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Standard Reference Data for the Thermophysical Properties of Biofuels*

ABSTRACT: The thermophysical properties of biofuels are required for the efficient design of their chemical processing, distribution, and utilization. We provide a review of biofuel properties research at the National Institute of Standards and Technology (NIST). We are expanding two Standard Reference Databases to include biofuels. The ThermoData Engine will collect and evaluate all published property data on biofuel components. The NIST Reference Fluid Thermodynamic and Transport Properties database is a calculational database providing properties of biofuel components and blends based on thermodynamic and transport models. The property models in the databases implement an equation of state approach based on well defined reference fluids. Complex mixtures, including blends of biofuels with conventional fuels, are modeled as “surrogate blends,” i.e., a blend of perhaps a dozen components that captures the essential characteristics of a complex fuel. Surrogate blends are formulated from a “suite” of well-characterized pure compounds. Property measurements for the pure compounds in the surrogate suite include but are not limited to density, speed of sound, and viscosity. We have also carried out measurements on actual biofuel samples. A recent extension of the distillation curve that we have developed at NIST is proving very valuable in characterizing fuels. This “advanced distillation curve method” provides much more quantitative information than the traditional method, including chemical characterization of the different “cuts” as the distillation proceeds. We present examples of our measurements and models completed to date and outline future plans.

KEYWORDS: biofuels, database, models, standards, thermodynamic properties, transport properties

Introduction

The sources and nature of transportation fuels will certainly undergo major changes in the coming years. Today’s fuels are based overwhelmingly on hydrocarbons derived from crude oil. It is certain that petroleum-based fuels must eventually be replaced, but it is highly uncertain what those replacements will be. Hydrogen may be the ultimate long-term replacement, but significant technical hurdles must be overcome to realize its potential. Liquid fuels derived from biological materials have bright prospects for more immediate utilization.

The thermophysical properties of biofuels are required for the efficient design of the processes involved in the chemical conversion of the biomass feedstock and then in the distribution and utilization of the resulting fuel. These properties include thermodynamic properties (density, heat capacity, enthalpy, etc.) and transport properties (viscosity, thermal conductivity, etc.). The thermophysical properties are just one part of a typical fuel specification. The thermodynamic and transport properties are most relevant for the design of engines or processes (e.g., production, purification, or distribution) and are equally important for chemical feedstocks and intermediaries as well as the finished fuel. Other specifications (e.g., acidity, oxidative stability, knock index, or the allowable levels of trace impurities such as water, metals, or sulfur) typically apply only to the finished fuel and often relate to the suitability of a fuel for a particular application, or they relate to materials compatibility issues. The thermophysical properties are generally not very sensitive to the presence of trace impurities or additives. This paper deals only with the thermophysical properties.

Modern engineering design relies on complex simulation packages. Thermophysical property data are required in such software. The design of new and innovative systems for biofuels can be no better than the

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input data. This becomes more of an issue when the fluids involved are different from the traditional fluids. The analysis of engine performance also demands reliable property data.

In the next 5–10 years, biofuels will be phased in by blending with hydrocarbons from fossil fuels—initially conventional gasoline or diesel fuel but later possibly with synfuels derived from coal. This is where the complications begin—the blend of a biofuel with gasoline or diesel may involve hundreds of chemical components (mostly from the hydrocarbon fraction). The biofuels have fundamentally different chemical characteristics compared to petroleum-derived hydrocarbons. For example, plants yield biofuels consisting of alcohols, esters, and/or carboxylic acids, molecules that are all highly polar and associating.

Biofuels thus present an enormous 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 many-component mixtures. Modeling approaches must be expandable to many components and to the various types of interactions between them.

Current methods to determine properties are highly empirical and approximate. The most important specification for a fuel is the distillation curve—a plot of the distillation temperature versus the volume fraction distilled. Properties of conventional fuels are obtained from empirical correlations between the distillation curve, specific gravity, and sometimes composition-related parameters (such as a measure of aromaticity). These correlations have been created based on years of experience and data. The current system works because systematic errors have been empirically compensated for and because conventional fuels, while having hundreds of components, are blends of similar compounds.

There is presently no comprehensive consensus source of reliable property data for the biofuels that can be called upon by industry, and that is the void we at NIST propose to fill. In this paper we summarize our research efforts on biofuels, focusing on two standard reference databases that will be the main vehicles for disseminating data to users in industry and the research community.

Summary

The biofuels program in the NIST Thermophysical Properties Division began in 2008, and we intend to ramp up a significant effort in the next 2–3 years. This program comprises experimental, modeling, and database components.

Two standard reference databases that have been developed at NIST over the last 20 years are being expanded to include biofuels and biofuel components. The NIST ThermoData Engine (TDE) and its associated TDE-SOURCE database of experimental data drawn from the literature provide the tools to identify and critically evaluate property data; TDE also provides expert system software to generate single-property correlations and preliminary equations of state (EOS). The focus of TDE is pure-component properties, although it has recently been expanded to include binary and ternary mixtures. The NIST Reference Fluid Thermodynamic and Transport Properties (REFPROP) database is a calculational database that implements comprehensive high-accuracy equations of state for the thermodynamic properties and also wide-ranging models for the transport properties. REFPROP can calculate essentially all the thermophysical properties at any temperature or pressure (within the validity limits of the models) for mixtures with up to 20 components. The number of biofuel-relevant compounds in REFPROP is currently limited, but the development of models is underway for alcohols, fatty acid methyl esters (FAMES) (biodiesel components), and conventional hydrocarbons that biofuels would be mixed with. These databases serve as our primary mechanism to deliver data to industry and the research community.

EOS that provide accurate values of the thermodynamic properties over wide ranges of temperature and pressure for pure compounds and mixtures have been developed and implemented in REFPROP. Experimental data are used in a multiparameter regression to generate the EOS; data can be combined with estimation techniques and thermodynamic constraints where necessary to generate reliable equations even when only limited data are available.

Biofuels are usually blends of many chemical compounds. In the case of blends composed of a small number of compounds (e.g., biodiesels), the blend can be explicitly modeled in REFPROP. For complex fuels (e.g., any blend of bio-derived components with conventional petroleum fuels), the concept of a

surrogate blend is used, where a complex fuel is characterized by a mixture with a limited number of components (usually less than 10–20). We have developed surrogate blends for a variety of conventional fuels and will be applying this methodology to biofuel blends.

