

EQUATION OF STATE MODEL DEVELOPMENT FOR EXTREME TEMPERATURES AND PRESSURES



NETL

NATIONAL ENERGY TECHNOLOGY LABORATORY

BACKGROUND

The density and viscosity of natural gas and crude oil at reservoir conditions are critical fundamental properties. Predicting these properties is required to accurately forecast the amount of recoverable petroleum within a reservoir, and to better understand the flow of these fluids within the porous subsurface material. These properties are also used to design appropriate drilling and production equipment, such as blow-out preventers and risers. A limited database currently exists for density and viscosity at extreme conditions associated with ultra-deep formations. Furthermore, currently available equations of state (EoS) models and transport models for viscosity are generally limited to less extreme conditions and do not predict accurately when extrapolated to extreme conditions. NETL diligently gathered data for crude oil density at extreme temperatures and pressures, then released the data to the public via the [EDX website](#). Such information is vital to estimate the domestic oil reserve hidden in ultradeep reservoirs beneath the sea floor where extreme temperature and pressure conditions prevail in the reservoirs.

Predictions of hydrocarbon fluid properties are essential to developing mitigation techniques for uncontrolled releases of oil/gas from a well, writing safety regulations, and designing surface and subsurface production equipment. EoS could be used to predict fundamental thermodynamics properties of multi-component hydrocarbon mixtures over a wide range of temperatures and pressures, extending from ambient conditions to the extreme conditions of very deep wells including pressures up to 40,000 psi (2,758 bars) and temperatures up to 260 °C. At present, oil companies use correlations based on lower temperature and pressure databases, but these correlations cannot be used to accurately predict fluid properties at extreme conditions due to their large margin of error (e.g., errors as great as ± 50 percent).

PRIMARY GOAL

The primary goal of this project was to develop and experimentally validate models for density and viscosity of crude oil and natural gas at high temperatures and high pressures (HTHP). The overarching objective was to develop thermodynamic EoS and transport property correlations for predicting the following properties/behaviors of systems composed of hydrocarbons, water, carbon dioxide, or mixtures of those constituents at HTHP conditions.

- physical properties: density and viscosity
- thermal properties: constant pressure, heat capacity, and thermal conductivity
- equilibrium phase behavior: number of phases and composition of phases at a specified temperature and pressure



NETL Phase and Composition Analysis Laboratory, Pittsburgh, PA.

OBJECTIVE

The overall objective of this work was to develop methodologies that provide crude oil thermodynamic and transport properties, including density and viscosity, and phase compositions at extreme temperatures and pressures to reduce uncertainties associated with deep drilling and to promote safe and secure processes for oil production.

PROJECT DESCRIPTION

The U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) combined pressure-volume-temperature (PVT) data and viscosity data from a comprehensive literature survey with PVT data and viscosity data from a focused experimental program to create a comprehensive database needed to develop new EoS and viscosity correlations. The EoS correlations have been used to determine the number of phases, composition of phases, phase densities, and phase boundaries (e.g., vapor pressure and dew points of pure components or mixtures) at extreme pressure and temperature conditions. NETL has also evaluate viscosity correlations for pure components and mixtures at the same conditions applicable to the vapor, liquid, or supercritical fluid phase. These correlations are designed to be accurate for the conditions associated with emerging technologies for deep aquifer sequestration and ultra-deep petroleum production.

BENEFITS

Rapid and systematic access to hydrocarbon fluid properties at ultra-deep reservoir conditions is a critical step to improving the understanding of crude oil behavior in an emergency situation, such as the 2010 Deepwater Horizon mishap (Macondo blowout) in the Gulf of Mexico. Accurate fluid properties are necessary for developing mitigation strategies and techniques. Reservoir in situ fluid properties are also needed for the development of effective safety regulations.

ACCOMPLISHMENTS

EXPERIMENTAL

NETL ENGINEERED DENSIMETER AND VISCOMETER FOR EXTREME CONDITIONS — The ability to accurately characterize the density and viscosity of hydrocarbons over an extremely wide range of temperatures and pressures, including conditions found in ultra-deep formations, will foster safer drilling and production operations and provide a means for obtaining more accurate predictions of the recoverable reserves and petroleum production rates from these critically important reservoirs.

