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Fluid Properties at High Pressures and Temperatures:

Experimental and Modelling Challenges

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Abstract

Thermophysical properties impact many aspects of the chemical process industries. Here three example areas, primarily in the energy sector, are highlighted to provide context for the experimental and modelling challenges associated with obtaining fluid property data at high pressures and temperatures (HPHT). These three areas include the recovery of petroleum reserves in ultra-deep reservoirs, the use of lubricants to reduce frictional losses in the automotive industries, and the use of high-pressure, common rail diesel fuel delivery to reduce soot emissions for greener environments. The accurate knowledge of thermodynamic and transport properties in these three focused areas minimizes associated operating uncertainties and accelerates safe, reliable, and robust process and product development.

Keywords

High pressure, High temperature, Phase equilibria, Density, Viscosity, modeling

1. Introduction

Accurate thermophysical fluid properties are crucial for the efficient and reliable operation of chemical processes used to manufacture specialty chemicals, lubricant additives, crude oil, polymers, pharmaceuticals, and a variety of other chemically-based products [1, 2]. Typically, equilibrium properties, such as vapor-liquid equilibria, determine the feasibility of the process however, density and transport properties are needed for equipment selection, design, and sizing. Although it is relatively straightforward to measure fluid properties at ambient conditions, applied product development in many fields requires accurate property data at extreme temperatures and pressures. Here we highlight the need for fluid property data at extreme temperatures and pressures encountered in the search for and recovery of petroleum reserves in ultra-deep reservoirs, in the general area of reducing friction losses via lubricants in the automotive and allied industries, and in the quest for increased efficiency of diesel engine performance leading to reduced soot emissions. The measurement and prediction of the properties of the fluids in all three areas is further exacerbated by the use of multicomponent mixtures that contain tens to hundreds of components differing in molecular weight and structure. A more complete, high-pressure, high-temperature (HPHT) fluid property data base is needed with entries for pure components and mixtures so that contemporary equations of state and transport models can be tested, verified, and refined to accurately describe fluid properties under extreme operating conditions. The following sections of this paper present the authors' opinions on the need for experimental data and improved modeling approaches for thermophysical fluid properties at HPHT conditions. Where appropriate, the reader is referred to original references for more detailed insight on the theory and application of HPHT property measurement and modeling techniques.

1.1 Ultra-deep petroleum reservoirs

The global increase in oil demand coupled with the depletion of available reserves has spurred the exploration for new oil resources located in remote and harsh locations, such as the deep waters in the Gulf of Mexico, frigid regions in the arctic, and deep wells in desert environments [3, 4]. Process failures can occur when drilling in such hazardous locations, as exemplified by the five million barrel, accidental oil release in the Macondo oil well blowout at a mile deep in the Gulf of Mexico. Figure 1 shows that the increased depth of new oil and gas wells can result in bottom hole pressures and temperatures reaching HPHT values of 240 MPa (35,000 psi) and 533K (500°F). Fluid property data at these HPHT reservoir conditions are essential for accurately determining the amount of available recoverable oil, for modeling the flow of the oil within porous media and into and up the wellbore and pipelines, and for safely operating production equipment, such as blow-out preventers, risers, etc. Unfortunately, there currently is a meager database of accurate fluid properties at these extreme conditions. A further complication is the multicomponent nature of petroleum fluids that taxes the performance of available equations of state and contemporary transport models used to predict fluid properties.

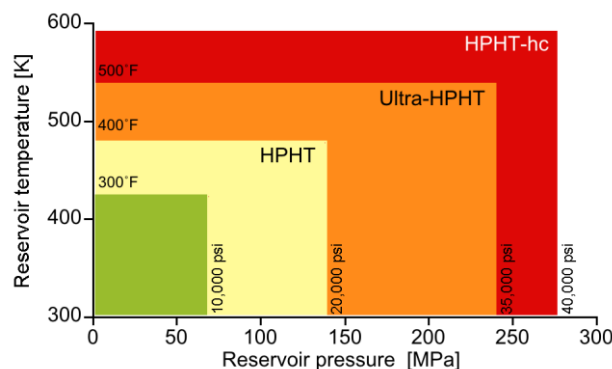


Figure 1. Reservoir classification based on bottom-hole pressure and temperature [5]. The authors use HPHT-hc to represent "beyond classification," which they say follows the practice used

