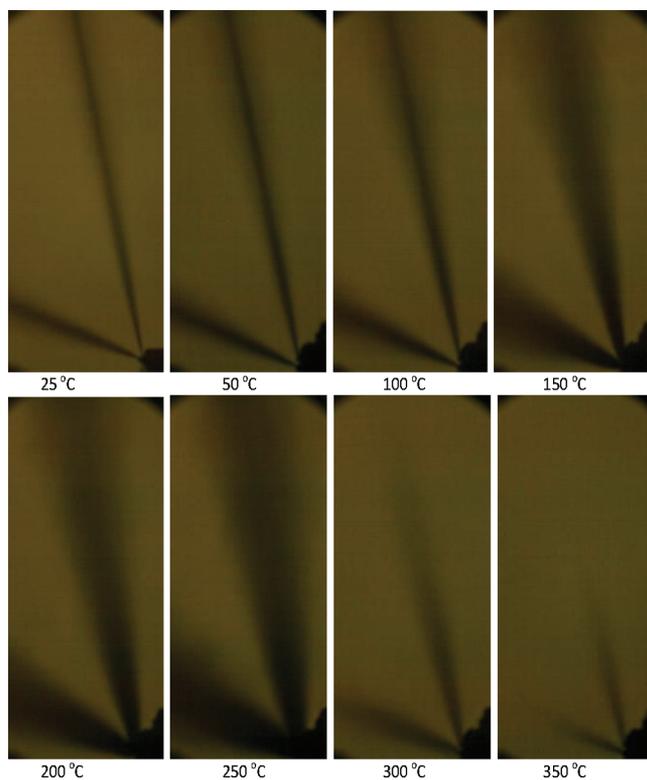


Figure 8. Shadowgraph images of ethanol injected into ambient atmosphere from 105 bar and various temperatures. The last two images are for supercritical ethanol.²¹⁴

it could be possible to implement an experimental method to determine fuel quality by studying its sprays/jets. Of particular interest will be to map the fuel concentration gradient in air upon injection. This is a difficult task, however, because of the harsh conditions in combustion chambers. An easier task could be to determine the spray/jet cone angle. A larger spray/jet cone angle indicates a better fuel–air mixing process. This method could well complement the volatility property of fuel determined by the ADC method.^{30–35,145–148}

Fuel Properties and Combustion Quality. The quality of fuel combustion is obviously closely connected with fuel properties. The highest useful work and engine efficiency require a rapid heat release after TDC. Combustion that takes place either before or late after TDC results in increased heat loss. The former has energy loss on the piston moving up while the latter has energy loss within exhaust gases. Under the tight conditions of an engine cycle, the fuel has to follow a complex sequence of events from injection to the evacuation of the exhaust gases. Figure 9 compares the main pathways of a typical volume of air–fuel in a plot of the local equivalence fuel–air ratio versus temperature.²¹¹ It includes fuel–air mixing, ignition and combustion events relative to two regions of major interest, zones of soot and NO_x production. To have clean combustion, the fuel events have to avoid these regions. While for conventional combustion it is almost impossible to reach such a performance over various engine loads, for the SC injection–combustion method this task is achievable both theoretically and technically. We note that the two curves in the plot above are not temporal profiles but are only pairs of fuel–air compositions under various temperatures from injection to the end of combustion. A temporal profile of the injection–combustion events for a HCCI mode is in the public

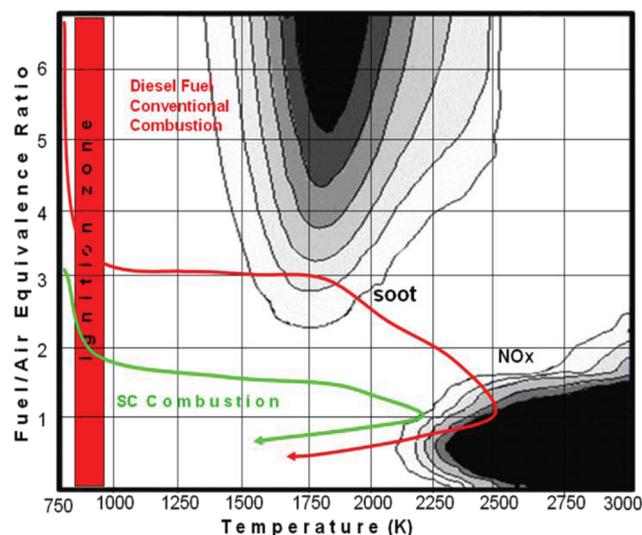


Figure 9. Local fuel/air equivalence ratio versus temperature. A comparative drawing.²¹⁴

domain.²¹⁵ The profile shown in the above reference could be close to that for SC fuels shown in Figure 9. Both of these profiles show just a few spikes of fuel-rich events.

The fluid properties needed to model the phenomena involved in fuel injection and combustion include fuel volatility, viscosity, thermal stability, reactivity with air, ignition delay, ignition T , heat of combustion, density, critical P – T , thermal conductivity, rate of heat release, C_p , etc. The influence of biodiesel fuel on the injection, spray, and engine characteristics with the aim to reduce harmful emissions is discussed in the literature.^{179,188,191–194,197,202,207} The injection, fuel spray, and engine characteristics obtained with biodiesel fuels are compared to those obtained with petrodiesel DF2 under various operating engine regimes. Ignition delay and combustion duration of biodiesel fuels, in accordance with the literature, are consistently shorter than those of petroleum-based diesel fuels.^{193,216} Biodiesel fuel density, viscosity, surface tension, and sound velocity, determined experimentally, are also compared to those of DF2. The results are used to analyze the most important injection, fuel spray, and engine characteristics. The injection characteristics are determined numerically under the operating regimes, and the fuel spray is obtained experimentally under peak torque condition. The results indicate that, by using biodiesel fuel, harmful emissions such as PM, NO_x, CO, and HC can be reduced to some extent by properly adjusting the timing of the injection pump.^{179,191–193,197,213–219}

■ SUMMARY

There is a remarkable amount of research on the transformation of various biomass feedstocks into potentially viable biofuels, chemicals, and other valuable products. In some cases, impressive results were obtained, while in many other cases there is the necessity to improve conversion and combustion to make possible a commercial implementation. With the concurrent advances made in fluid-property determination, it should be possible to better design processes that give the necessary improvements in a biofuel chain from feedstock logistics to fuel combustion. Moreover, these advances should allow for production of more environmentally friendly process than those previously reported and even used today.

Meanwhile, new comprehensive modeling tools will open more efficient synthetic routes to achieve the final products. The possibility that several reaction steps could be performed simultaneously will avoid costly intermediate separations with the current processes. Most biomass conversion processes have emerged with the goal of rapidly developing commercial technologies. The fundamental physicochemical characteristics of most of these reactions are not well understood; however, we contend that further fundamental understanding (including aspects of measurements and theory) will lead to improved processes. As we have discussed above, this must include not only additional work on the feed stocks, intermediates, and finished fuels (all of which are complex mixtures) but also on the constituents of them as well (in as pure a form as possible). Only such an approach will facilitate mixture modeling work which is important in process design.

