Hydrogen solubility of shale oil containing polar phenolic compounds

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Abstract

Many refineries use hydrogen to upgrade heavy fuel feedstocks, and therefore, hydrogen solubility is an important parameter. Shale oil is a fuel for which hydrotreatment is of interest, but no data about its hydrogen solubility can be found in the literature. This article presents experimental data for the hydrogen solubility of two shale oil samples measured at high temperatures and pressures (423 to 527 K and 40 to 140 bar). Experiments were performed using a continuous flow apparatus. Results show that the shale oil had a lower hydrogen solubility than most other fuels, probably due to the high content of polar phenolic compounds in the oil. Removing about 80% of the phenolic compounds increased the hydrogen solubility by approximately 0.1 mol H₂/kg oil (which is about 15 to 45%, depending on the solubility). Analysis also showed that current prediction methods used for petroleum and coal liquids cannot reliably be used for predicting the hydrogen solubility of this shale oil and other similar fuels.

Keywords: hydrogen solubility, shale oil, hydroxyl group, unconventional fuel, phenolic, phase equilibria

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1. Introduction

Hydrotreatment processes are commonly used to upgrade fuels, especially heavy fuels and fuels containing unwanted heteroatoms. The hydrogen solubility is needed for designing and operating these processes because the concentration of hydrogen in the liquid phase is important for reaction kinetics¹ and for accurately determining the material balance for hydrogen across a chemical plant². Experimental data for hydrogen solubility exists for a number of pure compounds³, including polar oxygenated compounds such as phenols^{4,5}, alcohols^{4,6–26}, ketones^{7,27–29}, esters^{30,31} and organic acids^{7,11,31}. Data also exists for many different fuels, including heavy oil samples^{32–35}, straight run gasoil³⁶, naphtha reformat³⁷, light naphtha³⁸, coal liquids^{39–45}, creosote oil⁴⁶ and bio oils^{47–50}. Data was also found for white oils^{51,52}. We compiled the literature data on fuels from most of these sources into a single spreadsheet that can be found on the Open Science Framework page for this research project (<https://osf.io/dhkew/>). However, no information could be found about the solubility of hydrogen in shale oils, even though shale oil is a fuel for which hydrotreatment would be of interest due to its high content of heteroatoms and aromatic compounds.

Shale oil is an unconventional liquid fuel produced from solid oil shale via pyrolysis^{53,54} (not to be confused with tight oil⁵⁵, which is conventional oil trapped inside a shale or sandstone formation). Shale oil has received attention due to the large quantities of oil shale present in deposits around the world⁵⁶. It has been estimated that 4.7·10¹² barrels of oil could be produced from these resources⁵⁷, but

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economic and environmental challenges have limited its production. And yet, shale oil industries exist in several countries, including Brazil, China and Estonia. Hydrotreating processes could help solve some of the challenges with shale oil by removing pollutants like sulfur and nitrogen and by increasing the economic value of the fuel. Indeed, a fair amount of research has been done on hydrotreating shale oil⁵⁸⁻⁶⁶, and Eesti Energia, a company which produces shale oil, has done preliminary investigations with the goal of incorporating a hydrotreating unit into their shale oil plant⁶⁷. Data on the hydrogen solubility of shale oil would be important for research and design work done in this field.

It is important to note that the composition and properties of shale oil can vary widely depending on the oil shale and retorting conditions used^{56,68-70}. Often shale oil contains significant amounts of olefins, aromatic compounds and heteroatoms, which make it compositionally different from conventional petroleum fuels. For example, shale oil produced from Kukersite oil shale (Estonia) contains large amounts of phenolic compounds^{71,72}. From experimental data for pure compounds³, it can be seen that, in general, the presence of a polar oxygen-containing functional group decreases the hydrogen solubility of a compound. For instance, at 298 K and about 100 bar the hydrogen solubility of hexane is 1.14 mol H₂/kg¹⁶, but for hexanol it is only 0.309 mol H₂/kg²². Because compositional differences affect the properties of the shale oil, many of the correlations developed using petroleum do not provide accurate results for these shale oils. This makes experimental data even more essential for shale oils, and only a limited amount of experimental data exists about the properties of shale oils⁷³.

