EQUATION OF STATE MODEL DEVELOPMENT FOR EXTREME TEMPERATURES AND PRESSURES

NATIONAL ENERGY TECHNOLOGY LABORATORY

BACKGROUND

The density and viscosity of natural gas and crude oil at reservoir conditions are critical fundamental properties required to accurately assess the amount of recoverable petroleum within a reservoir, and to model the flow of these fluids within the porous media and wellbore. These properties are also used to design appropriate drilling and production equipment, such as blow-out preventers and risers. A limited database 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 lower conditions and do not predict accurately when extrapolated to extreme conditions.

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 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 is to develop and experimentally validate models for density and viscosity of crude oil and natural gas at high temperatures and high pressures (HTHP). The ultimate goal of this project is to develop thermodynamic EoS and transport property correlations for predicting the physical properties (e.g., density and viscosity), thermal properties (e.g., constant pressure heat capacity and thermal conductivity), and equilibrium phase behavior (e.g., number of phases and composition of phases at a specified temperature and pressure) of systems composed of hydrocarbons, water, carbon dioxide, or mixtures of those constituents at HTHP conditions.

OBJECTIVE

The overall objective of this work is to develop methodologies that will 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) is combining 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 new EoS correlations will be 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 will 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.

NETL Phase and Composition Analysis Laboratory, Pittsburgh, PA.

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 BP Deepwater Horizon oil spill (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 in the final list of the 2014 Institution of Chemical Engineers Global Awards, Core Chemical Engineering category.

To learn more about this research. NETL publications are available electronically:

https://netl.doe.gov/advsearch?tid=107

REFERENCES

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_6

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., 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.; Bangbade, 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.

Research Partners

Leidos Research Support Team (LRST) | University of Pittsburgh | Virginia Commonwealth University | The Pennsylvania State University

Contacts

Isaac K. Gamwo
Principal Investigator
Research Chemical Engineer
isaac.gamwo@netl.doe.gov

Dushyant Shekhawant
Supervisor, Reaction Engineering Team
Energy Conversion Engineering Directorate
dushyant.shekhawant@netl.doe.gov