Glossary

$\Delta_r H(T)$ = heat of reaction (reaction enthalpy).
 $C_{p,i}$ = constant-pressure molar heat capacities of reactants and reaction products.
 A, B, C = fluid constants in eq 10.
 ABE = acetone–butanol–ethanol.
 ADC = advanced distillation curve.
 ASTM = American Society for Testing and Materials.
 B100 = unblended biodiesel fuel (100% biodiesel).
 B20 = blend of 20% biodiesel fuel and 80% petroleum diesel (v/v).
 BOB = blendstock for oxygenate blending.
 c = specific heat capacity.
 CEN = European Committee for Standardization.
 CFD = computational fluid dynamics.
 CN = cetane number.
 CP = cloud point.
 C_p = heat capacities at constant pressure.
 DF2 = diesel fuel no. 2.
 DG = diglyceride.
 DIPPR = Design Institute for Physical Properties.
 DSC = differential scanning calorimetry.
 E10 = blend of 10% ethanol and 90% gasoline (v/v).
 E_a = energy of activation.
 EN = European Standard (Norm).
 EOS = equation of state.
 FAMES = fatty-acid methyl esters.
 FFA = free fatty acid.
 FID = flame-ionization detector.
 FP = flash point.
 FR_0 = total volumetric flow rate at the reactor inlet.
 FTL = Fischer–Tropsch liquid.
 GDP = glycerol decomposition products.
 GHG = green house gases.
 HC = hydrocarbon.
 HCCI = homogeneous charge compression ignition.
 L = liquid phase.
 m = mass.
 MG = monoglyceride.
 MSD = mass selective detector.
 NIST = National Institute of Standards and Technology.
 NREL = National Renewable Energy Laboratory.
 NO_x = nitrogen oxides (noxes).
 PM = particulate matter.
 PP = pour point.
 PR = Peng–Robinson

$P-V-T-X$ = pressure–volume–temperature–molar composition.

Q = heat.

REFPROP = The NIST Reference Fluid Thermodynamic and Transport Properties.

SC = supercritical.

SC-TE = supercritical transesterification.

SPR = structure–property relationships.

TDC = top dead center of an engine cylinder.

TDE = the NIST ThermoData Engine.

TE = transesterification.

TG = triglyceride.

T_{nb} = normal boiling temperature.

V = volume of the reactor, vapor phase.

VLE = vapor–liquid equilibrium.

X = mole fraction, liquid phase.

x = mass or volume fraction, liquid phase.

β = average heat flow-rate; chemical-bond position.

η = kinematic viscosity.

ν_i = stoichiometric numbers.

ξ = extent of reaction.

ρ = fluid density.

τ = residence time.

Φ = heat flow-rate.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: bruno@boulder.nist.gov.

■ REFERENCES

- (1) Weber, R. S. Introduction to the virtual issue of *Energy & Fuels* on biofuels. *Energy Fuels* **2010**, *24*, 6221–6222.
- (2) Arai, K.; Smith, R. L. Jr.; Aida, T. M. Decentralized chemical processes with supercritical fluid technology for sustainable society. *J. Supercrit. Fluids* **2009**, *47*, 628–636.
- (3) Edenhofer, O.; Pichs-Madruga, R.; Sokona, Y.; Seyboth, K.; Arvizu, D.; Bruckner, T.; Christensen, J.; Devernay, J.-M.; Faaij, A.; Fishedick, M.; Goldstein, B.; Hansen, G.; Huckerby, J.; Jäger-Waldau, A.; Kadner, S.; Kammen, D.; Krey, V.; Kumar, A.; Lewis, A.; Lucon, O.; Matschoss, P.; Maurice, L.; Mitchell, C.; Moomaw, W.; Moreira, J.; Nadai, A.; Nilsson, L. J.; Nyboer, J.; Rahman, A.; Sathaye, J.; Sawin, J.; Schaeffer, R.; Schei, T.; Schlömer, S.; Sims, R.; Verbruggen, A.; von Stechow, C.; Urama, K.; Wisser, R.; Yamba, F.; Zwickel, T. Summary for Policy Makers. In *IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation*; Edenhofer, O., Pichs-Madruga, R., Sokona, Y., Seyboth, K., Matschoss, P., Kadner, S., Zwickel, T., Eickemeier, P., Hansen, G., Schlömer, S., Stechow, C. V., Eds.; Cambridge University Press: Cambridge, UK, and New York, USA, 2011.
- (4) Dalai, A. K.; Bassi, A. Bioenergy and green engineering. *Energy Fuels* **2010**, *24* (9), 4627.
- (5) Robertson, D. E.; Jacobson, S. A.; Morgan, F.; Berry, D.; Church, G. M.; Afeyan, N. B. A new dawn for industrial photosynthesis. *Photosynth. Res.* **2011**, *107*, 269–277.
- (6) Nigam, P.; Singh, A. Production of liquid biofuels from renewable resources. *Prog. Energy Combust. Sci.* **2010**, *37* (1), 1–17.
- (7) Larson, E. D. Biofuel production technologies: status, prospects and implications for trade and development, Report No. UNCTAD/DITC/TED/2007/10. *United Nations Conference on Trade and Development*, New York and Geneva, 2008.
- (8) Elbheri, A.; Coyle, W.; Dohman, E.; Kmak, H.; Ferrell, J.; Haq, Z.; Houghton, J.; Stokes, B.; Buford, M.; Nieh, W.; Patton-Mallory, M.; Perla, D.; Draucker, L.; Dodder, R.; Kaplan, P. O.; Okamuro, D.; Steiner, J.; Shapouri, H.; O'Toole, D. *The Economics of Biomass Feedstocks in the United States*, Technical Report, Biomass Research

and Development Board, Oct 2008. Available online: http://www.usbiomassboard.gov/pdfs/7_Feedstocks_Literature_Review.pdf

(9) *A Research Roadmap for Making Lignocellulosic Biofuels a Practical Reality; Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels: Hydrocarbon Biorefineries*; Huber, G. W., Ed.; University of Massachusetts Amherst, National Science Foundation, Chemical, Bio-engineering, Environmental, and Transport Systems Division: Washington, DC, 2008.

(10) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106*, 4044–4098.

(11) Hill, J.; Nelson, E.; Tilman, D.; Polasky, S.; Tiffany, D. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. *Proc. Natl. Acad. Sci.* **2006**, *103* (30), 11206–11210.

(12) *The Biodiesel Handbook*; Knothe, G., Van Gerpen, J., Krahl, J., Eds.; AOCs Press: Urbana, IL, 2005.

(13) McLinden, M. O.; Bruno, T. J.; Frenkel, M.; Huber, M. L. *Standard Reference Data for the Thermophysical Properties of Biofuels*; ASTM International: West Conshohocken, PA, 2010; Vol. 7, pp 1–18.

(14) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–70.

(15) Soave, G. Equilibrium constants from a modified Redlich–Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203.

(16) Geana, D.; Ferioiu, V. Thermodynamic properties of pure fluids using the GEOS3C equation of state. *Fluid Phase Equilib.* **2000**, *174*, 51–68.

(17) Huber, M. L.; Lemmon, E. W.; Kazakov, A.; Ott, L. S.; Bruno, T. J. Model for the thermodynamic properties of a biodiesel fuel. *Energy Fuels* **2009**, *23*, 3790–3797.

(18) Patel, N. C.; Teja, A. S. A new cubic equation of state for fluids and fluid mixtures. *Chem. Eng. Sci.* **1982**, *37* (3), 463–473.

(19) Diky, V.; Chirico, R. D.; Kazakov, A.; Muzny, C. D.; Frenkel, M. ThermoData Engine—TDE: Software implementation of the dynamic data evaluation concept. 3. Binary mixtures. *J. Chem. Inf. Model.* **2009**, *49*, 503–517.

