the ENERGY lab

R&D FACTS

Deep Petroleum Resources

Equation of State Model Development for Extreme Temperatures and Pressures

Goal

The ultimate, long term, five year, goal of this project is to develop thermodynamic equations of state or transport property correlations for predicting the physical properties (e.g. density, ρ, and viscosity, μ), the thermal properties (e.g. constant pressure heat capacity, Cp, and thermal conductivity, k) and the equilibrium phase behavior (e.g. the number of phases and composition of phases at a specified T and P) for systems composed of hydrocarbons, water, carbon dioxide, or mixtures at high temperature and high pressure conditions.

The EOS models developed in this project will be based on new and existing physical property data, compiled in a comprehensive data-base. The data-base will include previously reported physical property measurements made on petroleum reservoir compounds, including gas, organic liquid, and aqueous phase components. These existing data will be augmented with new data generated through laboratory experiments designed to track PVTμ changes under extreme conditions—pressures up to 40,000 psi and temperatures up to 500 °F. Finally, EOS models and viscosity models will be developed and modified to best fit the high pressure-high temperature data.

Background

The density and viscosity of natural gas and crude oil at reservoir conditions are critical fundamental properties required for accurate assessment of the amount of recoverable petroleum within a reservoir and the modeling of the flow of these fluids within the porous media and in the wellbore. These properties are also used to design appropriate drilling and production equipment such as blow out preventers, risers, etc. At present, there is NO accurate database for these fluid properties at extreme conditions associated with ultra-deep formations. As we have begun to expand this experimental database, it has become apparent that neither are there equations of state for density nor transport models for viscosity to predict these fundamental properties of multi-component hydrocarbon mixtures over the wide range of temperature and pressure that extends from ambient conditions to the extreme conditions of very deep wells; pressures up to 40,000 psi and temperatures up to 500 °F. Presently, oil companies are using correlations based on lower temperature and pressure databases that exhibit a very unsatisfactory predictive capability at extreme conditions (e.g. errors as great as ± 50%).

In order to accurately assess the extent of these deep petroleum resources, which are a significant portion of this ultra-deepwater resource base, and predict the rate at which they can be recovered, it is necessary to understand and model the behavior of deep reservoir fluids and gases under extreme pressure and temperature conditions. A very useful tool for modeling the number, composition, and density of phases within

CONTACTS

George Guthrie
Focus Area Lead
Geological and Environmental Sciences
Office of Research and Development
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-6571
george.guthrie@netl.doe.gov

Kelly Rose
Technical Coordinator
National Energy Technology Laboratory
1450 Queen Ave SW
Albany, OR 97321
541-967-5883
kelly.rose@netl.doe.gov

Isaac K. Gamwo
Principal Investigator
Earth and Mineral Science Division
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-6537
isaac.gamwo@netl.doe.gov

PARTNERS

NETL Office of Research and Development (including DOE, URS, University of Pittsburgh, and Virginia Commonwealth University).

a petroleum reservoir at a specified temperature and pressure is an equation of state (EOS). There is no single equation of state that can be used to describe and predict the properties of all substances under all conditions; it is therefore necessary to develop EOS models that describe the behavior of specific substances under a given range of pressure and temperature conditions. In this work we ultimately hope to model the mixtures of brine and petroleum that occur within the pores of ultra-deep formation, however our initial models will consider only the petroleum-rich phases (not the brine).

An extensive database of literature density and viscosity of hydrocarbons was compiled; new experimental data were obtained especially at extreme temperature and pressure conditions (i.e. up to 500°F and 40,000 psi) representative of ultra-deep formations, and new correlations for the density and viscosity of individual hydrocarbon compounds or multiple-component mixtures. The research team, composed of the National Energy Technology Laboratory, the University of Pittsburgh and Virginia Commonwealth University, proposes utilizing a systematic experimental and modeling approach in an effort to develop a pressure-specific volume-temperature-viscosity P-V-T-μ database, density (1/specific volume) models and viscosity models for hydrocarbons and hydrocarbon mixtures (the current work), water-hydrocarbon systems, and carbon dioxide-water mixtures at P-T conditions consistent with those for the exploration and characterization of ultradeep reservoirs at extreme operating depths.

