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Minimising hydrogen sulphide generation during steam assisted production of heavy oil

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The majority of global petroleum is in the form of highly viscous heavy oil. Traditionally heavy oil in sands at shallow depths is accessed by large scale mining activities. Recently steam has been used to allow heavy oil extraction with greatly reduced surface disturbance. However, in situ thermal recovery processes can generate hydrogen sulphide, high levels of which are toxic to humans and corrosive to equipment. Avoiding hydrogen sulphide production is the best possible mitigation strategy. Here we use laboratory aquathermolysis to reproduce conditions that may be experienced during thermal extraction. The results indicate that hydrogen sulphide generation occurs within a specific temperature and pressure window and corresponds to chemical and physical changes in the oil. Asphaltenes are identified as the major source of sulphur. Our findings reveal that for high sulphur heavy oils, the generation of hydrogen sulphide during steam assisted thermal recovery is minimal if temperature and pressure are maintained within specific criteria. This strict pressure and temperature dependence of hydrogen sulphide release can allow access to the world's most voluminous oil deposits without generating excessive amounts of this unwanted gas product.

Heavy oil represents the majority of petroleum on Earth with seven trillion barrels of resources in place. Major reserves of heavy oil exist within deposits of unconsolidated sand and clay. For example, the oil sands of Alberta, Canada, represent a staggering resource of 1.8 trillion barrels[1]. Initially, those reservoirs with a depth of less than 70 meters were accessed by straightforward mining[2]. Oil sands at depths greater than 70 meters cannot be economically developed by surface mining, and other recovery methods are needed. Using Alberta, Canada, as an example once more, 750 million barrels were recovered by steam assisted in situ methods in 2012 and production from in situ methods is expected to double by 2022[1]. The most popular variant of thermal in situ recovery is steam assisted gravity drainage[3] which uses an injection well to produce a steam saturated zone. The oil is heated and its viscosity reduced to promote flow. A second, lower, producer well collects the mobilized oil which is then pumped to the surface.

Gas generation due to thermally driven reactions is a recognized challenge during steam assisted in situ recovery of high sulphur heavy oils including that in the Alberta oil sands. Sulphur-rich organic matter is notoriously chemically reactive[4] and can lead to the release of hydrogen sulphide following treatment with steam. Many heavy oils are tainted by high sulphur contents (>2 w%[5]) owing to the concentration and generation of organic sulphur compounds during biodegradation[6]. Capture of the hydrogen sulphide produced during steam recovery is necessary. Owing to the large economic penalties of overestimating or underestimating sulphur production, accurate appraisals increase operational efficiency.

Here we investigate the chemistry, temperature and pressure dependence on gas production occurring during steam assisted recovery. We have used laboratory aquathermolysis to simulate subsurface conditions and monitor the change in product composition. A quantitative approach, with recovery and analysis of gas, water soluble organic compounds, liquid oil, asphaltene and mineral matrix adsorbed residue, allows the recognition of material transfer between solubility and volatility fractions.

