

HYDROGENATION OF COAL LIQUIDS  
IN THE PRESENCE OF SULFIDED Ni-Mo/Al<sub>2</sub>O<sub>3</sub>

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INTRODUCTION

Hydrogenation is one of the most important catalytic processing techniques applied to the petroleum industry. Although considerable work has been done on the hydrotreating of petroleum feedstocks(1,2) and model compounds(3), relatively few studies have been reported on hydrogenation of coal-derived liquids(4-9). Coal liquids contain much less hydrogen (6-8% b. wt.) and considerably more nitrogen (1-2%) and oxygen (4-5%) as compared to petroleum crudes and residua (hydrogen, 11%; nitrogen, <1%)(10). Coal liquids have much higher concentration of asphaltenes than petroleum residua (25-35% b. wt. vs 5-6% b. wt.), as well as higher overall aromaticity than the latter (60-75% b. wt. vs 20-35% b. wt. of aromatic carbon). This high concentration of condensed aromatic ring structures in coal liquids causes coke formation to a large extent in refining processes such as catalytic cracking. The heteroatoms, particularly nitrogen and sulfur, are severe poisons for many of the catalysts employed in petroleum refining. Hence, hydrotreatment of such liquids may be necessary to upgrade their quality and make them suitable for further refining processes. In this study, the hydrogenation of Synthoil and fractions derived from it, in the presence of sulfided Ni-Mo/Al<sub>2</sub>O<sub>3</sub> and Ni-W/Al<sub>2</sub>O<sub>3</sub> systems, was systematically investigated as a function of experimental conditions, such as, reaction temperature, pressure and process time. Results obtained with model compounds (11-13) were correlated with results of this study to elucidate the hydrogenation behavior of syncrudes.

EXPERIMENTAL

Feedstock

The Synthoil (from West Virginia coal) used in this study was supplied by the Pittsburgh Energy Research Center. The cyclohexane soluble fraction (maltene) and cyclohexane insoluble fraction (A-P) of Synthoil were prepared according to the following procedure. Synthoil was mixed with cyclohexane in a ratio of 1:40 and the mixture was heated to near the boiling point of cyclohexane with magnetic stirring for about 40 minutes. The mixture was cooled to room temperature and kept overnight with continued stirring. The maltene fraction with cyclohexane was separated from A-P by vacuum filtration. The maltene fraction of Synthoil was separated from cyclohexane by evaporating cyclohexane under slight vacuum. The A-P fraction was dried in an oven kept at 80°C. Data on properties of the Synthoil and fractions derived from it are given in Table 1.

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Table 1

Analysis and some Properties of Synthoil and Synthoil Fractions

| <u>Material</u>                      | <u>C</u> | <u>H</u> | <u>N</u> | <u>S</u> | <u>O</u> | <u>H-aromaticity %</u> |
|--------------------------------------|----------|----------|----------|----------|----------|------------------------|
| Synthoil <sup>a</sup>                | 86.4     | 7.2      | 1.3      | 0.7      | 4.4      | 30.7                   |
| Cyclohexane-soluble fr. <sup>b</sup> | 88.3     | 7.5      | 1.2      | 0.6      | 2.4      | 28.1                   |
| Cyclohexane-insoluble fr.            | 88.1     | 6.1      | 1.9      | 0.3      | 3.6      | 36.4                   |

(Asphaltene<sup>c</sup>-Preasphaltene<sup>d</sup>)

(a) Specific gravity, 1.14; viscosity SSF @ 82°C, 104; ash 1.6% b. wt.

(b) Represents 64.7% b. wt. of the total Synthoil; (c) Represents 28.1% b. wt. of the total Synthoil; (d) Represents 7.2% b. wt. of the total Synthoil

Catalyst

The catalysts used in this study were (i) HT100E, manufactured by Harshaw Chemical Company and (ii) Sphericat 550, manufactured by Nalco Chemical Company. The 1/16 inch HT100E extrudates contain 3.0% NiO and 15.0% MoO<sub>3</sub> on alumina. The 1/16 inch Sphericat 550 spheres contain 5.1% NiO and 20.2% WO<sub>3</sub> on alumina. These catalysts were chosen from several commercial catalysts for our study because of their high hydrogenation activity and low cracking characteristics in the hydrogenation of model compounds(11). Both catalysts were sulfided before use.

Hydrogenation Technique

All the experiments on hydrogenation of Synthoil were carried out in a fixed bed flow reactor (36" L. x 1.25" I.D. x 0.5" W.T.) system. An autoclave (11) of 300cc capacity was used in all the experiments on hydrogenation of maltene and A-P fractions of Synthoil.

