

BYU/DIPPR Biofuels Project
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Abstract: Efficient process design requires accurate thermophysical property information. Increasing focus on biofuels accentuates the need for accurate property values for these compounds. This proposal aims to produce a critically evaluated database of thermophysical properties for 30 important biofuel compounds. The project will include literature review, measurement, prediction, and critical review to provide the best possible recommended property values. The project team combines the expertise of the BYU-DIPPR Thermophysical Properties Laboratory and of industrial sponsors from the Design Institute for Physical Properties (DIPPR). This database will be a valuable resource for future biofuel process design and development.

Biofuel Property Needs: The biofuel industry is growing rapidly and it is anticipated that by 2020 close to 10% of all transportation fuels will come from renewable resources. The first generation of targeted biofuel components are bioalcohols – principally ethanol, esters of fatty acids (biodiesel) and biogas. Catalyzed transesterification of natural triglycerides, typically with methanol or ethanol, produces esters (biodiesel) and glycerol. The commonly used feedstocks are soybean, rapeseed, palm and other oils.

Emphasis is also growing for second generation biofuels, which are produced from a variety of low-value biomasses such as algae, grasses, and biomass wastes.

Efficient design and operation of biofuel production processes require accurate thermophysical property data for the components in question. Many biofuel components are chemicals that have been well-characterized for other uses, but are now being produced from different feedstocks or by different processes. Other components are relatively new compounds for which there is little accumulated thermophysical property information. Although new and innovative processes are being developed for the production of biofuels, these processes involve classic chemical engineering operations of fluid transport, heating and cooling, reactions, and separations, and hence will depend on fundamental properties. These include pure component properties such as critical constants, melting point, vapor pressure, and saturated liquid density; and mixture properties such as vapor-liquid equilibria.

The proposed work will produce a critically evaluated database of thermophysical properties for approximately 30 biofuel chemicals. The project will consist of the following elements:

1. Exhaustive literature searches to accumulate all available property data for these compounds,
2. Experimental measurements to provide essential data for inadequately characterized components including vapor pressure, density, viscosity, flash points, and vapor-liquid equilibria,
3. Prediction of missing property values using the best available methods,
4. Improvement of existing prediction techniques to more accurately estimate property values for biofuel compounds,
5. Critical evaluation of property values by BYU-DIPPR TPL staff and by DIPPR sponsors, who are experienced industrial thermophysical property experts, to provide a thermodynamically consistent set of recommended property values, and
6. Preparation of a relational database (using Microsoft Access) to contain all of the recommended property values, uncertainties, and associated raw data and reference information.

The BYU-TPL staff will complete the work in all of these areas and the DIPPR sponsors will provide critical evaluation of the recommended property values (part of element 5, above). Some of the measurement work may be subcontracted to other DIPPR investigators. The processes and tools developed as part of the DIPPR 801 project will be used to facilitate the work of this project.

The BYU-TPL has laboratory capabilities and equipment to measure the properties mentioned in element 2, above, and has software tools and extensive experience for property prediction and evaluation. Undergraduate and graduate research assistants will work with project staff and principal investigators in all aspects of the project.

Project Description

Compounds. Below is the proposed list of compounds to be included in this study. Included are compounds found in biodiesel processes including triglycerides, mono- and di-glycerides, fatty acids and methyl and ethyl esters of these fatty acids; sugars common to fermentation and other cellulosic processes; and glycerol, which is already well-characterized and is a product of both biodiesel and fermentation reactions. The availability of pure and relatively inexpensive samples of these chemicals will determine whether or not measurements can be performed on them. There is the possibility of substituting similar compounds if it is determined that other candidates will better meet the needs of the project.

Table 1. Proposed compounds for study.

Compound	Type	Molecular Formula
Trierucin	Triglyceride	C ₆₉ H ₁₂₈ O ₆
Triolein	Triglyceride	C ₅₇ H ₁₀₄ O ₆
Trilinolein	Triglyceride	C ₅₇ H ₉₈ O ₆
Tripalmitin	Triglyceride	C ₅₁ H ₉₈ O ₆
Trilaurin	Triglyceride	C ₃₉ H ₇₄ O ₆
Dirolein	Diglyceride	C ₃₉ H ₇₂ O ₅
Monolein	Monoglyceride	C ₂₁ H ₄₀ O ₄
Dipalmitin	Diglyceride	C ₃₅ H ₆₈ O ₅
Monopalmitin	Monoglyceride	C ₁₉ H ₃₈ O ₄
Methyl erucate	Methyl ester of fatty acid	C ₂₃ H ₄₄ O ₂
Ethyl erucate	Ethyl ester of fatty acid	C ₂₄ H ₄₆ O ₂
Methyl oleate	Methyl ester of fatty acid	C ₁₉ H ₃₆ O ₂
Ethyl oleate	Ethyl ester of fatty acid	C ₂₀ H ₃₈ O ₂
Methyl linoleate	Methyl ester of fatty acid	C ₁₉ H ₃₄ O ₂
Ethyl linoleate	Ethyl ester of fatty acid	C ₂₀ H ₃₆ O ₂
Methyl palmitate	Methyl ester of fatty acid	C ₁₇ H ₃₄ O ₂
Ethyl palmitate	Ethyl ester of fatty acid	C ₁₈ H ₃₆ O ₂
Methyl laurate	Methyl ester of fatty acid	C ₁₃ H ₂₆ O ₂
Ethyl laurate	Ethyl ester of fatty acid	C ₁₄ H ₂₈ O ₂
Erucic acid	Fatty acid	C ₂₂ H ₄₂ O ₂
Oleic acid	Fatty acid	C ₁₈ H ₃₄ O ₂
Linoleic acid	Fatty acid	C ₁₈ H ₃₂ O ₂
Palmitic acid	Fatty acid	C ₁₆ H ₃₂ O ₂
Lauric acid	Fatty acid	C ₁₂ H ₂₄ O ₂
Glucose	Sugar	C ₆ H ₁₂ O ₆
Xylose	Sugar	C ₅ H ₁₀ O ₅
Galactose	Sugar	C ₆ H ₁₂ O ₆
Arabinose	Sugar	C ₅ H ₁₀ O ₅
Mannose	Sugar	C ₆ H ₁₂ O ₆
Glycerol	Byproduct	C ₃ H ₈ O ₃