Results

Our aquathermolysis experimental products were comprehensively analysed using preparative chromatography, FTIR spectroscopy, gas chromatography-flame photometric detection, gas chromatography-mass spectrometry
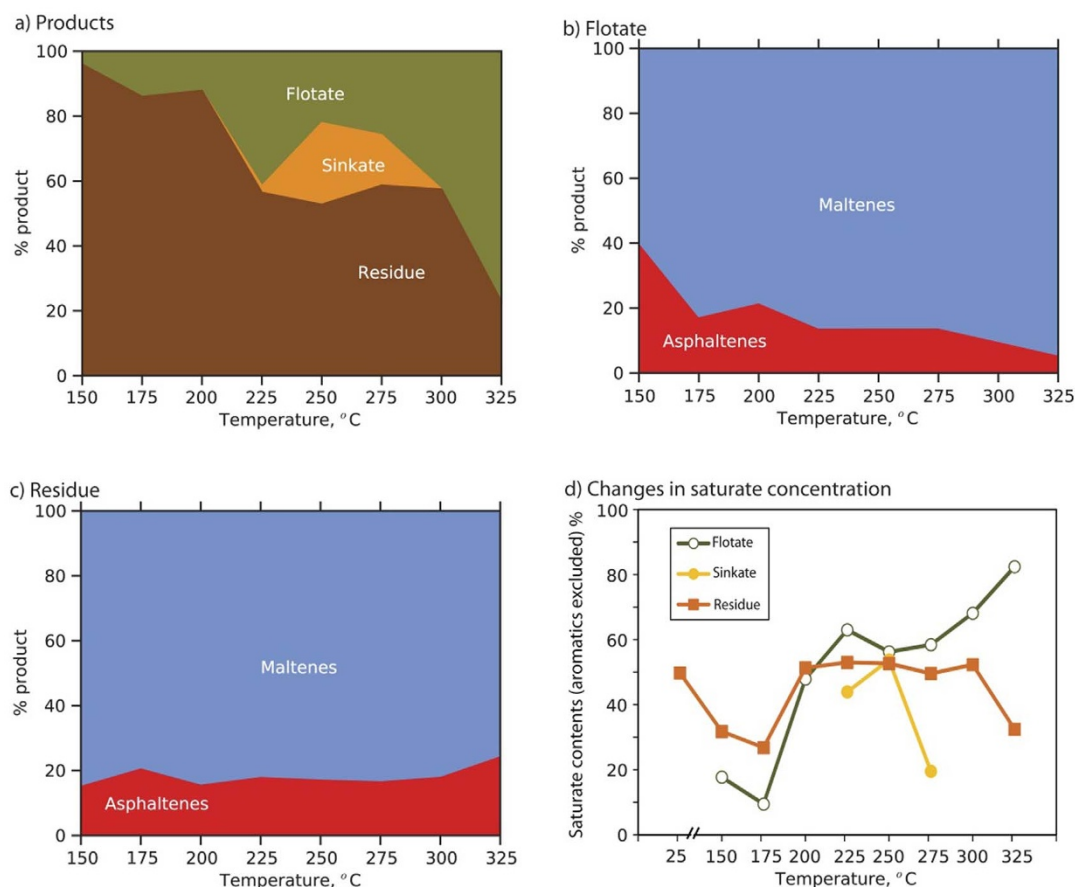
Figure 1 | (a) relative proportions of flotate, sinkate and residue, (b) relative proportions of maltenes and asphaltenes in the flotate, (c) relative proportions of maltenes and asphaltenes in the residue, (d) Changes in saturate concentration for the experimental products expressed as saturates/ (saturates + resins + asphaltenes) × 100. Aromatic hydrocarbons change little during aquathermolysis, consistent with published work[12], and so have been excluded. (See the Supplementary Information for details).

and pyrolysis-gas chromatography-mass spectrometry. Our data correspond to the following temperature and pressure intervals: 150°C (<690 kPa; <100 psig), 175°C (<690 kPa; <100 psig), 200°C (1030 kPa; 150 psig), 225°C (2760 kPa; 400 psig), 250°C (4140 kPa; 600 psig), 275°C (5520 kPa; 800 psig), 300°C (8620 kPa; 1250 psig) and 325°C (12070 kPa; 1750 psig). Each temperature and pressure combination represents a unique experiment run for 24 hours. The duration was chosen so as to avoid the short term (<12 hrs) kinetic effects which have been previously documented for similar oil sand samples[7–9] and to access the steady state chemistry of the system. Experimental pressure is a result of the volume increase of water and other fluids present and is read from a dedicated pressure gauge. For simplicity each experiment will be referred to hereafter using only its temperature. Our study uses a sulphur-rich oil sand from Canada as a typically problematic resource (discussed in Supplementary Fig. S1). The Alberta oil sands deposit in western Canada contains over 1.8 trillion barrels of heavy oil in Lower Cretaceous Mannville Group sands at typical depths of <100–500 m. In situ thermal methods are particularly appropriate for the Canadian oil sands because 80% are too deep to be accessed by mining[7]. The sulphur-rich nature of the oil suggests a source dominated by the Carboniferous Exshaw Formation in the eastern portion of the deposit and Jurassic Gordondale Member in the west[10–11]. Our oil sand came from the north east of the region and contained 18.5% extractable organic matter. The solvent-extracted oil had the following characteristics: C = 82.5%; H = 10.0%; N = 0.4%; S = 5.34%; saturates = 29.6%; aromatics = 40.5%; resins = 10.6%; asphaltenes = 19.3%.