This work presents the first known experimental data for the hydrogen solubility of shale oil. Experiments were performed at high temperatures and pressures, which are the conditions relevant for industrial plants. Additionally, a second sample of the shale oil was measured for which many of the phenolic compounds had been removed, which allowed the influence of these compounds to be examined. The applicability of using existing solubility prediction methods with this shale oil is also evaluated.

2. Experimental Methods

2.1. Sample preparation

The shale oil used in this study was obtained from Eesti Energia's Narva Oil Plant (Narva, Estonia). Kukersite oil shale (Estonia) is used as the raw material for the retort. The plant uses a solid heat carrier retort (also known as the Galoter process)⁷⁴. The shale oil is separated into three wide industrial fractions at the plant: shale gasoline, fuel oil and heavy oil. Even though the heavy oil fraction is the one most likely to be hydrotreated, a fuel oil sample was used because it could be measured without needing to dilute it with a solvent. Heavy samples need to be diluted to lower their viscosity and enable light to pass through, but then the more complex heavy oil + solvent + hydrogen system must be modeled, which would require significantly more research to develop appropriate models for the heavy shale oil.

As mentioned, Kukersite shale oil contains high quantities of phenolic compounds. To study the impact of those polar phenolic compounds on the hydrogen solubility, the fuel oil was split into two portions and the phenolic compounds were removed from one of the portions using extraction. The basic procedure is described in detail elsewhere^{71,75}, and involves extraction with 10% NaOH, washing with distilled water and drying the oil. Extraction was carried out in a glass cone with a volume of 5 liters that was fitted with a stopcock made of glass and teflon (see Figure 1). 2881 g of shale fuel oil was poured into the cone. A glass stirrer was inserted into the cone from above, which was turned using a motor. Then the NaOH solution was slowly added from the top of the cone using a peristaltic pump. The cone was allowed to fill, and then the NaOH with the extracted phenols was periodically removed from the bottom through the stopcock.

Figure 1. Picture of the liquid-liquid extraction vessel.

Approximately 12.5 L of the NaOH solution was sent through the oil, and at the end the water phase was translucent with an orange tint. Then about 5.5 L of distilled water was sent through the oil in the same manner to wash out any remaining NaOH. Distilled water was pumped in until the water removed from the device had a pH of 7. Some of the oil had been removed with the NaOH solution and had separated to the top of the container where the used NaOH had been placed. This oil was removed from the top and placed back in the extraction device by itself (the other oil had been removed first). 2 L of 10% NaOH was added to ensure that any phenols were removed from this additional oil, and then 8 L of distilled water was used to wash the oil. This oil was combined with the portion extracted first and then the oil was left to stand overnight to allow more of the remaining water to separate out of the oil. Then the oil was dried further by adding sodium sulfate salt to absorb water in the oil. The dried oil was then poured through a filter to ensure that the salt crystals were removed from the oil. 949 g of the fuel oil was left after extraction. Note that losses occurred during extraction and filtering, and therefore, the amount of recovered oil cannot be taken as an accurate representation of the amount of phenolic compounds in the oil.

Properties of both the fuel oil and dephenolated fuel oil samples are given in Table 1, and details about the measurement methods used can be found in the next section. Infrared spectra are presented in Figure 2, and files containing the spectral data can be found at <https://osf.io/dhkew/>.

Table 1. Properties of the shale oil samples used in this study.

