

UPGRADING HEAVY OIL/BITUMEN EMULSIONS VIA IN SITU HYDROGEN GENERATION

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Abstract

Canada has large reserves of heavy oils and tarsand bitumen. These heavy oils are recovered as emulsions via steam injection techniques. Current technologies for emulsion treatment and upgrading require multistage processing. Recently, we have developed a novel process for upgrading heavy oil emulsions in a single stage process where emulsion breaking and upgrading occurred in the same reactor. This process is based on the activation of water in an emulsion via the water gas shift reaction to generate hydrogen for in situ upgrading. This paper is focussed on the catalytic desulphurization in an emulsion using dispersed catalysts. The activity of in situ hydrogen will be compared with that of molecular hydrogen. Synthesis gas was found to be effective for upgrading emulsions. The emulsion upgrading technology could also be used to process emulsions derived from hot water extraction of tarsands bitumen.

Introduction

Canada has large reserves of high sulphur heavy oils and oil sand bitumen. As conventional oil reserves continue to decrease, it will become necessary to utilize more of the high sulphur heavy oil and oil sand bitumen in the future. Technologies for the recovery of heavy oils include steam flooding, cyclic steam injection or fire flooding of reservoirs while hot water was used to extract bitumen from tarsands. These methods of recovery of heavy oil and bitumen produce emulsions. In order to utilize the heavy oils and bitumen, the emulsions have to be broken and separated into water and oil phases in emulsion treatment plants. Subsequently, the bitumen or heavy oils are upgraded where sulphur removal and hydrocracking occurred before being utilized in conventional refineries. In summary, current technologies for emulsion treatment and upgrading require multistage processing and are costly. Thus alternative technologies for processing heavy oil/bitumen emulsions would be attractive.

We have developed in our laboratory a novel single stage process for upgrading emulsions via activation of water in the emulsion through the water gas shift reaction (WGSR) to provide hydrogen in situ for catalytic desulphurization and hydrocracking (1). This process could potentially reduce the environmental impact derived from the discharge of emulsions into tailings ponds. It is clear that in order to further develop the heavy oil/bitumen resources, new processes should be economically viable, flexible while assuring the quality of the environment. Our novel emulsion upgrading process could potentially achieve the above goals. It is envisaged that a single stage emulsion upgrading will minimize waste streams, lower the cost for hydrogen production and potentially break very stable emulsions which cause environmental hazards as in tailings pond.

In addition to our patents on emulsion upgrading, there are other patents related to the use of CO and synthesis gas for upgrading emulsions or heavy oils, including down hole upgrading (2). Aquathermolysis which utilizes water at 280 °C for hydrolysis of hydrocarbons in heavy oil, resulting in viscosity reduction and sulphur removal has been reported (3). There are also reports of the aqueous high temperature chemistry of hydrocarbons and heterocycles (4) with a view to elucidate the chemistry involved in the steam stimulation of heavy oil reservoirs (~ 200-300 °C).

Experimental

All experiments were performed either in a 300 mL or a 1000 mL stainless steel batch autoclave (Autoclave Engineers). The synthetic emulsions were prepared by using toluene, water and an emulsifier (BASF P105). Dispersed catalysts such as molybdic acid, phosphomolybdic acid, ammonium molybdate and ammonium tetrathiomolybdate were used. Model compounds such as benzothiophene (BTH) , dibenzothiophene were used to obtain kinetics of desulphurization (HDS) in an emulsion. HDS of a diesel fraction from Cold Lake bitumen was also studied.

The experiments were carried out over a temperature range of 320- 380 °C. The reactor was heated up at a rate of 2 °C per minute as recommended by Autoclave Engineers. The initial loading pressure of CO, synthesis gas (a 1:1 mol ratio of CO: H₂) or H₂ was between 300- 600 psig. For some of the experiments , samples of gas or liquid were taken for analysis. At the end of the reaction , the reactor was allowed to cool down overnight to room temperature. Gas, liquid and solids were then collected and analyzed. The gaseous product was collected in a gas bag and analyzed using gas chromatography (Perkin Elmer Model 8500) equipped with a thermal conductivity detector. The inlet system composed of a 1.5 m Hayesep C column in series with a 2 m molecular sieve column. Liquid analysis was carried out in the same GC using a 30 m DB-1701 fused silica capillary column and a flame ionization detector. X-ray fluorescence (Oxford Model Lab X-1000) was used to determine the sulphur content of the diesel fraction. X-ray diffraction, X-ray photoelectron spectroscopy and thermoanalysis techniques were used to characterize the spent catalysts.

