

Sulphur and viscosity reductions in heavy hydrocarbons by subcritical water processing

Citation for published version (APA):

Cuijpers, M. C. M., Boot, M. D., Deen, N. G., & Golombok, M. (2019). Sulphur and viscosity reductions in heavy hydrocarbons by subcritical water processing. *Journal of Petroleum Science and Engineering*, 172, 1069-1076. <https://doi.org/10.1016/j.petrol.2018.09.015>

Document license:

TAVERNE

DOI:

[10.1016/j.petrol.2018.09.015](https://doi.org/10.1016/j.petrol.2018.09.015)

Document status and date:

Published: 01/01/2019

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.



Sulphur and viscosity reductions in heavy hydrocarbons by subcritical water processing

M.C.M. Cuijpers^a, M.D. Boot^a, N.G. Deen^a, M. Golombok^{a,b,*}

^a *Multiphase and Reactive Flows, Department of Mechanical Engineering, Eindhoven University of Technology (TU/e), P.O. Box 513, 5600 MB Eindhoven, the Netherlands*

^b *Shell Technology Centre Amsterdam, Grasweg 3, 1031 HW Amsterdam, the Netherlands*

ARTICLE INFO

Keywords:

Subcritical water
Sulphur
Viscosity
Enhanced cracking

ABSTRACT

Viscosity and sulphur content are two important properties of heavy hydrocarbons for downstream processing. Both properties can be significantly reduced in value by processing in subcritical water. Subcritical water has advantages over steam recovery methods in terms of viscosity and sulphur reduction as well as energy consumption. In order to understand the mechanism of subcritical water treatment, the chemical structure of pre- and post-processed heavy hydrocarbons are compared to each other. For subcritical water processing, viscosity reduction coincides with a reduction in average molecular weight, average carbon chain length between branching points, and sulphur content, along with an increase in volatility and H₂S production. This suggests that not only are C–C bonds cracked, but also C–S(C) bonds. Subsequent comparison of subcritical water results with those obtained for pyrolysis treatment shows that the former is faster and more effective.

1. Introduction

Crude oils can be divided into three categories: light (LO), heavy (HO) and extra heavy (XHO). Typical benchmark oils all qualify as “light” (Fanchi and Christiansen, 2017). Unconventional oils, such as extra heavy hydrocarbons are typically more viscous and higher in sulphur concentration than their conventional counterparts. To be acceptable for crude transportation and petrochemical processing, heavy oils need to be upgraded in terms of sulphur and viscosity. The goal is typically characterised by the three traditional traded benchmarks of Brent, West Texas Intermediate (WTI) and Tapis (Gustavson, 1999). These all have viscosities < 10 mPa s qualifying them as “light oils”. Similarly they also have sulphur concentrations < 0.5 wt.-% which qualifies them as “low sulphur”. Heavy oils however have high levels of viscosity (> 0.5 Pa s) and often sulphur (> 0.5 wt.-%). Both levels can be considerably above the indicated boundaries.

Fig. 1 shows the sulphur content and viscosity of three target heavy crudes (Marmul, Schoonebeek and Peace River: light heavy, heavy and extra heavy respectively). These heavy oils are compared to the three light benchmarks mentioned above. The goal is to make the more viscous high sulphur crude oils acceptable for downstream refining to fuels and chemicals. The recovery of heavy crude oils usually involves thermal recovery technologies (Thomas, 2008). These are often applied in-situ when the overburden pressure is sufficiently high. For shallow

deposits (“tar sands”), this is not the case: these are obtained by open pit mining – which thus consumes a significant amount of energy for such a “recovery”. Subsequently hot water processing is used which leads to a lot of waste product (Cram and Redford, 1976; Miller and Misra, 1982).

For both cases, heat is transferred to the oil (either in-situ or following mining) and a portion of the original oil is obtained. This produced oil is not necessarily the same as that originally in place as regards the parameters of interest here, namely sulphur and viscosity. For example, heat can simply strip a lower boiling range fraction of the oil in place. This stripped portion is mobilised by the injected heat and transported to the well bore. Once cooled to ambient temperature, the stripped oil viscosity goes up again but not as high as for the original oil in place because it contains more light components (Shu and Hartman, 1986).

The heat transfer to reduce the oil viscosity to a pumpable level is thus transient (Alvarado and Manrique, 2010; Golombok and Ineke, 2013; Santos et al., 2014; Thomas, 2008). Such stripping of course does not change the sulphur content, except to the extent that the lighter components contain less sulphur. Transient processing does not address any problems for surface transport and processing following recovery. Ideally recovery would not just strip part of the oil in place, but would access all the oil in place and also permanently reduce oil viscosity as well as reducing sulphur content. A promising technology to this end

* Corresponding author. Multiphase and Reactive Flows, Department of Mechanical Engineering, Eindhoven University of Technology (TU/e), P.O. Box 513, 5600 MB Eindhoven, the Netherlands.

E-mail address: M.Golombok@tue.nl (M. Golombok).

<https://doi.org/10.1016/j.petrol.2018.09.015>

Received 2 March 2018; Received in revised form 17 August 2018; Accepted 4 September 2018

Available online 05 September 2018

0920-4105/ © 2018 Elsevier B.V. All rights reserved.

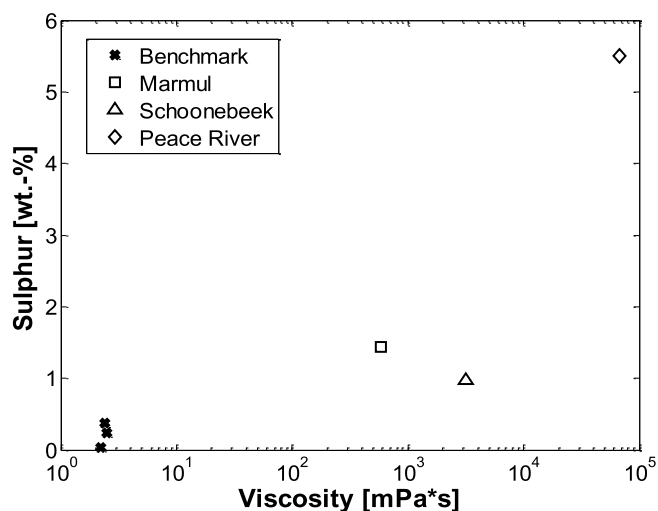


Fig. 1. Sulphur content as function of viscosity for crude oils.

involves the use of subcritical water (SCW) which has the potential to dissolve and crack heavy oil components (Duan et al., 2013; Kishita et al., 2005; Onwudili and Williams, 2014).