Underpinning all of the database and modeling efforts are experimental measurements of fluid properties. TDE mines the world's chemical literature for the bulk of its data. The experimental effort at NIST is focused in two areas. The first is the measurement of reference data for pure compounds and well-characterized mixtures; these are high-accuracy measurements, often over wide ranges of temperature and pressure. The resulting data are used to develop the models used in REFPROP. Measurements of real fuels provide the data needed to develop surrogate blends and verify mixture models; real fuels are also measured to provide data for a specific application. A key measurement on real fuels is the distillation curve, and we have recently extended the standard distillation curve method to provide temperature measurements that are thermodynamically well defined and to provide composition and other data as a function of the distillate cut.

Standard Reference Databases

ThermoData Engine and TDE-SOURCE

The first standard reference database to be discussed is NIST TDE [1–5], which also includes TDE-SOURCE, a local relational database of experimental data points drawn from the literature. TDE collects the raw experimental data from the literature and evaluates these data “on demand” to provide recommended data values and/or property models.

NIST TDE represents the first full-scale software implementation of the dynamic data evaluation concept for thermophysical property data. The traditional or “static” process for critical data evaluation is an extremely time- and resource-consuming process, requiring extensive efforts in data collection, data mining, analysis, fitting, etc. Because of this, it must be initiated far in advance of the need. By the time the data evaluation and fitting process for a particular chemical system or property group are complete (sometimes after years of data evaluation involving highly skilled data experts), new data have often been measured. But it is not practical to reinitiate the entire process, and as a result, a very significant part of the existing published data has never been used in any meaningful application. Essentially all existing data evaluation projects fall into this category. Moreover, this static data evaluation process is not responsive to rapidly developing fields, where the need to simulate many new technologies or processes each year demands property data for the fluids involved.

The new concept of dynamic data evaluation [6,7] requires the development of large electronic databases capable of storing essentially all relevant experimental data with detailed descriptions of relevant metadata (e.g., sample purities and experimental methods) and uncertainties. The combination of these electronic databases with artificial-intelligence (expert system) software, which can automatically evaluate the available experimental data and generate recommended property values, leads to the ability to produce critically evaluated data dynamically or “to order.” The dynamic data evaluation process dramatically reduces the effort and costs associated with anticipating future needs and keeping evaluations current. The implementation of the dynamic data evaluation concept consists of a number of major tasks [8]: (1) Design and development of a comprehensive database system that is structured on the principles of physical chemistry and is capable of supporting a large-scale data entry operation for the complete set of thermophysical and thermochemical properties of chemical systems, including pure compounds, mixtures, and chemical reactions; (2) development of software tools for automation of the data entry process with robust and internally consistent mechanisms for the automatic assessment of data uncertainty; (3) design and development of algorithms and software tools to ensure quality control at all stages of data entry and analysis; (4) development of algorithms and computer codes to implement the stages of the dynamic data evaluation concept; (5) development of algorithms to implement, target, and apply prediction methods depending on the nature of the chemical system and property, including automatic chemical structure recognition mechanisms; and (6) development of procedures allowing the generation of output in a format interoperable with major engineering applications, including commercial simulation engines for chemical-process design.

TABLE 1—Statistical information about availability of pure compound experimental thermophysical property data points from TDE-SOURCE (May 2009).

Compound Name	Formula	Critical Parameters	Phase Transition	Vapor Pressure	Density	Heat Capacity	Other Properties	Total
Ethanol	C ₂ H ₆ O	60	34	1877	3833	1457	1580	9823
1-butanol	C ₄ H ₁₀ O	31	17	1226	2586	542	748	5768
Methyl myristate	C ₁₅ H ₃₀ O ₂	0	25	123	25	106	13	331
Methyl palmitate	C ₁₇ H ₃₄ O ₂	0	49	130	20	205	13	469
Methyl linoleate	C ₁₉ H ₃₄ O ₂	0	1	22	9	0	9	66
Methyl oleate	C ₁₉ H ₃₆ O ₂	0	5	66	45	0	17	179
Methyl stearate	C ₁₉ H ₃₈ O ₂	0	47	121	32	104	14	362
Methyl arachidate	C ₂₁ H ₄₂ O ₂	0	20	34	1	104	0	175

Initially developed for the property-by-property evaluation of pure-compound thermophysical property data, TDE has been gradually expanded to properties of binary mixtures and chemical reactions as well as to the generation of EOS.

TDE-SOURCE is a local relational data storage facility of experimental data “feeding” TDE during data evaluation sessions [9]. As of May 2009, TDE-SOURCE contained more than 3.7 million data points for more than 19 000 pure compounds, 32 000 binary mixtures, 8000 ternary mixtures, and 5000 chemical reactions. TDE is one of the components of the Global Information System in Thermodynamics developed at NIST to collect, process, integrate, evaluate, and communicate the entire body of knowledge pertaining to a field of thermodynamics and thermophysics and to support any application requiring this knowledge in an on-demand mode with definitive information-quality assessments [10].

TDE-SOURCE strives to collect essentially all of the world’s published thermophysical property data, and as such, it contains substantial information on the chemical compounds that are the constituents of biofuels. Nevertheless, we have made a concerted effort over the past year to ensure that our data set is complete. Statistical information about the availability of experimental thermophysical and thermochemical property data points from TDE-SOURCE (as of May 2009) for some biofuel-relevant compounds, their binary and ternary mixtures, and chemical reactions with their participation is provided in Table 1 (pure compounds) and Table 2 (binary mixtures, ternary mixtures, and chemical reactions). It is obvious from the data presented in these tables that there is a dramatic difference in the quantity and diversity of the thermophysical property information for simple alcohols such as ethanol and 1-butanol compared to high

TABLE 2—Statistical information about the availability of experimental mixture and reaction thermophysical and thermochemical property data points from TDE-SOURCE (May 2009).

Compound Name	System									
	Binary Mixtures							Chemical Reactions		
	VLE	Liquid-Liquid Equilibria	Solid-Liquid Equilibria	Density	Excess Properties	Other Properties	Total	Ternary Mixture Properties	Thermo-dynamic State Change	Equilibria
Ethanol	41 151	899	1874	30 581	11 624	30 854	116 983	65 216	15	393
1-butanol	21 577	1310	1263	15 371	8517	13 279	61 317	18 464	13	132
Methyl myristate	208	1	84	58	113	182	646	202	1	0
Methyl palmitate	366	4	149	192	0	258	969	1105	0	0
Methyl linoleate	86	0	7	52	0	59	204	532	0	0
Methyl oleate	294	18	32	50	0	99	493	1060	1	0
Methyl stearate	82	3	135	344	0	525	1089	200	0	0
Methyl arachidate	0	0	0	0	0	0	0	0	0	0

