the ENERGY lab

R&D FACTS

Deep Petroleum Resources

Equation of State (EOS) Model Development for Extreme Temperatures and Pressures

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, as well as 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, no accurate database exists for these fluid properties at extreme conditions associated with ultra-deep formations. Expanding this experimental database revealed that equations of state (EOS) did not exist for density or transport models for viscosity. EOS could be used to predict 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, including pressures up to 40,000 psi and temperatures up to 500 °F. Presently, oil companies use correlations based on lower temperature and pressure databases that exhibit unsatisfactory predictive capability at extreme conditions (e.g., errors as great as ± 50%).

Predictions of hydrocarbon fluid properties are essential to develop mitigation techniques for uncontrolled releases of oil/gas from a well, for safety regulations, developments, and design of surface and subsurface production equipment.

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, long term goal of this project is to develop thermodynamic equations of state (EOS) 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 temperature (T) and pressure (P)) for systems composed of hydrocarbons, water, carbon dioxide, or mixtures of those constituents at high- temperature and high-pressure conditions.

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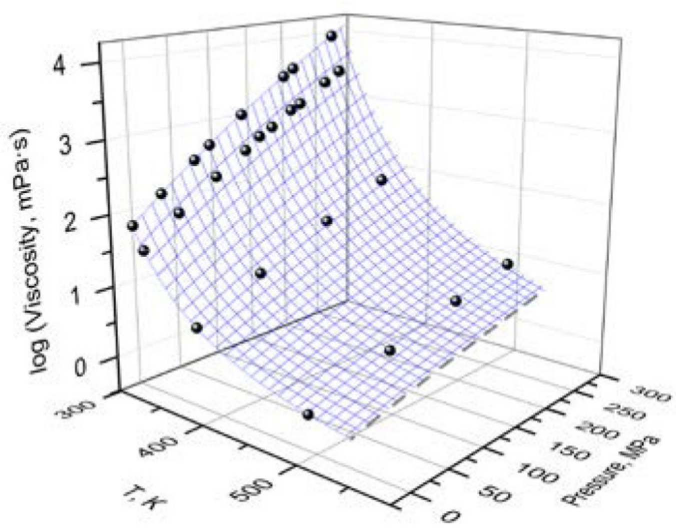

Surface Fitting of the Di-Ethyl Hexyl Phthalate (DEHP)viscosity data.

Objectives

The overall objective of this work is to develop methodologies to provide crude oil thermodynamic properties (including density and viscosity) and phase compositions at extreme temperature, pressure to reduce, uncertainties associated with deep drilling and to promote safe and secure processes for oil production.

Project Description

The National Energy Technology Laboratory (NETL) is combining pressure-volume-temperature (PVT) data and viscosity data (μ) from a comprehensive literature survey with PVT and μ data obtained from a focused experimental program to create the comprehensive database needed to develop new equation of state correlations. The new EOS correlations will be used to determine the number of phases, composition of phases, phase densities, phase boundaries (e.g., vapor pressure of pure components, dew points of mixtures) for pure components or mixtures at extreme pressure and temperature conditions. NETL will also evaluate viscosity correlations (μ) for pure components and mixtures at the same conditions that, like an equation of state, are applicable to the vapor, liquid, or supercritical fluid phase. These correlations will be designed to be accurate for the conditions associated with emerging deep aquifer sequestration and ultra-deep gas production technologies.

Benefits

Rapid and systematic access to hydrocarbon fluid properties at ultra-deep reservoir conditions is a critical step to improve the understanding of crude oil behavior in an emergency situation such as in the 2010 Deepwater Horizon Oil Spill. Accurate fluid properties are necessary to develop mitigation strategies and techniques. Reservoir in-situ fluid properties are also needed for the development of effective safety regulations.

Expanded view of the windowed variable-volume rolling-ball viscometer.