The objective of this work is to apply this technology to HO and XHO samples with elevated sulphur contents. In section 2 benchmark methods on heavy oil recovery and upgrading processes are reviewed and compared with the role of subcritical water with its enhanced dissolution and cracking potential. In addition, the energy balance of steam recovery technologies versus the described subcritical water process are assessed. Section 3 describes the experimental methodology and measurement. In section 4 the results are used to deduce the chemical nature of the products and a reaction mechanism.

2. Background

2.1. Process

The use of hot water to mobilise heavy hydrocarbons is a well-established technique in enhanced oil recovery (EOR) (Chen, 2009; Giacchetta et al., 2015). Low pressure hot water (steam) is injected as vapour at about 300 °C for an extended period of time. On reservoir contact the hot vapour ‘strips’ the lighter components from the crude oil although no cracking takes place because the temperature is too low. The recovered fluid is lighter than the original oil in place and its viscosity stays relatively low as long as heat is applied (Shu and Hartman, 1986). Such methods include cyclic steam simulation (CSS), steam assisted gravity drainage (SAGD) and steam drive (SD) (Adams and Khan, 1969; Chen, 2009; Giacchetta et al., 2015; Van Dijk, 1968). Once removed from the heat source, the stripped fluid reverts to a higher viscosity – although not as high as the original oil in place.

By contrast subcritical water aims to access all the oil in the reservoir. The water is injected as a fluid under subcritical conditions i.e. between the boiling point (100 °C at 1 bar) and subcritical point (374 °C at 220 bar) (Alenezi et al., 2009). There are two interesting properties of the subcritical water:

- The dielectric constant decreases from 80 to 6 when water approaches subcritical conditions (Alenezi et al., 2009; Goto et al., 2004; Miller et al., 1998). This allows more oil to dissolve in the water, particularly the more polar molecules associated with the heavy ends such as polyaromatics and heterocyclic compounds.
- Simultaneously, enhanced water dissociation boosts cracking to lighter fractions (Akiya and Savage, 2002; Hageman et al., 1996; Patrick et al., 2001; Ryan et al., 1997). The dissociation constant of water increases by a factor 1000 compared to the value at standard

conditions. The simultaneous increase in OH^-/H^+ concentrations assists cracking.

Note that the more commonly studied supercritical water methods rely solely on higher temperature and increased thermal cracking (Akiya and Savage, 2002; Cuijpers et al., 2017; Golombok and Ineke, 2013; Patrick et al., 2001; Ryan et al., 1997). Moreover, in these methods there is no dissolution of the heavy oil feed. Cracking of C–C and C–S bonds has been referred to by other workers (Kamimura et al., 1998). Supercritical water reduces average molecular weight and sulphur content in heavy oils (Demirbas, 2016; Kishita et al., 2005; Timko et al., 2015). This process requires high temperatures and pressures, making the desulphurisation process unattractive. In addition, the sulphur removal is strongly affected by changes of the fluid around the critical point of the solution. Supercritical desulphurisation requires a significant investment in operating, maintenance and control (Demirbas, 2016; Demirbas, 1999). The use of a catalyst (ZnO) reduces sulphur content and decreases average molecular weight even further (Patrick et al., 2001; Timko et al., 2015).

In contrast to steam or supercritical water, the subcritical water process maintains water in a liquid state and is seen as a green chemistry area (Bicker et al., 2005; Isa et al., 2015; Oliveira et al., 2011; Ramos et al., 2002; Yang et al., 1998). The reduced dielectric constant increases dissolution of organic components, which allows for heavy oil molecule isolation and thus better heat transfer for cracking purposes. This is demonstrated in a previous study on a light heavy oil (Marmul in Fig. 1) where subcritical water led to both a permanent reduction in viscosity of 80% and a decrease in sulphur content of 60% (Cuijpers et al., 2017; Golombok and Ineke, 2013). The novelty of subcritical water processing is thus the *permanent* reduction in viscosity and the fact that all oil is accessed.

It is easy to see why a permanent reduction in viscosity is desirable – not just for the time during which heat is applied. Surface facilities for post processing and pumping HO and XHO are significant energy consuming operations. If the heavy oil viscosity can be reduced permanently during production then the energy costs are significantly reduced. Moreover, the dissolution and enhanced cracking potential of subcritical water mean that less injected energy is required for the production part of the process. This may be parametrised by an energy yield parameter based on the ratio of the heating value of produced oil to the “injected” energy.

2.2. Benchmark

The classical recovery parameter from an oil reservoir can be stated either on volume (R_v) or mass basis (R_m) i.e.

$$R_v = \frac{V_{op}}{V_{or}}; R_m = \frac{m_{op}}{m_{or}} \quad (1)$$

where the numerator is the quantity of oil produced to the stock tank on the surface (V_{op} , m_{op}) and the denominator is the estimated oil originally in place i.e. oil in reservoir (V_{or} , m_{or}). Primary recovery involves practically no energy input, but on proceeding through secondary and tertiary recovery processes, it is necessary to consider the energy efficiency – i.e. is more energy recovered in terms of oil compared to the energy invested in the recovery process? Note that this excludes any consideration of more arcane costs such as well to wheel type electric conversion, etc. By analogy with Eq. (1) one may consider the heating value of the produced hydrocarbon Q_p ratioed to the energy invested in its recovery Q_i to give an energy gain factor ε by

$$\varepsilon = \frac{Q_p}{Q_i} \quad (2)$$

Clearly it is necessary that $\varepsilon > 1$ in order to make any process worthwhile. Turning to each of the terms in the ratio, Q_p is simply derived from the recovered volume of oil (and is thus related to eq. (1))

and the associated heating value (HV_p).

$$Q_p = m_{op} * HV_p \quad (3)$$

The amount of energy required is very dependent on the type of thermal recovery. The most common thermal recovery method uses water in the form of steam. The main variable here is the water to oil ratio WOR. This is the ratio of *injected* water (m_w) to *produced* oil (m_{op}).

$$WOR = \frac{m_w}{m_{op}} \quad (4)$$

The injected water is either in the form of steam, normally heated water or subcritical water. Classical steam processes include steam assisted gravity drainage (SAGD), cyclic steam stimulation (CSS) and steam drive (SD). For these processes the WOR varies from 2 to 6. (This is in contrast to processing of mined tar sands where the WOR is around 10).