1 by the Tour de France bicycle race to represent the steepest mountain-grade classification
2 (hc, hors categorie) [5].
3

4 1.2. Lubricant performance at HTHP conditions

5 Lubricant technology impacts automobile fuel economy, reduces friction losses, and
6 improves wear protection to name just a few areas. Improved vehicle fuel efficiency is a critical
7 focus and market driver for vehicle and engine manufacturers worldwide due to mandated
8 reductions in CO₂ emissions by the United States Environmental Protection Agency and other
9 worldwide government agencies. For example, at a 2016 Society of Automotive Engineering
10 (SAE) conference, a panel discussion consisting of key automotive, oil, and supplier industry
11 executives and top ranking federal and state regulators focused solely on the enormous task of
12 balancing mandated vehicle fuel economy improvements with consumer expectations of
13 performance and cost [6]. The majority of the SAE presentations at this meeting emphasized
14 enhanced mechanical and hardware design to meet performance targets. Yet, the missing
15 component of these presentations is the recognition that improved lubricant fluid properties can
16 result in as much as an 9% increase in overall efficiency. There is a 5% of efficiency losses result
17 from internal engine friction and 4% of the losses result from driveline friction [7]. Note that a 1%
18 improvement in fuel economy in the U.S. alone amounts to more than \$300 million/yr savings to
19 the automobile manufacturers in non-compliance penalties [8]. Left unsaid at this conference are
20 the vast research and development approaches by automobile additives companies to improve the
21 performance of lubricants operating at extreme pressures, especially found in gears [9].

22 Typical lubricant base oils are refinery blends of paraffinic, naphthenic, and aromatic
23 compounds. Base oils are augmented with polymer additives to impart specific lubrication
24 properties to the composite fluid mixture [10], such as improved bulk fluid viscosity over the entire

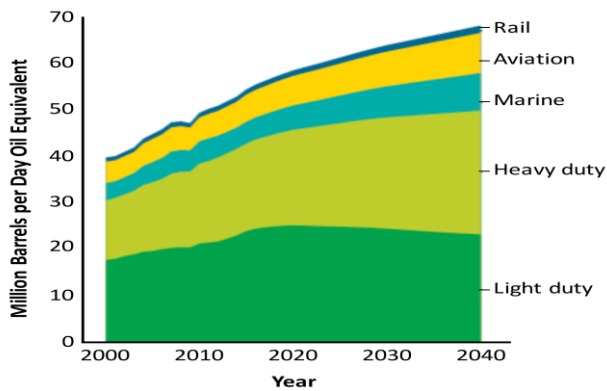
1 ambient to HPHT operating conditions encountered in normal automotive applications. Hence, the
2 need for fundamental fluid property data becomes more important as new types of polymers, such
3 as star polymers, are formulated into base oils for improved product performance. However, the
4 key to understanding and predicting the benefits of these polymers as versatile additives to increase
5 fuel efficiency, while simultaneously protecting mechanical hardware, requires a deep
6 understanding of how polymer architecture impacts solution viscosity over wide ranges of pressure
7 and temperature.

8 A substantial amount of physical property data already exist in the literature on the
9 performance characteristics of conventional, petroleum-derived base oils with and without
10 additives at atmospheric pressure and temperatures to 373K (212°F), although very little data exist
11 at HPHT conditions. Empirical performance data from simulated real world automotive-like
12 conditions suggest that polymer architecture can be tailored to provide superior and highly
13 beneficial properties. Further advances in lubrication technology is directly dependent on a more
14 thorough understanding of viscosity and density behavior at HPHT conditions.