Properties. The set of properties included in the DIPPR 801 database are for the most part the properties that will be included for the Biofuel Property Database, with a few additions. Water solubility, Henry's

constant, and octanol-water partition coefficient will be included. Vapor-liquid equilibrium data from the literature and from measurements will also be included. The list of properties to be included is given in Table 2.

Table 2. Properties to be included in Biofuel Property Library.

Constant Properties
Molecular Weight
Critical Temperature
Critical Pressure
Critical Volume
Critical Compressibility Factor
Melting Point at 1 atm
Triple Point Temperature
Triple Point Pressure
Normal Boiling Point
Liquid Molar Volume at a reference temperature and pressure
Enthalpy of Formation for Ideal Gas at 298.15 K
Gibbs Energy of Formation for Ideal Gas at 298.15 K and 1 bar
Absolute Entropy of Ideal Gas at 298.15 K and 1 bar
Standard State Enthalpy of Formation at 298.15 K and 1 bar
Standard State Gibbs Energy of Formation at 298.15 K and 1 bar
Standard State Absolute Entropy at 298.15 K and 1 bar
Enthalpy of Fusion at the Melting Point
Net Standard State Enthalpy of Combustion at 298.15 K
Acentric Factor
Radius of Gyration
Solubility Parameter at a reference temperature and pressure
Dipole Moment
van der Waals Reduced Volume
van der Waals Area
Refractive Index
Flash Point
Lower Flammability Limit Percent/Temperature
Upper Flammability Limit Percent/Temperature

Auto Ignition Temperature Heat of Sublimation at the triple point Parachor Dielectric Constant

Temperature-dependent Properties

Density of Liquid Density of Solid Heat Capacity of Ideal Gas Heat Capacity of Liquid Heat Capacity of Solid Heat of Vaporization Second Virial Coefficient Surface Tension Thermal Conductivity of Liquid Thermal Conductivity of Solid Thermal Conductivity of Vapor Vapor Pressure of Liquid Vapor Pressure of Solid or Sublimation Pressure Viscosity of Liquid
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Mixture Properties

Henry's Law Constant Water Solubility Octanol-Water Partition Coefficient Vapor-Liquid Equilibria
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Measurements. Measurements will play a critical role in this project. The specific list of properties to be measured for each compound will depend on the results of the literature research. If adequate data are available for given properties then measurement efforts will shift to other properties or to other compounds. The project budget includes funding for measurements of vapor pressure, density, viscosity, and flash point on approximately 10 compounds each, and for 20 binary VLE studies. These funds will be shifted between properties and compounds as dictated by the literature evaluation and by the potential impact on the proposed database.

Most of the experimental apparatuses needed for the experimental measurements are currently available in BYU-TPL facilities. A small amount of capital equipment expenditures will be made to upgrade vapor pressure and vapor-liquid equilibrium measurement capabilities. Vapor pressure and vapor-liquid equilibrium measurements will be performed using a variety of glass and stainless steel apparatuses with

appropriate temperature control and pressure and temperature measurement. Densities will be measured using an Anton Paar oscillating tube densitometer. Viscosity will be measured using a Schott Geräte viscometer. Flash points will be measured using either a Pensky-Martens or Setaflash apparatus, both of which are available in the BYU-TPL facility.

Vapor-liquid equilibrium (VLE) measurements will be made using a standard binary PTx method in which total pressure measurements are made across the entire composition range. Activity coefficient model parameters are determined from a least-squares fit of these data. (This method is described in W.V. Wilding, K.L. Adams, A.E. Carmichael, J.B. Hull, T.C. Jarman, K.P. Jenkins, T.L. Marshall, and H.L. Wilson, "Vapor-Liquid Equilibrium Measurements on Three Binary Mixtures: Difluoromethane / Hydrogen Chloride, *cis*-1,3-Dichloropropene / *trans*-1,3-Dichloropropene, Pyrrole / Water," *J. Chem. Eng. Data*, **47**(4), 748-756, 2002.) The selection of VLE studies will depend upon the availability of literature data, the practical relevance of these data to separations process design, and upon the availability of the compounds.

Critically evaluated prediction techniques will be used to estimate properties for which measured data are not available either from the literature or from the measurements included in this project.

Process. The process for the proposed work is as follows:

1. Literature search to find all available property values will be completed.
2. Literature values will be evaluated for accuracy and completeness.
3. Measurements will be completed to provide property values unavailable in the literature.
4. Each compound's properties will be evaluated for thermodynamic consistency and chemical family consistency. Appropriate prediction techniques will be used to estimate remaining properties.
5. Existing prediction techniques will be improved based on literature and measured data to better represent biofuel components.
6. The recommended property values will be evaluated by DIPPR sponsors.
7. Modifications will be made to respond to this review and once values are agreed upon by the project staff and DIPPR sponsors, the compound properties are finalized.
8. A relational database of recommended properties and of literature references will be compiled.

As part of a biofuels initiative within the DIPPR 801 project literature searches and preliminary evaluations have already begun on many of the proposed compounds.