There are three thermal stages to calculate the energy invested in steam processes (Q_i): (1) heating the water up to the phase transition Q_{wl} , (2) the latent heat of vaporisation Q_{vap} and (3) heating the steam Q_{wg} .

$$Q_i = Q_{wl} + Q_{vap} + Q_{wg} \quad (5)$$

Each of the three terms on the right hand side consists of known parameters. The first stage is given by

$$Q_{wl} = m_w c_{pwl} (T_b - T_0) = WOR m_{op} c_{pwl} (T_b - T_0) \quad (6)$$

where m_w is substituted from Eq. (4). Here c_{pwl} represents the specific heat capacity of liquid water, T_b and T_0 are the boiling point and the ambient temperature, respectively. The second term is the energy to vaporise liquid water (Q_{vap}) and is given by

$$Q_{vap} = WOR m_{op} * L \quad (7)$$

where L is the latent heat of vaporisation. The last component is the heating of steam (Q_{wg}) to operation temperature.

$$Q_{wg} = WOR m_{op} * c_{pwg} * (T_{op} - T_b) \quad (8)$$

Where c_{pwg} represents the specific heat constant of water in gas phase and T_{op} the operation temperature.

Substituting equations (6)–(8) into 5 the result is

$$Q_i = WOR m_{op} (c_{pwl} (T_b - T_0) + L + c_{pwg} (T_{op} - T_b)) \quad (9)$$

Now the energy gain factor ε can be obtained by substituting eqs. (3) and (9) into eq. (2)

$$\varepsilon = \frac{HV_p}{WOR (c_{pwl} (T_b - T_0) + L + c_{pwg} (T_{op} - T_b))} \quad (10)$$

Based on this analysis there are two cases: steam recovery and subcritical water. For steam there is an expression identical to eq. (10) i.e.

$$\varepsilon_{ste} = \frac{HV_p}{WOR (c_{pwl} (T_b - T_0) + L + c_{pwg} (T_{op} - T_b))} \quad (11)$$

This process includes all three thermal stages including the energy intensive vaporisation process. By contrast, for subcritical water, there is no vaporisation process nor is there any steam heating process. The result is that the energy gain factor for subcritical water is given by

$$\varepsilon_{scw} = \frac{HV_p}{WOR c_{pwl} (T_{op} - T_0)} \quad (12)$$

The subcritical water energy gain can be benchmarked against steam recovery methods by dividing the two to obtain

$$\frac{\varepsilon_{scw}}{\varepsilon_{ste}} = \frac{c_{pwl} (T_b - T_0) + L + c_{pwg} (T_{op} - T_b)}{c_{pwl} (T_{op} - T_0)} \quad (13)$$

With all constants known, vaporising 1 kg of water consumes

Table 1
Unconventional crude oil properties.

Feedstock	Viscosity at 25 °C [Pa s]	Sulphur content [wt.%]	API gravity [°]
Schoonebeek 2401	3.2	0.97	25–30
Peace River	67.7	5.5	< 10

approximately the same amount of energy as required to increase the temperature of liquid water to around 500 °C. i.e. well above the critical temperature. Our operating temperature is 300 °C and we use the normal boiling point of water along with the specific heat constants of liquid water and water vapour to estimate $\varepsilon_{scw}/\varepsilon_{ste} \approx 2.6$. This means that the relative energy gain factor for subcritical water is considerably higher than for the steam process. Since we are accessing the same hydrocarbon source, the advantage is that the subcritical water process consumes much less energy compared to classical steam recovery methods. Even without post-processing operations included (i.e. viscosity and sulphur decreasing technologies), SCW already benefits over classical steam recovery processes in terms of energy.

3. Methodology

3.1. Set-up

The heavy oils evaluated during this study originate from Schoonebeek (The Netherlands) and Peace River (Alberta, Canada). The properties are summarized in Table 1: these have already been compared to the desired changes to be implemented in the introduction (see Fig. 1). The oil is processed in the presence of water – typically a 1:1 mixture is used as reported in previous studies.

The sample is placed in a 200 ml Hastelloy C Premex autoclave. A silver gasket is installed between the lid and reactor in order to prevent leakages at high temperatures. The autoclave is heated by an electric mantle. The pressure is set by an Isco 500 d high pressure pump, which is controlled by a back pressure regulator. This regulator neutralizes sudden pressure eruptions due to impurities or volatile components. A magnetically coupled fluid suction stirrer ensures a homogenous mixture of heavy hydrocarbons and water. The setup is installed with various controllers for temperature, pressure, residence time, and rotational speed of the stirrer. Bursting disks are installed at two locations: in the pipework near the Isco high pressure pump and directly on top of the 200 ml reactor. The installed bursting disks are designed and calibrated to break at a pressure of 250 bar at 330 °C. The exit stream from the disk on bursting leads directly to the exhaust ventilation system. Gas detectors are installed to trigger any gas flushing if poisonous gases are detected. A schematic overview of the setup is shown in Fig. 2.

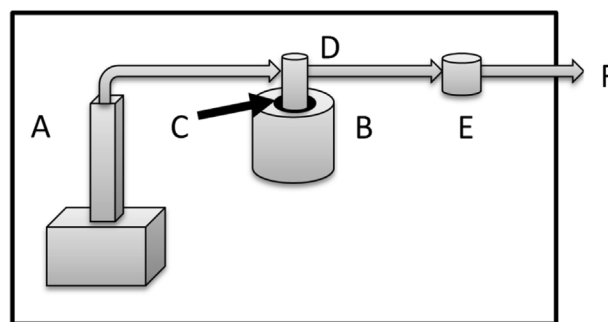


Fig. 2. Schematic overview of the subcritical water setup (A: Isco 500D Syringe pump; B: Premex electric heating mantle; C: Hastelloy C Premex autoclave; D: Premex magnetic stirrer; E: Backpressure regulator; F: External exhaust).

3.2. Procedure

Excess air is expelled by filling and flushing the reactor to the desired 1:1 ratio of oil and demineralised water. Afterwards, the mixture is pressurized to a level in the range of 150–200 bar. Once pressurized, the reactor is heated. Once the desired temperature and pressure are reached, the process time is considered to start. Any sudden pressure eruptions ensuing from released volatile components or impurities are vented to an external exhaust.