Physical and chemical fractions. Our data set (Figure 1) allows us to define a number of physical products observable following aquathermolysis experiments. Gas is generated in the reactor headspace, flotate is a light oil that floats on the surface of the water, sinkate is a heavier oil that sinks in the water and residue is an oil that coats mineral surfaces. The relative abundances in the three liquid products in each of the experiments are displayed in Figure 1a.

There is evidence that the physical properties of the products are controlled by their chemical constitution. Each of the recovered products can be separated into the relatively high molecular weight asphaltenes and lower molecular weight maltenes (Figure 1b, c). Division of the maltenes into saturate, aromatic and resin fractions (Figure 1d) completes "SARA" analysis. (Data provided in Supplementary Tables S1a–d). The relative abundances of SARA fractions within the flotates, sinkates and residues are different and vary with changing temperature and pressure of aquathermolysis. Some patterns exist and aromatic hydrocarbons change little during aquathermolysis[12] and can be considered relatively constant: resins and asphaltenes display similar trends with temperature and pressure and can be summed into a single fraction. Chemical variations can, therefore, be expressed simply as saturates/(saturates + resins + asphaltenes) × 100 (Figure 1d; Supplementary Table S1d).

The flotate first appears in the 150°C experiment and its abundance then increases with experimental temperature (Figure 1a). The chemistry of the flotate changes with temperature and its asphaltene content decreases (Figure 1b) to produce an increasingly lighter and less viscous oil. Aquathermolysis treatment up to 325°C progressively reduces viscosity in the flotate from 1105 Pa*s to 1.5 Pa*s

(numerical details are provided in Supplementary Table S2). Examination of the chemical fractions within the flotate reveals that the flotate maltenes become more saturate rich with temperature and pressure (Figure 1b) implying that hydrocarbons are being introduced from degradation of the functionalised resin or high molecular weight asphaltene structures. FTIR data of all fractions support these interpretations and are available in the Supplementary Fig. S2.

A sinkate joins the flotate in experiments carried out above 225°C (Figure 1a) and a divergence in chemical composition begins, with the flotate becoming more saturate rich and the sinkate becoming more resin and asphaltene rich (Figure 1d). The chemical dichotomy which appears to maintain the two phases disappears above 275°C. The saturated compounds appearing in the flotate must be derived from a reservoir within the resins and asphaltenes which becomes exhausted above 275°C. In the context of in situ steam assisted production the appearance of a two-phase liquid between 225°C and 300°C driven by thermally induced chemical changes in the oil may affect fluid flow characteristics in the reservoir with each phase being capable of movement at different rates.

Our chemical composition data reveal that there is a notable difference in susceptibility to chemical change for oil coating mineral surfaces relative to that free in the experimental products. While the chemical composition of the flotate and sinkate begins to vary in experiments above 225°C, the residue appears to resist chemical change (Figure 1 c, d). Between 200°C and 300°C the relative abundance of maltenes relative to asphaltenes and the saturates/ (saturates + resins + asphaltenes) × 100 values for the residue are relatively constant. In terms of heat energy, the protective effects of mineral scaffolding equates to a differential of 75°C, highlighting the importance of geological and mineralogical context in oil sand reservoirs.

Hydrogen Sulphide Production. Aquathermolysis also leads to significant changes in headspace gas composition. Hydrogen sulphide is quantifiable by gas chromatography-flame photometric detection at experimental temperatures above 200°C. Notably the onset of hydrogen sulphide generation directly precedes the temperature at which a loss of resins and asphaltenes begins and at which there is a divergence in the saturate contents of the flotate and sinkate (Figures 1d & 2). The correlation implies an origin for hydrogen sulphide by the degradation of sulphur-containing units in the resin or asphaltene fractions.