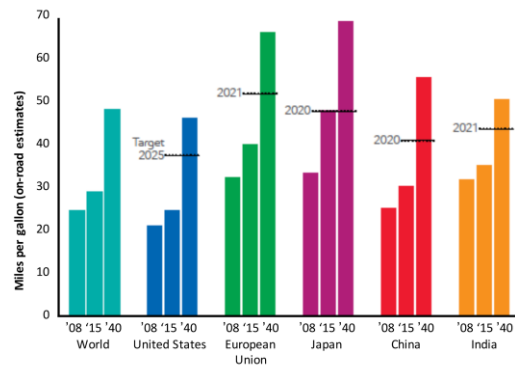
15 16 1.3 Advanced diesel engine performance at HPHT conditions

17 As living standards improve for billions of people across the globe, especially in
18 developing economies, more people will have access to cars with diesel engines. In addition a high
19 percentage of commercial transportation needs are currently met with diesel engines. Figure 2
20 shows the projected global transportation demand and the fuel economy goals for the year 2040
21 [11]. Coupled with the increased global transportation demand is an expected 75% increase in CO₂
22 and soot emissions (particulates) over the next two to three decades. Although particulate
23 formation processes are inherent to diffusion flames, the dominant mode of combustion in diesel

engines, the amount of particulates can be controlled by the quality of the spray and atomization of the diesel fuel [12]. Currently, Fuel Injection Equipment (FIE) manufacturers are developing high-pressure, common rail fuel injectors that operate at or above 450 MPa [13] to improve fuel spray quality and atomization. The efficient performance and control of FIE with ultra-fine tolerances is directly related to fuel density, viscosity, compressibility, and bulk modulus, all at HPHT conditions. Market deployment of high-pressure FIE is anticipated once these novel injectors are validated with a range of commercial diesel fuels whose composition depends on the global source. Given the meager HPHT fuel property data base that currently exists, prototype injector design and development programs have been burdened with costly, time-intensive, trial-and-error protocols. Understanding the effect of fuel composition on HPHT diesel fuel properties is key for optimizing the formulation of fuels and additives that maximize the advantages inherent with modern FIE, or stated differently, this is an instance of physical chemistry struggling to keep pace with advanced mechanics.



(a) Global transportation demand in million barrels per day oil equivalent.



(b) Projected fuel economy targets for light-duty cars

Figure 2. Outlook for global transportation demand and fuel economy goals of light-duty cars [11].

1
2 Interestingly, transcritical fuel injection is an alternative approach proposed to improve the
3 atomization of fuel, reduce spray inhomogeneity, and subsequently reduce particulate formation
4 [14]. In this approach, a subcritical fuel is injected into a supercritical gas in the combustion
5 chamber where the fuel is rapidly heated to supercritical temperatures. Transcritical fuel injection
6 leads to improved diffusive mixing and fuel-air mixture homogeneity, given that the hydrocarbon
7 fuel-air mixture now exhibits a single phase due to extremely low, or ideally, no interfacial tension.
8 In a controlled apparatus, Dahms et al. [15] observed the absence of fuel spray ligaments or
9 droplets when the fuel becomes supercritical. Further development and refinement of this novel
10 technology to improve combustion and emission performance requires a database of HPHT fuel
11 properties and a thorough understanding of effect of fuel composition on these properties.

12 2. Current Status

13 2.1. Phase equilibria

14 Phase equilibria data are crucial for the efficient design and optimization of a wide range
15 of high-pressure chemical and separation processes. The reader is directed to the excellent review
16 by Dohrn et al. [16] who describe experimental methods and techniques for the study of phase
17 equilibria at high pressures. For each method these authors examined the measurement principle,
18 application areas, advantages, disadvantages, and the common sources of errors that affect data
19 quality and the techniques to overcome these errors. Currently, many research laboratories use the
20 synthetic technique with a variable-volume, view cell to visually observe and map the pressure,
21 temperature, and composition of phase transitions. The versatility of the view cell apparatus is
22 exemplified by its use for a wide range of applications, including the determination of vapor-liquid
23 equilibria [17, 18], the solubility of a polymer in pure and multicomponent solvents [19], the

1 solubility of a solid in a supercritical fluid, the formation of gas hydrates, and the cloud point
2 behavior of ionic liquid-CO₂ systems.

