



Full Length Article

Effect of process conditions on the hydrothermal partial oxidation of phenanthrene as a heavy oil model structure



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ABSTRACT

The decline in light oil production has triggered the necessity to develop effective processes to upgrade heavy oil feedstocks. An alternative to traditional heavy oil upgrading processes is the hydrothermal partial oxidation in near-critical or supercritical conditions. Partial oxidation leads to the formation of oxygen functionalities in aromatic rings located in central positions within the molecule. These functionalities destabilize the aromatic ring structure, making it more prone to cracking reactions. In this work, the effect of pressure, the ratio between the initial oxygen loaded into the system with respect to the stoichiometric oxygen needed for total combustion (O/O_{stoich} ratio) and temperature were studied using phenanthrene as model compound for structures commonly found in asphaltene molecules. The process was studied at a range of pressures between 210 and 275 bar, O/O_{stoich} ratio from 0.1 to 0.75 and temperatures between 360 and 450 °C. Changes in pressure did not affect phenanthrene conversion, but had a great impact on product selectivities and the gas and organic-soluble fraction compositions. Increases in O/O_{stoich} ratio resulted in higher phenanthrene conversions and greater yields to gas. Selectivity to organic-soluble products increased with O/O_{stoich} ratio to find a maximum at a ratio around 0.2 to then decrease with further increments due to an increase in gas production. Any increase in temperature resulted in higher phenanthrene conversions and also higher yields to organic-soluble products. Yields to gas and coke remained low at all reaction temperatures. Higher selectivity to organic-soluble products was obtained at 230 bar, 0.2 O/O_{stoich} ratio and 425 °C.

1. Background

Increasing world energy consumption combined with the gradual decline in conventional oil resources has made heavy oil production and upgrading crucial for the future of the global oil market. A raise in global heavy oil production to an approximate of 13 mbpd in 2035 is expected to meet the estimated future demand of liquid fuels [1]. Heavy crude oil is commonly defined as a feedstock with API less than 20 and viscosity greater than 100 cP at reservoir conditions [2]. These feedstocks present great challenges during processing and refining stages due to their high heteroatom and metal content as well as their highly asphaltenic nature, density and viscosity [1–5]. Asphaltenes represent the most complex and heaviest constituent of heavy oil fractions. They contain condensed polycyclic aromatic hydrocarbons (PAH) as well as heteroatoms and metals in their chemical structure [6].

Traditional oil conversion processes consist of a combination of hydrogen addition and carbon rejection processes that can be performed in the presence or absence of a catalyst [7]. These technologies are not effective as a standalone method to process heavy oil feedstocks

due to operational disadvantages such as high yields to coke, poor conversions, low yields to light fractions, high volumes of hydrogen required, large amounts of catalyst needed, catalyst deactivation and poisoning, which represent elevated operational costs [6,7]. These issues increase the importance of developing alternative or complementary processes to upgrade heavy oil more efficiently.

One such alternative is the hydrothermal upgrading of heavy oil feedstocks in near-critical water (NCW) or supercritical water (SCW). Water turns supercritical above 374 °C and 221 bar where it has a density of 0.32 g mL⁻¹. At these conditions water becomes a good solvent for non-ionic rather than ionic species due to the almost completely disrupted hydrogen bonding as well as the important changes in the auto-dissociation capacity, viscosity and an important decrease in the dielectric constant [8]. In addition, it has been reported that water at these conditions can play the role of solvent, reactant and catalyst in organic chemical reactions [9]. Potential applications have also been shown in oil upgrading processes, as NCW and SCW can inhibit coke production and decrease the viscosity of the feedstock. In heavy oil upgrading reactions, water acts as a solvent that allows greater

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diffusivity of molecules and as a dispersant for heavy components like asphaltenes, which favours the formation of lighter fractions [10–12]. In SCW, asphaltenes undergo cracking reactions mainly through the cleavage of peripheral aliphatic chains rather than the more stable polycyclic aromatic clusters to produce lighter fractions, gas and carbonaceous solids [13].

Studies using PAH as model compounds showed that in NCW or SCW alone, low conversions are achieved with low yields to ring opening and reduction products [14,15]. To increase the reactivity of the medium, the inclusion of a catalyst has been considered, resulting in the formation of reactive hydrogen or oxygen species that increase conversions and yields to lighter products [16–21]. Moreover, the presence of an added oxidizing agent improves conversions compared to reactions in water alone [22]. Studies on the hydrothermal oxidation of PAHs have shown that in the presence of an excess of a strong oxidizer, destruction rates as high as 99% are achieved [23–25]. In addition, hydrothermal partial oxidation of PAHs in NCW and SCW start preferentially at central ring positions rather than in peripheral rings [26]. The oxygen incorporated in the aromatic structure weakens its aromaticity making it more reactive. As a result, weaker reactive sites are formed, which make the molecule more prone to cracking reactions in central positions of the polyaromatic cluster. Therefore, hydrothermal partial oxidation presents a potential alternative process for heavy oil upgrading.

The aim of this work is to study the effect of pressure, O/O_{stoich} ratio and temperature on the partial oxidation of heavy oil model compound phenanthrene. O/O_{stoich} ratio is defined as the ratio between the amount of oxygen fed into the system and the required stoichiometric oxygen to achieve the complete oxidation of phenanthrene. Special emphasis is placed in targeting reaction conditions at which yields and selectivity to organic-soluble products are high.