Comprehensive analysis of headspace gas is achieved by gas chromatography-mass spectrometry (Figures 2 and 3a). Hydrogen sulphide increases markedly with experimental temperatures above 200°C and is accompanied by the generation of methane and C_2 to C_6 saturated hydrocarbons (ethane, propane, butane and hexane). The presence of C_2 to C_6 saturated hydrocarbons is commonly interpreted as evidence of the thermal degradation of higher molecular weight organic matter, supporting the proposal that hydrogen sulphide has an origin by the thermal dissociation of an organic fraction. At experimental temperatures at and above 300°C the responses of C_5 and C_6 diminish and the responses of shorter chain saturated hydrocarbons (C_1 and C_2) are enhanced, features which are in harmony with a greater number of bond breaking events occurring at higher temperatures.

A full appreciation of hydrogen sulphide generation during aquathermolysis requires identification of transformable sulphur in the starting materials. Inorganic sulphur is an unlikely source in an oil-stained sandstone, because sandstone rocks contain no sulphur-bearing minerals, leaving organic sources as the remaining possibility. The proposal that hydrogen sulphide is derived from thermal degradation of sulphur-containing organic units can be tested by subjecting the generated intermediate molecular weight hydrocarbon liquids to gas chromatography-mass spectrometry and the relatively high molecular weight asphaltenes to on-line pyrolysis gas
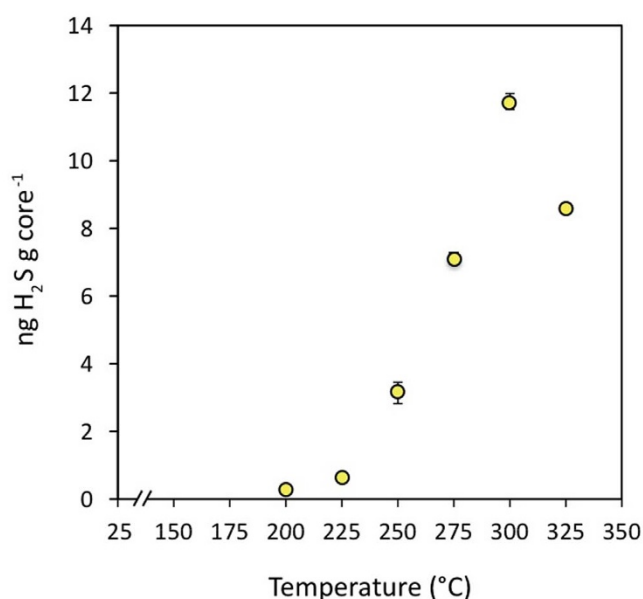

Figure 2 | Hydrogen sulphide produced by aquathermolysis of sulphur rich heavy oil. 300 and 325°C data points represent minimum values (see the Supplementary Information for details). Error bars are generated from the variation in multiple measurements on the gas produced from a single experiment.

chromatography-mass spectrometry (detailed analysis presented in Supplementary Fig. S3).

Organic sulphur is absent in the saturate fractions, limited in the resin fractions but clearly present in the aromatic and asphaltene fractions. Data from the flotate aromatic fraction are displayed in Figure 3b and data from on-line pyrolysis of asphaltenes are presented in Figure 3c. A number of products are present in the total ion current which can be filtered using partially reconstructed ion chromatograms (m/z = 147 + 161 + 198) to reveal the presence of thiophenes, benzo- and dibenzo- thiophenes (Figure 4). Specifically, the aromatic fractions of the flotates and residues generated in experiments at 275°C and above contain various benzo- and dibenzothiophenes. Complete lists of sulphur compounds in the flotates and residues are presented in Supplementary Table S4.

The asphaltene fractions of flotates and residues generated at all experimental temperatures contained a plethora of sulphur-bearing molecules including thiophenes, benzo- and dibenzo- thiophenes. The population of sulphur-bearing molecules in the asphaltene fraction did not vary greatly between flotate and residue, nor were there any trends observed in the size or composition of sulphur-bearing molecules with increasing experimental temperature. Full lists of sulphur compounds identified in the flash pyrolysates of flotates and resides of asphaltenes are presented in Supplementary Table S5.