3 4 2.2 Density and Viscosity

5 The HPHT operating conditions encountered in automotive applications [6, 8] and in ultra-
6 deep petroleum reservoirs [20] place a premium on accurate experimental fluid properties, such as
7 density and viscosity. Cibulka et al. reviewed and critically evaluated experimental density data
8 for pentane to hexadecane at pressures to 1000 MPa (145,000 psi) and temperatures to 610K
9 (635°F) [21]. However, there is still only a modest amount of density data for higher alkanes at
10 temperatures greater than 373K (212°F), likely due to the temperature sensitivity of the highly
11 accurate electronic techniques used for these measurements. Similarly, a modest amount of density
12 data exists for simple binary mixtures, such as hexane + propylene, toluene + propylene, and
13 toluene + ethylene [17, 18]. The techniques used to measure HPHT density are oftentimes coupled
14 with those used to measure viscosity, and these techniques are briefly mentioned in the next
15 section.

16 Likewise, a very meager HPHT data base exists for pure component and mixture
17 viscosities, an important transport properties. Consider for example the viscosity database
18 available for hexane, a very simple compound. Hexane viscosity studies are shown in Figure 3
19 originally published in the excellent, extensive and detailed review by Michailidou and coworkers
20 [22]. Note the lack of hexane viscosity data at pressures greater than 50 MPa (~7,000 psi) at
21 temperatures greater than ~373K (~200°F). Evidently the technical challenges from the
22 combination of high pressures with high temperatures limits many of the HPHT fluid property
23 studies to modest temperatures. The following section provides a very brief description of the

techniques reported in the literature for measuring HPHT viscosity, including the oscillating body, vibrating wire, falling body [23, 24], and rolling ball viscometers [25, 26]. Although not described here, it is worth mentioning that diamond-anvil viscometers are used for viscosity measurements to pressures of $\sim 1,200$ MPa ($\sim 175,000$ psi) but modest temperatures of less than 373K ($\sim 200^\circ\text{F}$).

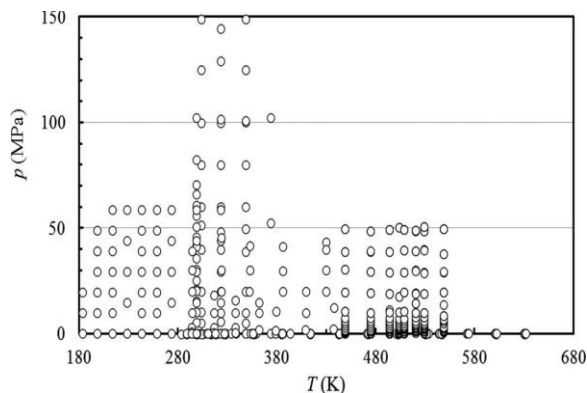


Figure 3. Pressure and temperature range of available viscosity data for *hexane* adapted from Michailidou et al. [22] Each circle represents experimental conditions where hexane viscosity can be found in the literature as of 2013.

Oscillating body viscometer

Torsional oscillating body or quartz-crystal viscometers have been extensively used to measure the viscosity of gases and liquids including aqueous solutions, organic liquids, and liquid metals. With these instruments, it is possible to simultaneously measure both density and viscosity at temperatures to 300°C , but typically at low pressures of 30 MPa ($\sim 4,500$ psi) [27, 28]. Although both density and viscosity can be measured to a typical uncertainty of 0.4 % with this type of apparatus, the working equations to convert experimental measurements to viscosity are complex and the pressure range is limited. Typical reported viscosity ranges from 0.01 mPa•s to ~ 10 mPa•s.

Vibrating wire viscometer

A vibrating-wire apparatus is capable of measuring both density and viscosity simultaneously at pressures to ~ 200 MPa ($\sim 30,000$ psi) and temperatures to ~ 473 K ($\sim 400^\circ\text{F}$) [29-31]. Typical expanded uncertainty of the data with this apparatus are 2% for viscosity and 0.2% for density at a 95% confidence level. Very accurate data, without the need for calibration, can be generated with this instrument, although its operation can be complex, there is the potential for mechanical failure at high temperatures, and data analysis is complex. These instruments are reported to measure viscosities in the range of 0.1 mPa $\cdot$ s to 500 mPa $\cdot$ s [32], depending on the selected vibrating-wire sensor for the viscometer.

Capillary viscometer

Among all the methods, capillary viscometers are well known and firmly established both in theory and in experimentation [33]. Interestingly, these viscometers have been adapted to operate at extremely high pressures. For example, lubricant viscosity data, up to viscosities of $112,000$ mPa $\cdot$ s, are reported to pressures of ~ 690 MPa ($\sim 100,000$ psi) and temperatures of ~ 423 K ($\sim 300^\circ\text{F}$) measured with a capillary viscometer [34]. The uncertainty of measured viscosity data is typically between 1% and 3%.