The fixed-bed hydrotreating unit (11) was flushed with hydrogen to remove air, and the system was brought to reaction temperature and pressure. Synthoil was heated to about 80°C and pumped at a rate of 30 cc/hr. to maintain a LHSV of 0.5 hr<sup>-1</sup> (catalyst:60cc) in each experiment. A hydrogen flow rate of 2 litres/min. was used. The product was cooled in the condenser and the liquid product was collected from the low pressure separator. The gaseous product was passed through a series of scrubbers (to remove H<sub>2</sub>S and NH<sub>3</sub>) and wet test meter. The liquid product was dissolved in CCl<sub>4</sub>, filtered and analyzed.

The hydrogenation procedure in the autoclave unit is as follows. After placing known amounts of Synthoil fraction and catalyst in the autoclave, the autoclave was purged with H<sub>2</sub> and then pressurized with H<sub>2</sub> to half the reaction pressure. The reactor was heated to the reaction temperature and the pressure was adjusted to the experimental pressure. The total pressure in the system was maintained constant throughout the reaction period by the automatic addition of hydrogen whenever necessary from the cylinder through the regulator and check valve. At the end of each experiment, the reactor was cooled rapidly, and the pressure was released. The product was mixed with CCl<sub>4</sub>, filtered to remove the catalyst and analyzed.

Due to the complex nature of coal-derived liquids and their products of hydrogenation, no attempt of structural analysis of the liquid products was made. Elemental analysis was done for all samples. A simple analytical method, using PMR (Proton Magnetic Resonance), was developed(11) to determine the overall aromatic saturation. The extent of saturation was estimated as

$$\% \text{ decrease in H-aromaticity} = \frac{(\text{H-aromaticity})_{\text{feed}} - (\text{H-aromaticity})_{\text{product}}}{(\text{H-aromaticity})_{\text{feed}}} \times 100$$

## RESULTS AND DISCUSSION

### Effect of Experimental Conditions upon the Hydrogenation of Synthoil

Coal derived liquids consist of condensed polycyclic aromatic hydrocarbons (mainly 3 to 5 rings), as well as aromatic-naphthenic, aromatic-heterocyclic and aromatic-naphthenic heterocyclic systems. The extent of hydrogenation and heteroatom removal depend on several factors, e.g., (a) reaction temperature, (b) reaction pressure, (c) hydrogen/substrate ratio, (d) liquid hourly space velocity (LHSV), (e) catalyst structure and type, and (f) composition of the feedstock (structural characteristics of the starting substrate components and of partially hydrogenated intermediates). The effect of some of these variables upon hydrogenation of Synthoil over Ni-Mo/Al<sub>2</sub>O<sub>3</sub> was studied in a fixed bed reactor, using a hydrogen flow rate of 2 litres/min., and a LHSV of 0.5 hr<sup>-1</sup>.

### Effect of Process Time

Figure 1 summarizes the observed hydrogen uptake, viz. the % decrease in H-aromaticity, in the product from hydrogenation of Synthoil as a function of process time (between 60-260 min.). Initially (process time, 60-140 min.), a rapid decrease in hydrogen uptake, is observed. However, as the process time is extended (140-300 min.), the % decrease in H-aromaticity and the hydrogen uptake reach a plateau. This indicates that the catalyst deactivates appreciably at the beginning of the experiment, but subsequently its activity is stabilized. Product analysis shows a hydrogen content of ca 10% b.wt., and a 55-60% decrease in H-aromaticity under steady state conditions (Figure 1).

### Effect of Temperature

Figure 2 shows the observed change in hydrogen content and in H-aromaticity of the product from hydrogenation of Synthoil as a function of temperature (between 300-400°C at 2900 psig). As seen, the hydrogen uptake increases with increase in temperature up to ca 370°C (maximal % decrease in H-aromaticity, 62.4%; and maximal hydrogen content, ca 10%). Above 370°C, there is apparently a tendency of decrease in the hydrogen uptake. Experimental and calculated data (14,15) on hydrogenation equilibria of polycyclic aromatics indicate that at high hydrogen pressures, e.g., above 2000 psig and temperatures below 390°C, the equilibrium is displaced almost entirely in the direction of hydrogenation. On the other hand, at temperatures above 390°C (this temperature may vary depending upon the type of aromatics), there should be some of the free aromatic reactant at equilibrium. The concentration of this aromatic component increases with increase in temperature. For example, upon hydrogenation of phenanthrene, the concentration of the latter at equilibrium decreases with increase in temperature up to 375°C, but then increases with further increase in temperature (14). Hence, this provides a plausible explanation for the observed hydrogenation behavior of Synthoil. The observed increase in aromatic content of the product from hydrogenation of Synthoil at temperatures above 370°C may be also due to some increase in the extent of cracking reactions.

