



High temperature reactions of water with heavy oil and bitumen: Insights into aquathermolysis chemistry during steam-assisted recovery



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HIGHLIGHTS

- Heavy oil is transformed by higher temperature and pressure water.
- Aliphatic hydrocarbons are generated at the expense of polars and asphaltenes.
- Carbon dioxide and methane are notable gaseous products.
- Steam-assisted recovery of heavy oil will generate important gases and some lighter oil.

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ABSTRACT

To better understand the hot water-mediated organic transformation process (aquathermolysis) that occurs during the steam-assisted recovery of heavy oils and bitumen we have performed a series of experiments that subject a heavy oil to progressively higher temperatures and pressures in the presence of liquid water. As temperature and pressure increases, from ambient conditions to 300 °C and 1250 psig (8.6 MPa), a floating oil (flotate) is generated and is composed of mostly aliphatic hydrocarbons that appear to be generated at the expense of polars and asphaltenes. Analyses of hopane maturity parameters for the flotate indicate lower temperatures than the starting material suggesting the liberation of hopanes and, therefore, other hydrocarbons, from asphaltenes. Infrared spectra confirm changes in overall organic constitution as the relative abundance of hydrocarbons to oxygen-containing functional groups increases in the flotate. At the highest temperatures and pressures (325 °C, 1750 psig (13.8 MPa)) the flotate is at a maximum relative amount, the untransformed heavy oil is at a minimum and significant amounts of methane are generated indicating the onset of cracking. Steam-assisted recovery of heavy oil, therefore, leads to changes in the chemical constitution of a number of chemical fractions generating a lighter oil and gases that must be taken into account when planning field operations for production.

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1. Introduction

Heat and water are known modifiers of organic matter but the particular type of organic transformation observed can be dependent on the conditions under which modification has taken place. When heat, with or without water, leads to the decomposition of organic matter it is termed pyrolysis [1]. Anhydrous pyrolysis is the thermal decomposition of organic matter in a water-free environment while hydrous pyrolysis has been defined as those conditions in which the heated samples are in contact with liquid water for the duration of the experiment. Supercritical water pyrolysis denotes experiments in which a sample is pyrolyzed in contact with a supercritical fluid containing more than 50 mol% water [2] while steam pyrolysis indicates experiments in which a sample is

pyrolyzed in contact with water vapour at partial pressures in excess of 20% of its saturated vapour pressure [2]. Hydrous, supercritical, and steam pyrolysis are all covered by the umbrella terms hydrothermal pyrolysis or aquathermolysis, e.g. [3].

The influence of water is perhaps most profound when considered in relation to processes for the generation and exploitation of fossil fuels. When compared to anhydrous conditions, pyrolysis of organic-rich shales in the presence of water produces organic products that are physically, chemically and isotopically more similar to natural crude oils suggesting a closer replication of natural subsurface maturation conditions [4]. Moreover, hydrous pyrolysis experiments display product yields that are greater, by up to 100%, than in comparable anhydrous experiments [5,6]. When water is present, its state represents an important control on pyrolysis product yields [7]; historical data reveal that steam reduces yields of oil from oil shale during retorting [8] whereas liquid water increases the yield of soluble materials from heated coals by an order

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of magnitude [9]. Experimental data also reveal that ratios of water to organic compounds can exert an influence on product yields; for example ratios between 2.5:1 and 5:1 are optimal for hydrolysis reactions [10]. Reviews of the chemical consequences of organic reactions in hot water [11,12,3] and their geochemical and technological implications [13] are available in the literature. Hydrous pyrolysis studies have been widely applied to simulating the production of crude oil in the subsurface [4]. An extensive review of the use of hydrous pyrolysis to understand the geochemistry of oil has been published [6]. Crude oil is a staple energy resource and accounts for over 35% of the world's energy consumption but the demand for refined products is outstripping the supply of conventional oil and so focus is turning to unconventional hydrocarbon deposits. One such unconventional hydrocarbon deposit is represented by heavy oil and bitumen where "technical reserves," those which are technically viable although not necessarily commercially viable today, total > 1 trillion bbl where a large proportion will likely require (in situ) steam stimulation for production [14]. A good example of this is the province of Alberta in Canada which has 169 billion bbl of crude bitumen reserves (technically and commercially viable today using steam-assisted in situ recovery methods) which is just 9% of the initial volume in place; in 2011 Alberta produced on average 630,000 bbl/day of bitumen through steam stimulation methods and this rate is expected to triple by 2021 [15].

