

BITUMEN UPGRADING IN SUPERCRITICAL FLUIDS

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ABSTRACT

This research is concerned with use of supercritical fluids (SCFs) to develop a more efficient procedure for upgrading heavy oils and bitumens. Catalytic hydrogenation studies of a range of model polycyclic aromatic hydrocarbons (PAHs) in supercritical carbon dioxide (scCO₂) and *n*-heptane are reported. High levels of hydrogenation were achieved using reaction conditions significantly milder than those previously reported. Solubility studies of real bitumen samples in SCFs are currently underway.

INTRODUCTION

The bitumen deposits in the Alberta tar sands are estimated to contain at least 1.7 trillion barrels of oil, representing around one-third of the world's total petroleum resources, and their high concentration makes them economically recoverable [1]. An improved bitumen upgrading technology will thus confer direct economic advantages to the tar sands petroleum industry, as well as enabling major reductions in greenhouse gas emissions through a more efficient overall operation.

Bitumen is a viscous, tar-like material composed primarily of polycyclic aromatic hydrocarbons (PAHs) with a low hydrogen-to-carbon content that are difficult to extract and process. The high solubility of hydrogen in SCFs will allow us to increase the hydrogen content of these bituminous materials, and at higher temperatures rearrangement and fragmentation of their carbon skeletons will produce smaller, more tractable compounds. We aim to demonstrate a viable process at the end of this project that can be subsequently integrated into a more efficient overall process for the extraction and processing of these materials.

Phase one of this project was to carry out hydrogenation reactions on a variety of model PAHs in scCO₂ and also in conventional solvents for comparison using commercially available heterogeneous catalysts. Conventional catalytic hydrogenation of simple PAHs such as naphthalene and anthracene have been achieved using severe reaction conditions (>300 °C, 5 MPa H₂) [2,3]. Deeply aromatic systems such as phenanthrene and pyrene have been shown to be significantly more difficult to hydrogenate, leading to lower reaction rates (Benzene to cyclohexane = 1, phenanthrene to tetrahydroanthracene = 0.7) [4]. There have been sporadic reports in the literature describing the hydrogenation of PAHs under milder conditions. Thus, conversion of naphthalene to decalin in scCO₂ was achieved at 60 °C with a Rh/C catalyst and H₂ (6 MPa) [5,7], and Marshall *et al.* reported catalytic hydrogenation of a variety of PAHs (μmol scale) under mild conditions in the presence of Pd/Al₂O₃ using hexane as a solvent [8]. However, there remains a significant scope for improvements through a systematic approach.

MATERIALS AND METHODS

Commercially available naphthalene, anthracene, phenanthrene, pyrene, Rh and Pd supported catalysts (charcoal and alumina 5 %) were obtained from Sigma Aldrich. All materials were used without further purification.

Typical experimental procedure: A 20 mL pressure vessel was charged with substrate (0.84 mmol) and catalyst (50 mg) and a stirrer bar. The vessel was attached to a high pressure system and heated to the desired temperature. H₂ (6.2 MPa) was introduced into the vessel, then CO₂ (10 MPa) was added *via* syringe pump and the reaction mixture was stirred for the designated time, after which the vessel was cooled to room temperature. The gases were vented through an ether trap and the catalyst was separated by filtration. The contents of the vessel were extracted with Et₂O, and the resulting solution was filtered to separate catalyst from the products. The reaction products were analysed quantitatively using GC-MS analysis (Agilent 7890A and 5975MSD).