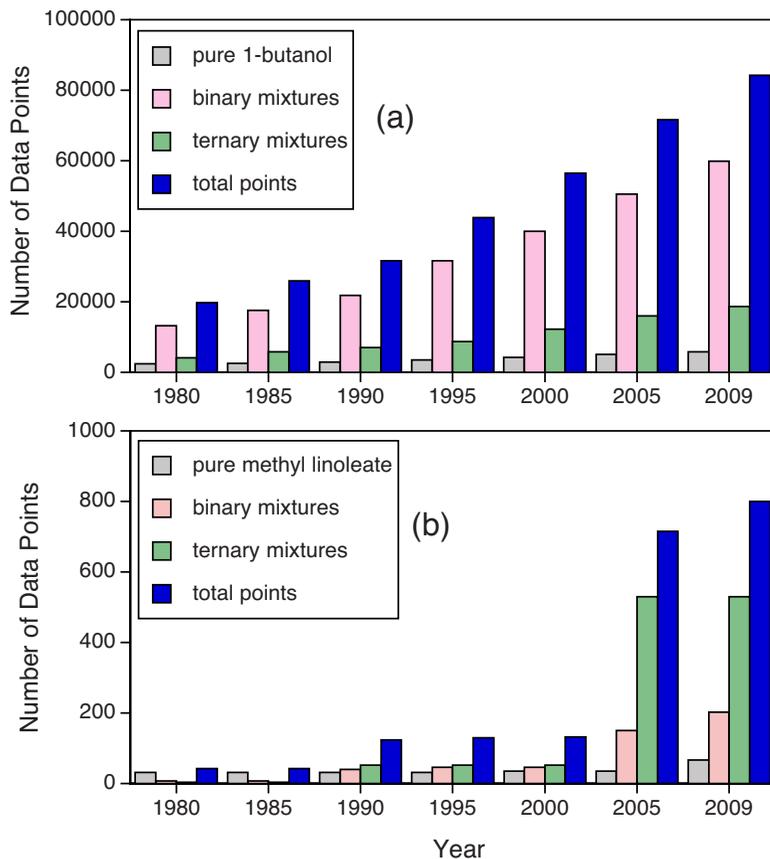


FIG. 1—The growth of experimental thermophysical property data points for (a) pure 1-butanol and its mixtures and (b) pure methyl linoleate and its mixtures.

molar mass esters such as methyl myristate, methyl palmitate, methyl linoleate, methyl oleate, methyl stearate (also known as methyl octadecanoate), and methyl arachidate, i.e., the FAMES that are major constituents of biodiesel.

While the data for these esters are currently sparse, the interest in studying and measuring their properties has significantly increased over the past 10 years compared to a more steady rise in the data for the alcohols, as illustrated in Fig. 1 for 1-butanol and methyl linoleate. It is highly probable that thermophysical property information for biofuel-relevant compounds will continue growing rapidly in the near future. This, in turn, will create the need for an on-going re-evaluation of these properties. TDE is well suited to perform such a task in an on-demand mode. Continuous analysis of data availability will also allow the identification of the most critical measurements to be performed for broad-based property modeling.

The NIST REFPROP Database

The second standard reference database to be discussed, the NIST REFPROP database [11,12], is a calculational database—it implements property models based on experimental data rather than storing the experimental data themselves. The fluids covered by the database are much more limited compared to TDE (Version 8.0 of REFPROP covers 84 pure fluids compared to more than 19 000 compounds in TDE). But, for the fluids that are included, REFPROP provides all of the thermodynamic properties, over wider ranges of temperature and pressure, and at much lower uncertainties compared to TDE. REFPROP focuses on industrially important fluids and mixtures including refrigerants, cryogenics, natural gases (i.e., mixtures of methane with other light hydrocarbons, nitrogen, and CO₂), and hydrocarbons up to C₁₂. It is the de facto standard for refrigerants and incorporates the internationally accepted models for natural gases. Its coverage of biofuels is, however, limited at present.

REFPROP calculates a wide range of thermodynamic and transport properties; the more common ones are listed in Table 3. Mixtures with up to 20 components may be specified from among the pure fluids, and

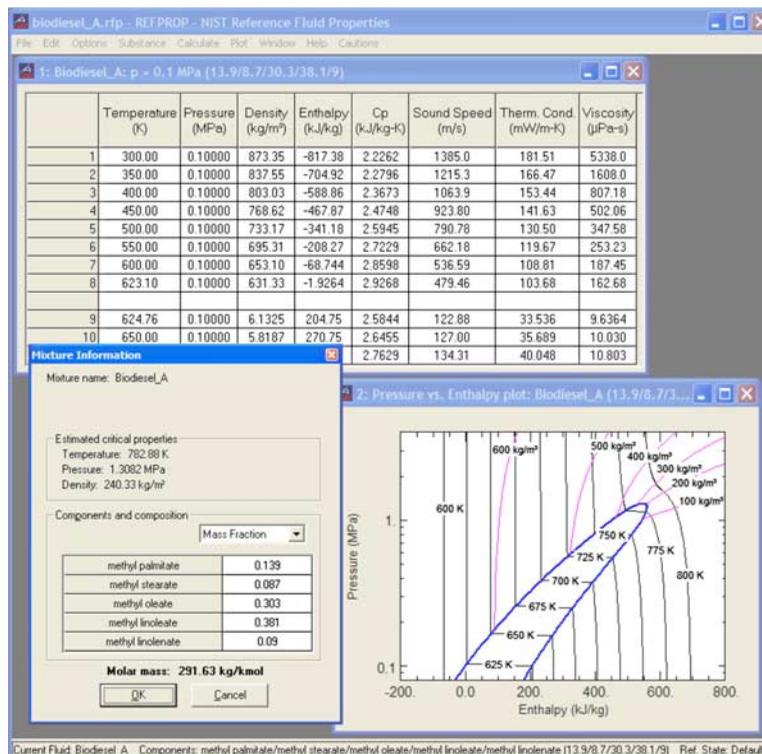


FIG. 2—Screen shot of the NIST REFPROP database showing a data table and pressure-enthalpy diagram for biodiesel “A” studied by Huber et al. [13].

virtually any combination is allowed. The program is based on the most accurate EOS and transport property models currently available. Whenever possible, we implement models published in peer-reviewed sources, and these sources are internally documented in the database. The thermodynamic properties are computed by use of comprehensive EOS (described in the next section). This approach ensures thermodynamic consistency and allows calculations at all conditions.

The property models implemented in REFPROP may be accessed in several ways. A graphical user interface provides a convenient means to calculate and display properties in tabular or graphical form. Figure 2 gives a screen shot of the program depicting data for one of the biodiesels described below in the Modeling section. The models are implemented in a suite of subroutines written in standard Fortran, and the source code is provided. They are also compiled into a standard dynamic link library that can be linked with other applications, such as spreadsheets, laboratory data acquisition systems, or symbolic math packages. REFPROP has also been incorporated into comprehensive commercial process simulation packages.