The role of water in organic transformation has been studied in relation to heavy oil and bitumen primarily because of the use of steam and water in recovery (e.g. see [16] for a review). Steam injection into the sub-surface has been used for decades to assist the recovery of heavy oil primarily through three methods: steam-flooding, Cyclic Steam Stimulation (CSS), and more recently Steam-Assisted Gravity Drainage (SAGD). Operating temperatures and pressures used in these methods differ widely, but SAGD temperatures are typically 180–240 °C and CSS can operate at temperatures in excess of 300 °C. These processes all offer intimate contact between the oil, condensed water and mineral matter for residence times of multiple days permitting even slow chemical processes to produce quantifiable changes to the oil and the generation of significant quantities of gas. Even using the simplest model, these processes can be seen to involve a number of variables that will change over distance and time, including: (i) temperature (ii) phase, (iii) water/oil ratio and (iv) opportunity for static vs. dynamic reaction conditions. More complex variables involve the chemistry of the starting materials, e.g. [17], and mineralogy of the reservoir rocks, e.g. [18]. It is accepted that both the temperatures involved in steam stimulation and the unavoidable juxtaposition of bitumen and steam condensate ensure that laboratory hydrous pyrolysis is a valuable predictor of steam chamber aquathermolysis reactions [19].

Owing to its ability to produce high yields of lower molecular weight products from higher molecular weight starting materials, the area of the steam chamber which is experiencing hydrous pyrolysis is perhaps most interesting. A key consideration is that, with respect to both economics and engineering, maintaining hydrous pyrolysis conditions over large areas of the steam chamber is more plausible compared to other higher temperature pyrolysis conditions involving water. Hydrous pyrolysis studies that aim to provide insights into steam-assisted recovery processes should ideally be comprehensive in that all of the solid, liquid and gaseous material is monitored during the experiments. For instance, untransformed residues are related to the recovery efficiency while gas contents could reflect diagnostic products of aqueous or thermal chemical reactions. Gas contents also reveal whether these processes will generate any production engineering issues owing to acid gas generation (hydrogen sulphide and carbon dioxide). Inevitably this approach involves multiple analytical instruments.

Previous hydrous pyrolysis experiments on source rocks have demonstrated the utility of studies that are comprehensive and partially [20] or fully [7] quantitative.

In this paper we report on a series of hydrous pyrolysis experiments. A sample of well-characterised biodegraded heavy oil was subjected to various temperatures and pressures. Although the experiment durations are relatively short, it is expected that the reactions that take place will reflect those occurring in the presence of liquid water across the temperature and pressure gradients experienced in steam-assisted recovery. These data indicate the progressive transformation of organic matter with temperature through different bond breaking events to produce an increasingly less viscous oil. Higher temperatures also lead to greater quantities of gas. The gas becomes progressively more hydrocarbon-rich at higher temperatures. Organic transformations are relatively concentrated into specific chemical fractions. The data provide insights into how management of steam-assisted processes can lead to in situ changes in heavy oil.

2. Experimental

2.1. Samples

For the oil sand extraction experiments, degraded oil in a sand matrix was obtained from Osmington Mills, Dorset, United Kingdom. Although by no means an economic prospect, the oil sand provides a well-characterised analogue for study. Examination of the cliff face at Osmington Mills (Grid Ref.: 50.63391°N, 2.37571°W) reveals clays, limestones and sandstones of Upper Jurassic age. At sea level, the six metre thick Bencliff Grits are found and comprise fine grained sands with occasional mudstone layers. Large scale cross bedding, dewatering structures and the presence of land plant material suggest rapid sedimentation in a near shore setting [21]. The sands exhibit porosities of 15–20% and permeabilities of 10–1000 mDa [22]. The Bencliff Grits display a notable and widespread oil stain the most likely source of which is the Lower Jurassic Blue Lias shales which contain marine type II kerogen. Tertiary inversion in the Wessex Basin resulted in the breach of the Bencliff Grit oil accumulation to produce a sulfur-poor heavy oil with densities in the 18.4–18.9° API range [23] and a viscosity of 1538 Pa s at 25 °C.

2.2. Hydrous pyrolysis

Approximately 50 g of Osmington Mills sample were added to a high pressure and temperature reactor (Model 4740, Parr Instruments). Using the measured reactor volume, 75 ml, and 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 nitrogen and the reactor was sealed and placed in an oven for 24 h. Pressure was monitored throughout the experiment using a dedicated pressure gauge attached to the reactor. Subcritical water experiments were performed on samples of oil sands at a range of temperatures and pressures as follows: 25 °C, 14.5 psig; 250 °C, 600 psig; 275 °C, 800 psig; 300 °C, 1250 psig; 325 °C, 1750 psig.

2.3. 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 chamber with a septum. Gas was collected from this chamber 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

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