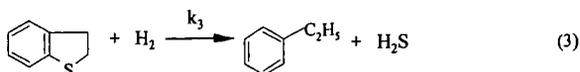
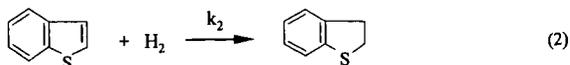
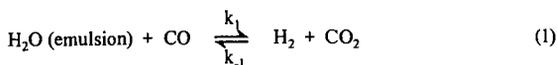
Results and Discussion

Our initial research was based on the desulphurization of a synthetic emulsion (toluene/water) containing benzothiophene, a model compound for sulphur species in heavy oil. Simulated emulsions were used to provide a better understanding of the chemical and physical processes involved in upgrading heavy oil emulsions. Such information serves to provide a basis for the interpretation of data from experiments involving heavy oil emulsions.

Under the reaction conditions of 320 -380 °C and 300 -600 psig initial loading pressure of CO, the dispersed Mo catalysts were found to be effective catalysts for the HDS of BTH in an emulsion. The emulsion was found to be broken completely into 2 separate oil and water phases, with some black solids identified to be some form of MoS_x accumulated at the bottom of the reactor. Essentially complete sulphur removal could be achieved. Gas samples taken during the reaction showed that CO decreases as a function of time, while that CO₂ and H₂ increases as a function of time. In the absence of sulphur compounds ,the amount of CO₂ and H₂ were found to be equimolar as expected according to the stoichiometry of the water gas shift reaction shown in equation 1 (Fig 1). However, in the presence of sulphur compounds, the amount of H₂ was found to be less than CO₂ which was attributed to the consumption of H₂ during the reaction (Fig. 2).

A kinetic study was carried out for the production of hydrogen from the water gas shift reaction. In the absence of benzothiophene, the reaction followed a reversible pseudo first order kinetics. In the presence of benzothiophene, an irreversible first order reaction was observed (5). Similar behaviour was observed for molybdc acid and phosphomolybdc acid. The rate constants obtained for both catalysts were very similar suggesting that probably the same catalytic species was involved in the reaction (Table 1). It is interesting to note that the rate constant obtained in the presence of benzothiophene is higher than in the absence of benzothiophene. This could be attributed at least partly to the formation of a MoS_x species when benzothiophene was present and it has been reported that MoS_x is more active for the water gas shift reaction than Mo oxides (6). Indeed we found that the WGSR reaction proceeded at a faster rate when ammonium tetrathiomolybdate was used. Variation of the initial CO loading pressure from 300 - 600 psig also indicated a first order dependence on CO.

The kinetics of the HDS of BTH was obtained by analysis of liquid samples taken from the reactor. GC analysis indicated that dibenzothiophene was the intermediate of the reaction and that ethylbenzene was the final product (Fig 3). Therefore the reaction pathway for the desulphurization of benzothiophene could be represented by equations 1-3.



Mechanisms for the desulphurization of benzothiophene have been reviewed by a number of researchers (7). Two reaction schemes have been proposed. One involves the initial hydrogenation of benzothiophene to dihydrobenzothiophene, followed by sulphur removal to give ethylbenzene and H₂S. The second scheme is the direct desulphurization via C-S bond cleavage resulting in H₂S and styrene which is then hydrogenated to give ethylbenzene. Since dihydrobenzothiophene was detected as an intermediate in our reaction, the predominant pathway for desulphurization is hydrogenation of benzothiophene to give dihydrobenzothiophene which then undergoes hydrogenolysis to give ethylbenzene.

The desulphurization of benzothiophene in an emulsion with externally supplied molecular hydrogen was carried out. The reactivity of in situ hydrogen was found to be about 7 times that of supplied molecular hydrogen. This may be attributed to the fact that the in situ hydrogen may be more like atomic hydrogen and hence has a higher reactivity than molecular hydrogen. A higher reactivity of in situ hydrogen for HDS reactions has also been reported (8).

Results of HDS of dibenzothiophene in an emulsion indicated the rate constant for water gas shift reaction is essentially the same as that obtained with benzothiophene (10). The rate constant for sulphur removal is about a factor of 5 smaller than that of benzothiophene. This result is in accordance with the data by Ma et al (10). The activity of in situ hydrogen was found to be higher than that of molecular hydrogen. Product analysis revealed that the major pathway for desulphurization is via the hydrogenation of the aromatic ring to give tetrahydrodibenzothiophene. Since hydrogenation rather than hydrogenolysis apparently is the main pathway for the desulphurization of benzothiophene and dibenzothiophene, it may account for the higher activity of in situ hydrogen compared with molecular hydrogen.