A number of biofuel-relevant compounds are currently included in the NIST REFPROP database. For example, REFPROP implements the ethanol EOS of Dillon and Penoncello [14] as well as comprehensive viscosity and thermal conductivity models. Equations for other alcohols, including the butanols, are under development. Preliminary EOS for the most important FAMES are now available, as described below. A model for ethanol/water mixtures is under development. Additional fluids will be added as the data and models are developed. A large number of hydrocarbons that would be applicable for the petroleum fraction of biofuel blends are included.

Compared to the dynamic data evaluation of TDE, REFPROP implements the more traditional static property models. For well-studied fluids or those important to commerce (e.g., steam and natural gas) this approach is preferred: Detailed evaluations by data experts will always yield the most accurate formulations, and in many cases, consistency and stability of values are preferable over absolute accuracy; these would be undermined by continual reevaluation of the data. But the two databases are complementary; TDE can generate EOS and output the results as a file compatible with REFPROP.

TABLE 3—Partial list of properties computed with REFPROP database.

Thermodynamic Properties				
T Temperature		C_p Heat capacity, const. p		A Helmholtz free energy
ρ Density		w Speed of sound		G Gibbs free energy
p Pressure		Z Compressibility factor		Δh_v Heat of vaporization
h Enthalpy		μ_J Joule–Thompson coefficient		f Fugacity
u Internal energy		q Vapor quality		ϕ Fugacity coefficient
s Entropy		B Second virial coefficient		K K value
C_V Heat capacity, const. V		C Third virial coefficient		V Specific volume
Critical Parameters				
T_{crit} Critical temperature		p_{crit} Critical pressure		ρ_{crit} Critical density
Transport Properties				
η Viscosity		λ Thermal conductivity		
Other Properties				
σ Surface tension		M Molar mass		κ Isothermal compressibility
β Volume expansivity		k Isentropic coefficient		β_s Adiabatic compressibility
Ξ Exergy		ν Kinematic viscosity		α Thermal diffusivity
Pr Prandtl number		θ Specific heat input		
Derivatives				
$(\partial p / \partial \rho)_T$	$(\partial^2 p / \partial \rho^2)_T$	$(\partial p / \partial T)_\rho$	$(\partial \rho / \partial T)_p$	$(\partial \rho / \partial p)_T$

Modeling

Pure-Fluid Equations of State

The thermodynamic properties of pure fluids are represented by EOS. An EOS is a mathematical expression relating the state variables of a system. All of the thermodynamic properties, including those not directly measured, such as enthalpy and entropy, may be calculated from an EOS. Most of the EOS in REFPROP (including all of the more recent formulations) are written in terms of the reduced molar Helmholtz free energy as a function of temperature and density. The equation is composed of separate terms arising from ideal-gas behavior (superscript *id*) and a “residual” or “real-fluid” (superscript *r*) contribution

$$\phi \equiv \frac{A}{RT} = \phi^{\text{id}} + \phi^r \quad (1)$$

where:

A = molar Helmholtz energy and
 R = molar gas constant.

The ideal-gas contribution is represented in terms of the heat capacity of the ideal-gas state. The residual or real-fluid contribution is given by

$$\phi^r = \sum_k N_k \tau^{t_k} \delta^{l_k} \exp[-a_k(\delta - \varepsilon_k)^{l_k}] \exp[-b_k(\tau - \gamma_k)^{m_k}] \quad (2)$$

where the temperature and density are expressed in the dimensionless variables $\tau = T^*/T$ and $\delta = \rho/\rho^*$, where T^* and ρ^* are reducing parameters that are often equal to the critical parameters. The N_k are numerical coefficients fitted to experimental data. The multipliers a_k and b_k and the exponents t_k , d_k , l_k , and m_k are optimized for a particular fluid or group of fluids. The development of the functional form of the equation is described by Lemmon and Jacobsen [15]. For the biofuels, a subset of Eq 2 with 13 terms in the summation is used where many of the parameters are 0 or 1. Given an EOS all of the thermodynamic properties can be calculated from derivatives of the Helmholtz energy. These relationships are given in the work of Lemmon and Jacobsen [18].

Traditionally, the Helmholtz energy form required a large quantity of high-quality experimental data to determine the multiple parameters of the equation. Different types of thermodynamic property data, such as the phase boundary (saturated liquid and vapor densities and vapor pressures) and single-phase properties (density, heat capacity, speed of sound), are used simultaneously in a multi-parameter regression.

Different weights can be assigned to each type of data as well as to each individual point. Recently a new form of the Helmholtz energy equation and regression procedure has been developed [16], which imposes a significant number of thermodynamic constraints that allow even very limited experimental data to be used to develop a well-behaved equation that extrapolates in a physically reasonable manner. Since the coefficients of the equation are empirical, in cases with very limited data, it is possible to obtain a set of coefficients that result in unphysical behavior (such as negative heat capacities at low temperatures) in regions where data are unavailable. The use of appropriate constraints in the regression removes this problem.

The critical temperature and density are used as reducing parameters in the EOS, and these parameters are often unknown for biofuel components (as indicated in Table 1). Thus they must often be estimated. (Indeed, the critical temperature is often above the thermal stability limit of the molecule.) Another feature of this particular formulation is that although uncertainty in the critical values will increase the uncertainty of properties in the critical region, it will not greatly affect properties outside of the critical region that are based on a regression of experimental data. This is in contrast to some of the simple EOS (e.g., cubic EOS such as Peng–Robinson) that have parameters expressed in terms of the critical parameters; these can be much more sensitive to the values of the critical parameters used.

An additional option is the extended corresponding states (ECS) model of Huber and Ely [17]. It is used for fluids with very limited data. Simple corresponding states are based on the assumption that with the appropriate scaling of temperature and density, the reduced residual Helmholtz energies and compressibilities ($Z=p/RT\rho$) of an unknown fluid and a reference fluid (for which an accurate EOS is available) are equal. When combined with the ideal-gas heat capacity, all other thermodynamic properties can be calculated. Simple corresponding states were developed for spherically symmetric molecules. The ECS model extends this method to other types of molecules by the introduction of the “shape factors,” which are functions of temperature and density. These shape factors are fitted to experimental data.