	Fuel oil	Dephenolated oil
Density at 293 K (g/cm ³)	1.0170	0.9682
Refractive index at 293 K	1.5567	1.5411
Molecular weight (g/mol)	242	250
Hydrogen content (wt%)	9.4	10.7
Carbon content (wt%)	80.9	82.5

Atomic H/C ratio	1.38	1.55
Hydroxyl group content (wt%)	5.3	1.1
Hydroxyl groups per molecule	0.75	0.16
Density at 313 K (g/cm ³)	1.0026	0.9542
Density at 333 K (g/cm ³)	0.9880	0.9399
Density at 353 K (g/cm ³)	0.9733	0.9254
Volumetric expansion coefficient at 293 K (K ⁻¹)	0.0007166	0.0007371

Figure 2. Infrared spectra of the shale oil samples measured in this study and a heavy shale oil sample (for comparison). The numbers denote the main functional groups associated with a given region⁷⁶: (1) O-H, (2) saturated C-H, (3) C-H for aromatic and double bonded carbon, (4) carbon bonds in an aromatic ring, (5) C=O, (6) C-O.

2.2. Measurement of characteristic properties

Characteristic properties of the shale oil samples were measured, and are presented in Table 1. Infrared spectra were also measured, as well as densities at higher pressures.

2.2.1. Density

Densities were measured using a DMA 5000M density meter (Anton Paar GmbH, Graz, Austria) and had a standard uncertainty of 0.00015 g/cm³ (expanded uncertainty of 0.0003 g/cm³ at the 95% level). The density was measured at 293, 313, 333 and 353 K, and volumetric expansion coefficients were calculated from the density data.

To be able to accurately calculate the flow rate of the oil feed, the densities of the samples at high pressures were also measured. These measurements were performed using a DMA HPM density measurement cell (Anton Paar GmbH, Graz, Austria), which was calibrated with nitrogen and pure water. These densities were estimated to have an expanded uncertainty of ± 0.0004 g/cm³ at the 95% level. The densities showed a linear dependence on temperature and pressure. Therefore, because the feed pump was always at room temperature, only a few data points at room temperature were needed for the hydrogen solubility calculations. For shale fuel oil the densities at 293.15 K were 1017.9 and 1022.9

kg/m³ at pressures of 1.52 and 99.29 bar, respectively. At 298.15 K the densities were 1014.7 and 1019.3 kg/m³ at pressures of 10.22 and 99.62 bar. For the dephenolated shale fuel oil the densities at 293.15 K were 969.5 and 975.6 kg/m³ at 5.18 and 119.22 bar. At 298.15 K and pressures of 5.1 and 119.19 bar the densities were 965.9 and 972.2 kg/m³, respectively. A complete set of experimental density data, including data at higher temperatures, will soon be published as part of separate article that investigates the thermodynamic properties of these oil samples.

2.2.2. Refractive index

The refractive index at 589.592 nm was measured using an Abbemat HT refractometer (Anton Paar GmbH, Graz, Austria) and had a standard uncertainty of 0.0011 (expanded uncertainty of 0.0021 at the 95% level).

2.2.3. Molecular weight

The average molecular weight was measured using vapor pressure osmometry (Knauer K-7000, Wissenschaftliche Gerätebau Dr. Ing. Herbert KNAUER GmbH, Germany), which had a standard uncertainty of 7 g/mol (expanded uncertainty of 14 g/mol at the 95% level).

2.2.4. Infrared spectra and chemical composition

Infrared spectra were measured using an Interspec 301-X portable mid-infrared spectrometer (Interspectrum OÜ, Tõravere, Estonia). The hydroxyl group content of the oils was determined from the infrared spectra using a model created with support vector regression. More details about the creation of these models is given in our earlier articles^{71,77}. The model had a root mean squared error (RMSE) of 0.35 wt%. These values for the hydroxyl group content were then used to calculate the number of hydroxyl groups per average molecule by multiplying by the average molecular weight of the sample and dividing by the molecular weight of a hydroxyl group.

Hydrogen and carbon content were also calculated from infrared spectra. Support vector regression was used to create the model for doing so, and was performed using experimental data for the hydrogen and carbon content of over 250 shale oil fractions. The RMSEs of these models were 0.133 wt% for hydrogen and 0.564 wt% for carbon. The process for creating these models was similar to that used for creating a model for density in our earlier paper⁷⁷. These values for the hydrogen and carbon content were then used to calculate the H/C ratios given in Table 1.