(20) Lemmon, E. W.; Huber, M. L.; McLinden, M. O. *NIST Standard Reference Database 23, NIST Reference Fluid Thermodynamic and Transport Properties—REFPROP*, Version 9.0; Standard Reference Data Program, National Institute of Standards and Technology: Gaithersburg, MD, 2010.

(21) Rowley, R. L.; Wilding, W. V.; Oscarson, J. L.; Zundel, N. A.; Marshall, T. L.; Daubert, T. E.; Danner, R. P. *DIPPR Data Compilation of Pure Compound Properties*; Design Institute for Physical Properties, New York, 2004.

(22) <http://aspenplus.com/products/aspen-plus.aspx>. Retrieved May 19, 2011.

(23) CHEMCAD, Version 5.6.4; Chemstations Inc.: Houston, TX, 2007.

(24) Mowry, G. A portable, automated and environmentally friendly biodiesel processing system. *Int. J. Sustainable Energy* **2011**, DOI: 10.1080/1478646X.2010.542816.

(25) Daubert, T. E.; Danner, R. P.; Sibul, H. M.; Stebbins, C. C.; Rowley, R. L.; Wilding, W. V.; *Physical and thermodynamic properties of pure chemicals*; AIChE: Available online: <http://dippr.byu.edu/>; Retrieved May 19, 2011.

(26) *Physical and Chemical Characteristics of Oils, Fats, and Waxes*, 2nd ed.; American Oil Chemists Society: Urbana, IL, 2006.

(27) Deshpande, A.; Anitescu, G.; Rice, P. A.; Tavlarides, L. L. Supercritical biodiesel production and power cogeneration: technical and economic feasibilities. *Biores. Technol.* **2010**, *101*, 1834–1843.

(28) Anitescu, G.; Bruno, T. J. Fluid properties needed in supercritical transesterification of triglyceride feedstocks to biodiesel fuels—A review. *J. Supercrit. Fluids*, In press.

(29) West, A. H.; Posarac, D.; Ellis, N. Assessment of four biodiesel production processes using HYSYS.Plant. *Biores. Technol.* **2008**, *99* (14), 6587–6601.

(30) Bruno, T. J.; Baibourine, E. Comparison of biomass-derived turbine fuels with the composition-explicit distillation curve method. *Energy Fuels* **2011**, *25*, 1847–1858.

(31) Windom, B. C.; Lovestead, T. M.; Mascal, M.; Nikitin, E. B.; Bruno, T. J. Advanced distillation curve analysis on ethyl levulinate as a diesel fuel oxygenate and a hybrid biodiesel fuel. *Energy Fuels* **2011**, *25*, 1878–1890.

(32) Bruno, T. J.; Ott, L. S.; Smith, B. L.; Lovestead, T. M. Complex fluid analysis with the advanced distillation curve approach. *Anal. Chem.* **2010**, *82*, 777–783.

(33) Bruno, T. J.; Smith, B. L. Enthalpy of combustion of fuels as a function of distillate cut: application of an advanced distillation curve method. *Energy Fuels* **2006**, *20*, 2109–2116.

(34) Ott, L. S.; Bruno, T. J. Variability of biodiesel fuel and comparison to petroleum-derived diesel fuel: application of a composition and enthalpy explicit distillation curve method. *Energy Fuels* **2008**, *22*, 2861–2868.

(35) Smith, B. L.; Ott, L. S.; Bruno, T. J. Composition-explicit distillation curves of commercial biodiesel fuels: Comparison of petroleum derived fuel with B20 and B100. *Ind. Eng. Chem. Res.* **2008**, *47*, 5832–5840.

(36) Kamm, B.; Hille, C.; Schönicke, P.; Dautzenberg, G. Green biorefinery demonstration plant in Havelland (Germany). *Biofuels, Bioprod. Biorefin.* **2010**, *4*, 253–262.

(37) Mascal, M.; Nikitin, E. B. Co-processing of carbohydrates and lipids in oil crops to produce a hybrid biodiesel. *Energy Fuels* **2010**, *24*, 2170–2171.

(38) Thamsiriroj, T.; Murphy, J. D. Can rape seed biodiesel meet the European Union sustainability criteria for biofuels? *Energy Fuels* **2010**, *24* (3), 1720–1730.

(39) Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107* (6), 2411–2502.

(40) Sawangkeaw, R.; Bunyakiat, K.; Ngamprasertsith, S. A review of laboratory-scale research on lipid conversion to biodiesel with supercritical methanol (2001–2009)—Review article. *J. Supercrit. Fluids* **2010**, *55*, 1–13.

(41) Pinnarat, T.; Savage, P. E. Assessment of noncatalytic biodiesel synthesis using supercritical reaction conditions. *Ind. Eng. Chem. Res.* **2008**, *47*, 6801–6808.

(42) Vasiliu, M.; Guynn, K.; Dixon, D. A. Prediction of the thermodynamic properties of key products and intermediates from biomass. *J. Phys. Chem. C* **2011**, *115*, 15686–15702.

(43) Yuan, Z.; Xia, S.; Chen, P.; Hou, Z.; Zheng, X. Etherification of biodiesel-based glycerol over tungstophosphoric acid to synthesize glyceryl ethers. *Energy Fuels* **2011**, *25*, 3186–3191.

(44) Kleinert, M.; Barth, T. Towards a lignocellulosic biorefinery: Direct one-step conversion of lignin to hydrogen-enriched biofuel. *Energy Fuels* **2008**, *22* (2), 1371–1379.

(45) Cherubini, F.; Stromman, A. H. Production of biofuels and biochemicals from lignocellulosic biomass: Estimation of maximum theoretical yields and efficiencies using matrix algebra. *Energy Fuels* **2010**, *24* (4), 2657–2666.

(46) Dinh, L. T. T.; Guo, Y.; Mannan, M. S. Sustainability evaluation of biodiesel production using multicriteria decision-making. *Environ. Prog. Sustainable Energy* **2009**, *28*, 38–46.

(47) Green, N. Getting biofuels on the green and narrow path: Why we must get advanced biofuels started and started in the right way. *Biofuels, Bioprod. Biorefin.* **2011**, *5*, 10–17.

(48) Zakrzewska, M. E.; Bogel-Lukasik, E.; Bogel-Lukasik, R. Solubility of carbohydrates in ionic liquids. *Energy Fuels* **2010**, *24* (2), 737–745.

(49) Zakrzewska, M. E.; Bogel-Lukasik, E.; Bogel-Lukasik, R. Ionic liquid-mediated formation of 5-hydroxymethylfurfural—A promising biomass-derived building block. *Chem. Rev.* **2011**, *111* (2), 397–417.

(50) Bunyakiat, K.; Makmee, S.; Sawangkeaw, R.; Ngamprasertsith, S. Continuous production of biodiesel via transesterification from vegetable oils in supercritical methanol. *Energy Fuels* **2006**, *20*, 812–817.