Recently we examined the desulphurization of a diesel fraction from Cold Lake (11). Water was added to the diesel to simulate an emulsion. The reaction was carried out under the same reaction conditions as the model compounds benzothiophene and dibenzothiophene. The rate constant for the water gas shift reaction was found to be similar to that obtained in the presence of model compounds. However, the rate constant for desulphurization with in situ hydrogen was found to be similar to that of molecular hydrogen. It has been reported that diesel contains a mixture of sulphur compounds including substituted dibenzothiophenes which are very resistant to desulphurization. The difference between the reactivity of in situ hydrogen and molecular hydrogen towards model compounds and diesel may be due to the presence of highly substituted dibenzothiophene type compounds. Due to the steric hindrances of the substituted alkyl groups, the in situ hydrogen that was produced from the water gas shift reaction will decompose to give molecular hydrogen before it could be utilized for the desulphurization process.

Similar rate constants for desulphurization were observed when synthesis gas (1:1 mol ratio of CO: H₂) was used for the upgrading of diesel. This is an important result since this implies that CO is not an inhibitor for HDS. Since the cost of hydrogen for upgrading is high, the use of a cheaper source of hydrogen for upgrading will be attractive for the process economics.

Conclusions

Dispersed molybdenum catalysts are effective for catalyzing the water gas shift reaction to generate hydrogen in situ for the desulphurization and upgrading of heavy oil/bitumen emulsions. The in situ hydrogen was found to be more active for the desulphurization of model compounds such as benzothiophene and dibenzothiophene. However, the reactivity of in situ hydrogen and molecular hydrogen was found to be about the same for the desulphurization of diesel. Synthesis gas could be utilized for the upgrading of heavy oil/bitumen emulsions.

Acknowledgement

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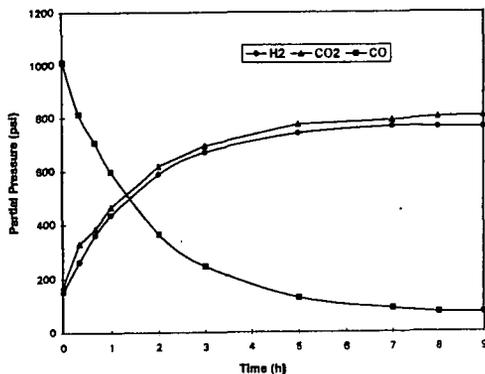
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Table I. Rate Constants for WGSR and HDS of BTH at 340 °C
 (4775 ppm Mo, 600 psig CO loading pressure, 49 mL toluene,
 9.8 mL BTH, 21 mL water, stirring speed = 500 rpm)

Catalyst	Pseudo First Order Rate Constant ^a		
	$k_1' \times 10^4 (s^{-1})$	$k_2' \times 10^4 (s^{-1})$	$k_3' \times 10^4 (s^{-1})$
MA	2.3 1.4 ^b	2.0	4.1
PMA	2.2 1.1 ^b	2.3	3.8

^a $k_1' = k_1[H_2O]$, $k_2' = k_2[H_2]$, $k_3' = k_3[H_2]$
^b WGSR runs, no BTH added
 MA = molybdc acid
 PMA = phosphomolybdc acid

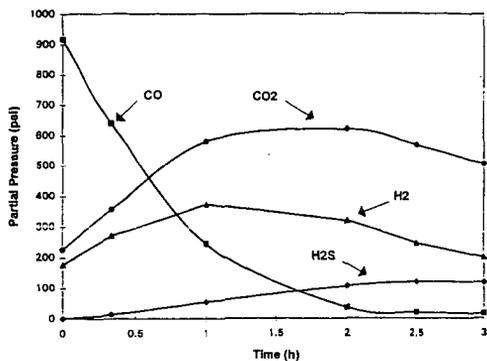
Figure 1. Product Distribution with time for the WGSR



REACTION PROFILE FOR WGSR @ 380 °C.

($P_{CO_0} = 600$ psig ; 70 ml H₂O/196 ml TOLUENE;
 1.78 g MoO₃; 1300 rpm).

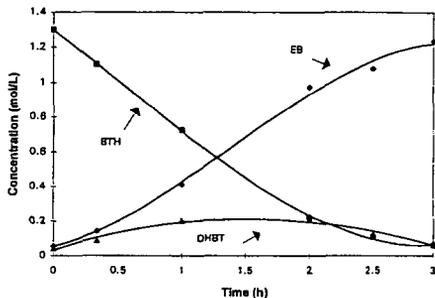
Figure 2. Product distribution of the WGSR with time in the presence of BTH



REACTION PROFILE FOR WGSR @ 380 °C.

($PCO_0 = 600$ psig ; $BTH_0 = 267$ mmol; 70 ml H_2O /163 ml TOLUENE; 1.78 g MoO_3 ; 1300 rpm).

Figure 3. Product distribution for the HDS of BTH with *in situ* H_2



REACTION PROFILE FOR HDS @ 380 °C.

($PCO_0 = 600$ psig ; $BTH_0 = 267$ mmol; 70 ml H_2O /163 ml TOLUENE; 1.78 g MoO_3 ; 1300 rpm).