Falling body viscometer

This is one of the oldest types of apparatus used to measure HPHT viscosity. Some of the earliest reports with a falling-body viscometer date to 1926 with the work of Bridgman [35]. Density and viscosity data are reported for many fluids with this apparatus to very high pressures in excess of ~ 400 MPa ($\sim 60,000$ psi) but typically only to temperatures of ~ 373 K ($\sim 200^\circ\text{F}$) [36-

40]. Viscosity data obtained with the falling-body viscometer has a reported expanded uncertainty between 1% and 5%, which is higher than that observed with the oscillating wire and vibrating wire viscometers, although now the data extend over a much wider pressure range. These viscometers are successfully used to measure viscosities in the range of 0.1 mP•s to 5500 mP•s

Rolling ball viscometer

Rolling ball viscometers, a variant of the falling body viscometer, are widely used to measure both density and viscosity because of their ease of operation, straightforward correlation equations used to convert experimental measurements to viscosity, and the wide range of operating temperatures and pressures. Hubbard and Brown established the fundamental working equation for the rolling ball viscometer in 1943 [41], although the use of this type of apparatus dates to the early 1900s [42]. Data can be measured to very high pressures of 150,000 psi (1,000 MPa) and temperatures of ~533K or higher (~500°F) [43-45]. These viscometers are used to measure viscosity of gases [46] as well as highly viscous fluids with viscosity of 5,800 mP•s [20]. The typical expanded uncertainty in measured viscosity data is 1 to 4 % at a 95% confidence level.

2.3. Interfacial Tension and Thermal Conductivity

Accurately measuring surface and interfacial tension data (here the modifiers surface and interfacial are used interchangeably) for immiscible mixtures at elevated pressures and temperatures are critical for industrial and environmental applications such as CO₂ sequestration [47-50], enhanced oil recovery (EOR) [48, 49, 51-53], process development [54], and HPHT fuel injection [55]. A number of techniques are available to measure the interfacial tension of gas-liquid, vapor-liquid, and liquid-liquid systems at HPHT conditions. A few of these techniques,

used at ambient condition and adapted to high pressure operation, include the pendant drop [47-53, 56-61], capillary rise [54, 62, 63], capillary wave [55], and maximum bubble pressure [64-66] methods. The most commonly used HPHT interfacial tension technique is the pendant drop method due to ease of adaptability to high pressure operation and ease of operation to obtain reproducible data. The bulk of available interfacial tension data are for pure components at saturation conditions. See for example the study by Jasper [67] who compiled data for many different chemical families and the work of Mulero and Cachadiña [68] who developed a reference correlation for 37 different fluids. Several interfacial tension studies are reported for binary hydrocarbon mixtures in air at elevated temperatures and at ambient pressure that have led to the development and validation of a number of predictive models [69-71]. However, these models have yet to be verified for HPHT data. Another important concern when interpreting interfacial tension data is that the density for each phase is needed to accurately determine the interfacial tension. However, density data are often unavailable and, therefore, many studies resort to using pure component or calculated densities, which can affect the accuracy of the data.

Interfacial tension data for CO₂-water/brine [47, 48, 62] and CO₂-hydrocarbon systems [52, 58, 61, 62] have been measured and used to develop EOR and carbon sequestration processes. High pressure interfacial tension data for N₂-hydrocarbon systems [55-57, 63, 65, 66, 72, 73] have also been measured and used to develop applications in EOR and FIE for combustion engines. However, in both cases typically the hydrocarbons only include n-alkanes. Very few studies on the effect of pressure on interfacial tension have been reported for other hydrocarbon families such as cyclics, olefins, and aromatics, components that are all present in diesel and gasoline. Fuels vary in composition both geographically and batch to batch and can consist of up to 250 components

[74]. Hence, mixture data are needed to model and understand the behavior of industrially relevant systems such as crude oil, diesel, or gasoline.