2. Experimental

Experiments were performed in a stainless steel microbomb batch reactor detailed in Fig. 1. The reactor consists of a 12 mL reaction section and a 6 mL gas recovery and sampling section. The reaction section is made of a 1/2" Swagelok bore through tee with two ends plugged and connected to a high pressure and high temperature resistant needle valve through a 1/4" stainless steel tubing with a wall thickness of 0.065". The function of this valve is to isolate the reaction zone and keep the system at the desired pressure. The reaction section is also connected by means of a 1/8" stainless steel tube to a pressure relief valve calibrated to open at a pressure of 300 bar. Temperature in the reactor is monitored with a type K thermocouple located in the centre of the 1/2" tee.

The reactor was loaded with 1.2 mL of H_2O_2 30% m/v (from VWR), varying amounts of Sigma-Aldrich phenanthrene 98% from (0.075 g–0.5 g) depending on the target O/O_{stoich} ratio and varying volumes of DI water (2.1–3.0 mL) depending on the pressure and temperature required. The required volume of water to reach the desired operating pressure inside the reactor was obtained from a calibration curve built from experimental measurements. For the subcritical temperature experiment at 360 °C, the reactor was loaded with an initial helium pressure to provide 230 bar after reaction temperature was reached. This was determined taking into account the thermal expansion of the helium loaded and the pressure resulting from the oxygen formed in the thermal decomposition of hydrogen peroxide. Once filled, the reactor was leak tested and repeatedly purged with helium to remove any air present inside the reactor. Then the reactor was depressurized and the needle valve was closed to isolate the reaction section.

The reactor was immersed in a TECHNE SBL-2D fluidised sand bath, which provides heating, and attached to a shaking mechanism, leaving the needle valve 10 cm above the surface of the sand bath. The time required for the system to reach reaction temperature was less than

3 min in all experiments performed. Reaction time was measured from the moment the reactor reached the desired reaction temperature. Experiments were performed at a fixed reaction time of 60 min.

Once reaction time was reached, the reactor was removed from the sand bath and quenched in a chilled water bath to stop reactions in the system. After cooling, gas products were obtained and analysed in a Perkin Elmer Clarus GC equipped with a Carboxen plot 1010 capillary column and thermal conductivity detector. The reactor was then opened and rinsed with chloroform/methanol mixture (4:1 v/v) to recover the remaining products. The product mixture was then filtered to separate the organic-soluble products from the solids. The amount of solids obtained was measured and then analysed through thermogravimetric analysis (TGA) in a Perkin Elmer Pyris 1 to determine yield to coke. An organic phase and an aqueous phase were recovered and separated using a separation funnel. A series of chloroform extractions were performed on the aqueous phase to recover any remaining product until further analysis of the water showed no reaction products. The organic-soluble products were analysed in a Perkin Elmer Clarus GC with flame ionization detector and in a Varian Star 3400/Saturn 2000 GC/MS to determine the amount and nature of the products obtained. Both instruments were equipped with a non-polar HT-5 (25 m × 0.32 mm) column. Identification of individual organic soluble products was performed through GC–MS by comparing the spectrum of each product with those in spectrum library of the National Institute of Standards and Technology (NIST). The amount of organic soluble products was quantified through the determination of the GC–MS peak area of each product and converted to carbon moles using calibration curves built with standards supplied by Sigma-Aldrich.

Experimental conditions for this study are detailed in Table 1. Phenanthrene conversion, yield and selectivity to different product fractions and composition of the gas and organic-soluble fractions are reported. Phenanthrene conversion is defined as the carbon moles of phenanthrene that reacted divided by the carbon moles of phenanthrene originally fed. Yields to products are defined as the carbon moles present in the organic-soluble, gas and coke fractions respectively divided by the carbon moles in the original phenanthrene. Finally, selectivity to organic-soluble products is defined as the carbon moles in the organic-soluble product divided by the carbon moles of phenanthrene converted. The total gas produced was determined by mass balance difference. To determine the error in these measurements, a fixed experimental condition (450 °C, 230 bar and O/O_{stoich} ratio of 0.4) was repeated four times and its product fractions analysed. Then, the mean value, standard deviation and standard error were calculated in order to determine the experimental variability. The standard deviation for the yields was as follows: 0.0106 for the organic soluble products, 0.0041 for coke and 0.0085 for gas. This led to standard errors of ± 0.0104 for organic soluble products, ± 0.004 for coke and ± 0.0083 for gas at a 95% confidence interval. This resulted in error percent's at a 95% confidence interval of $\pm 3.9\%$ for organic soluble products yield, $\pm 3.7\%$ for coke yield and $\pm 6.8\%$ for gas yield.

3. Results and discussion

Products of reaction were analysed and classified as organic-soluble products, gas products (H_2 , CH_4 , CO and CO_2) and coke. Most of the organic-soluble products obtained were oxygenated aromatic species, such as furans and quinones, with less production of PAHs. This is in good agreement with product distributions obtained in supercritical water oxidation processes previously reported in literature [22,24].

3.1. Effect of pressure

The effect of pressure on the process was assessed at 210, 230, 250 and 275 bar, which includes operation at near-critical and supercritical water conditions. Changes in pressure had a small impact on the overall phenanthrene conversion, as shown in Fig. 2. A slight increase in

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