Accomplishments

1) Thermodynamic and Transport Property Database Development

- Detailed and thorough reviews of the literature density and viscosity data were done to develop a comprehensive P-V-T-μ database. Selected components of interest include propane, pentane, n-octane, n-decane, n-hexadecane, n-octadecane, n-eicosane, 2,2,4 trimethyl pentane, methyl cyclohexane, ethylcyclohexane and toluene at pressures and temperatures ranging from 2,000 to 35,000 psi and 40 to 500 °F, respectively.

- We have begun the measurement of hydrocarbon density values at extreme conditions to fill in the large gaps in density data. Our group has provided experimental density data for selected hydrocarbons, ranging at temperatures to 500 °F (260 °C) and pressures to 40,000 psi. Various linear alkanes, branched alkanes, cyclic compounds and aromatics were selected.

- Based on the proven capabilities and elegant design of the windowed densimeter, we have designed and constructed a windowed rolling ball viscometer that is rated to 500 °F and 40000 psi. This is the first windowed rolling ball viscometer built for measuring the viscosity of hydrocarbons or hydrocarbon mixtures at extreme conditions up to 500 °F and 40,000 psi. This viscometer has been calibrated with n-decane using various size balls in order for it to be used for other hydrocarbons exhibiting a wide range of viscosity values.

2) EOS Model Assessment & Development

- NETL has developed the most accurate "cubic" equations of state for predicting the density of selected hydrocarbons at extreme conditions. These cubic equations of state include a high temperature high pressure (HTHP) volume-translated Peng-Robinson equation of state, and a HTHP volume-translated Soave-Redlich-Kwong equation of state; and they provide density values within 1-2% of experimental values over the 70 – 500 °F and 1000 – 40,000 psi range. Because cubic equations of state are provided as an option in virtually every reservoir simulator, our new cubic formulations allow users to quickly incorporate these results into powerful reservoir simulation tools.

- NETL has developed the most accurate "SAFT-based" equations of state for predicting the density of these hydrocarbon at extreme conditions. SAFT models are complex three-parameter models, but they provide a more accurate description of the molecule and its interactions with other molecules than the cubic equations of state. New Hybrid PC-SAFT parameters were developed that can predict the density with ± 1% at HTHP conditions.

- We have determined that when the PC-SAFT density model is used in conjunction with the free volume theory viscosity model, the resultant PC-SAFT-FVT model consistently gives the lowest mean absolute percent deviations (MAPDs) of ±3% from reference values for the compounds examined in this work. Notably, it can be employed to successfully predict viscosities for normal and branched alkanes, aromatics, and cycloalkanes.

3) Deepwater Viscosity Standard: 20cP at 500 °F and 35,000 psi

- We are the first research group to successfully suggest a fluid that can satisfy the requirements of a desired "Deepwater Viscosity Standard" and to experimentally verify that it exhibits the desired viscosity at extreme conditions. We have determined, using both the rolling ball viscometer and the NETL HTHP Couette viscometer that the perfluorpolyether oils known as DuPont Krytox 101 and 102 are excellent candidates. Krytox 101 has a viscosity of ~16 cP at 500 °F and 35,000 psi, while Krytox 102 (a higher molecular weight version of the same polymer) has a viscosity of ~26 cP; both are sufficiently close to 20 cP that either could be chosen as the Deep-water Viscosity Standard. We worked with scientists at NIST and Georgia Tech to suggest this chemical to serve as the standard, and our team at NETL, the University of Pittsburgh and Virginia Tech was the first to provide viscosity data for these Krytox oils at extreme conditions. We have already presented these results to the rheology community.

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