Notably, while present in the asphaltene fraction of the flotate phase at all reaction temperatures, the sulphur-bearing compounds are present in the flotate phase only at temperatures at and above 275°C, coincident with the onset of peak hydrogen sulphide production observed in Figure 2. Hence it appears that sulphur-rich portions of the asphaltenes are degrading at and above 200°C to produce a relatively small amount of hydrogen sulphide gas; more extensive degradation at and above 275°C leads to the main phase of hydrogen sulphide release and the additional liberation of moderate molecular weight sulphur containing units which then pass into the liquid flotate.

Discussion

As the quantitatively dominant phase degrading during hydrogen sulphide production the asphaltene fraction should exert overall
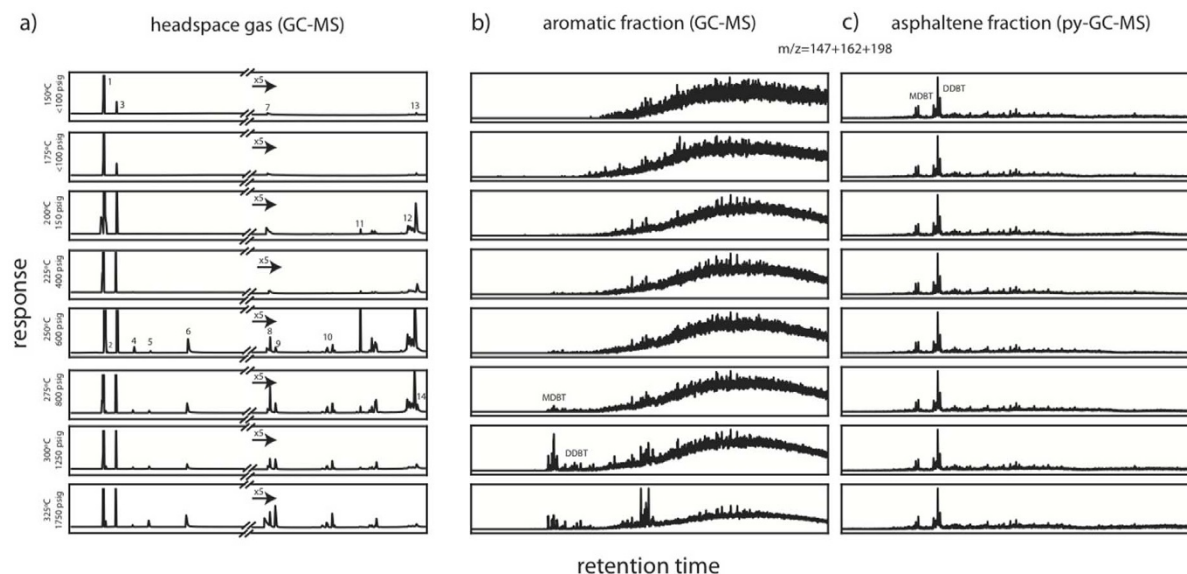
Figure 3 | (a) Total ion current of gas species generated by aquathermolysis of sulphur-rich heavy oil. (1) argon(from purge), (2) methane, (3) carbon dioxide, (4) ethylene, (5) ethane, (6) hydrogen sulphide, (7) water, (8) propene, (9) propane, (10) butene isomers, butane, (11) dichloromethane (DCM contamination), (12) pentane, (13) hexane, (14) benzene, alongside a comparison of selected ions (m/z = 147 + 162 + 198) from the (b) aromatic (GC-MS) and (c) asphaltene (py-GC-MS) fractions of the flotates. MDBT – methyldibenzothiophene, DDBT – dimethyldibenzothiophene. Full lists of sulphur compounds identified in the flotate and asphaltene flash pyrolysate are presented in Table S5.

control on headspace gas composition. Assessments of the ability of oils to produce deleterious sulphur gases should therefore focus on this relatively high molecular weight material. Pyrolysis gas chromatography-mass spectrometry of asphaltenes from a heavy oil will immediately indicate whether hydrogen sulphide generation at and above 200°C will occur.