Important process parameters in addition to the already mentioned process time (τ), are the temperature and pressure. As stated, sufficient pressure is needed to ensure that the mixture remains liquid. After the desired process time, the reactor is cooled down to ambient conditions. Once cooled down, the system is flushed with compressed air to ensure any gaseous components - including sulphur containing products (e.g. H_2S) - are expelled via an external exhaust. The reactor is opened and the product is extracted. 15 ml of this product is centrifuged - 6500 rpm for 30 min - in order to separate water and organics. The latter is then subjected to a number of analyses.

3.3. Analysis

Viscosity measurements, using the plate and cone technique, are conducted on a Physica MCR 302 rheometer at a temperature of 25 °C. The average molecular weight, or mean molecular weight, is determined using gel permeation chromatography (GPC) in a Shimadzu Prominence-I LC-2030C 3D apparatus at 25 °C with tetrahydrofuran (THF) as eluent. The thermal and phase behavior is analysed by thermogravimetric analysis (TGA) on a Netzsch STA 449F3 instrument. The apparatus heats up a about 10 mg sample from 35 °C to 350 °C at a fixed temperature rise rate of 1 °C/min.

Elemental analyses (C, N, H, S, and O) were carried out on a Thermo Scientific Flash 2000 combustion analyser with GC and thermal conductivity detection. $1H-13C$ NMR spectra were recorded using a Varian 400 MHz spectrometer. The samples were dissolved in deuterated chloroform whose solvent peak was used as an internal standard (7.2 ppm). Data processing was performed using Bruker topspin software.

4. Results and discussion

4.1. Viscosity and sulphur

Fig. 3 shows viscosity-sulphur data points for different degrees of

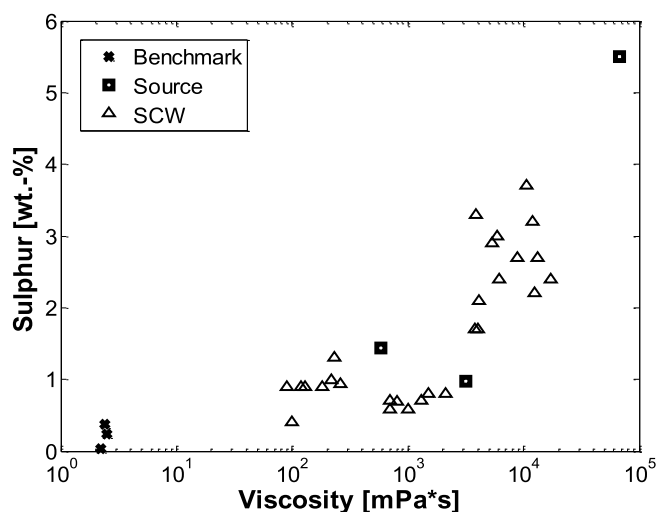


Fig. 3. Sulphur viscosity plot as in Fig. 1 with addition of subcritical (SCW) processed crude points.

subcritical water processing (marked SCW). We have also shown for reference values from Fig. 1 for the “benchmark” crudes and the “source” crudes used in this study. These processed crudes (triangles marked “SCW”) fall between the undesirable properties of the unprocessed oils (“source”) and the desirable properties associated with the “benchmark” (light) crude oils. There is an apparent correlation between viscosity and sulphur content with correlation coefficient 0.78.

Fig. 4 shows the viscosity (a) and sulphur content (b) as a function of processing time at 340 °C for the Schoonebeek and Peace River heavy samples discussed above. The Marmul oil from Oman (a medium heavy crude) has been added from previous studies for comparison (Cuijpers et al., 2017). Another reference shown is the pyrolytic conversion (i.e., heating in the absence of water) of Peace River (PR). The comparison of pure pyrolysis with the other results indicates the effect of subcritical water.

In every case there is a clear decrease in the viscosity and some (although highly scattered) decrease in sulphur. Looking back at the original crudes in Fig. 1, this means that the oils are processed from their starting points as shown in Fig. 1 towards the more desirable properties of the benchmarks on the bottom left indicated on the same figure. Of course each of the samples has a different starting viscosity and sulphur. In Fig. 4 we have normalised results to the initial values for both viscosity and sulphur content for each sample. In the case of viscosity we use

$$\mu_N(\tau) = \frac{\mu_{25}(\tau)}{\mu_{25}(0)} \quad (14)$$

where $\mu_{25}(\tau)$ is the viscosity at time τ , and the denominator ($\mu_{25}(0)$) the original viscosity (all viscosities are measured at 25°C). The same comparison is used for normalising the sulphur content (S_N) which is derived from the sulphur mass fraction from the elemental analyser.

$$S_N = \frac{S(\tau)}{S(0)} \quad (15)$$

$S(\tau)$ is the sulphur content at a certain process time and S_0 the original sulphur content.

A first order cracking mechanism is used to derive the form of the exponential decay of the viscosity in the experiments. Any viscosity reduction treatment of a heavy oil with viscosity μ_h leads to a product mixture of viscosity μ_m . This is a mixture of viscosities of the uncracked oil, μ_h along with that of a cracked lighter fraction, μ_l . Because both mixtures consist of similar organic molecules of comparable polarizability, one can assume that the viscosities blend linearly

$$\mu_m = \mu_h x_h + \mu_l x_l \quad (16)$$

Every cracked heavy molecule leads to 2 light molecules



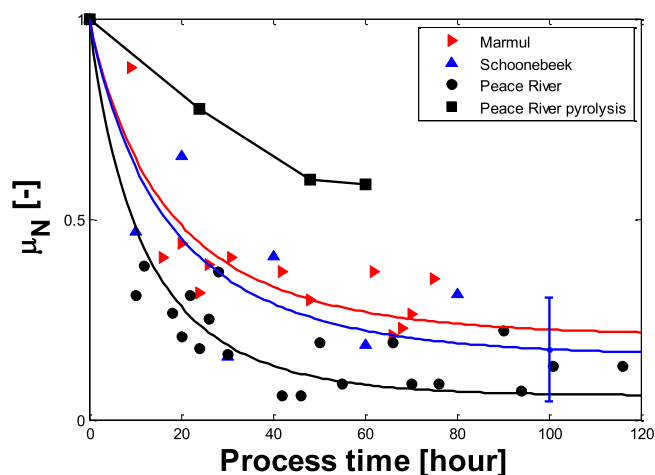
Suppose the reaction is stopped after time τ . Then the reaction mixture has a heavy fraction x_h and a light fraction x_l . The total number of molecules changes during the reaction so that the conversion is difficult to define in terms of mole fractions – so volume concentrations are used since the volume remains constant.

