Fuel 137 (2014) 393–404

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Hydrogen solubility in heavy oil systems: Experiments and modeling

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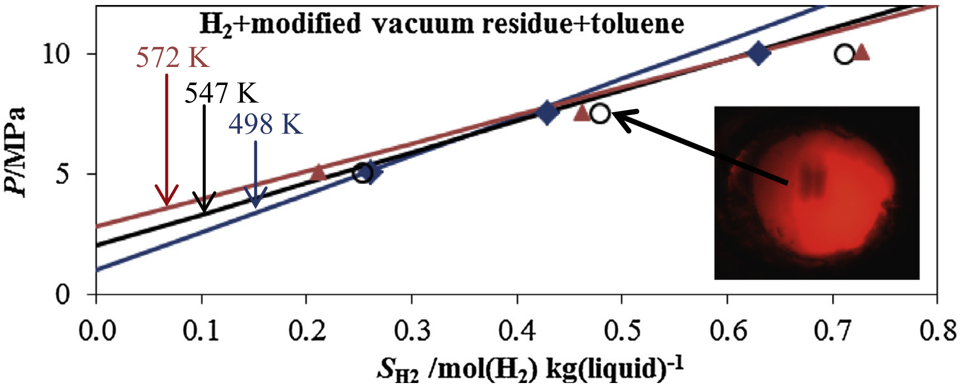
HIGHLIGHTS

- Hydrogen solubility was measured in heavy oil systems at high temperature and pressure.
- Measurements were performed with a continuous flow apparatus with visual method.
- Hydrogen solubility in heavy oil systems was predicted with four models.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 May 2014
Received in revised form 30 July 2014
Accepted 5 August 2014
Available online 19 August 2014

Keywords:
Hydrogen solubility
Heavy oil
Experiments
Modeling
PC-SAFT

ABSTRACT

Hydrogen solubility measurements in heavy oils are required in order to develop accurate process models. Nevertheless, these solubility measurements are challenging at elevated temperatures and pressures and the amount of data points is scarce in the literature. This paper presents measured hydrogen solubilities in heavy oil systems at a temperature range from 498 to 598 K and a pressure range from 2 to 11 MPa. The experiments were conducted with a continuous flow apparatus. One of the well-characterized heavy oil systems was a hydrocracked vacuum gas oil and the second system consisted of a modified vacuum residue from Urals crude and toluene. The modified vacuum residue and toluene mixtures were prepared gravimetrically (mass fractions of vacuum residue: 0.25, 0.34 and 0.50). The experiments demonstrated that increasing the partial pressure of hydrogen and temperature increased the hydrogen solubility. Another finding was that the amount of toluene in the system had great impact to the hydrogen solubility. Four modeling approaches were compared based on their predictions on the hydrogen solubility in heavy oil systems measured in this work and four heavy oils found from the literature. The chosen models were PC-SAFT, Peng–Robinson, a simple correlation based on the corresponding theory and a method based on the Scatchard–Hildebrand theory. PC-SAFT with applied a heavy oil characterization method and the correlation based on the corresponding theory were found to predict the hydrogen solubility equally well and accurately. The benefit of using PC-SAFT instead of the simple correlation is that with PC-SAFT, phase behavior of multicomponent systems can be predicted and other properties, such as densities, can be obtained simultaneously. Peng–Robinson with a single carbon number characterization method overestimated the hydrogen solubility in the studied heavy oils and the method based on the Scatchard–Hildebrand theory could model the hydrogen solubility well after parameter regression.

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http://dx.doi.org/10.1016/j.fuel.2014.08.015
0016-2361/

Nomenclature

A	parameter in the generalized distribution model
AAD	average absolute deviation
B	parameter in the generalized distribution model
EoS	equation of state
F	flow rate ($cm^3\ min^{-1}$)
k	binary interaction parameter in the PC-SAFT equation of state
l	property: density ($g\ cm^{-3}$) or pressure (MPa)
m	number of segments in PC-SAFT equation of state
M	molar mass ($g\ mol^{-1}$)
N	number of measured data points
P	pressure (MPa)
PS	pseudocomponent
RAD	relative average deviation
SCN	single carbon number
S_{H2}	hydrogen solubility ($mol(H_2)\ kg(liquid)^{-1}$)
T	temperature (K)
u	uncertainty
V_m	molar volume of ideal gas ($22\ 414\ cm^3\ mol^{-1}$)
w	mass fraction
wt%	mass percent