The observation of physical separation into light saturate-rich and heavy asphaltene-rich oil phases and the relative unreactivity of the heavy residue suggests the possibility of in situ upgrading. The res-idue does not respond until the very highest temperature (325°C) and the saturate-rich flotate will be much more mobile that the relatively saturate-poor sinkate. The two free phases will flow at different rates allowing the selective recovery of lighter hydrocarbons that are more easy to handle and of higher economic value. There are also substantial economic benefits derived from leaving the less eco-nomic resins and asphaltenes behind in the reservoir related to the avoidance of extensive and expensive surface refining. Allowing a substantial part of the refining to occur in the reservoir also confers
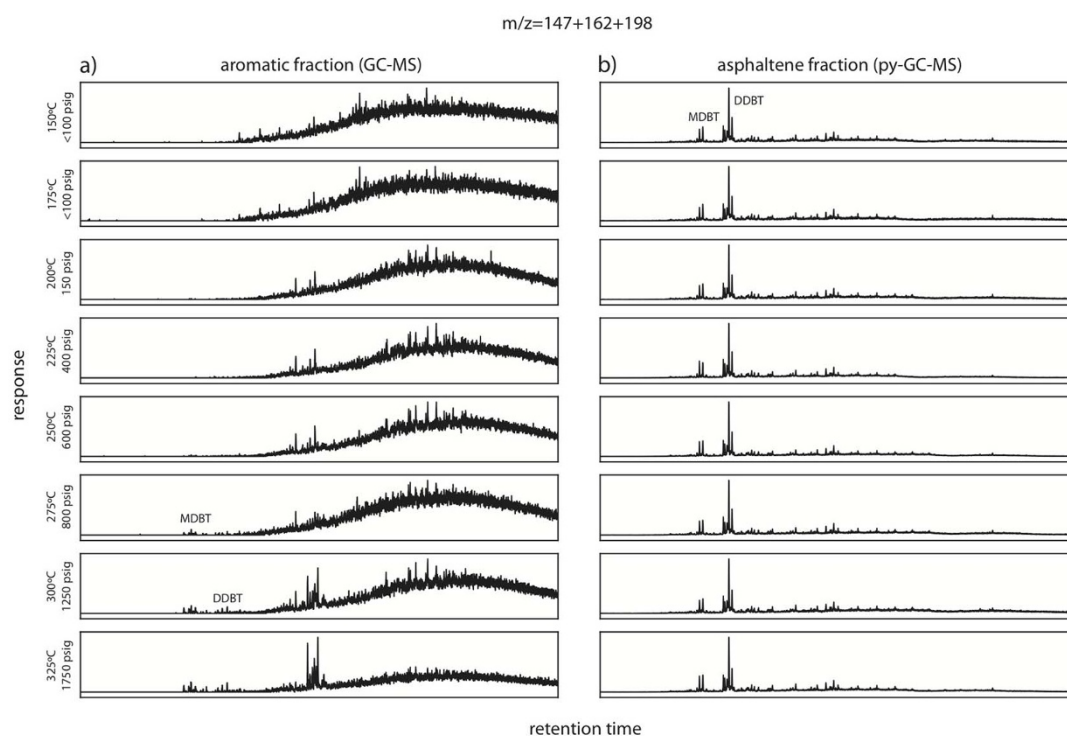

Figure 4 | **Comparison of selected ions from the (a) aromatic (GC-MS) and (b) asphaltene (py-GC-MS) fractions of the residues.** (Equivalent data for the flotate fraction is presented in Figure 3b and 3c. MDBT – methyldibenzothiophene, DDBT – dimethyldibenzothiophene

Table 1 | Experimental temperatures and corresponding pressures

Temperature, °C	150	175	200	225	250	275	300	325
Pressure (kPa)	<690	<690	1030	2760	4140	5520	8620	12070
Pressure (psig)	<100	<100	150	400	600	800	1250	1750

substantial environmental benefits. In the reservoir, the two phase oil generated by medium temperature (225°C to 300°C) aquathermolysis may be a characteristic of sulphur rich heavy oil which ensures the presence of resin and asphaltene structures that can be degraded at relatively low temperatures owing to the relative weakness of sulphur-containing bonds[4,12].