- (51) Ceriani, R.; Goncalves, C. B.; Coutinho, J. A. P. Prediction of viscosities of fatty compounds and biodiesel by group contribution. *Energy Fuels* **2011**, *25*, 3712–3717.
- (52) Kazakov, A.; Muzny, C. D.; Diky, V. V.; Chirico, R. D.; Frenkel, M. Predictive correlations based on large experimental datasets: Critical constants for pure compounds. *Fluid Phase Equilib.* **2010**, *298*, 131–142.
- (53) Saldana, D. A.; Starck, L.; Mougin, P.; Rousseau, B.; Pidol, L.; Jeuland, N.; Creton, B. Flash point and cetane number predictions for fuel compounds using quantitative structure property relationship (QSPR) methods. *Energy Fuels* **2011**, *25*, 3900–3908.
- (54) Huber, M. L.; Ely, J. F. A predictive extended corresponding states model for pure and mixed refrigerants including an equation of state for R134a. *Int. J. Refrig.* **1994**, *17*, 18–31.
- (55) Pitz, W. J.; Mueller, C. J. Recent progress in the development of diesel surrogate fuels. *Prog. Energy Combust. Sci.* **2011**, *37*, 330–350.
- (56) Anand, K.; Ra, Y.; Reitz, R. D.; Bunting, B. Surrogate model development for fuels for advanced combustion engines. *Energy Fuels* **2011**, *25*, 1474–1484.
- (57) Herbinet, O.; Pitz, W. J.; Westbrook, C. K. Detailed chemical kinetic mechanism for the oxidation of biodiesel fuels blend surrogate. *Combust. Flame* **2010**, *157* (5), 893–908.
- (58) ASTM International. *Standard Specification for Biodiesel Fuel Blendstock (B100) for Middle Distillate Fuels*, ASTM D6751; ASTM International: West Conshohocken, PA, 2011.
- (59) *Biodiesel: ASTM International Specifications (B100)*, World Energy, http://www.worldenergy.net/products/biodiesel/us_specs.php; Retrieved August, 2010.
- (60) US Environmental Protection Agency. *Life cycle assessment (LCA)*, <http://www.epa.gov/nrmrl/lcaccess/>; Retrieved Aug 6, 2010.
- (61) Clarens, A. F.; Resurreccion, E. P.; White, M. A.; Colosi, L. M. Environmental life cycle comparison of algae to other bioenergy feedstocks. *Environ. Sci. Technol.* **2010**, *44*, 1813–1819.
- (62) http://www.algepower.com/organic_waste.php; Retrieved June 20, 2011.
- (63) Kalnes, T.; Marker, T.; Shonnard, D. R. Green diesel: A second generation biofuel. *Int. J. Chem. React. Eng.* **2007**, *5*, A48.
- (64) Yu, Y.; Wu, H. Bioslurry as a fuel. 2. Life-cycle energy and carbon footprints of bioslurry fuels from mallee biomass in Western Australia. *Energy Fuels* **2010**, *24* (10), 5660–5668.
- (65) Stephenson, A. L.; Kazamia, E.; Dennis, J. S.; Howe, C. J.; Scott, S. A.; Smith, A. G. Life-cycle assessment of potential algal biodiesel production in the United Kingdom: a comparison of raceways and air-lift tubular bioreactors. *Energy Fuels* **2010**, *24* (7), 4062–4077.
- (66) Dale, B. E. Thinking clearly about biofuels: Ending the irrelevant “net energy” debate and developing better performance metrics for alternative fuels. *Biofuels, Bioprod. Biorefin.* **2007**, *1*, 14–17.
- (67) Campbell, J. E.; Lobell, D. B.; Field, C. B. Greater transportation energy and GHG offsets from bioelectricity than ethanol. *Science* **2009**, *324*, 1055–1057.
- (68) Farrell, A. E.; Plevin, R. J.; Turner, B. T.; Jones, A. D.; O’Hare, M.; Kammen, D. M. Ethanol can contribute to energy and environmental goals. *Science* **2006**, *311*, 506–508.
- (69) Shapouri, H.; Duffield, J.; McAloon, A.; Wang, M. *The 2001 Net Energy Balance of Corn-Ethanol*; U.S. Dept. of Agriculture: Washington, DC, 2004.
- (70) Fritsche, U. R.; Sims, R. E. H.; Monti, A. Direct and indirect land-use competition issues for energy crops and their sustainable production. *Biofuels, Bioprod. Biorefin.* **2010**, *4* (6), 692–704.
- (71) Zegada-Lizarazu, W.; Elbersen, H. W.; Cosentino, S. L.; Zatta, A.; Alexopoulou, E.; Monti, A. Agronomic aspects of future energy crops in Europe. *Biofuels, Bioprod. Biorefin.* **2010**, *4*, 674–691.
- (72) Peterson, A. A.; Vogel, F.; Lachance, R. P.; Froling, M.; Antal, M. J. Jr.; Tester, J. W. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy Environ. Sci.* **2008**, *1*, 32–65.
- (73) Kargbo, D. M. Biodiesel production from municipal sewage sludge. *Energy Fuels* **2010**, *24* (5), 2791–2794.