Greek letters

ε/κ	segment energy parameter (K) in PC-SAFT equation of state
ρ	density ($g\ cm^{-3}$)
σ	segment diameter (Å) in PC-SAFT equation of state

Subscripts

0	parameter in the generalized distribution model
2-P	two-phase region
A	aromatic fraction
b	boiling point
C	cumulative
calc	calculated value
H_2	hydrogen
i	component i
j	component j
L	liquid sample
Li	liquid phase region
P	polyaromatic fraction
S	saturate fraction

Superscripts

*	equilibrium point

1. Introduction

Energy consumption is increasing worldwide all the time. One third of the consumed energy is produced from petroleum, and the most of the liquid fuels are refined from oil. Meanwhile, light crude oil wells are being exhausted and the utilization of heavy and extra-heavy oils is increasing. Simultaneously, refineries are maximizing their capacity and the heaviest fractions are processed into an even more valuable form [1].

Heavy crude oil is dense and viscous and usually has a high content of asphaltenes. In addition, heavy oil contains usually a high amount of heteroatoms, such as sulfur and nitrogen, and metals, mostly nickel and vanadium. Vacuum residue has similar properties in comparison to heavy crude oil and it is normally classified as heavy oil. In addition, heavy crude oil and vacuum residue is refined in similar process units [1].

Refining of heavy oils is challenging due to their complex nature. However, processing increases the value of the product substantially. Refining is usually conducted in hydroprocesses, where heavy hydrocarbons are hydrocracked to the more valuable light components. In addition, most of the heteroatoms and metals have to be removed from the system due to the environmental legislation and the subsequent refining processes [1].

Knowledge of hydrogen solubility in heavy oil is required for designing and operating hydroprocesses and it has a major role in process models [2–4]. Hydrogen solubility data is also needed in kinetic models of hydrocracking and hydrotreating reactions [4,5]. Unfortunately, the hydrogen solubility measurements are challenging due to the thermal instability of heavy oils at elevated temperatures and pressures. Further challenges are the complex phase behavior of heavy oils and the low hydrogen solubility in such systems [2]. Only three data sets for hydrogen solubility in heavy oils and heavy oil cuts were found in the literature [2,5,6]. In addition, there are a few measurements of hydrogen solubility in coal liquids [7–14]. Hydrogen solubility in hydrocarbons and oils are reviewed in details in the paper by Chávez et al. [4]. As to conclude, there is still a need for hydrogen solubility data in well-characterized heavy oil systems.

Accurate hydrogen solubility predictions are an essential part in hydroprocess models as discussed above. Challenge to the modeling work is caused by the complexity of heavy oils – a huge number of components of which a large fraction is unidentified [15] – hence oil characterization must be conducted carefully. In the previous studies, hydrogen solubility in heavy oils is predicted with several models. At early stages, correlations for predicting hydrogen solubility in hydrocarbons and hydrocarbon mixtures have been suggested by Chao and Seader [16], Grayson and Streed [17] and Sebastian et al. [18]. Shaw [19] has proposed a correlation for predicting hydrogen solubility in alicyclic and aromatic solvents based on the corresponding theory. The correlation has predictive nature. It requires mean boiling point and density of the solvent and estimation of density difference between the lightest and the heaviest component of oil sample. Lal et al. [5] has predicted the hydrogen solubility in Athabasca bitumen with the Peng–Robinson with a modified repulsive term. One challenge of applying the cubic equations of state is defining critical properties for heavy oil or alternatively for pseudocomponents. In addition, binary interaction parameters may easily be unreasonable with the cubic equations of state [5]. Riazi and Vera [20] and Riazi and Roomi [3] has developed a method for modeling H_2 + hydrocarbons and H_2 + heavy oil systems based on the Scatchard–Hildebrand theory. The method requires mean boiling point and density of solvent but not require the critical parameters or binary interaction parameters. In addition, user might have to estimate one solvent depended parameter if the solvent is highly aromatic. Luo et al. [21] are proposed a model, which combines the Pierotti method together with the Henry's law. In practice, four oil specific parameters are regressed against measured data of H_2 + oil system. Thus, the model cannot be applied for modeling hydrogen solubility without experimental data. Torres et al. [22] modeled hydrogen