Our data reveal that reservoir heterogeneity may also be an important factor. The main source of sulphur is the asphaltene fraction. Asphaltenes and associated organic sulphur compounds are enhanced following biodegradation and this process can be highly variable depending on access to microbes, water and oxidants and the pasteurizing effects of reservoir temperature. An example of variation in biodegradation levels is provided by the Canadian oil sands in which biodegradation increases to the east and north within the oil sands deposit and anti-correlates with maturity in the region[13].

The quantification of hydrogen sulphide allows predictions to be made for the amounts of this gas released during steam assisted production. Significant hydrogen sulphide generation begins at 200°C and amounts become substantial above 250°C. Our data are in accord with that of previous laboratory aquathermolysis studies[14] that defined 200°C for the onset of hydrogen sulphide generation. Field data display a less precise agreement[15] but may reflect less well constrained subsurface conditions and chemistries relative to laboratory experiments. Notably, 200°C is above that normally associated with steam assisted gravity drainage, although local hot spots occur. Other thermal methods such as cyclic steam simulation do breach the 200°C threshold. It must be noted that our hydrogen sulphide values are specific to the heavy oil used in the experiments. Substantial natural variation in sulphur contents are expected. Yet, although total yields may vary the basic principles of gas production with temperature are widely applicable and it is clear that hydrogen sulphide generation can be avoided if temperatures in the reservoir are not allowed to exceed 200°C. If minimizing hydrogen sulphide gas production is not a priority, the in situ upgrading characteristics of medium temperature (225°C to 300°C) aquathermolysis can be exploited. As the two phases observed have differing densities, it may be possible to extract the saturate-rich flotate while leaving the more sulphurous sinkate behind.

Methods

Post experiment sampling. Once the experiment was complete and the reactor cooled, gases were extracted from the reactor headspace by releasing a needle gauge and allowing the gas to flow into a Tedlar collection bag with a septum. Gas was collected from this bag using a gas-tight syringe. The gas quantities in the syringe were scaled to reveal the total quantities in the reactor headspace. Following gas sampling, the reactor was opened and any oil floating on the surface of the water (the flotate) was transferred to a test tube using a polytetrafluoroethylene (PTFE)-coated spatula. To isolate any water-soluble organic matter, the water contents were pipetted from the vessel into test tubes, aided by rinsing with deionised water. If a layer of separated oil lay under the water but over the sediments, this was transferred to a test tube using a PTFE coated spatula. The remaining contents were transferred to the test tubes containing the water. These test tubes were centrifuged at 3000 rpm for 10 minutes to settle and combine any suspended fines with the solid residue, following which the supernatant was pipetted off. Two cycles of further addition of deionized water, centrifugation and pipetting followed. The separated water, containing the water-soluble fraction of the liquid water treatment products, was subjected to solid phase extraction (SPE). Then the solvent was allowed to evaporate to produce a water soluble oil fraction (the liquid-liquid extract). The residual oil still coating the sand was extracted with 93:7 dichloromethane/methanol (DCM/MeOH) by sonication for 15 minutes, followed by centrifugation and collection of the supernatant as described above. The remaining residual organic material was then extracted as above using toluene as the solvent. Any material remaining in the vessel is removed with 93:7 DCM/MeOH and any material resistant to that (cake) is removed using force.

Viscosity and elemental analysis. Rheological measurements were carried out using a Brookfield R/S Plus rheometer and analysed with RHEO3000 software. The flow curves were obtained by registering viscosity and shear stress at shear rates from 1 to 100 s^{-1}. Where possible, measurements were performed twice, at a temperature of 25°C ± 0.1. Determination of carbon, nitrogen and hydrogen was performed by the ASTM D5291 method where the sample is combusted in a pure oxygen environment and measured by Thermal Conductivity or IR. Measurement of sulphur was achieved by the ASTM D2622 method where the sample is placed in an X-ray beam and the peak intensity of the sulphur Kα line at 5.373 A is determined.