2.3. Measurements with the continuous flow apparatus

The hydrogen solubility of the samples was measured using the continuous flow apparatus described by Saajanlehto⁷⁸. The heart of this device is an optical cell in which the formation of a gaseous phase in the liquid sample can be observed using a video camera. This cell is maintained at a constant temperature and pressure. The sample and hydrogen gas are continuously fed into the cell. The flow rate of hydrogen gas is controlled using a mass flow controller (F230MI-AAD-11-V, Bronkhorst High-Tech, Ruurlo, Netherlands), and the liquid sample is fed using a syringe pump (Teledyne ISCO 260D, Teledyne ISCO, Lincoln, NE, USA). These flow rates determine the composition. The sample and hydrogen streams are combined in a T-joint, and then the mixture flows through a 3 meter long capillary tube to ensure complete mixing before it enters the optical cell.

Temperature was measured using a calibrated K-type thermocouple (Nokeval Oy, Nokia, Finland) that was placed in the metal housing of the optical cell. The temperature of the feed pump was also measured using one of these thermocouples. Pressure was measured using a Trafag pressure sensor (type 8253.74.2317, Trafag AG, Bubikon, Switzerland). The pressure in the system is maintained using a second syringe pump (Teledyne ISCO 500D, Teledyne ISCO, Lincoln, NE, USA), which also serves to collect the spent sample. Note that the third syringe pump shown in the original scheme of the apparatus⁷⁸ (designated as “measurement pump”) was not used. Hydrogen was obtained from AGA (Oy AGA Ab, Espoo, Finland) and was stated to have a purity of at least 99.995%.

The thermocouples and pressure sensor were calibrated immediately after measurements with the shale oil samples were completed. The thermocouples were calibrated against a Tempcontrol F200 thermometer (Tempcontrol Industrial Electronic Products B.V., Nootdorp, Netherlands) equipped with a Pt-100 RTD, which had been calibrated at the Finnish National Standards Laboratory (MIKES). The standard uncertainty of the thermocouples was estimated to be 0.06 K (expanded uncertainty of 0.13 K at the 95% level). The pressure sensor was calibrated using a Beamex MC2-PE calibrator with an EXT600 external pressure module, which had been calibrated by Beamex Oy Ab. Based on the calibration, the standard uncertainty of the Trafag pressure sensor was estimated to be 0.015 bar (expanded uncertainty of 0.034 bar at the 95% level). The mass flow controller was also calibrated to ensure the accuracy of the flow rate of hydrogen, and had a standard uncertainty of 0.30 mL/min (that is, normal milliliters per minute at the standard temperature and pressure of 1 atm and 273.15 K) and an expanded uncertainty of 0.84 mL/min.

Before beginning a measurement the sample was degassed by placing the bulb with the sample in an ultrasonic bath that contained ice water and using a vacuum pump to remove gases in the bulb. The sample was degassed for a minimum of 30 minutes. The sample was weighed before and after degassing, and on average 0.15 g (0.07%) of the sample was lost during degassing (the maximum amount lost was 0.3 g, or 0.18%). The feed pump was also connected to a vacuum pump to remove any gases and remaining solvents. Then the degassed sample was fed into the evacuated feed pump. Feeding the sample into the pump took a long time (about 1 hour for the dephenolated fuel oil and 3 to 7 hours for the fuel oil) because small capillary tubing is used in the continuous flow apparatus and the shale oil samples were fairly viscous (we estimate that the viscosity at room temperature was about 1000 mPa·s for the shale fuel oil and about 20 mPa·s for the dephenolated sample). To enable the sample to be fed in a reasonable timeframe, the sample was heated using a hair dryer or hot air gun. Safety was ensured during heating by keeping the temperature low enough that the vapor pressure of the sample was still well below atmospheric pressure.