Modeling of Biodiesel Components

Biodiesel produced from vegetable oil consists primarily of FAMES. The modeling of biodiesel thus requires EOS for the FAMES, and we recently completed preliminary models for the five FAMES that are the major components of biodiesel produced from soybeans, namely, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linoleate [13]. Our own measurements of the boiling point, density, and speed of sound [13,19] over a range of temperature were combined with literature data, which were retrieved from TDE-SOURCE database.

The EOS requires the critical point temperature, pressure, and density. Experimental values of the critical parameters of the FAMES are not available; therefore we used estimation methods. The critical temperature and pressure were estimated by the use of a novel procedure based on quantitative structure-property relationship methodology. The procedure made use of evaluated critical parameter data for more than 700 compounds in TDE-SOURCE; from these, a subset of 200 compounds that are most structurally similar to the FAMES was selected. The critical parameters were then correlated using multiple descriptors. The entire procedure is detailed by Kazakov et al. [20]. The resulting estimates for the critical temperature and pressure were put back into TDE, which combined these points with densities at the normal boiling point to estimate the critical density. The critical temperature, pressure, and density have estimated uncertainties of 5–15 K, 50 kPa, and 2.0–2.7 kg/m³, respectively. The ideal-gas properties were also estimated using methods built into TDE.

The experimental and estimated data were used to develop EOS explicit in Helmholtz energy for each FAME; specifically, the form of Eq 2 was used with a total of 13 terms. Finally, the EOS were put into the data file format required by REFPROP database. The EOS developed by this process must be considered preliminary because of the limited set of experimental data. Nevertheless, they do allow modeling of actual biodiesel feedstocks, as described below.

As an example of the data situation common for many of the biofuel components, a comparison of experimental vapor pressures for methyl palmitate with the values computed with the EOS is shown in Fig. 3. This figure illustrates several challenges. While numerous data sets are available, many report data at just one or a few temperatures. The uncertainties (depicted by the error bars) are often very large. Different data sets can disagree by large factors, especially at low temperatures (i.e., low vapor pressures). To help remedy this situation, our regression procedure simultaneously uses all available data. Because of thermo-

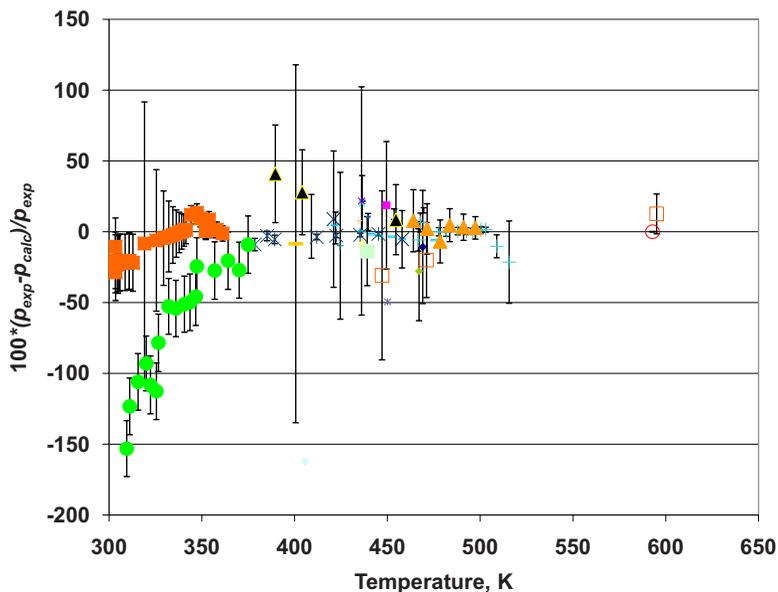


FIG. 3—Comparison of the vapor pressure calculated from the EOS and experimental data for methyl palmitate. The different symbols represent distinct literature data sources.

dynamic consistency, all of the thermodynamic properties are interrelated, and knowledge of other data, such as heats of vaporization and heat capacity, will guide the behavior of the vapor-pressure curve at low temperatures.

Mixture Equations of State

For calculations of the thermodynamic properties of mixtures, we use a mixture model explicit in Helmholtz energy that can utilize any EOS, provided that it can be expressed in terms of the Helmholtz energy [18,21]. This form of model has been used successfully for refrigerant mixtures [18] and for natural gas mixtures [22]. Details on the mixture model are given in Refs 18 and 21.

In REFPROP, the model contains one generalized function for each class of mixture and three mixture-dependent parameters for each binary pair. Multicomponent mixtures are modeled using only the constituent binary parameters. With this model, all of the thermodynamic properties can be calculated for a mixture.

Transport Property Models

In general, models for transport properties are not as well developed as those for the thermodynamic properties. When there are sufficient data present, fluid-specific empirical correlations for viscosity and thermal conductivity are used.

The transport properties of viscosity and thermal conductivity are modeled with the residual concept. In this model, the property (either viscosity or thermal conductivity) is composed of three contributions: A dilute-gas term that is a function only of temperature, a residual term accounting for the behavior at higher densities, including liquid densities, and a term to account for critical enhancement. The thermal conductivity approaches infinity at the critical point, and the enhancement term is significant for thermal conductivity even quite far from the critical point. For viscosity, the enhancement is small except extremely close to the critical point and can usually be ignored. A variety of fluid-specific correlations for viscosity and thermal conductivity has been taken from the literature and implemented in REFPROP database.

Where fluid-specific correlations are not available, the transport properties are modeled with the ECS method of Klein et al. [23] for viscosity and McLinden et al. [24] for thermal conductivity. The critical enhancement for thermal conductivity is the model by Huber et al. [25]. This method shares many of the concepts of the ECS model for the thermodynamic properties described above, but it employs a third shape factor that is a simple function of density. Separate functions for viscosity and thermal conductivity are

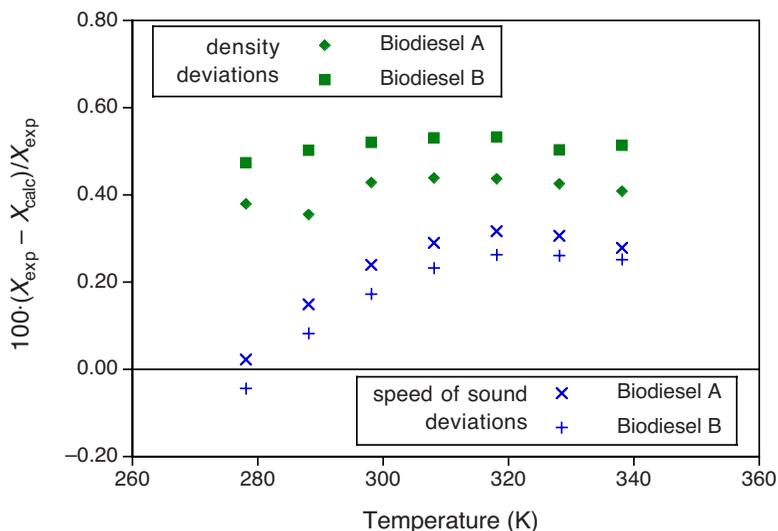


FIG. 4—Comparison of the density and speed of sound calculated from the EOS mixture model and experimental data for the B100 biodiesel fuel samples.

fitted to data or supplemented with predictive methods such as those recommended by Poling et al. [26]. Where no data are available, the functions are set to 1; this is a “predictive mode.”