First the concentration of heavy reactant remaining is calculated along with the light fraction of product formed after the process has run for a time τ . This then yields the dimensionless viscosity of the mixture. The conversion is the fraction of initially present molecules of heavy oil N_h which have been cracked. In terms of number concentration ($c = N/V$) this conversion is

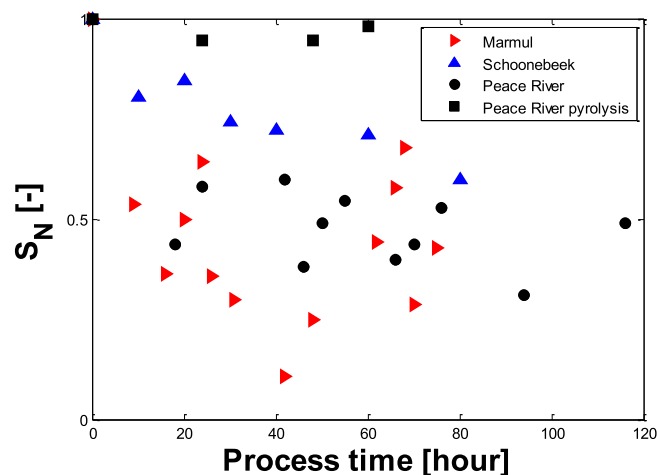
$$X = \frac{c_{0h} - c_h}{c_{0h}} \quad (18)$$

Since $1-X$ molecules have reacted, then based on eq. (17) there are $2X$ molecules of reactant.

The mole fractions in the final mixture are then given by



(a)



(b)

Fig. 4. Effect of SCW processing of various heavy oil samples on (a) viscosity and (b) sulphur content. Results of pyrolysis processing are shown as reference. (in colour). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

$$x_h = \frac{1 - X}{1 + X}; \quad x_l = \frac{2X}{1 + X} \quad (19)$$

A first order reaction corresponds to a concentration of heavies at any time given by

$$c_h = c_{h0} e^{-k\tau} \quad (20)$$

where c_{h0} is the initial concentration of the heavy component (In mole fraction terms of course by definition $x_{h0} = 1$). By inserting eq. (20) into eq. (18) the conversion X is given by

$$X = 1 - e^{-k\tau} \quad (21)$$

Inserting eq. (21) into eq. (19) gives

$$x_h = \frac{e^{-k\tau}}{2 - e^{-k\tau}} \text{ and } x_l = \frac{2 - 2e^{-k\tau}}{2 - e^{-k\tau}} \quad (22)$$

It then remains to insert eq. (22) into eq. (16), to yield the time response of the viscosity of the mixture given by

$$\mu_m(\tau) = \frac{\mu_h e^{-k\tau} + \mu_l (2 - 2e^{-k\tau})}{2 - e^{-k\tau}} \quad (23)$$

If no cracking has taken place ($X = 0$), the viscosity of the mixture is equal to the viscosity of the pure feed μ_h . After long exposure to subcritical conditions (process time is infinite) the conversion approaches the asymptotic viscosity μ_l . When $X = 1$, the infinite time viscosity is equal to μ_l as seen from eq. (23)

$$\mu_m(0) = \mu_h; \quad \mu_m(\infty) = \mu_l \quad (24)$$

Generalising eq. (23) using eq. (14) one obtains

$$\mu_{mN}(\tau) = \frac{e^{-k\tau}}{2 - e^{-k\tau}} + \frac{\mu_l (2 - 2e^{-k\tau})}{\mu_h (2 - e^{-k\tau})} \quad (25)$$

The asymptotic limiting (normalised) viscosity is given by μ_l/μ_h at large time.

Applying this model, Fig. 4a shows the feedstocks fitted to the form of eq. (25) (see Table 2 for parameter fits). The time constant k is approximately the same, but the extent of cracking (μ_l/μ_h) to light components is much more for Peace River than for the other feeds – the cracked product viscosity is 6% of the initial value – possibly due to the easier solubility and crackability of the heavier feeds.

While the viscosity reduction time is thus quite similar for all samples, the concurrent sulphur reduction (Fig. 4b) in the heavy oil samples does not display such a clear trend. For the pyrolysis process of

Table 2

Initial viscosity, reaction times, extent of viscosity reduction and fit parameters for 3 feeds.

Sample	μ_h (Pa s)	k [hr^{-1}]	μ_l/μ_h [-]	R^2 [-]
Peace River	67.7	0.05	0.06	0.83
Schoonebeek	3.2	0.03	0.16	0.74
Marmul	0.57	0.03	0.21	0.85

Peace River, there is no change in sulphur content indicating that cracking in and of itself is not enough to attain this. The Schoonebeek feed showed some slight consistent decrease but the values for the other feeds are much more scattered and do not show any exponential decay – typical end values are in the band 30–60%. The values for each feed are fully distributed all over this range so the feeds cannot be differentiated. For both viscosity and sulphur, there are thus correlated and less well correlated drops respectively during subcritical water treatment. This suggests that the mechanism behind the viscosity reduction might be linked to hetero bond cleavage (C–S–C) – a mechanism validated elsewhere (Caniaz and Erkey, 2014; Kamimura et al., 1998). As mentioned in the experimental section, H_2S is vented during the process and this could be a source of the fluctuating values of sulphur observed in the product. H_2S formed near the gas vent is more likely to be lost whereas H_2S formed far away from the vent has more chance of being reabsorbed in the reaction mixtures. This also suggests cleavage of sulphur bonds – see 4.2.1 below for further discussion of this.

The subcritical water process is more effective for lowering viscosity and sulphur content compared to the pure pyrolysis process. Given that temperature, pressure and reaction time were kept constant in all experiments, the superior performance of the SCW process could be attributed to the higher H^+/OH^- concentrations which are not present during pyrolysis. Further evidence to this effect will be presented in the later NMR section.

4.2. SCW mechanism

In order to check our model assumptions and further understand the viscosity reductions, we carried out a range of extensive analyses of the products obtained from cracking Peace River feed. This was chosen because it yielded the largest viscosity decrease (Table 2).