- (74) Pienkos, P. T.; Darzins, A. The promise and challenges of microalgal-derived biofuels. *Biofuels, Bioprod. Biorefin.* **2009**, *3*, 431–440.
- (75) van Beilen, J. B. Why microalgal biofuels won’t save the internal combustion machine. *Biofuels, Bioprod. Biorefin.* **2010**, *4*, 41–52.
- (76) Knothe, G.; Dunn, R. O.; Bagby, M. O. Biodiesel: The use of vegetable oils and their derivatives as alternative diesel fuels. In *Fuels and Chemicals from Biomass*, ACS Symposium Series; American Chemical Society: Washington, DC, **1997**; Ch 10, pp 172–208.
- (77) Bartle, J. R.; Abadi, A. Toward sustainable production of second generation bioenergy feedstocks. *Energy Fuels* **2010**, *24*, 2–9.
- (78) Banerjee, S.; Sandeep Mudliar, S.; Sen, R.; Giri, B.; Satpute, D.; Chakrabarti, T.; Pandey, R. A. Commercializing lignocellulosic bioethanol: Technology bottlenecks and possible remedies. *Biofuels, Bioprod. Biorefin.* **2010**, *4*, 77–93.
- (79) Vicente, G.; Bautista, L. F.; Gutierrez, F. J.; Rodriguez, R.; Martinez, V.; Rodriguez-Frometa, R. A.; Ruiz-Vazquez, R. M.; Torres-Martinez, S.; Garre, V. Direct transformation of fungal biomass from submerged cultures into biodiesel. *Energy Fuels* **2010**, *24* (5), 3173–3178.
- (80) Brown, T. M.; Duan, P.; Savage, P. E. Hydrothermal liquefaction and gasification of *Nannochloropsis* sp. *Energy Fuels* **2010**, *24* (6), 3639–3646.
- (81) Levine, R. B.; Pinnarat, T.; Savage, P. E. Biodiesel production from wet algal biomass through in situ lipid hydrolysis and supercritical transesterification. *Energy Fuels* **2010**, *24*, 5235–5243.
- (82) Ogihara, Y.; Smith, R. L. Jr.; Hiroshi Inomata, H.; Arai, K. Direct observation of cellulose dissolution in subcritical and supercritical water over a wide range of water densities (550–1000 kg/m³). *Cellulose* **2005**, *12*, 595–606.
- (83) Rogalinski, T.; Ingram, T.; Brunner, G. Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures. *J. Supercrit. Fluids* **2008**, *47*, 54–63.
- (84) Chen, W.; Wang, C.; Ying, W.; Wang, W.; Wu, Y.; Zhang, J. Continuous production of biodiesel via supercritical methanol transesterification in a tubular reactor. Part I: Thermophysical and transitive properties of supercritical methanol. *Energy Fuels* **2009**, *23* (1), 526–532.
- (85) Satyarthi, J.; Srinivas, D.; Ratnasamy, P. Estimation of free fatty acid content in oils, fats, and biodiesel by ¹H NMR spectroscopy. *Energy Fuels* **2009**, *23* (4), 2273–2277.
- (86) Anitescu, G.; Deshpande, A.; Tavlarides, L. L. Integrated technology for supercritical biodiesel production and power cogeneration. *Energy Fuels* **2008**, *22*, 1391–1399.
- (87) Marulanda, V. F.; Anitescu, G.; Tavlarides, L. L. Investigations on supercritical transesterification of chicken fat for biodiesel production from low-cost lipid feedstocks. *J. Supercrit. Fluids* **2010**, *54*, 53–60.
- (88) Marulanda, V. F.; Anitescu, G.; Tavlarides, L. L. Biodiesel fuels through a continuous flow process of chicken fat supercritical transesterification. *Energy Fuels* **2010**, *24*, 253–260.
- (89) Zhou, H.; Lu, H.; Liang, B. Solubility of multicomponent systems in the biodiesel production by transesterification of *Jatropha curcas* L. oil with methanol. *J. Chem. Eng. Data* **2006**, *51*, 1130–1135.
- (90) Glisic, S.; Montoya, O.; Orlovic, A.; Skala, D. Vapor–liquid equilibria of triglycerides–methanol mixtures and their influence on the biodiesel synthesis under supercritical conditions of methanol. *J. Serb. Chem. Soc.* **2007**, *72*, 13–27.
- (91) Geana, D.; Steiner, R. Calculation of phase equilibrium in supercritical extraction of C54 triglyceride (rapeseed oil). *J. Supercrit. Fluids* **1995**, *8*, 107–118.
- (92) Hegel, P.; Mabe, G.; Pereda, S.; Brignole, E. A. Phase transitions in a biodiesel reactor using supercritical methanol. *Ind. Eng. Chem. Res.* **2007**, *46*, 6360–6365.
- (93) Glisic, S. B.; Skala, D. U. Phase transition at subcritical and supercritical conditions of triglycerides methanolysis. *J. Supercrit. Fluids* **2010**, *54*, 71–80.