Accomplishments

NETL researchers have been successful in various aspects of this project, including:

1) Thermodynamic and Transport Property Database Development

An NETL team is the First to Report Cyclic Hydrocarbon Solidification Data.

The formation of solid deposits in crude oil can clog processing lines during production, potentially leading to severe equipment damage. Therefore, it is important to determine the liquid-solid transition data. This is a major issue experienced during the oil recovery process for high-temperature, high-pressure ultra-deep petroleum reservoirs such as those typically encountered beneath the deep waters of the Gulf of Mexico (GOM). Yet, no high-pressure solidification data exists for saturated cyclic hydrocarbons. The NETL research team has recently addressed the gap in available aromatic and cyclic hydrocarbon solidification data by measuring solid-liquid transition data for several branched cycloalkanes and three isomeric xylenes. A visualization technique coupled with a high-pressure, variable-volume view cell was used for these solidification measurements at pressures to 300 MPa and over a wide range of temperatures starting at 293K. These findings were released in the journal *Fuel*, volume **111**, pages 75-80 (2013).

2) Equation of State (EOS) Model Assessment and Development

NETL Extended Viscosity Models for Hydrocarbons to High-Temperature and High-Pressure Conditions.

NETL, in collaboration with research partners, extensively evaluated various combinations of equation of state-viscosity models for hydrocarbon components at high-temperature and high-pressure conditions. These conditions are encountered in ultra-deep porous sandstone or carbonate layers that retain crude oil or natural gas. Two viscosity theories, the frictional theory viscosity model and the free volume theory viscosity model, show great promise for predicting pure components or mixtures. However, none of these viscosity models could be extended to accurately predict viscosity of hydrocarbons at high-pressure and high-temperature conditions. In fact, the frictional theory model under-predicts viscosity by as much as 20% at pressures near 276 MPa. Therefore, the perturbed-chain statistical associating fluid theory (PC-SAFT) model was used to calculate the fluid density, which is an input into the improved Frictional Theory (FT) viscosity model referred to as PC-SAFT-FT. This model predicts viscosity values within ± 2% of the reference value for normal alkanes at pressures up to 276 MPa. These newly developed models have been released in the *Industrial & Engineering Chemistry Research*, Volume **51**, 16721, 2012.

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

An NETL Research Group is the First to Identify Krytox 102 as a Viable Fluid for Deep Water Viscosity Standard (DVS).

An NETL research group is the first to successfully suggest and experimentally verify a fluid that exhibits the requirements of a desired "Deepwater Viscosity Standard (DVS)." Using both the rolling ball viscometer and the NETL HTHP Couette viscometer, determined that the perfluorpolyether oil known as DuPont Krytox 102 is a good candidate. Krytox 102 has a viscosity of ~26 cP at 500 °F and 35,000 psi. This viscosity is sufficiently close to 20 cP and has been suggested, in collaboration with the National Institute of Standards and Technology (NIST), as the Deep-water Viscosity Standard. If accepted, this fluid will allow industry and researchers to calibrate high-pressure viscometers and rheometers prior to studying oils at extreme conditions. Results have been presented to the rheology community.

NETL Filled Density Data Gap for a Reference Fluid

Di-Ethyl Hexyl Phthalate (DEHP) has been suggested as a reference fluid for viscosity measurements in the high-temperature, high-pressure regions consistent with ultra-deep reservoir conditions. DEHP is preferred over the current fluid reference, Di-Iso Decyl Phthalate (DIDP), since DEHP is commercially available in high purity while DIDP is only available as a mixture of phthalates esters of the isomers of isodecyl alcohols.

An exhaustive literature review revealed a lack of density data in the open literature for DEHP at both high-temperature and high-pressure conditions. NETL filled this literature gap by reporting high-temperature, high-pressure DEHP density data in the August 2013 issue of the *Journal of Chemical Thermodynamics*, **63**, 102-107, 2013.

Compositional Density Cell (NETL-PGH).

Chandler HTHP Couette VIscometer (NETL-MGN).