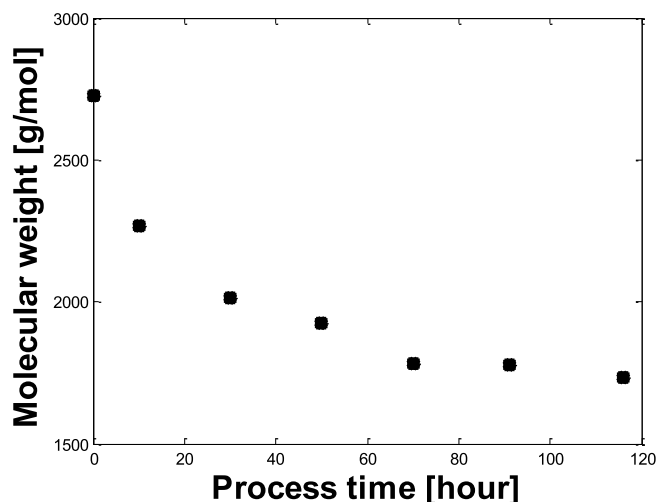


Fig. 5. Mean molecular weight as function of process time for different processed samples of Peace River oil.

4.2.1. Mean molecular weight

As is clear from Fig. 4a, a significant part of the reduction in viscosity appears to be a result not so much of pure thermally induced (i.e., pyrolytic) cracking, but rather for the greater part of chemistry specific to the SCW process. As already noted, in the first order cracking reaction model, the decay constant (k) of the viscosity is more or less same for all the observed oil samples (Table 2). The mechanisms will be similar - namely, both C–S and C–C covalent bonds are cleaved, resulting in lower average molecular weights and associated drops in viscosity. To validate whether or not this mechanism also applies to the PR sample, Fig. 5 shows how the mean molecular weight of Peace River feed changes as a function of process time. Fig. 6 shows that viscosity correlates quite well with mean molecular weight.

4.2.2. Volatility

Further evidence that cracking has indeed occurred as a result of SCW, can be found in the apparent change in volatility. Analysis using thermogravimetric analysis (TGA) shows that the fraction that evaporates below 350 °C increases. 350 °C is taken as the reference point because it is close to the pyrolysis boundary. The fraction that is evaporated at 350 °C is denoted by $E(350)$ – analogous to the parameter in distillation. The fraction that remains solid at 350 °C is then defined by $S(350) = 1 - E(350)$. For the unprocessed feed, $S(350)$ is about 70%.

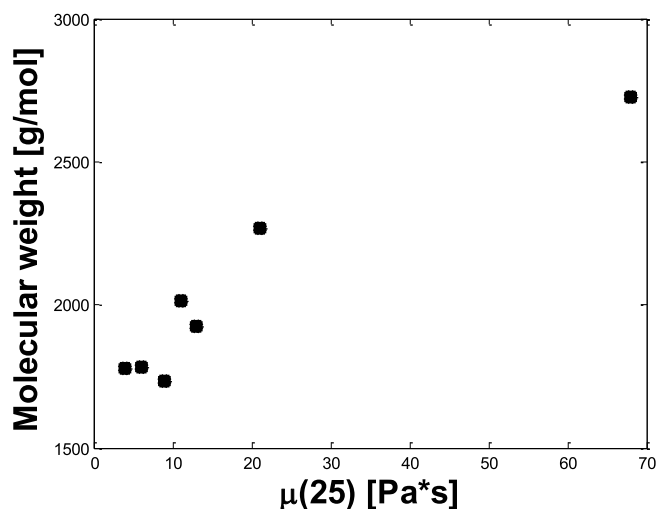


Fig. 6. Mean molecular weight as function of viscosity for different processed samples of Peace River oil.

However from a processing time of 24 h onwards, $S(350)$ is more or less constant at 57%. This means that the 13% transfer of oil content to the lower boiling range has resulted from the subcritical water processing. This value appears to be more or less constant irrespective of the reaction time above 24 h – so most of the cracking has happened beforehand.

4.2.3. NMR

A more sophisticated method to ascertain the SCW cracking mechanism is NMR. A ^1H NMR analysis identifies which bond types are present in the heavy oil sample and oil product. From the raw NMR results, there are two regions of interest, namely the peaks marking CH_2 (δ shift 1.5–1.2 ppm) and CH_3 (δ shift 1.2–0 ppm) groups. These regions are integrated: the amount of CH_2 (I_β) indicates the uninterrupted sequence between any branching points. The integrated value of CH_3 (I_α) shows the number of alkane chain terminations. These numbers do not mean anything in themselves – but their ratio (I_β/I_α) tells us the average ratio of CH_2/CH_3 in the sample. A representation of the average unbranched segment length (N), is given by

$$N = \left(\frac{1.5 I_\beta}{I_\alpha} \right) + 1 \quad (26)$$

where I_α is the intensity of the three methyl protons and I_β is the total intensity of the methylene bridge protons (note, 1.5 derives from the difference in protons, the factor “+1” is the alkyl end group) (Speight et al., 2011). It is thus not a measure of the total carbon length of the molecule but of the average unbranched segment length. This ignores here the presence of sulphur, alkene and aromatics effects.

The original PR sample was analysed, along with four processed PR oils. The original crude oil has an average unbranched segment length of 3.0. The processed samples (process time greater than 24 h) have an average unbranched segment length of about 2.4. This correlates nicely with the findings of $S(350)$ mentioned above (i.e. increased volatility after 24 h). The observed reduction in N could result from chain branching, breaking or a combination thereof. Fig. 7 resolves this uncertainty - a lower N clearly and consistently coincides with a reduced mean molecular weight. This correlation rules out isomerization which merely generates branched isomers of a molecule where cracking does occur but is followed by reattachment of the branched components at different molecular positions so that the original molecule is re-generated but as a different isomer. This would have yielded a flat trend in the same figure.

Thus if chain breaking is the main source of the measured increase of CH_3 over CH_2 groups, then a hydrogen source, apart from the PR

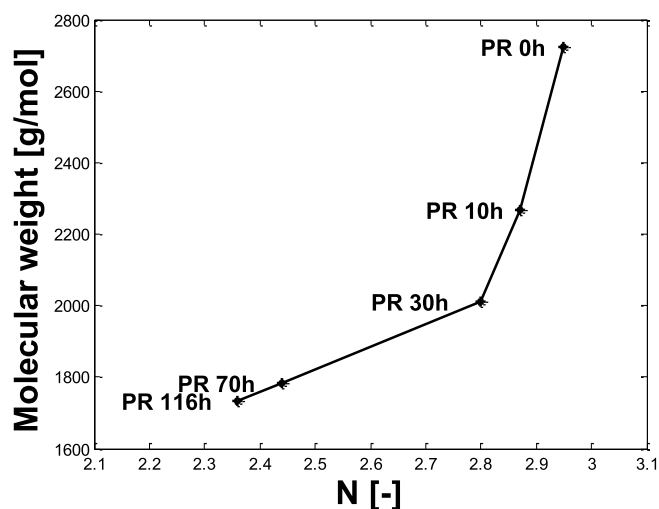


Fig. 7. Molecular weight as function of the average unbranched segment length for processed samples of Peace River.

sample itself, is required. Under pyrolytic conditions only ions are generated. However under subcritical water conditions, significant quantities of hydrogen ions are present. (Akiya and Savage, 2002; Hageman et al., 1996; Hata et al., 2008; Patrick et al., 2001; Ryan et al., 1997; Watchararujji et al., 2008). This could explain why cracking can occur, maintaining paraffins – avoiding gummy olefins – and thus reducing viscosity.