RESULTS

Naphthalene (1.17 mmol) was the subject of initial investigations and reactions were carried out at 60 °C for up to four hours using Rh/C (50 mg) and H₂ (6.2 MPa) in scCO₂ (10 MPa) (Scheme 1, Figure 1). Reactions were carried out in a 20 ml stainless steel high pressure vessel and were also in *n*-heptane for comparison. Initial reaction conditions were established following procedures from Shirai *et al.*[5]

Scheme 1:

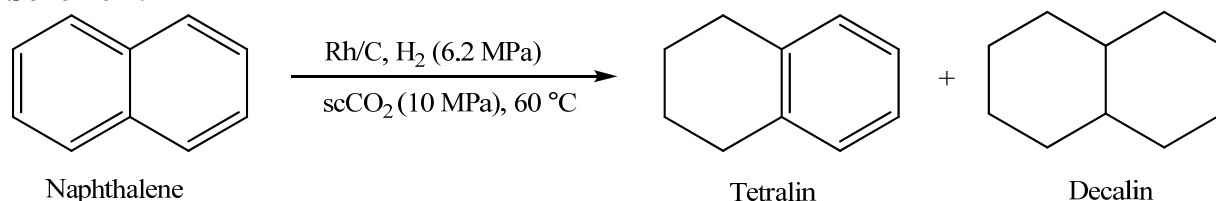
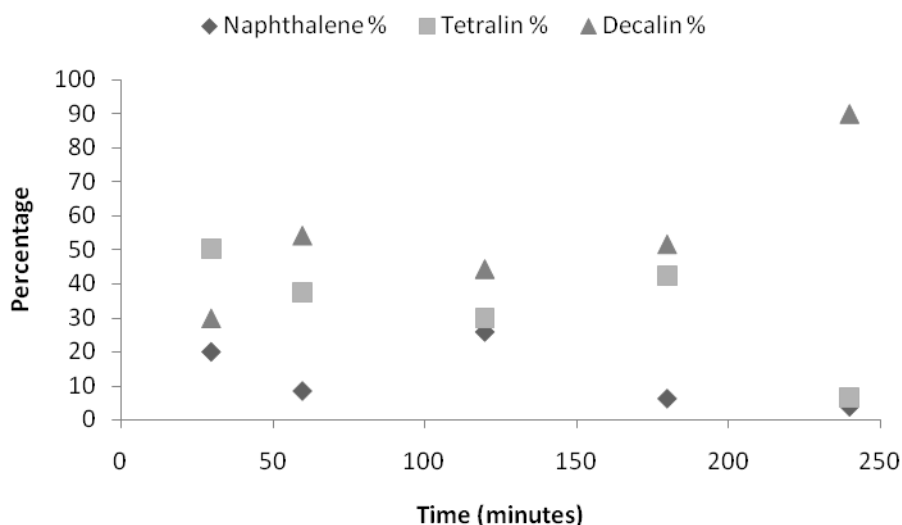


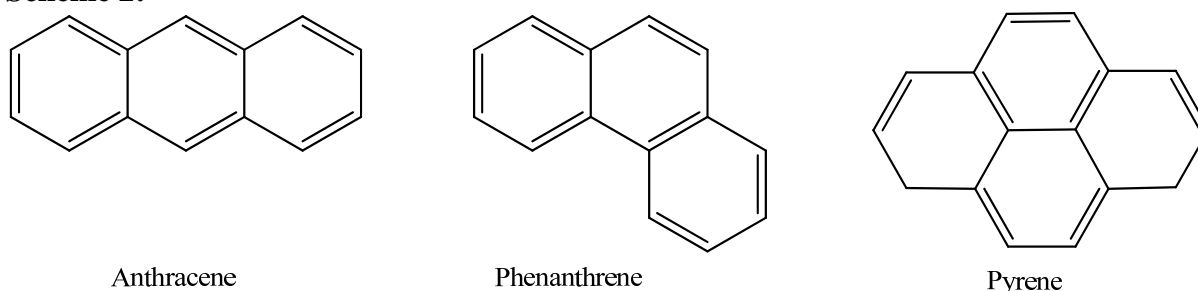
Figure 1: Variation of products with reaction time in scCO₂ (10 MPa)



The results of the reaction determined the repeatability of previous literature findings, with complete hydrogenation within 4 hours in $scCO_2$. Naphthalene was converted to a mixture of tetralin and decalin within one hour, with longer reaction times leading to fully hydrogenated products. Reactions in *n*-heptane were also shown to go to completion within four hours using identical reaction conditions (99.6 % conversion, 95.2 % decalin).