For this purpose, NETL's research team designed, developed, and commissioned the specialized apparatus and methodologies needed to measure thermodynamic and transport properties, such as density and viscosity of hydrocarbons and their mixtures at the extreme temperatures and pressures (260 °C and 40,000 psi) representative of the conditions found in ultra-deep oil reservoirs. Using this unique equipment, hydrocarbon density and viscosity values were measured at extreme conditions for more than 19 pure component hydrocarbon fluids and three fluid binary mixtures. This research filled major gaps in datasets present in the literature.

These data, released in a number of peer-reviewed journals including *Fuel*, *The Journal of Chemical Thermodynamics*, and *Fluid Phase Equilibria*, are used to develop new EoS and modify contemporary EoS to improve the quality of the predictions of hydrocarbon properties at extreme operating conditions.

As part of this research, the team addressed an issue of great interest to the energy industry. An excellent Deepwater Viscosity Standard candidate fluid was identified—a thermally stable perfluoropolyether oil known as Krytox® GPL 102— that exhibits a viscosity of 20 cP at 260 °C and 35,000 psi. If accepted, Krytox® GPL 102 would enable researchers studying the viscosity of petroleum fluids found in ultra-deep formations to reliably calibrate and validate their equipment at the relevant conditions. The NETL results are being used for comparison with data obtained with different techniques by several internationally recognized rheology research laboratories: the University of Western Australia, University of New South Wales (Australia), University of Santiago de Compostela (Spain), Imperial College London (United Kingdom), Aristotle University of Thessaloniki (Greece), Université de Pau et des Pays de l'Adour (France), Universidad Nacional Autonoma (Mexico), Georgia Institute of Technology, and National Institute of Standards and Technology (NIST).

MODELING

NETL RESEARCHERS DEVELOPED PREDICTIVE MODELS FOR HTHP HYDROCARBON DENSITY — An NETL research team extended a group contribution method to calculate the perturbed-chain statistical associating fluid theory (PC-SAFT) parameter sets for polymers to accurately determine parameters for normal and branched alkanes, aromatics, and cycloalkanes at temperatures to 260 °C and pressures to 40,000 psi—conditions encountered in ultra-deep reservoirs. The researchers anticipate that this method can be further extended to predict PC-SAFT parameter sets for hydrocarbon mixtures, including crude oil. Density predictions of pure hydrocarbons using the new model agree with NIST's reference data within ± 1 percent throughout the HTHP range. Derivative properties—isothermal compressibility, isobaric heat capacity, and sound speed in hydrocarbons—are within 10 percent of NIST's reference values. These predictive models have been published in *Industrial & Engineering Chemistry Research* and are available via NETL's Energy Data eXchange (EDX) website.

NETL EOS MODELS CAPTURED ISOMERIC STRUCTURE ON DENSITY PREDICTIONS

NETL researchers and collaborators have extended their modeling studies to address whether the PC-SAFT EoS can accurately model the effect of isomer structure on density. The results from these studies represent the first step in ascertaining the fundamental information needed to predict other fluid properties at HTHP conditions, such as solution viscosity, which directly impacts the efficacy of operating ultra-deep petroleum reservoirs. The predictive approach used in this study elucidated the structural impact on these densities. Details of these findings were released in *The Journal of Physical Chemistry B*.

This project was also included as the finalist of the 2014 Institution of Chemical Engineers Global Awards, Core Chemical Engineering category.