In addition to phase behavior, density, viscosity, surface tension, there is an acute need for thermal conductivity, heat capacity, and thermal diffusivity data. In a series of papers Assael et al. critically assessed the available literature data and developed reference correlations for the thermal conductivity of normal alkanes [75], aromatics [76], and fluorinated compounds [77] covering wide ranges of temperature and pressure. Even though a significant body of thermal property data exists, there still remains gaps in the database. For example, Figure 5 shows the pressure-temperature conditions of thermal conductivity data for n-heptane, which highlights the lack of data at high pressures between 445 K and 545 K [75]. Transient Plane Source (TPS) and Transient Hot-Wire (THW) techniques are widely used methods to measure the thermal conductivity of liquids [78]. The challenge here is the accurate measurement of transient temperature changes, especially at high temperatures. Fine control of temperature fluctuations during an experiment is needed to ensure resolving transient temperature signals. In our opinion, the TPS technique is the preferred technique for HPHT measurements given the ease of operation of this technique relative to hot-wire methods.

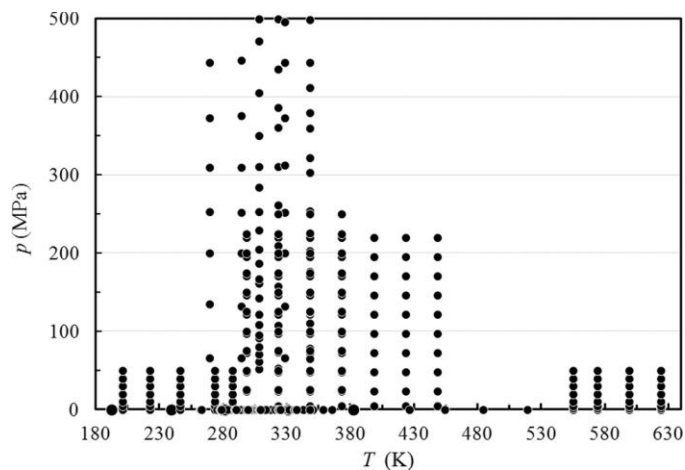


Figure 4. Pressure and temperature range of available thermal conductivity data for n-heptane adapted from Assael et al. [75]. Each circle represents conditions where heptane data can be found in the literature.

3. Challenges

3.1. Experimental Challenges

There are three routes to determining thermophysical property data: (1) retrieval from literature, (2) estimation from theory and models or correlation, and (3) experimental measurement. When developing a new process or designing a process improvement, the hope is literature data are available for the actual mixtures of interest at precisely the needed pressures and temperatures, or model calculations can provide highly accurate estimates of the needed data. The third alternative, experimental measurement, is time consuming and expensive. In addition, when dealing with HPHT conditions, the experimentalist must have more than just a conversant familiarity with high pressure techniques in addition to grounding in thermodynamic principles. Hence, simplicity in design should be the paramount objective.

Usually the first HPHT experimental challenge is to map phase transition boundaries in pressure-temperature-composition space so that reliable and coherent fluid property measurements can be obtained. These experiments are usually done with a mixture at a fixed composition, the so-called synthetic method. A windowed cell is the most straightforward apparatus to use to measure phase-transition, phase inversions (where phases flip positions due to changes in density, so-called barotropic phenomena), and solidification and melting phenomena. The reader is directed to the excellent text by Sherman and Stadtmuller [79] to ascertain the design criteria needed to build a robust and safe HPHT view cell. The high pressure view cell must be of sufficient thickness, which means heat transfer into and out of the cell will suffer a time lag with this

essentially adiabatic cell. Given that pressure can be changed quite rapidly by the displacement of an internal piston or bellows, the time to thermal equilibrium, within desired bounds, becomes the rate-determining factor to obtain data within a normal day of operation. For simultaneous high pressure and high temperature operation, it is necessary to remove any elastomeric o-rings used to seal windows. Likewise, metal bellows are typically used to adjust the cell internal pressure rather than a floating piston sealed with an o-ring. Metal-to-metal seals based on a cone-and-threaded principle are needed rather than sealing based on a lower-pressure, compression-fitting principle. Careful attention is also needed as to the choice of metal used for the body of the cell since certain metals, such as 316 stainless steel (SS), experience a reduction in ultimate tensile strength after cold working at elevated pressures and moderate temperatures, which means a single HPHT experiment with a 316 SS cell can permanently reduce the future safe operating range of the cell. Typically mixing the contents of a view cell is accomplished via a magnet coupling with an internal stir bar and external magnet, which means the cell body must also be nonmagnetic and the solution cannot be very viscous. Of course, attention should be paid to the resistance of the metal to chemical attack. The Inconel series of metals, specifically 625 and 718, offer many of the desired properties for a reliable HPHT cell.