Aquathermolysis. For the oil sand extraction experiments, sulphur-rich (%) oil in a sand matrix was obtained from north eastern of the Alberta oil fields. Approximately 50 g of oil sand were added to a high pressure and temperature reactor (Model 4740, Parr Instruments). Using the measured reactor volume, 75 ml, calculated sample density, and the pressure required, the mass of water needed was determined and added. The remaining headspace within the reactor was purged with argon and the reactor was sealed and placed in an oven for 24 hours. Pressure was monitored throughout the experiment using a dedicated pressure gauge attached to the reactor. Aquathermolysis experiments were performed on samples of oil sands at 25°C intervals from 150–325°C and corresponding pressures ranging from 100–2000 psi (Table 1). The experimental approach has been previously proved successful for heavy oil samples[16].

Fractionation and quantitative analysis. Samples of the flotates, sinkates and 93:7 DCM/MeOH-soluble fractions were further separated into saturate, aromatic, resin (polar) and asphaltene (collectively termed SARA) fractions. Asphaltenes were precipitated from the sample using an excess of n-heptane with a 12 hour settling time; further separation was achieved by centrifugation. The precipitation process was repeated three times in total. The maltene fraction was further separated into saturate, aromatic, and polar fractions using alumina micro-column chromatography. The aliphatic fraction was eluted with hexane, the aromatic fraction with DCM, and the polar fraction with MeOH. Fractions were allowed to dry and were weighed.

Gas chromatography-Flame Photometric Detector (FPD). Gases produced were analysed using a Perkin Elmer AutoSystemXL gas chromatograph-flame photometric detector (GC-FPD). Samples (500 μl) were injected using a gas tight lockable syringe at a 10:1 split at with the injector at 220°C. Separation was performed on a J&W GS-Q column (30 m length, 0.32 mm internal diameter). Helium at column flow rate of 2 ml min^{-1} (constant flow rate) was used as the carrier gas. The GC oven temperature was held for 4 min at 35°C and then programmed at 10°C min^{-1} to 220°C, the final temperature was held for 6 min. The FPD was held at 300°C with a hydrogen flow of 75 ml min^{-1} and air 90 ml min^{-1}.

Gas chromatography-mass spectroscopy and on-line pyrolysis-gas chromatography-mass spectroscopy. Gases produced were analysed using an Agilent Technology 7890–5975 gas chromatograph-mass spectrometer (GC-MS). Samples (500 μl) were injected using a gas tight lockable syringe at a 5:1 split at with the injector at 220°C. Separation was performed on a J&W GS-Q column (30 m length, 0.32 mm internal diameter). Helium at column flow rate of 2 ml min^{-1} (constant flow rate) was used as the carrier gas. The GC oven temperature was held for 4 min at 35°C and then programmed at 10°C min-1 to 220°C, the final temperature was held for 6 min. The MS was run in full scan mode (10–200 a.m.u.) at 3.7 Hz. For on-line pyrolysis, asphaltene samples were placed in quartz sample tubes and loaded into a CDS Analytical Model 2500 Plus autosampler pyrolysis unit then subjected to pyrolysis (610°C at a heating rate of 20°C min^{-1}). The products were introduced to the GC via split injection at a 25:1 split ratio with the injector at 270°C. Separation was performed on a J&W DB-5 column (30 m length, 0.32 mm internal diameter). Helium at column flow rate of 2 ml min^{-1} (constant flow rate) was used as the carrier gas. The GC oven temperature was held for 2 min at 40°C and then programmed at 5°C min^{-1} to 310°C, the final temperature was held for 8 min. The MS was run in full scan mode (10–200 a.m.u.) at 3.7 Hz. Sample pyrolysis analysis is shown in Supplementary Fig. S3.

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Acknowledgments

Author contributions

W.M. carried out the experiments, analysed the data and wrote the paper, M.A.S. designed the experiments, analysed the data and wrote the paper, J.S.W. designed the experimental equipment and analysed the data, H.Z. provided the samples, analysed the data and wrote the paper, A.C.R. designed the experiments, provided the samples, and wrote the paper. All authors discussed the results and implications and commented on the manuscript at all stages.

Additional information