- (94) Anitescu, G.; Tavlariades, L. L.; Geana, D. Phase transitions and thermal behavior of fuel–diluent mixtures. *Energy Fuels* **2009**, *23* (6), 3068–3077.
- (95) Geana, D. Department of Applied Physical Chemistry and Electrochemistry University Politehnica of Bucharest, private communication, 2011.
- (96) Anitescu, G. Supercritical fluid technology applied to the production and combustion of diesel and biodiesel fuels. Ph.D. Thesis, Syracuse University, 2008.
- (97) Outcalt, S. L.; McLinden, M. O. Automated densimeters for the rapid characterization of industrial fluids. *Ind. Eng. Chem. Res.* **2007**, *46*, 8264–8269.
- (98) Outcalt, S. L.; Laesecke, A.; Freund, M. B. Density and speed of sound measurements of Jet A and S-8 aviation turbine fuels. *Energy Fuels* **2009**, *23*, 1626–1633.
- (99) Ott, L. S.; Huber, M. L.; Bruno, T. J. Density and speed of sound measurements on five fatty acid methyl esters at 83 kPa and temperatures from 278.15 to 338.15 K. *J. Chem. Eng. Data* **2008**, *53*, 2412–2416.
- (100) Acosta, G. M.; Smith, R. L. Jr.; Arai, K. High pressure PVT behavior of natural fats and oils, trilaurin, triolein, and *n*-tridecane from 303 to 353 K from atmospheric pressure to 150 MPa. *J. Chem. Eng. Data* **1996**, *41*, 961–969.
- (101) Anand, K.; Ranjan, A.; Mehta, P. S. Predicting the density of straight and processed vegetable oils from fatty acid composition. *Energy Fuels* **2010**, *24* (5), 3262–3266.
- (102) Perkins, E. G. Composition of soybeans and soybean products. In *Practical Handbook of Soybean Processing and Utilization*; Erikson, D. R., Ed.; AOCS Press: Champaign, IL, 1995.
- (103) Höhne, G. W. H.; Hemminger, W. F.; Flammersheim, H.-J. *Differential Scanning Calorimetry*, 2nd ed.; Springer, Verlag Berlin: Heidelberg, Germany, 2003.
- (104) http://en.wikipedia.org/wiki/Smoke_point; Retrieved August, 2010.
- (105) Babu, A. K.; Devaradjane, G. *Vegetable oils and their derivatives as fuels for CI engines: An overview*, SAE Technical Paper No. 2003-01-0767, 2003.
- (106) Anitescu, G. Syracuse University, unpublished data.
- (107) Chupka, G. M.; Yanowitz, J.; Chiu, G.; Alleman, T. L.; McCormick, R. L. Effect of saturated monoglyceride polymorphism on low-temperature performance of biodiesel. *Energy Fuels* **2011**, *25* (1), 398–405.
- (108) Tolan, J. S. Iogen's process for producing ethanol from cellulosic biomass. *Clean Technol. Environ. Policy* **2002**, *3*, 339–345.
- (109) Guerrero, H.; Lafuente, C.; Royo, F.; Lomba, L.; Giner, B. *PpT* behavior of several chemicals from biomass. *Energy Fuels* **2011**, *25*, 3009–3013.
- (110) Christensen, E. D.; Williams, A.; Paul, S.; Burton, S.; McCormick, R. L. Properties and performance of levulinic esters as diesel blend components. *Energy Fuels* **2011**, DOI: dx.doi.org/10.1021/ef201229j.
- (111) Biofuels for transport—An international perspective. International Energy Agency (IEA), <http://www.iea.org/textbase/nppdf/free/2004/biofuels2004.pdf>; 2004. Retrieved May 11, 2011.
- (112) Escobar, J. C.; Lora, E. S.; Venturini, O. J.; Yanez, E. E.; Castillo, E. F.; Almazan, O. Biofuels: environment, technology and food security. *Renewable Sustainable Energy Rev.* **2009**, *13*, 1275–1287.
- (113) Morjanoff, P. J.; Gray, P. P. Optimization of steam explosion as method for increasing susceptibility of sugarcane bagasse to enzymatic saccharification. *Biotechnol. Bioeng.* **1987**, *29*, 733–741.
- (114) Biobutanol. European Biofuels Technology Platform (EBTP), <http://www.biofuelstp.eu/butanol.html>; 2009. Retrieved May 11, 2011.
- (115) Ramey, D. Butanol advances in biofuels. The Light Party, <http://www.lightparty.com/Energy/Butanol.html>; 2004. Retrieved May 5, 2011.
- (116) http://en.wikipedia.org/wiki/Acetone-butanol-ethanol_fermentation. Retrieved May 5, 2011.
- (117) Murata, K.; Liu, Y.; Inaba, M.; Takahara, I. Production of synthetic diesel by hydro-treatment of *Jatropha* oils using Pt–Re/H-ZSM-5 catalyst. *Energy Fuels* **2010**, *24* (4), 2404–2409.
- (118) Li, L.; Coppola, E.; Rine, J.; Miller, J. L.; Walker, D. Catalytic hydrothermal conversion of triglycerides to non-ester biofuels. *Energy Fuels* **2010**, *24*, 1305–1315.
- (119) Knothe, G. Biodiesel and renewable diesel: A comparison. *Prog. Energy Combust. Sci.* **2010**, *36*, 364–373.
- (120) Liu, G.; Larson, E. D.; Williams, R. H.; Kreutz, T. G.; Guo, X. Making Fischer–Tropsch fuels and electricity from coal and biomass: performance and cost analysis. *Energy Fuels* **2011**, *25*, 415–437.
- (121) Moutsoglou, A.; Sunkara, P. P. Fischer–Tropsch synthesis in a fixed bed reactor. *Energy Fuels* **2011**, *25*, 2242–2257.
- (122) Nuru, D.; Pabst, K.; Schaub, G. Fischer–Tropsch synfuels from biomass: maximizing carbon efficiency and hydrocarbon yield. *Energy Fuels* **2010**, *24* (4), 2634–2641.
- (123) Salehi, E.; Abedi, J.; Harding, T. Bio-oil from sawdust: Effect of operating parameters on the yield and quality of pyrolysis products. *Energy Fuels* **2011**, *25*, 4145–4154.
- (124) Oasmaa, A.; Kuoppala, E.; Ardiyanti, A.; Venderbosch, R. H.; Heeres, H. J. Characterization of hydrotreated fast pyrolysis liquids. *Energy Fuels* **2010**, *24* (9), 5264–5272.
- (125) Saddawi, A.; Jones, J. M.; Williams, A.; Wojtowicz, M. A. Kinetics of the thermal decomposition of biomass. *Energy Fuels* **2010**, *24* (2), 1274–1282.
- (126) Varhegyi, G.; Bobaly, B.; Jakab, E.; Chen, H. Thermogravimetric study of biomass pyrolysis kinetics. A distributed activation energy model with prediction tests. *Energy Fuels* **2011**, *25*, 24–32.
- (127) Sharma, Y. C.; Singh, B.; Korstad, J. Advancements in solid acid catalysts for eco-friendly and economically viable synthesis of biodiesel. *Biofuels, Bioprod. Biorefin.* **2011**, *5*, 69–92.
- (128) Janaun, J.; Ellis, N. Perspectives on biodiesel as a sustainable fuel. *Renewable Sustainable Energy Rev.* **2010**, *14*, 1312–1320.
- (129) Baig, A.; Ng, F. T. T. A single-step solid acid-catalyzed process for the production of biodiesel from high free fatty acid feedstocks. *Energy Fuels* **2010**, *24* (9), 4712–4720.
- (130) Shibasaki-Kitakawa, N.; Tsuji, T.; Chida, K.; Kubo, M.; Yonemoto, T. Simple continuous production process of biodiesel fuel from oil with high content of free fatty acid using ion-exchange resin catalysts. *Energy Fuels* **2010**, *24* (6), 3634–3638.
- (131) Satyarthi, J. K.; Radhakrishnan, S.; Srinivas., D. Factors influencing the kinetics of esterification of fatty acids over solid acid catalysts. *Energy Fuels* **2011**, *25* (9), 4106–4112.
- (132) Satyarthi, J. K.; Srinivas, D.; Ratnasamy, P. Influence of surface hydrophobicity on the esterification of fatty acids over solid catalysts. *Energy Fuels* **2010**, *24*, 2154–2161.
- (133) Lee, J.-S.; Saka, S. Biodiesel production by heterogeneous catalysts and supercritical technologies. *Biores. Technol.* **2010**, *101*, 7191–7200.
- (134) Urbanchuk, J. *Statewide Feasibility Study for a Potential New York State Biodiesel Industry*, Final Report NYSERDA 7681; New York State Energy Research and Development Authority, April 2004.
- (135) Tsuji, T.; Kubo, M.; Shibasaki-Kitakawa, N.; Yonemoto, T. Is excess methanol addition required to drive transesterification of triglyceride toward complete conversion? *Energy Fuels* **2009**, *23*, 6163–6167.
- (136) Hillier, J.; Bezzant, T.; Fletcher, T. H. Improved method for the determination of kinetic parameters from non-isothermal thermogravimetric analysis (TGA) data. *Energy Fuels* **2010**, *24* (5), 2841–2847.
- (137) He, H.; Sun, S.; Wang, T.; Zhu, S. Transesterification kinetics of soybean oil for production of biodiesel in supercritical methanol. *J. Am. Oil Chem. Soc.* **2007**, *84*, 399–404.
- (138) Tat, M. E.; van Gerpen, J. H. The kinematic viscosity of biodiesel and its blends with diesel fuel. *J. Am. Oil Chem. Soc.* **1999**, *76* (12), 1511–1513.
- (139) Yuan, W.; Hansen, A. C.; Zhang, Q. Predicting the temperature dependent viscosity of biodiesel fuels. *Fuel* **2009**, *88*, 1120–1126.