3.2. Modeling Challenges

We offer a few observations on modeling fluid properties at HPHT conditions for the development of advanced fuel injection equipment and engine performance, since the challenges in these areas provide an overview of the challenges currently confronting process design engineers in many different industries. Diesel fuel properties are needed to model cavitation in the injector nozzle and the processes occurring in the combustion chamber including fuel atomization,

1 heating, vaporization, and combustion. Engineers are increasingly using Computational Fluid
2 Dynamics (CFD) tools to accelerate the development of improved injector designs and engine
3 combustion technologies. Despite the significant investments and advances realized in CFD codes,
4 surprisingly inaccurate fuel properties and poor EoS are often used in the CFD simulations. Lin et
5 al. [14] suggest that many, if not most, CFD codes used for modeling fuel injection and combustion
6 require inputs of the critical temperature, latent heat of vaporization, and liquid viscosities for n-
7 **hexadecane in the absence** of measured properties for diesel, a multicomponent mixture. Although
8 it would be advantageous to have a data base for the particular diesel fuel of interest, this is likely
9 unrealistic given the variation of fuel composition with diesel from different global sources.
10 Therefore, it is more logical to populate a HPHT fluid property data base with data on well-
11 characterized, diesel surrogate mixtures [21] with a limited number of components. The HPHT
12 surrogate mixture properties can be used to validate fluid property estimation techniques applied
13 to complex, multicomponent diesel fuel. Currently fluid properties are calculated with correlations
14 created from diesel property data bases, from surrogate hydrocarbon property databases calculated
15 with the NIST REFPROP program, from calculations with commercially available software, such
16 as ASPEN [21] or SUPERTRAPP, or from calculations using cubic or more contemporary
17 equations of state (EoS). Unfortunately, the best collection of diesel fuel properties [21] is limited
18 to pressures and temperatures far from supercritical or saturated vapor conditions and the
19 REFPROP data base is defined for hydrocarbons up to dodecane, which leaves out the C13 to C20
20 hydrocarbons found in diesel fuels [21]. Fluid property estimations obtained with a cubic EoS are
21 known to be inaccurate when calculated at HPHT conditions or when the molecular weight of the
22 component exceeds approximately ~ 170 g/mol [21]. A more accurate, molecular-based EoS is the
23 family of statistical associating fluid theory (SAFT) EoS, but the SAFT model is also less

frequently used directly in simulations given the mathematical complexity of the SAFT equation. In our research group the perturbed chain (PC)-SAFT EoS has been used to model the phase behavior for many classes of organic compounds including normal and branched alkanes, cycloalkanes, alkenes, gases, ethers, esters, benzene derivatives, halogenated hydrocarbons, polymers, and polymer-solvent mixtures [80, 81]. The challenge remains on how best to integrate the PC-SAFT EoS with the CFD simulation without creating extreme computation times.

While there is an appreciable amount of available HPHT density data, there is still a significant gap in the literature viscosity database that ultimately could be populated with model calculations. A wide selection of viscosity models are available that purport to describe the high-pressure viscosity of pure compounds, binary, and multicomponent mixtures. The Free Volume Theory (FVT) [82] and the Friction Theory (f-theory) [83, 84] models have shown potential for predicting viscosity data for hydrocarbons and their mixtures at both low pressures and HPHT conditions. An equation of state (EoS) model is needed for both viscosity models since the FVT model requires density as an input and f-theory requires values for the repulsive and attractive pressure. Burgess et al. [85] provide an excellent assessment of the modeling performance of these two viscosity models for pure hydrocarbons using four different EoS models. The authors found that characteristic pure component parameters for each viscosity model, obtained from fitting experimental viscosity data, vary significantly depending on which EoS model is used. Further, there is no apparent agreement among researchers for the choice of mixing rules needed for the FVT when calculating mixture viscosity data [86-92]. In addition, the applicability of these models for complex systems, such as polymer solutions at extreme operating conditions, remain uncertain [93].