The ECS model is also applicable to mixtures. Other approaches may be necessary for polar compounds such as alcohols; research is in progress in this area.

Application to Commercial Biodiesel Samples

We have recently applied the above modeling approach to two commercial biodiesel feedstocks [13]. The biodiesels were chemically analyzed and found to consist primarily of five FAMES: methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linoleate. The first step in modeling these biodiesels was to develop EOS for each of the five constituent FAMES, as described above. The actual concentrations of the five component FAMES were used to “construct” the biodiesels in REFPROP. No experimental data on mixtures of the FAMES were available, and thus, the mixture interaction parameters were set to their “ideal mixing” values. Comparisons of calculated values of density and speed of sound are shown in Fig. 4. The calculated density is within 0.6 % of the experimental values, and the calculated sound speed is within 0.4 % of the experimental values. The predicted bubble-point temperatures at atmospheric pressure for the two blends were 1.0–2.2 K lower than the measured values or to within 0.4 %. Although these deviations exceed the experimental uncertainties of approximately 0.1 %, we feel these results demonstrate the promise of this modeling approach.

Surrogate Fluid Approach for Complex Mixtures

While the B100 biodiesels (i.e., a fuel derived 100 % from biological sources) discussed above could be modeled as mixtures of the five or so major components making up the blend, most fuels are complex mixtures of hundreds, even thousands, of chemical compounds. It is not practical to model such a complex mixture explicitly: The exact composition is often unknown, many of the components have insufficient data to allow the fitting of an EOS, and the computation time required for a 1000-component mixture would be prohibitive. Petroleum-derived fuels are complex mixtures, and at least for the short term, most biofuel feedstocks are blended with conventional petroleum fuels for retail sale to yield, for example, E85 (85 % ethanol/15 % gasoline) or B10 (10 % biodiesel/90 % petroleum-diesel).

A different approach is required for complex mixtures, and we use the concept of a surrogate mixture. The general principle is to use a mixture of a relatively small number of components (usually less than 20) to represent the behavior of the actual complex fuel. Edwards and Maurice [27] reviewed some of the surrogates available for aviation and rocket fuels and provided an overview of the general requirements and expectations of fuel surrogates. Active working groups are currently developing experimental data-

bases and surrogate models for the kinetics of jet, diesel, and gasoline fuels [28–30], and various groups have proposed and studied surrogate fuel mixtures for gasoline, diesel fuel, and aviation turbine fuel.

Surrogate fuel mixtures vary in complexity, and most are intended for specific purposes. Single-component surrogates (e.g., *isooctane* for gasoline) may be adequate for simple applications such as assessing combustion efficiency [31]. However, more complex multicomponent surrogate mixtures are necessary for applications that are dependent on fuel chemistry, such as soot formation, emissions, radiation loading, combustion staging, or applications involving lean premixed flames. Surrogate mixtures are also relevant to the study of physical properties. Specifically, the properties that describe fuel volatility (distillation properties, vapor pressures, etc.) are needed for the study of preferential vaporization phenomena and pool fire hazards. A surrogate mixture designed for one specific purpose may not be adequate for alternative tasks.

The procedure for developing the surrogate mixture can be summarized as follows. First, a chemical analysis is performed to identify the composition of the fuel sample. From this analysis, a list of candidate fluids is constructed, including compounds representative of the various chemical families (branched or linear paraffins, alkenes, aromatics, mono- or polycyclic paraffins, etc.) found in the sample. For each of these possible pure-fluid constituents, an EOS, a viscosity surface, and a thermal conductivity surface are developed. A mixture model is used that incorporates the pure-fluid equations for both thermodynamic and transport properties. The fluids in the surrogate mixture and their compositions are then chosen by determining the composition that minimizes the difference between the predicted and experimental data for the distillation curve, density, sound speed, viscosity, and thermal conductivity. The intent is to match the thermophysical properties of a fuel, but the concept of using species representative of what is actually present in the fuel is also applicable to selection of components for studies of soot formation [32], as well as extinction and autoignition [33].

Models developed at NIST to date have been for conventional fuels, but blends with biofuels will be modeled in the future. The surrogate approach requires an EOS for each component in the fluid suite, and the development of these equations will constitute a major effort for us in the coming years.

Experimental

Underpinning all of the modeling and database work are experimental fluid property data. The experimental effort at NIST is focused in two areas. The first is the measurement of reference data for pure compounds and well-characterized mixtures. The resulting data are used to develop the models used in REFPROP. Measurements of real fuels provide the data needed to develop surrogate blends and verify mixture models. A key measurement on real fuels is the distillation curve.

Reference Data for Pure Compounds and Mixtures

The development of accurate EOS requires a minimum set of accurate experimental data. The $(p$ - ρ - T) behavior of a fluid over a wide range of temperature, pressure, and density is the key data for the fitting of a thermodynamic EOS. Vapor pressures are the key data needed to define the saturation boundary of a pure fluid. Heat capacity and/or speed of sound data in the low-temperature liquid region are also vital. While, in principle, an EOS can be fitted to just $(p$ - ρ - T) data, the calculation of thermal properties such as enthalpy and entropy involves derivatives of the $(p$ - ρ - T) data so that any systematic errors in the $(p$ - ρ - T) data would be greatly amplified in such calculations. When high-accuracy $(p$ - ρ - T) data are available, only a few heat capacity or speed of sound data are required to give the EOS the proper behavior. While estimation methods and thermodynamic constraints can supplement data in fitting an EOS and allow the generation of an EOS even with very limited data, these ultimately require reference EOS for chemically similar compounds that are based on extensive data. Thus, a reliable EOS could be developed for *t*-butanol, for example, with limited data, but only if a reference EOS were available for another alcohol, such as ethanol.

The measurements made are dictated by the data required for EOS fitting. We have completed limited density and speed of sound measurements on five FAMES [19]. Forthcoming NIST Standard Reference Materials for fuel ethanol and biodiesel will include our recent measurements of density, speed of sound, and viscosity. Wide-ranging density $(p$ - ρ - T) measurements on the butanols and FAMES are in progress.