- (140) *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids*, ASTM D 445-88; American Society for Testing and Materials: West Conshohocken, PA1986.
- (141) Robertson, L. X.; Schaschke, C. J. Combined high pressure and low temperature viscosity measurement of biodiesel. *Energy Fuels* **2010**, *24*, 1293–1297.
- (142) Freitas, S. V. D.; Pratas, M. J.; Ceriani, R.; Lima, A. S.; Coutinho, J. A. P. Evaluation of predictive models for the viscosity of biodiesel. *Energy Fuels* **2011**, *25*, 352–358.
- (143) Duncan, A. M.; Ahosseini, A.; McHenry, R.; Depcik, C. D.; Stagg-Williams, S. M.; Scurto, A. M. High pressure viscosity of biodiesel from soybean, canola, and coconut oils. *Energy Fuels* **2010**, *24* (10), 5708–5716.
- (144) Bucy, H. Oxidative stability and ignition quality of algae derived methyl esters containing varying levels of methyl eicosapentaenoate and methyl docosahexaenoate. Masters Thesis, Colorado State University, Fort Collins, CO, 2011.
- (145) Bruno, T. J. Improvements in the measurement of distillation curves—Part 1: A composition-explicit approach. *Ind. Eng. Chem. Res.* **2006**, *45*, 4371–4380.
- (146) Bruno, T. J.; Ott, L. S.; Lovestead, T. M.; Huber, M. L. Relating complex fluid composition and thermophysical properties with the advanced distillation curve approach. *Chem. Eng. Technol.* **2010**, *33*, 363–376.
- (147) Bruno, T. J.; Wolk, A.; Naydich, A. Stabilization of biodiesel fuel at elevated temperature with hydrogen donors: Evaluation with the advanced distillation curve method. *Energy Fuels* **2009**, *23*, 1015–1023.
- (148) Lovestead, T. M.; Windom, B. C.; Bruno, T. J. Investigating the unique properties of cuphea-derived biodiesel fuel with the advanced distillation curve method. *Energy Fuels* **2010**, *24*, 3665–3675.
- (149) ASTM Standard D 86-04b, Standard test method for distillation of petroleum products at atmospheric pressure. In *Book of Standards*; ASTM International: West Conshohocken, PA, 2004.
- (150) Anitescu, G.; Bruno, T. J. Characterization of biodiesel fuel from supercritical fluid processing by the advanced distillation curve method. In preparation.
- (151) Yuan, W.; Hansen, A. C.; Zhang, Q. Vapor pressure and normal boiling point predictions for pure methyl esters and biodiesel fuels. *Fuel* **2005**, *84*, 943–950.
- (152) Bachler, C.; Schober, S.; Mittelbach, M. Simulated distillation for biofuel analysis. *Energy Fuels* **2010**, *24* (3), 2086–2090.
- (153) Perkins, R. A.; Huber, M. L. Measurement and correlation of the thermal conductivities of biodiesel constituent fluids: methyl oleate and methyl linoleate. *Energy Fuels* **2011**, *25* (5), 2383–2388.
- (154) Pratas, M. J.; Oliveira, M. B.; Pastoriza-Gallego, M. J.; Queimada, A. J.; Pineiro, M. M.; Coutinho, J. A. P. High pressure biodiesel density: experimental measurements, correlation, and cubic-plus-association equation of state modeling. *Energy Fuels* **2011**, *25*, 3806–3814.
- (155) U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Alternative Fuels Data Center, <http://www.afdc.energy.gov/afdc/fuels/properties.html>; Retrieved August, 2010.
- (156) Coutinho, J. A. P.; Goncalves, M.; Pratas, M. J.; Batista, M. L. S.; Fernandes, V. F. S.; Pauly, J.; Daridon, J. L. Measurement and modeling of biodiesel cold-flow properties. *Energy Fuels* **2010**, *24* (4), 2667–2674.
- (157) Knothe, G. Biodiesel derived from a model oil enriched in palmitoleic acid, macadamia nut oil. *Energy Fuels* **2010**, *24* (3), 2098–2103.
- (158) Black, G.; Curran, H. J.; Pichon, S.; Simmie, J. M.; Zhukov, V. Bio-butanol: Combustion properties and detailed chemical kinetic model. *Combust. Flame* **2010**, *157* (2), 363–373.
- (159) Cardona, C. A.; Sanchez, O. J. Fuel ethanol production: Process design trends and integration opportunities. *Biores. Technol.* **2007**, *98*, 2415–2457.
- (160) Sanchez, O. J.; Cardona, C. A. Trends in biotechnological production of fuel ethanol from different feedstocks. *Biores. Technol.* **2008**, *99*, 5270–5295.
- (161) Roychoudhury, P. K.; Ghose, T. K.; Ghosh, P. Operational strategies in vacuum-coupled SSF for conversion of lignocellulose to ethanol. *Enzyme Microb. Technol.* **1992**, *14*, 581–585.
- (162) Cysewski, G. R.; Wilke, C. R. Rapid ethanol fermentations using vacuum and cell recycle. *Biotechnol. Bioeng.* **2004**, *19* (8), 1125–1143.
- (163) Nolte, M. W.; Liberatore, M. W. Viscosity of biomass pyrolysis oils from various feedstocks. *Energy Fuels* **2010**, *24* (12), 6601–6608.
- (164) Oasmaa, A.; Elliott, D. C.; Korhonen, J. Acidity of biomass fast pyrolysis bio-oils. *Energy Fuels* **2010**, *24* (12), 6548–6554.
- (165) ASTM International. *Standard Specification for Biodiesel Fuel Blendstock (B100) for Middle Distillate Fuels*, ASTM 7467; ASTM International: West Conshohocken, PA, 2010.
- (166) EN 590, http://www.worldenergy.net/products/biodiesel/us_specs.php
- (167) ASTM International. *Standard Specification for Diesel Fuels*, ASTM 975; ASTM International: West Conshohocken, PA, 2010.
- (168) Alleman, T. A.; Fouts, L.; McCormick, R. L. *Analysis of Biodiesel Blend Samples Collected in the United States in 2008*, Technical Report NREL/TP-540-46592, March 2010.
- (169) Andersen, V. F.; Anderson, J. E.; Wallington, T. J.; Mueller, S. A.; Nielsen, O. J. Vapor pressures of alcohol–gasoline blends. *Energy Fuels* **2010**, *24* (6), 3647–3654.
- (170) Andersen, V. F.; Anderson, J. E.; Wallington, T. J.; Mueller, S. A.; Nielsen, O. J. Distillation curves for alcohol–gasoline blends. *Energy Fuels* **2010**, *24* (4), 2683–2691.
- (171) Alleman, T. L.; Wright, K.; Hogan, D. National survey of E85 quality (CRC Report No. E-85); Publisher: Coordinating Research Council, November 2009.
- (172) ASTM International. *Standard Specification for Diesel Fuels*, ASTM D5798; ASTM International: West Conshohocken, PA, 2010.
- (173) Torres-Jimenez, E.; Svoljsak-Jerman, M.; Gregorc, A.; Lisec, I.; Dorado, M. P.; Kegl, B. Physical and chemical properties of ethanol–biodiesel blends for diesel engines. *Energy Fuels* **2010**, *24* (3), 2002–2009.
- (174) Di Serio, M.; Casale, L.; Tesser, R.; Santacesaria, E. New process for the production of glycerol *tert*-butyl ethers. *Energy Fuels* **2010**, *24* (9), 4668–4672.
- (175) McCormick, R. L.; Westbrook, S. R. Storage stability of biodiesel and biodiesel blends. *Energy Fuels* **2010**, *24*, 690–698.
- (176) Tang, H.; De Guzman, R. C.; Ng, K. Y. S.; O. Salley, S. O. Effect of antioxidants on the storage stability of soybean-oil-based biodiesel. *Energy Fuels* **2010**, *24* (3), 2028–2033.
- (177) Shah, R.; Mahajan, D.; Patel, S.; Ball, J.; Colantuoni, V.; Maraj, R. Oxidation stability in biodiesel: A brief review of current technology. *Biodiesel Magazine*, June 9, 2009; Available online: <http://www.biodieselmagazine.com/articles/3541/oxidation-stability-in-biodiesel-a-brief-review-of-current-technology/>.
- (178) Benjumea, P.; Agudelo, J. R.; Agudelo, A. F. Effect of the degree of unsaturation of biodiesel fuels on engine performance, combustion characteristics, and emissions. *Energy Fuels* **2011**, *25* (1), 77–85.
- (179) Corporan, E.; Edwards, T.; Shafer, L.; DeWitt, M. J.; Klingshirn, C.; Zabarnick, S.; West, Z.; Striebich, R.; Graham, J.; Klein, J. Chemical, thermal stability, seal swell, and emissions studies of alternative jet fuels. *Energy Fuels* **2011**, *25*, 955–966.
- (180) Abou-Neme, I. The effect of fuel additives on biodiesel (B-100) long-term oxidative stability and performance. *19th World Petroleum Congress*, Madrid, Spain, June 29–July 3, 2008.
- (181) Knothe, G. Some aspects of biodiesel oxidative stability. *Fuel Process. Technol.* **2007**, *88*, 669–677.
- (182) Dunn, R. O. Effect of antioxidants on the oxidative stability of methyl soyate (biodiesel). *Fuel Process. Technol.* **2005**, *86* (10), 1071–1085.
- (183) Alberici, R. M.; Simas, R. C.; Abdelnur, P. V.; Eberlin, M. N.; de Souza, V.; de Sa, G. F.; Daroda, R. J. A highly effective antioxidant and artificial marker for biodiesel. *Energy Fuels* **2010**, *24* (12), 6522–6526.