When using an EoS for fluid property estimates it is necessary to have reliable estimates for the pure component parameters used with the EoS. Group contribution (GC) methods and generalized correlations are becoming more important for predicting the pure component parameters needed with an equation of state since sufficient physical property data for each pure component in a mixture may not be available to determine these parameters. Consider, for instance, the variety of GC methods used to predict the three pure component parameters used with the PC-SAFT equation of state. GC methods have been developed by Peng et al.[94], Vijende et al.[95], Huynh et al.[96], Tamouza et al.[97], just to name a few approaches, to predict PC-SAFT parameters. One limitation of these methods is that the GC parameters are typically adjusted to fit vapor pressure and liquid density data at relatively low pressures, which can lead to poor predictions at HPHT conditions. Burgess et al. [85] addressed this issue by determining GC parameters fit with HPHT data, although further studies are needed to improve and extend this method. Even GC methods become problematic when dealing with multicomponent, ill-defined mixtures. To remedy this situation, correlation schemes have been developed to predict parameters for ill-defined mixtures, such as diesel, knowing only molecular weight and a single mixture density at ambient pressures as described in [98]. More studies are needed to refine these promising correlation approaches.

4. Knowledge Gaps/Needs

As previously mentioned, the exploration and recovery of petroleum from ultra-deep formations is currently ongoing, engine manufactures are actively pursuing development of high-pressure, common rail diesel fuel deliver systems to reduce soot emissions, and chemical additives companies are investigating the use of polymers with novel backbone architectures to improve lubricant properties, reduce friction, and increase fuel efficiencies. These pursuits are progressing

1 even with major gaps in the HPHT data bases of fluid properties for pure components and
2 multicomponent mixtures. The pace of future advances in these areas can be accelerated with the
3 creation of an expanded HPHT data on density, viscosity, and heat capacity – to name perhaps the
4 three most important needed fluid properties. Density and viscosity data are available for many
5 normal alkanes up to ~C₂₄, but the data base for branched alkanes, cyclic hydrocarbons, aromatics,
6 alkylated saturated cyclic hydrocarbons, and alkylated aromatics is more sparse. To a first
7 approximation it is reasonable to fill in missing entries with calculated predictions using a reliable
8 equation of state, such as the PC-SAFT EoS. However, calculated fluid properties have their own
9 limitations. For example, Wu et al. [99] showed that the densities of cis-trans isomers of
10 dimethylcyclohexane vary as much as 4 to 6% at high pressures, yet calculated densities with the
11 PC-SAFT EoS virtually superpose.

12 In this article, we have highlighted a few technologies in need of both a reliable HPHT data
13 base and reliable calculation methods to fill the gaps in the data base. Modern computational
14 techniques are certainly advancing rapidly to the point where one might question the wisdom of
15 further HPHT studies, given the time, expense, and difficulty associated with HPHT experiments.
16 However, HPHT data are needed with well-characterized model mixtures to verify new EoS and
17 simulation approaches. Model mixtures should encompass a wide range of compounds to test the
18 ability of an EoS to not only capture the effect of polarizability, the dominant interaction with
19 saturated normal hydrocarbons, but also polar interactions exhibited by ketones and aromatics,
20 hydrogen bonding exhibited by alcohols and acids, etc. In addition, with the advent of new polymer
21 synthetic routines being developed, there are many opportunities to investigate the impact of
22 polymer backbone composition and, now, unique polymer architecture on fluid properties.

1 Systematic studies are needed to enhance the development of new model approaches to calculate
2 fluid properties for these unique polymer solutions.

3 It is fitting to conclude this opinion paper with the observation of Professor Wakeham, a
4 distinguished thermodynamics researcher, made at the end of his plenary lecture at the Forum 2000
5 Meeting [100]. Professor Wakeham argued that even if there were only 15 pure fluids in the world,
6 300,000 man-years would be needed to create a representative sample of properties of those fluids
7 and all of their mixtures. He concluded by saying "... argument about the debate between
8 simulation, theory, and experiment is a balance between them all. You can't do away with
9 experiment, but neither can you do all of the experiments. They will have to be balanced."

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