Once the sample was in the feed pump and the temperature in the optical cell had stabilized then the system was filled with the oil sample and pressurized to the desired pressure. Low oil and hydrogen flow rates were then set to allow the system to stabilize, and then the flow rates were set to get the first composition to be measured. When measuring at a given composition, the system was allowed to stabilize for at least the residence time of the sample at the given flow rate and usually longer. The volume of the cell and the capillary tubes before the cell was approximately 5 ml and oil flow rates of 0.4 to 1.4 mL/min were used. Once the system had stabilized the optical cell was observed for several minutes, using the video camera, to determine whether or not the mixture was in the 2-phase region. This procedure was repeated at different compositions to find the saturation composition, or the highest hydrogen concentration at which a single liquid phase still exists. The solubility limit at the given conditions is taken to be the average of the two compositions closest to the saturation composition; in other words, the average of the highest hydrogen concentration where a liquid phase is observed and the lowest hydrogen concentration where two phases are observed. Then, if there was still enough sample in the feed pump, the pressure or temperature was changed and measurements were performed at the new conditions.

The hydrogen solubility was calculated from the experimental data using Equation 1

$$S = \frac{\dot{V}_{H_2}}{\dot{V}_{oil}\rho_{oil}\dot{V}_{H_2}} \cdot 1000 \quad (1)$$

where S is the hydrogen solubility (mol H_2 /kg oil), $\dot{V}_{H_2}$ is the volumetric flow rate of hydrogen (mL/min, normal milliliters per minute) at standard conditions (1 atm and 273.15 K), $\dot{V}_{oil}$ is the volumetric flow rate of the oil sample, ρ_{oil} is the density of the oil at the temperature and pressure in the feed pump

during the experiment and $\hat{V}_{H_2}$ is the molar volume of hydrogen at standard temperature and pressure (1 atm and 273.15 K). The molar volume of hydrogen was taken from the NIST webbook⁷⁹ and was 22250 ml/mol.

2.4. Reactions during the study

Some problems arose during the experiments that seem to be caused by reactions that occurred with the shale oil. This was first noticed when particles formed in the fuel oil sample at 573 K. The oven was heated to 573 K to prepare for experiments at that temperature, and fuel oil from the previous run was still in the system. The oven was at this temperature for about 6 hours while a new portion of fuel oil was loaded into the feed pump. When the camera was turned on to begin the experiment then it was observed that the optical cell contained some sort of heavy residue. As the new fuel oil was fed through the system this residue was broken up into particles. The long time period spent at a high temperature and pressure seems to have caused the shale fuel oil to react.

Particle formation was observed only once at the short residence times used during actual experiments. This occurred with the dephenolated oil at 527.2 K and 139.71 bar. This run had the lowest oil flow rate of any of the experiments (0.4 ml/min), which means the oil also had the longest residence time in the hot zone (about 13 min). For comparison, the average residence time for all the measurements was 6 min. A picture of these particles is given in Figure 3. This data point still had a hydrogen solubility value that lined up with the remaining data for the dephenolated sample, and it was not removed. However, it should be noted that changes in the composition may have been large enough to affect the hydrogen solubility for that data point. At the same temperature and lower pressures (and also higher flow rates) particle formation was not observed. The residence times for these runs were 8 min and 3 min.

Figure 3. Pictures from the experiments. **Left:** the liquid phase; **center:** a small bubble flowing through the optical cell; **right:** particles formed when measuring dephenolated shale fuel oil at 527.2 K and 139.71 bar.

2.5. Uncertainty analysis

The uncertainty in the measured solubility values was assessed using a Monte Carlo method (see ISO/IEC Guide 98-3⁸⁰). This involved specifying a probability distribution for each parameter that could affect the uncertainty of the measurements, randomly sampling these distributions and then using each set of sampled values to calculate a solubility. A distribution of solubility values was then obtained; the variance of this distribution was taken to be the standard uncertainty of the measured value. The expanded uncertainty at the 95% level was also calculated from the probability density function. 9 parameters were varied in the Monte Carlo simulation, and the statistical sample size used with this method was 100,000. In addition to the uncertainties of the parameters used in Equation 1, the uncertainty in the measured temperature and pressure of the cell were also included in the error model

by multiplying the deviation of these values from the mean by the sensitivity of the hydrogen solubility to the temperature and the pressure. The sensitivity was calculated as the partial derivative of the hydrogen solubility with respect to temperature or pressure at the measurement conditions.