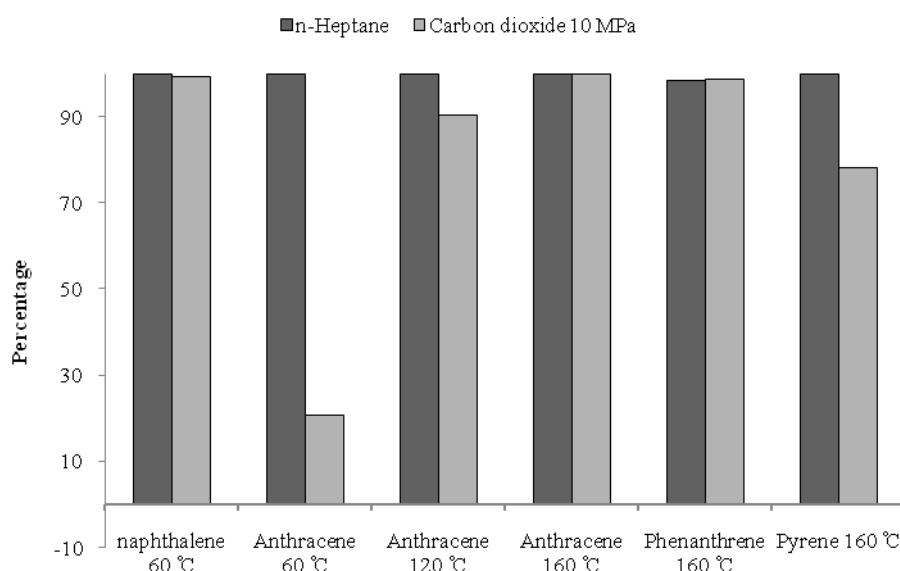
Accordingly, the investigation was extended to hydrogenation of other simple PAHs with tri- and tetracyclic ring systems (Scheme 2). The results are summarized in Figs. 2 and 3.

Scheme 2:



Hydrogenation of anthracene (0.84 mmol) in *n*-heptane proceeded to the fully hydrogenated product perhydroanthracene in 4 h at 120 °C. Lower temperatures (60-100 °C) resulted in a mixture of partially hydrogenated materials, with <5 % of the perhydro product. In $scCO_2$ (10 MPa) lower temperatures (60-80 °C) were found to give poor conversions (<50 %); however higher yields (up to 100 %) were obtained at higher temperatures (100-160 °C) over a period of 16 h (Fig. 2). Although high conversions of anthracene to a mixture of partially and fully hydrogenated materials were observed, only low amounts (17 %) of perhydroanthracene were obtained. The yield of fully hydrogenated product in $scCO_2$ improved to 77 % within 4 h by raising the H_2 pressure to 12.4 MPa (Fig. 3).

Figure 2: Conversion of PAHs to products in *n*-heptane and $scCO_2$ (10 MPa).