REFERENCES

- Hseen Baled and Isaac Gamwo; Viscosity Models Based on the Free Volume and Entropy Scaling Theories for pure hydrocarbons over a wide range of temperatures and pressures, Thermophysical properties of complex fluids. Intechopen, **2019**. <https://www.intechopen.com/chapters/69006>
- Gamwo I. K.; Bamgbade B. A.; Burgess W. A. Experimental Investigation and Molecular-Based Modeling of Crude Oil Density at Pressures to 270 MPa and Temperatures to 524 K. **Chapter 6**, *Application of Thermo-fluid Processes in Energy Systems. Green Energy and Technology*. Springer, Singapore, 141-155, **2018**. <https://doi.org/10.1007/978-981-10-0697-5>
- Baled, H. O.; Gamwo, I. K.; Enick, R. M.; McHugh, M. A.; Viscosity Models for Pure Hydrocarbons at Extreme Conditions: A Review and Comparative Study. *Fuel*, **2018**, 89, 2018. <https://doi.org/10.1016/j.fuel.2018.01.002>
- Rowane, A. J.; Mallepally, R. R.; Bamgbade, B. A.; Newkirk, M. S.; Baled, H. O.; Burgess, W. A.; Gamwo, I. K.; Tapriyal, D.; Enick, R. M.; McHugh, M. A. High-Temperature, High-Pressure Viscosities and Densities of Toluene. *Journal of Chemical Thermodynamics*, **2017**, 115, 34.
- Baled, O. H.; Tapriyal, D.; Gamwo, I. K.; Bamgbade, A. B.; McHugh, M. A.; Enick, M. R. Viscosity Measurements of Two Potential Deepwater Viscosity Standard Reference Fluids at High Temperature and High Pressure. *Journal of Chemical & Engineering Data*, **2016**, 61, 2712.
- Baled, O. H.; Koronaios, P.; Xing, D.; Miles, R.; Tapriyal, D.; Gamwo, I. K.; Newkirk, M. S.; Mallepally, R. R.; McHugh, M. A.; Enick, R. High-temperature, High-pressure Viscosity of n-octane and isooctane. *Fuel*, **2016**, 164, 199.
- Baled, H. O.; Tapriyal, D.; Gamwo, I. K.; Bamgbade, A. B.; McHugh, M. A.; Enick, M. R. Viscosity Measurements of Two Potential Deepwater Viscosity Standard Reference Fluids at High Temperature and High Pressure. *Journal of Chemical & Engineering Data*, **2016**, 61, 2712.
- Baled, H. O.; Koronaios, P.; Xing, D.; Miles, R.; Tapriyal, D.; Gamwo, I. K.; Newkirk, M. S.; Mallepally, R. R.; McHugh, M. A.; Enick, M. R. High-temperature, High-pressure Viscosity of n-octane and isooctane. *Fuel*, **2016**, 164, 199-205.
- Bamgbade, A. B.; Wu, Y.; Burgess, A. W.; Tapriyal, D.; Gamwo, I. K.; Baled, O. H.; Enick, M. R.; McHugh, M. A. Measurements and Modeling of High-temperature, High-pressure Density for Binary Mixtures of Propane with n-decane and propane with n-eicosane. *Journal of Chemical Thermodynamics*, **2015**, 84, 108-117.
- Burgess, W. A.; Tapriyal, D.; Gamwo, I. K.; Wu, Y.; McHugh, M. A.; Enick, R. M. New Group-Contribution Parameters for the Calculation of PC-SAFT Parameters for Use at Pressures to 276mpa and Temperatures to 533k. *Industrial & Engineering Chemistry Research*, **2014**, 53, 2520-2528.
- Wu, Y.; Bamgbade, B. A., Burgess, W.A., Tapriyal, D., Baled, H.O., Enick, R.M., and McHugh, M. A. Effect of Isomeric Structures of Branched Cyclic Hydrocarbons on Densities and Equation of State Predictions at Elevated Temperatures and Pressures. *Journal of Physical Chemistry B*, **2013**, 117, 8821-8830.
- Baled, H. O.; Xing, D.; Katz, H.; Tapriyal, D.; Gamwo, I. K.; Soong, Y.; Bamgbade, B. A.; Wu, Y.; Liu, K.; McHugh, M. A.; Enick, R. M. Viscosity of n-hexadecane, n-octadecane and n-eicosane at Pressures up to 243 MPa and Temperatures up to 534 K. *Journal of Chemical Thermodynamics*, **2012**, 72, 108-116.

NETL is a U.S. Department of Energy national laboratory that drives innovation and delivers technological solutions for an environmentally sustainable and prosperous energy future. By leveraging its world-class talent and research facilities, NETL is ensuring affordable, abundant and reliable energy that drives a robust economy and national security, while developing technologies to manage carbon across the full life cycle, enabling environmental sustainability for all Americans.

Research Partners

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