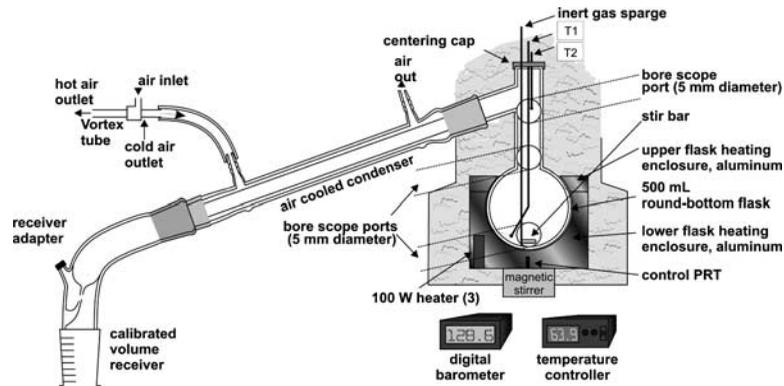


FIG. 5—Schematic diagram of the apparatus used for the measurement of distillation curves.

Measurements of the heat capacity of ethanol and 1-butanol are planned for late 2009. Future work will include mixtures of alcohols with hydrocarbons to provide data for the development of mixture models, for example, ethanol+*isooctane* as a surrogate for E85.

Advanced Distillation Curve

Critical among the properties required for the successful application of a new fuel are its volatility characteristics usually described by the distillation curve [34–36]. The distillation curve is a graph of boiling temperature plotted against volume fraction distilled, and it provides the only practical avenue to assess the vapor-liquid equilibrium (VLE) (volatility) of a complex mixture such as a fuel. This has become a standard method, as embodied in ASTM D86-09e1 [37]. It is possible to relate the distillation curve to operational parameters of complex liquid fuels. For a spark-ignition engine operating with gasoline as the fuel, these parameters include engine starting ability, vehicle drivability, fuel system icing and vapor lock, the fuel injection schedule, fuel autoignition, and others [38,39]. The low-temperature region of the distillation curve of gasoline (up to approximately 70°C) is used to assess and optimize the ease of starting and the potential for hot-weather vapor lock. The mid range of the gasoline curve (up to a temperature of approximately 100°C) is used to assess and optimize cold-weather performance, the operational readiness of a hot engine, and the acceleration behavior of a hot engine under load. The top range of the distillation curve is used to assess and optimize fuel economy in a hot engine.

We recently introduced an improved method for measuring distillation curves of complex fluids. The standard method, ASTM D86-09e1 [37], suffers from significant limitations. Our method, called the composition-explicit or advanced distillation curve (ADC) approach, is a significant improvement featuring (1) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis) [40,41], (2) temperature measurements that are well-defined thermodynamic state points that can be modeled with an EOS [40–44], (3) temperature, volume, and pressure measurements of low uncertainty suitable for EOS development [45,46], (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction [47], (6) trace chemical analysis of each distillate fraction [48], and (7) corrosivity assessment of each distillate fraction [49–52]. Related to a classical VLE phase diagram, the ADC provides the coexisting bubble-point temperature and the dew-point composition [53]. As an analytical strategy for complex fluids, the ADC presents the analyst with a sample that has been simplified on the basis of a physical property (VLE). One can often apply simpler analytical methods to fractions, avoiding complexities such as multiple chromatographic columns, backflushing, etc. We have applied the ADC to mixtures that include simple *n*-alkanes, gas turbine fuels, diesel and biodiesel fuels, gasolines, rocket propellants, and crude oils [48,54–67].

The ADC apparatus (shown schematically in Fig. 5) consists of a stirred boiling flask that is placed in an aluminum enclosure that is itself well insulated. Observation of the fluid inside the flask is done through small observation ports or a flexible bore scope, to optimize temperature uniformity. The fluid temperature is measured with thermocouples in two locations. One thermocouple monitors the temperature directly in the fluid (kettle); this temperature is called T_k . Another thermocouple is placed at the bottom of the take-off position in the distillation head; this temperature is called T_h . Electrical heating is applied to the enclosure (and ultimately to the kettle) with a model predictive controller [45]. This is a temperature controller that

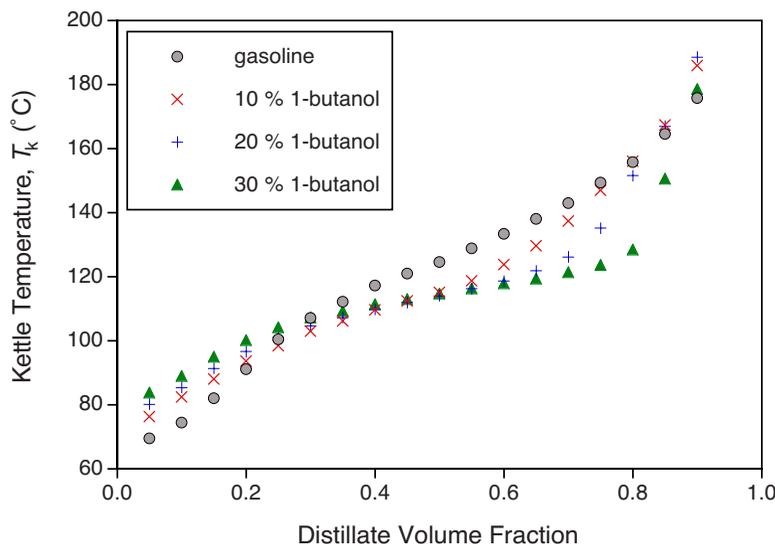


FIG. 6—The distillation curves of 91 AI Summer-quarter gasoline with mixtures of 1-butanol. Here we present T_k , the temperature measured directly in the boiling fluid. The data shown are the average of three or more distillation experiments.

mimics the shape of a distillation curve but leads the temperature of the fluid in the flask by approximately 20°C . This produces a constant heat flux and thus nearly constant mass flow rate of vapor through the distillation head. Following the distillation head, the vapor is condensed in a straight glass condenser chilled with air from a vortex tube [68]. An adapter that allows for instantaneous sampling of the distillate follows the condenser, after which the distillate drops into a level-stabilized receiver.

Our recent study of blends of gasoline with butanols [57] illustrates the insight that can be obtained with the ADC methodology. Butanol can be produced from biomass with the ABE fermentation, making use of the bacterium *Clostridium acetobutylicum*. Butanols can also be produced from algae and from a three-step thermal catalysis and reformulation process. Compared to ethanol, butanols have more carbon-hydrogen bonds and thus a higher energy content. The butanols are significantly less volatile than ethanol, and they appear to lower sulfur and nitrogen oxide emissions in mixtures when compared to gasoline [69]. Butanol blends do not have the serious phase-separation problems seen with ethanol, and they are also much more compatible with the materials found in typical engines. It is likely that distribution of butanol/gasoline mixtures can be done with the existing fuels infrastructure, including pipeline transport.