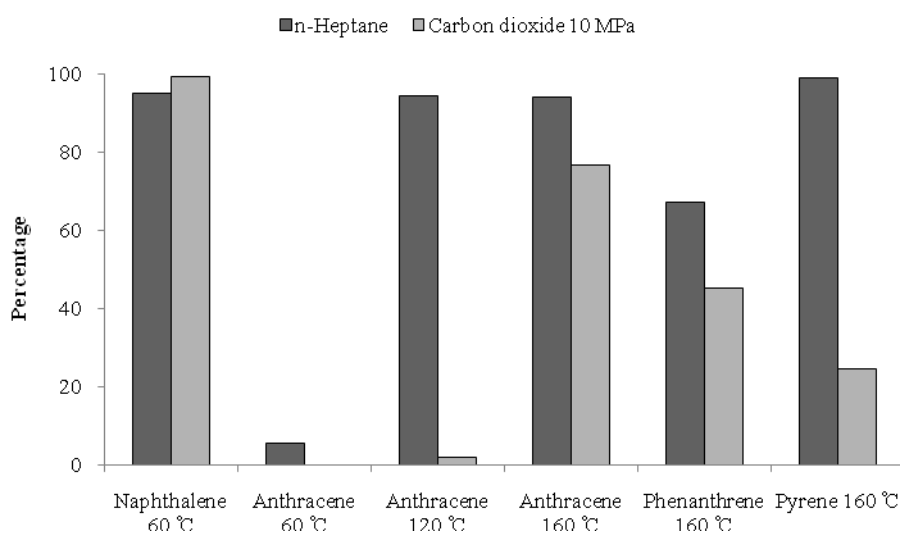


Hydrogenation of phenanthrene proved to be significantly more difficult than anthracene. In order to overcome low reaction rates, a higher reaction temperature (160 °C) was employed. Low conversions were obtained in *n*-heptane at higher substrate concentrations (39 %; 0.84 mmol). Higher conversions were obtained in $scCO_2$ at the same substrate concentration (45 %). The dependence of the reaction rate on concentration was explored in *n*-heptane (0.14-

0.84 mmol), which established that the reaction proceeds fastest at lower concentrations, with almost quantitative conversion (97 %, 0.14 mmol) to the fully hydrogenated perhydrophenanthrene (Fig. 3).

We extended the study to encompass the tetracyclic PAH pyrene; Scheme 2. The hydrogenation of pyrene in conventional solvents has not been widely explored, although two reports document low conversion to perhydropyrene [9,10]. Drawing on our successes with other PAHs, pyrene was hydrogenated in *n*-heptane and *scCO*₂, using Rh/C at 160 °C. A concentration study (0.12-0.74 mmol pyrene) revealed that lower concentrations of substrate (0.24 mmol) were converted quantitatively to perhydropyrene within 16 h at 160 °C in *n*-heptane using a Rh/C catalyst and 6.2 MPa H₂ (Figs. 2 and 3). To date, only preliminary experiments have been conducted on pyrene in *scCO*₂: (0.24 mmol) was transformed into hydrogenated products in 78 % yield in the presence of Rh/C (50 mg) and H₂ (6.2 MPa) within 4 h at 160 °C (Figs. 2 and 3).

Figure 3: Conversion to fully hydrogenated materials in *n*-heptane and *scCO*₂ (10MPa).



Another aspect of this project is concerned with solubility and upgrading of actual bitumen samples from the oil sands in Alberta. Solubilities of tar sand bitumen in *scCO*₂ have been reported at temperatures between 84 and 120 °C [11,12]. These studies reveal that its solubility is temperature- and pressure-dependent, with low temperatures and higher pressures giving optimal solubilities. It has also been shown that asphaltenes, a heavier constituent of bitumen, are soluble in toluene but insoluble in *n*-heptane at reasonable temperatures, which indicates that it is possible to form bituminous solutions [13]. We will investigate the solubility of bitumen from real tar sand samples in a variety of SCFs, in order to optimize temperature and pressure conditions. We will also explore the addition of modifiers such as methanol to enable dissolution of more complex asphaltenes. Sonication has recently been claimed to accelerate chemical reactions in an SCF medium [14]; therefore, we will also investigate the efficacy of this technique in the extraction of bitumen in tar sand samples from the inorganic matrix.

CONCLUSIONS

The preliminary results described in this paper demonstrate the potential of scCO₂ as a highly suitable medium for the hydrogenation of simple PAHs using commercially available Rh and Pd catalysts. Increased reaction rates and higher conversions are obtained using significantly milder conditions in scCO₂ and in *n*-heptane than have been reported elsewhere in the literature. Optimization of catalysts, reaction conditions and hydrogenation of other PAHs are currently being investigated and will be reported shortly. Understanding bitumen solubility in SCFs will enable us to develop a process towards combined extraction and upgrading; this aspect of the project is under investigation.

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