- (184) Lutterbach, M. T. S.; Galvão, M. M. Fuel for the future: Biodiesel—A Case study. *Appl. Microbiol. Mol. Biol. Oilfield Syst.* **2011**, *5*, 229–235.
- (185) Aktas, D. F.; Lee, J. S.; Little, B. J.; Ray, R. I.; Davidova, I. A.; Lyles, C. N.; Sufliya, J. M. Anaerobic metabolism of biodiesel and its impact on metal corrosion. *Energy Fuels* **2010**, *24* (5), 2924–2928.
- (186) Dec, J. E. Advanced compression ignition engines—Understanding the in-cylinder processes. *Proc. Combust. Inst.* **2009**, *32*, 2727–2742.
- (187) Yoon, S. H.; Lee, C. S. Lean combustion and emission characteristics of bioethanol and its blends in a spark ignition engine. *Energy Fuels* **2011**, *25*, 3484–3492.
- (188) Allen, C. M.; Toulson, E.; Hung, D. L. S.; Schock, H.; Miller, D.; Lee, T. Ignition characteristics of diesel and canola biodiesel sprays in the low-temperature combustion regime. *Energy Fuels* **2011**, *25*, 2896–2908.
- (189) Som, S.; Longman, D. E. Numerical study comparing the combustion and emission characteristics of biodiesel to petrodiesel. *Energy Fuels* **2011**, *25*, 1373–1386.
- (190) Tzanetakis, T.; Moloodi, S.; Farra, N.; Nguyen, B.; Thomson, M. J. Spray combustion and particulate matter emissions of a wood derived fast pyrolysis liquid–ethanol blend in a pilot stabilized swirl burner. *Energy Fuels* **2011**, *25*, 1405–1422.
- (191) Park, S. H.; Kim, H. J.; Sik Lee, C. S. Fuel spray and exhaust emission characteristics of an undiluted soybean oil methyl ester in a diesel engine. *Energy Fuels* **2010**, *24* (11), 6172–6178.
- (192) Fisher, B. T.; Knothe, G.; Mueller, C. J. Liquid-phase penetration under unsteady in-cylinder conditions: soy- and cuphea-derived biodiesel fuels versus conventional diesel. *Energy Fuels* **2010**, *24* (9), 5163–5180.
- (193) Bittle, J. A.; Knight, B. M.; Jacobs, T. J. Interesting behavior of biodiesel ignition delay and combustion duration. *Energy Fuels* **2010**, *24* (8), 4166–4177.
- (194) Ye, P.; Boehman, A. L. Investigation of the impact of engine injection strategy on the biodiesel NO_x effect with a common-rail turbocharged direct injection diesel engine. *Energy Fuels* **2010**, *24* (8), 4215–4225.
- (195) Cheng, A. S.; Fisher, B. T.; Martin, G. C.; Mueller, C. J. Effects of fuel volatility on early direct-injection, low-temperature combustion in an optical diesel engine. *Energy Fuels* **2010**, *24* (3), 1538–1551.
- (196) *Proceedings of the Annual DEER Conference* Detroit, MI, 2002 to 2011; Available online: <http://www1.eere.energy.gov/vehiclesandfuels/resources/proceedings/index.html>.
- (197) Jindal, S.; Nandwana, B. P.; S. Rathore, N. S. Comparative evaluation of combustion, performance, and emissions of *Jatropha* methyl ester and karanj methyl ester in a direct injection diesel engine. *Energy Fuels* **2010**, *24* (3), 1565–1572.
- (198) Toulson, E.; Allen, C. M.; Miller, D. J.; Lee, T. Modeling the autoignition of oxygenated fuels using a multistep model. *Energy Fuels* **2010**, *24* (2), 888–896.
- (199) Reitz, R.; Arcoumanis, D.; Kamimoto, T.; Johannsson, B. *Int. J. Engine Res.* **2007**, *8*, 1–3, Special issue on homogeneous charge compression ignition engines.
- (200) De Boer, C.; Chang, J.; Shetty, S. Transonic combustion—A novel injection ignition system for improved gasoline engine efficiency, SAE Paper No. 2010-01-2110; 2010.
- (201) Anitescu, G.; Lin, R.-H.; Tavlarides, L. L. Preparation, injection, and combustion of supercritical fuels. *Poster P-2, Directions in Engine-Efficiency and Emissions Research (DEER) Conference*, Dearborn, MI, Aug 3–6, 2009.
- (202) Um, S.; Park, S. W. Numerical study on combustion and emission characteristics of homogeneous charge compression ignition engines fueled with biodiesel. *Energy Fuels* **2010**, *24* (2), 916–927.
- (203) Singh, S.; Reitz, R. D.; Wickman, D.; Stanton, D.; Tan, Z. Development of a hybrid, autoignition/flame-propagation model and validation against engine experiments and flame liftoff, SAE Paper No. 2007-01-0171; 2007.
- (204) Dec, J. Factors affecting HCCI combustion phasing for fuels with single- and dual-stage chemistry. *10th DEER Conference*, Coronado, CA, Aug 29–Sept 2, 2004.
- (205) Ryan, T. W.; Callahan, T. J. Homogeneous charge compression ignition of diesel fuel. SAE Paper No. 961160; 1996.
- (206) Yelvington, P. E.; Rallo, M. B. I.; Liput, S.; Tester, J. W.; Green, W. H.; Yang, J. Prediction of performance maps for homogeneous-charge compression ignition engines. *Combust. Sci. Technol.* **2004**, *176* (8), 1243–1282.
- (207) Patel, A.; Kong, S.-C.; Reitz, R. D. Development and validation of a reduced reaction mechanism for HCCI engine simulations. SAE Paper No. 2004-01-0558; 2004.
- (208) Christensen, E. D.; Chupka, G. M.; Luecke, J.; Smurthwaite, T.; Teresa L. Alleman, T. L.; Iisa, K.; Franz, J. A.; Elliott, D. C.; McCormick, R. L. Analysis of oxygenated compounds in hydrotreated biomass fast pyrolysis oil distillate fractions. *Energy Fuels* **2011**, *25*, 5462–5471.
- (209) Murphy, M. J.; Taylor, J. D.; McCormick, R. L. Compendium of experimental cetane number data, Technical Report NREL/SR-540-36805; National Renewable Energy Laboratory, Sept 2004.
- (210) Knothe, G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Process. Technol.* **2005**, *86* (10), 1059–1070.
- (211) Knothe, G. “Designer” biodiesel: Optimizing fatty ester composition to improve fuel properties. *Energy Fuels* **2008**, *22* (2), 1358–1364.
- (212) Knothe, G.; Dunn, R. O. A comprehensive evaluation of the melting point of fatty acids and esters determined by differential scanning calorimetry. *J. Am. Oil Chem. Soc.* **2009**, *86* (9), 843–856.
- (213) Kegl, B. Effects of biodiesel on emissions of a bus diesel engine. *Biores. Technol.* **2008**, *99*, 863–873.
- (214) Anitescu, G. Syracuse University. Unpublished data.
- (215) Computational Modeling Group, University of Cambridge, Department of Chemical Engineering, <http://como.cheng.cam.ac.uk/index.php?Page=Research&Section=Engines>; Retrieved Aug 12, 2011.
- (216) Vaughn, T.; Hammill, M.; Harris, M.; Marchese, A. J. Ignition delay of bio-ester fuel droplets. SAE Technical Paper No. 2006-01-3302; 2006.
- (217) Bunce, M.; Snyder, D.; Adi, G.; Hall, C.; Koehler, J.; Davila, B.; Kumar, S.; Garimella, P.; Stanton, D.; Shaver, G. Stock and optimized performance and emissions with 5 and 20% soy biodiesel blends in a modern common rail turbo-diesel engine. *Energy Fuels* **2010**, *24* (2), 928–939.
- (218) Fisher, B. C.; Marchese, A. J.; Volckens, J.; Lee, T.; Collett, J. L. Measurement of gaseous and particulate emissions from algae-based fatty acid methyl esters. *SAE Int. J. Fuels Lubr.* **2010**, *3* (2), 292–321.
- (219) Williams, A.; Black, S.; McCormick, R. L. Biodiesel fuel property effects on particulate matter reactivity. *6th International Exhaust Gas and Particulate Emissions Forum*, Ludwigsburg, Germany, March 9–10, 2010.