5. Conclusions

1. Subcritical water (SCW) heavy oil processing was compared to the more classical steam recovery approach. The former consumes roughly 60% less energy per unit of oil recovered than the latter. Moreover, as will be elaborated on below, SCW processing requires less post-processing operations.
2. Whereas steam recovery strips off a light portion of the oil in place, SCW yields a permanent viscosity reduction of up to 80% for all oil processed after some 24 h.
3. Contrary to steam recovery, SCW treatment reduces sulphur content in different heavy oils by up to 40%.
4. The SCW induced viscosity reduction correlates well with reductions in sulphur content, average molecular weight and an increase in volatility. NMR measurements also show a reduction of around 20% in average unbranched segment length – probably paraffinic chains. This all suggests that the heavy oil is being cracked.
5. SCW treatment results in the formation of H₂S, which suggests that not only C–C, but also C–S or C–S–C bonds are cleaved.
6. In order to discern between thermal cracking and that induced by the hydroxyl and hydrogen ions that are characteristic to SCW, a pyrolysis experiment was carried out under similar process conditions. There is no H₂S generation and a viscosity reduction of only 22% is observed, where the viscosity using SCW is reduced by about 70% at similar conditions.
7. These combined observations suggest that the superior viscosity and sulphur reductions seen for SCW processing vis-à-vis pyrolysis owe much to the presence of hydroxyl and hydrogen ions in the former.
8. This paper generalizes analytical results from the heaviest oil sample which was selected because of the relatively large viscosity reduction observed. Different crude oils can have different compositions (saturates, aromatics, resins and asphaltenes etc.) This means that the generalisation from one feed needs to be treated with some care.

Acknowledgements

We gratefully acknowledge the funding provided by Shell Global Solutions International BV under grant No. PT 13670.

Abbreviations/symbols

EOR	Enhanced oil recovery
(X)HO	(extra) Heavy oil
CSS	Cyclic steam stimulation
HV	Heating value
LO	Light oil
MM	Marmul
PR	Peace River
SAGD	Steam assisted gravity drainage
SB	Schoonebeek
SCW	Subcritical water
SD	Steam drive
WOR	Water oil ratio
c	concentration
C _p	Specific heat constant
E	Evaporation
I	Intensity
k	Rate of time

K _w	Dissociation constant
L	Latent heat of vaporisation
m	Mass of oil
m _w	Molecular weight
N	Average unbranched segment length
Q _i	Energy invested
Q _p	Energy produced
R	Recovery factor
T	Temperature
V	Volume of oil
x	Fraction of feed
X	Conversion of heavy feed
ε	Energy gain factor
μ	Viscosity
τ	Process time
σ _x	Standard deviation

References

- Adams, H., Khan, A.M., 1969. Cyclic steam injection project performance analysis and some results of a continuous steam displacement pilot. *J. Petrol. Technol.* 21, 95–100.
- Akiya, N., Savage, P.E., 2002. Roles of water for chemical reactions in high-temperature water. *Chem. Rev.* 102, 2725–2750. <https://doi.org/10.1021/cr000668w>.
- Alenezi, R., Leeke, G.A., Santos, R.C.D., Khan, A.R., 2009. Hydrolysis kinetics of sunflower oil under subcritical water conditions. *Chem. Eng. Res. Des.* 87, 867–873. <https://doi.org/10.1016/j.cherd.2008.12.009>.
- Alvarado, V., Manrique, E., 2010. Enhanced oil recovery: an update review. *Energies* 3, 1529–1575. <https://doi.org/10.3390/en3091529>.
- Bicker, M., Endres, S., Ott, L., Vogel, H., 2005. Catalytic conversion of carbohydrates in subcritical water: a new chemical process for lactic acid production. *J. Mol. Catal. Chem.* 239, 151–157. <https://doi.org/10.1016/j.molcata.2005.06.017>.
- Camaz, R.O., Erkey, C., 2014. Process intensification for heavy oil upgrading using supercritical water. *Chem. Eng. Res. Des.* 92, 1845–1863. <https://doi.org/10.1016/j.cherd.2014.06.007>.
- Chen, Q., 2009. Assessing and Improving Steam-assisted Gravity Drainage: Reservoir Heterogeneities, Hydraulic Fractures, and Mobility Control Foams.
- Cram, P., Redford, D., 1976. Thermal recovery of hydrocarbons from tar sands. *US Pat* 3 993,132.
- Cuijpers, M.C.M., Boot, M.D., Golombok, M., 2017. Enhanced viscosity reduction in heavy oils by subcritical water. *J. Pet. Explor. Prod. Technol.* <https://doi.org/10.1007/s13202-017-0370-y>.
- Demirbas, A., 2016. Sulfur removal from crude oil using supercritical water. *Petrol. Sci. Technol.* 34, 622–626. <https://doi.org/10.1080/10916466.2016.1154871>.
- Demirbaş, A., 1999. Sulfur removal from coal by oxydesulfurization using alkaline solution from wood ash. *Energy Convers. Manag.* 40, 1815–1824. [https://doi.org/10.1016/S0196-8904\(99\)00075-8](https://doi.org/10.1016/S0196-8904(99)00075-8).
- Duan, P., Xu, Y., Bai, X., 2013. Upgrading of crude duckweed bio-oil in subcritical water. *Energy Fuels* 27, 4729–4738. <https://doi.org/10.1021/ef4009168>.
- Fanchi, J.R., Christiansen, R.L., 2017. *Introduction to Petroleum Engineering*. Wiley, Hoboken NJ.
- Giacchetta, G., Leporini, M., Marchetti, B., 2015. Economic and environmental analysis of a Steam Assisted Gravity Drainage (SAGD) facility for oil recovery from Canadian oil sands. *Appl. Energy* 142, 1–9. <https://doi.org/10.1016/j.apenergy.2014.12.057>.
- Golombok, M., Ineke, E., 2013. Oil mobilisation by subcritical water processing. *J. Pet. Explor. Prod. Technol.* 3, 255–263. <https://doi.org/10.1007/s13202-013-0066-x>.
- Goto, M., Obuchi, R., Hirose, T., Sakaki, T., Shibata, M., 2004. Hydrothermal conversion of municipal organic waste into resources. *Bioresour. Technol.* 93, 279–284. <https://doi.org/10.1016/j.biortech.2003.11.017>.
- Gustavson, J.B., 1999. Valuation of international oil and gas properties, SPE 5957. In: *SPE Symp. Hydrocarb. Econ. Eval. SPE Richardson TX*.
- Hageman, K.J., Mazeas, L., Grabanski, C.B., Miller, D.J., Hawthorne, S.B., 1996. Coupled subcritical water extraction with solid-phase microextraction for determining semi-volatile organics in environmental solids. *Anal. Chem.* 68, 3892–3898. <https://doi.org/10.1021/ac960751c>.
- Hata, S., Wiboonsirikul, J., Maeda, A., 2008. Extraction of Defatted rice Bran by Subcritical Water Treatment, vol. 40. pp. 44–53. <https://doi.org/10.1016/j.bej.2007.11.016>.
- Isa, K.M., Snape, C.E., Uguna, C., Meredith, W., Deng, H., 2015. Pyrolysis oil upgrading in high conversions using sub- and supercritical water above 400°C. *J. Anal. Appl. Pyrolysis* 119, 180–188. <https://doi.org/10.1016/j.jaap.2016.03.004>.
- Kamimura, H., Takahashi, S., Kishita, A., ChengXie, H., Enomoto, H., 1998. Upgrading of bitumen with supercritical water for a system combined with sagd. *Abstr. Pap. Am. Chem. Soc.* 216 U879–U879.
- Kishita, A., Takahashi, S., Jin, F., Yamasaki, Y., Moriya, T., Enomoto, H., 2005. Decomposition of benzothiophene, dibenzothiophene, and their derivatives in subcritical and supercritical water with alkali. *J. Japan Pet. Inst.* 48, 272–280. <https://doi.org/10.1627/jpi.48.272>.
- Miller, D.J., Hawthorne, S.B., Gizir, A.M., Clifford, A.A., 1998. Solubility of polycyclic aromatic hydrocarbons in subcritical water from 298 K to 498 K. *J. Chem. Eng. Data* 43, 1043–1047. <https://doi.org/10.1021/je980094g>.