The accuracy of the measurements was also checked by measuring the hydrogen solubility of toluene. The toluene used was obtained from Merck and had a purity of $\geq 99.9\%$ (as measured by the producer using gas chromatography). The measured value is shown in Table 2 along with literature values at approximately the same conditions measured by Saajanlehto et al.⁷⁸ and Simnick et al.⁸¹. This analysis confirms that the experimental procedure gave accurate values, with uncertainties at a level that is commonly expected for hydrogen solubility measurements.

Table 2. Measured and literature values for the mole fraction of hydrogen that is soluble in toluene (x_{H_2}).

Source	Temperature (K)	Pressure (bar)	x_{H_2}
this work	505.6	49.72	0.038 ± 0.0027
Saajanlehto et al. ⁷⁸	501.6	50.0	0.037
Saajanlehto et al. ⁷⁸	502.0	49.9	0.037
Simnick et al. ⁸¹	502.2	50.7	0.0375

3. Results and Discussion

3.1. Measured data

In total, 15 data points were measured for the shale oil samples from 424 to 527 K and from 40 to 140 bar. This data is presented in Table 3. The data is also presented graphically in Figure 4 and Figure 5. The solubility of hydrogen in the oil samples increases with pressure and temperature, as would be expected³. The dephenolated sample had a hydrogen solubility that was about 0.1 mol H₂/kg oil higher than the shale fuel oil, which is an increase of about 15 to 45%, depending on the hydrogen solubility. This increase is reasonable given that oxygenated pure compounds generally have lower solubilities than comparable hydrocarbons that do not contain oxygen³. As shown in Table 1, the average molecule in the shale fuel oil contains 0.75 hydroxyl groups, which means that roughly 3 out of 4 molecules contain a hydroxyl group. For the dephenolated shale fuel oil only 1 in 6 molecules contain a hydroxyl group, which is a significant decrease. In addition to the difference in hydroxyl group content, it is likely that the aromatic structure in the phenols also decreases the hydrogen solubility. Therefore, the increase in hydrogen solubility for the dephenolated sample is probably also related to the decrease in aromatic rings that occurs when removing the phenolic compounds.

Table 3. Measured values for the hydrogen solubility (S_{H_2}) and mole fraction of hydrogen in the liquid phase (x_{H_2}) for the shale oil samples. $u(_)$ denotes the expanded uncertainty at the 95% level.

Temperature	Pressure	Shale fuel oil		x_{H_2}	$u(x_{H_2})$
		S_{H_2}	$u(S_{H_2})$		
K	bar	mol H ₂ /kg oil	mol H ₂ /kg oil		
527.1	119.92	0.47	± 0.034	0.103	± 0.0084
475.9	139.93	0.45	± 0.025	0.098	± 0.0070
475.9	100.01	0.32	± 0.029	0.072	± 0.0072
475.9	60.11	0.18	± 0.020	0.041	± 0.0051
423.9	139.97	0.32	± 0.019	0.073	± 0.0055
423.9	80.12	0.17	± 0.019	0.040	± 0.0048
527.1	80.07	0.31	± 0.029	0.070	± 0.0072

501.5	139.91	0.51	±0.038	0.109	±0.0091
501.6	100.02	0.35	±0.033	0.078	±0.0079
501.6	60.16	0.19	±0.020	0.044	±0.0051

Dephenolated shale fuel oil					
Temperature	Pressure	S_{H_2}	$u(S_{H_2})$	x_{H_2}	$u(x_{H_2})$
<i>K</i>	<i>bar</i>	<i>mol H₂/kg oil</i>	<i>mol H₂/kg oil</i>		
423.9	139.72	0.45	±0.031	0.102	±0.0080
423.9	79.86	0.25	±0.028	0.058	±0.0069
527.2	139.71	0.68	±0.069	0.145	±0.0144
527.2	99.85	0.45	±0.046	0.102	±0.0106
527.2	39.86	0.13	±0.018	0.032	±0.0045

Figure 4. Measured hydrogen solubilities for the shale fuel oil and dephenolated shale fuel oil.