The gasoline used as the base fluid in this work was a 91 antiknock index (AI) summer-grade gasoline formulated with no oxygenate additive. It was blended with 1-butanol, 2-butanol, 2-methyl-2-propanol (*t*-butanol), and 2-methyl-1-propanol (isobutanol) to form blends with 10, 20, and 30 vol % butanol. The butanols were obtained from a commercial source and had purities of 99.5 mass % or higher, as verified by gas chromatography.

Three to six complete distillation curve measurements were made of the base gasoline and each of the gasoline/butanol blends. The initial boiling temperatures of the butanol blends were $2.1\text{--}9.6^{\circ}\text{C}$ higher compared to straight gasoline. The distillation curves for the gasoline/1-butanol blends are shown in Fig. 6. A gross examination of the distillation curves shows that the early behavior of the curves (for distillate volume fractions of up to 0.15) is consistent with the observed initial boiling points. The butanol mixtures start out less volatile than gasoline, and then a crossover point is observed, after which the mixtures are more volatile than gasoline. (The crossover points are different for each of the butanols, and these points correlate with the normal boiling temperature of each butanol, with the crossover being progressively later for higher boiling alcohols.) As the concentration of the butanol increases, the distillation curves show a pronounced flattening, approximating the behavior of a pure fluid. While this behavior is observed whenever a single component composes a large fraction of the mixture (as is the case with these mixtures), it is especially pronounced when azeotropic pairs are present. Indeed, 1-butanol is known to form azeotropes with cyclohexane, *n*-heptane, *n*-octane, and toluene, compounds typical of the hydrocarbons found in gasoline.

The composition channel of the ADC approach provides further understanding and information con-

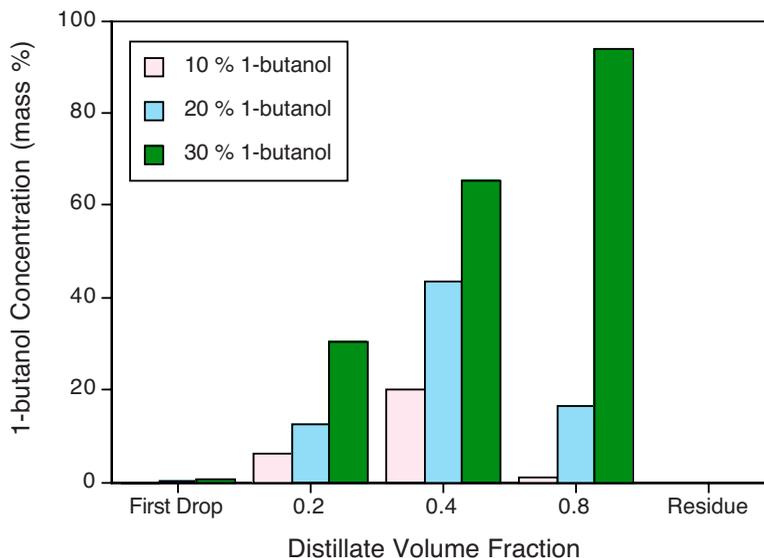


FIG. 7—Analysis for 1-butanol as a function of distillate volume fraction for the three starting mixtures (10 %, 20 %, and 30 % 1-butanol) in gasoline. There was no detectable 1-butanol in the residue left behind after the distillation.

tent. The individual fractions were sampled and analyzed as they emerged from the condenser. Chemical analyses of each fraction were done by gas chromatography with flame ionization detection and mass spectrometric identification. As an example of the quantitative analysis of a butanol and its relation to the distillation curve, Fig. 7 presents the results for the 1-butanol content at selected distillate cuts. At the first drop (representative of the 0.025 distillate fraction), we observed very little 1-butanol, and indeed for the 10 % starting mixture, it was barely detectable. The concentrations increased for the 0.2 and the 0.4 distillate fractions in the expected ratio corresponding to the starting mixture concentration. At the 0.8 distillate volume fraction, the 30 % mixture was nearly pure 1-butanol. The temperature at this point in the distillation is nearly equal to the normal boiling point of pure 1-butanol, as observed in the distillation curve. At a distillate fraction of 0.8, the departure from the neat gasoline is maximized for the 30 % mixture. In contrast, for the 20 % mixture the curve closely approached the gasoline curve, while for the 10 % mixture, the convergence was nearly complete as the 1-butanol distilled out of the mixture. In this way, the composition-explicit data channel can provide insight into the structure of distillation curves.

As another example of the ADC approach, we mention briefly our measurements on biodiesel fuel. In this area, we have measured neat biodiesel fuel produced from soy and olive oil (B100) and also mixtures of petroleum-derived diesel fuel with biodiesel. We note that the application of the classical ASTM D86-09e1 on B100 is not generally done because of the high temperatures required and the poor results obtained. Indeed, upon our initial application of the ADC on B100, our repeatability was of the order of 25 °C for replicate distillations. This is unacceptable for fuel specification purposes and completely useless for the modeling of thermophysical properties. We found that the difficulty was in the thermal and oxidative stability of the fluid during the measurement, and an inert gas (argon) sparge was added to the protocol. This change made an immediate and dramatic improvement, with successive curves becoming repeatable to within 0.3 °C.

Concluding Remarks

The engineer applying biofuels faces a considerable challenge in obtaining the needed property data. Data range from individual points measured at some temperature and pressure to extensive data sets covering wide ranges of temperature and pressure; models range from simple empirical correlations of single properties to comprehensive EOS models. These data and models are widely scattered through the literature. The design engineer is typically not a properties specialist but nevertheless is often forced to find, evaluate, and model the data needed for the task at hand.

In this paper, we have reviewed the biofuels program in the Thermophysical Properties Division of

NIST. We are expanding two of our standard reference databases to include biofuels and biofuel components. In support of the databases, we have initiated substantial efforts in modeling and experimental measurement. The NIST REFPROP database will provide comprehensive models for fluids and fluid mixtures; it provides critically evaluated data that can be used directly in process simulations, but it will always be limited in the number of fluids covered. TDE captures essentially all of the world's published data and provides the tools to retrieve and evaluate on demand these data and generate property correlations, including preliminary EOS. TDE is more of a research tool directed towards the property specialist or researcher investigating a novel fluid. The two databases are complementary and should prove very valuable in the development of biofuels.

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