- Miller, J.D., Misra, M., 1982. Hot water process development for Utah tar sands. *Fuel Process. Technol.* 6, 27–59. [https://doi.org/10.1016/0378-3820\(82\)90038-8](https://doi.org/10.1016/0378-3820(82)90038-8).
- Oliveira, E.L.G., Silvestre, A.J.D., Silva, C.M., 2011. Review of kinetic models for supercritical fluid extraction. *Chem. Eng. Res. Des.* 89, 1104–1117. <https://doi.org/10.1016/j.cherd.2010.10.025>.
- Onwudili, J.A., Williams, P.T., 2014. Catalytic depolymerization of alkali lignin in subcritical water: influence of formic acid and Pd/C catalyst on the yields of liquid monomeric aromatic products. *Green Chem.* 16, 4740–4748. <https://doi.org/10.1039/C4GC00854E>.
- Patrick, H.R., Griffith, K., Liotta, C.L., Ckert, C., Glaser, R., 2001. Near-critical water: a benign medium for catalytic reactions. *Ind. Eng. Chem. Res.* 40, 6063–6067. <https://doi.org/10.1021/ie010178+>.
- Ramos, L., Kristenson, E.M., Brinkman, U.T., 2002. Current use of pressurised liquid extraction and subcritical water extraction in environmental analysis. *J. Chromatogr. A* 975, 3–29. [https://doi.org/10.1016/S0021-9673\(02\)01336-5](https://doi.org/10.1016/S0021-9673(02)01336-5).
- Ryan, E.T., Xiang, T., Johnston, K.P., Fox, M.A., 1997. Absorption and fluorescence studies of acridine in subcritical and supercritical water. *J. Phys. Chem.* 101, 1827–1835. <https://doi.org/10.1021/jp962676f>.
- Santos, R.G., Loh, W., Bannwart, A.C., Trevisan, O.V., 2014. An overview of heavy oil properties and its recovery and transportation methods. *Braz. J. Chem. Eng.* 31, 571–590. <https://doi.org/10.1590/0104-6632.20140313s00001853>.
- Shu, W.R., Hartman, K.J., 1986. Thermal visbreaking of heavy oil during steam recovery processes. *Soc. Pet. Eng.* 474–482. <https://doi.org/10.2118/12783-PA>.
- Speight, R.J., Rourke, J.P., Wong, A., Barrow, N.S., Ellis, P.R., Bishop, P.T., Smith, M.E., 2011. 1H and 13C solution- and solid-state NMR investigation into wax products from the Fischer–Tropsch process. *Solid State Nucl. Magn. Reson.* 39, 58–64. <https://doi.org/10.1016/j.ssnmr.2011.03.008>.
- Thomas, S., 2008. Enhanced oil recovery - an overview. *Oil Gas Sci. Technol. - Rev. IFP* 63, 9–19. <https://doi.org/10.2516/ogst:2007060>.
- Timko, M.T., Ghoniem, A.F., Green, W.H., 2015. Upgrading and desulfurization of heavy oils by supercritical water. *J. Supercrit. Fluids* 96, 114–123. <https://doi.org/10.1016/j.supflu.2014.09.015>.
- Van Dijk, C., 1968. Steam-drive project in the Schoonebeek field, The Netherlands. *J. Petrol. Technol.* 20, 295–302.
- Watchararужи, K., Goto, M., Sasaki, M., Shotipruk, A., 2008. Value-added Subcritical Water Hydrolysate from rice Bran and Soybean Meal, vol. 99. pp. 6207–6213. <https://doi.org/10.1016/j.biortech.2007.12.021>.
- Yang, Y., Belghazi, M., Lagadec, A., Miller, D.J., Hawthorne, S.B., 1998. Elution of organic solutes from different polarity sorbents using subcritical water. *J. Chromatogr. A* 810, 149–159. [https://doi.org/10.1016/S0021-9673\(98\)00222-2](https://doi.org/10.1016/S0021-9673(98)00222-2).