Figure 5. Measured hydrogen solubilities of the shale oil samples.

By comparing the measured data to data found in the literature (available at <https://osf.io/dhkew/>), it can be seen that the shale fuel oil has a relatively low hydrogen solubility. This is illustrated in Figure 6, which compares the literature data and the shale oil samples. The hydrogen solubility of the shale fuel oil sample falls below almost all of the other fuel samples. Two of the main molecular structures in shale oil produced from Kokersite oil shale, such as the samples in this study, are aromatic rings and functional groups containing oxygen. In general, compounds with these structures have lower hydrogen solubilities than n-alkanes, as seen from general trends in data for pure

compounds³ (see Figure 7). For example, benzene has a lower hydrogen solubility than hexane, as does hexanol. The Kukersite shale oil samples match most closely with compounds that have aromatic rings, such as m-cresol, eugenol and methylnaphthalene. Therefore, it is reasonable to expect that Kukersite shale oil would have a relatively low hydrogen solubility. In support of this reasoning, the dephenolated fuel oil has a higher hydrogen solubility that is similar to many of the other fuel samples, which indicates that the phenolic compounds present in Kukersite shale oil decrease the hydrogen solubility. Interestingly, the bio oil samples also have a higher solubility than the shale fuel oil. The bio oils were cottonseed, jojoba and tall oils, and they consisted mainly of acids and esters with long straight chain alkenes that had one or two double bonds^{47,48,50}. The added aromatic rings in the phenols of the shale oil are likely the reason for its lower hydrogen solubility. The dephenolated shale oil had a hydrogen solubility that was more comparable to those bio oils.

Figure 6. A comparison of the hydrogen solubilities of the shale oil samples and other oils at approximately 60 and 100 bar (data at <https://osf.io/dhkew/>).

Figure 7. Comparison of the hydrogen solubilities of selected pure compounds at about 100 bar. Data taken from Young³ and Qureshi et al.⁶.

3.2. Modeling hydrogen solubility in Kukersite shale oil

Hydrogen solubility is generally modelled and predicted using equations of state; however, this requires the equation of state parameters to be predicted or fit to experimental data. Because there is no method for predicting these parameters for Kukersite shale oil that is known to be reliable and experimental data necessary for fitting was not available, an equation of state was not used for modeling the hydrogen solubility. Instead, the method presented by Riazi and Roomi⁸² was used. This method only requires the average molecular weight of the fuel and a rough estimate of the composition.

The core of this method is the vapor liquid equilibria relationship given as Equation 4 in the reference⁸² (shown here as Equation 2).

$$x_1 = \frac{\phi_1^V P_1}{\gamma_1 f_1^L} \quad (2)$$

where x_1 is the mole fraction of component 1 (in this case hydrogen) in the liquid phase, ϕ_1^V is the fugacity coefficient of component 1 in the gas phase, P_1 is the partial pressure, γ_1 is the activity coefficient in the solvent liquid phase, and f_1^L is the fugacity of component 1 as a pure liquid at the given pressure and temperature. For light gases like hydrogen f_1^L is taken to be the fugacity of a hypothetical liquid.

The activity coefficient γ_1 is estimated using Scatchard–Hildebrand theory, and the solubility parameter and molar volume of the fuel needed for this calculation are predicted from correlations given in the reference⁸² that are based on model pure compounds. The liquid phase fugacity f_1^L is estimated using Equation 8 in the reference⁸² (shown here as Equation 3)

$$f_1^L = f_r^{oL} P_c \exp \left[\frac{V_1^L (P - 1.013)}{RT} \right] \quad (3)$$

where f_r^{oL} is the reduced hypothetical liquid fugacity at 1 atm, P_c is the critical pressure of component 1, V_1^L is the molar volume, P is the pressure, R is the ideal gas constant and T is the temperature. Riazi and Roomi treat f_r^{oL} as an adjustable parameter to enable a better fit. They also introduce a second adjustable parameter α which functions as a correction factor for the hypothetical solubility parameter and molar volume of liquid hydrogen at 298 K. These two parameters are chosen depending on the composition of the solvent or fuel.

When using this method for the shale oil samples the solubility parameter was estimated using only the correlation for alkylbenzenes (Equation 22 in the reference⁸²), and the molar volumes were calculated directly from the measured molecular weights and densities. Riazi and Roomi suggest that for aromatic fuels the parameters α and f_r^{oL} be set to 1.27 and 30, respectively, and these suggested values were used first. When using these parameters a poor fit was obtained: for the shale fuel oil the RMSE of the mole fraction was 0.080 (an average relative deviation, %AAD, of 111%) and for the dephenolated fuel oil the RMSE was 0.062 (%AAD of 74%). Figure 8 shows the predicted values graphically. The method, as is, significantly over predicts the hydrogen solubility.

Figure 8. A comparison of the hydrogen solubility predicted using the method given by Riazi and Roomi⁸² and the experimental data for the shale fuel oil sample. Deviation calculated as predicted minus experimental.

The immediate question is whether or not the method can be modified to provide a good fit for the shale oil samples. This method takes composition into account in two places: in calculation of the solubility parameter of the fuel and in choosing the values for α and f_r^{oL} . Based on data and estimates for pure alkylphenols⁸³ it seems that the solubility parameter should be close to that of alkylbenzenes, so

the solubility parameter was left unchanged. Therefore, it seems likely that α and f_r^{ol} would need to be optimized for use with Kukersite shale oil samples. Directly optimizing these parameters does give a good fit, with an RMSE at about the level of the experimental uncertainty (RMSE of the mole fraction of 0.0016; %AAD of 2.1%). However, it seems unlikely that these parameters could be inferred from compositional trends identified for other fuels by Riazi and Roomi⁸², especially because both values are significantly lower than any values used for other solvents or fuels (optimal values were -0.045 and 12.5 for α and f_r^{ol}). Also, these shale fuel oil parameters do not provide a good fit for the dephenolated sample, for which the optimal values were 0.42 and 20 (also lower than expected). Therefore, it seems doubtful that these optimized values would provide good predictions for other Kukersite shale oil products, and data for more samples would be needed to take compositional differences into account.

When analyzing the solution space of the Riazi and Roomi method it was seen that the accuracy of the fit was quite sensitive to changes in alpha, at least for the experimental data presented here. Deviations from the optimal value of more than 0.05 quickly resulted in a %AAD of more than 10%. This also makes it seem unlikely that the parameters for this shale fuel oil sample would give good results when used for other shale oil samples.

For modeling, a more accurate approach for shale oil samples like these could be to estimate parameters for an equation of state by using the pseudocomponent approach, where the fuel is represented as a mixture of a small number of compound classes whose values can be predicted from data for pure compounds⁸⁴. Future modeling studies could take this approach, but to do so more detailed information would be needed about the samples, such as a distillation curve and density data for the distilled fractions. Also, the main class of compound in this shale oil, alkylphenols, is not found in petroleum, and new correlations would have to be developed for predicting the properties of alkylphenolic pseudocomponents. Likely this would require more experimental data to be measured for pure alkylphenols.

4. Conclusions

Experimental data presented here shows that Kukersite shale oil has a hydrogen solubility that is lower than most other fuels, which is most likely due to the high amount of polar aromatic compounds (phenolic compounds) in the oil. Some of these phenolic compounds were removed from the oil using extraction, and the hydrogen solubility of this dephenolated oil was noticeably higher. Signs of chemical reactions were also observed when the oil had a longer residence time in the hot zone, and thus, maintaining low residence times seems to be important for obtaining trustworthy measurements for these oils.

It seems probable that the data for the shale fuel oil also gives a good indication of the solubility behavior of the heavy shale oil because they have similar molecular structures (see Figure 2). In the future it would be useful confirm this assumption by performing experiments with the heavy shale oil.

Prediction methods developed for petroleum and coal liquid fuels cannot currently be used for predicting the solubility of Kukersite shale oil. More accurate predictions could be obtained if additional measurements were made for other shale oil samples or if methods were developed for predicting equation of state parameters for shale oil.

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