Figure 3 shows the change in nitrogen and sulfur content of the product from hydrogenation of Synthoil as a function of temperature (between 300-400°C). As expected, the extent of N and S removal increases with increase in temperature,

since the equilibrium data indicate that heteroatom removal proceeds irreversibly and is, therefore, not equilibrium controlled. Nitrogen removal ranges from 18% to 70% whereas the S removal ranges from 45% to 86%. This indicates that the former process is generally a slower one. The observed incomplete removal of heteroatoms may be due to the stereochemical characteristics of some more complex nitrogen-and sulfur-containing heterocyclics, and of partially hydrogenated intermediates (11,13). Another reason for incomplete saturation of polyaromatics and incomplete removal of heteroatoms in feedstocks such as Synthoil and their fractions may be due to diffusion effects (1,16).

### Effect of Pressure

Figure 4 shows the observed change in H-aromaticity of the product from hydrogenation of Synthoil as a function of pressure (between 2500-2900 psig). As seen, the saturation of aromatics increases with increase in pressure. It is indicated(11) that nitrogen removal increases with increase in pressure (51% at 2500 psig and 70% at 2900 psig), but the extent of S removal changes only to a small extent (83 to 89%) with increase in pressure (between 2500-2900 psig). A similar behavior was observed in the Texaco work on hydrodesulfurization of heavier intermediate cracked gas oil(1).

### Hydrogenation of Maltene (Cyclohexane-Soluble) and Asphaltene-Preasphaltene (Cyclohexane-Insoluble) Fractions of Synthoil

A Synthoil sample was separated into a maltene (cyclohexane-soluble) fraction and an asphaltene-preasphaltene (cyclohexane-insoluble) fraction as described in experimental section. These fractions derived from Synthoil were hydrogenated in an autoclave under severe conditions (pressure, 2900 psig; temperature, 288-377°C; reaction time, 7 hr.) using sulfided Ni-W/Al<sub>2</sub>O<sub>3</sub> catalyst and the results are summarized in Table 2. As seen from experiment 1, the cyclohexane-soluble fraction is readily hydrogenated (% decrease in H-aromaticity=71.2%, corresponding to a residual H-aromaticity of only 8.1%). On the other hand, hydrogenation of the cyclohexane insoluble fraction (asphaltenes plus preasphaltenes), under the same set of conditions, (expt. 3) is very limited (% decrease in H-aromaticity of 23.6% corresponding to a residual H-aromaticity of 27.8%). Table 2 also shows that the saturation of the cyclohexane-insoluble fraction increases with increase in temperature.

Table 2

Change of Quality in the Product from Hydrogenation of Synthoil Fractions<sup>a-c</sup>

| <u>Expt. No.</u>            | <u>Cyclohexane soluble fr.<sup>d</sup></u> | <u>Cyclohexaneinsoluble fr.<sup>e</sup> (asphaltenes-preasphaltenes)</u> |          |          |
|-----------------------------|--------------------------------------------|--------------------------------------------------------------------------|----------|----------|
|                             | <u>1</u>                                   | <u>2</u>                                                                 | <u>3</u> | <u>4</u> |
| Reaction temperature, °C    | 341                                        | 288                                                                      | 341      | 377      |
| H-aromaticity, %            |                                            |                                                                          |          |          |
| in feed                     | 28.1                                       | 36.4                                                                     | 36.4     | 36.4     |
| in product                  | 8.1                                        | 34.5                                                                     | 27.8     | 25.3     |
| % decrease in H-aromaticity | 71.2                                       | 5.6                                                                      | 23.6     | 30.5     |
| % heteroatom removed        |                                            |                                                                          |          |          |
| N                           | 86.1                                       | 8.5                                                                      | 31.9     | 51.6     |
| S                           | 62.9                                       | --                                                                       | --       | 62.5     |
| O                           | 96.7                                       | 33.1                                                                     | 63.6     | 82.4     |

(a) Catalyst: sulfided Ni-W/Al<sub>2</sub>O<sub>3</sub>; (b) Pressure: 2900 psig; (c) Reaction time: 7 hr.; (d,e) For elemental composition of reactant, see Table 1.

A probable reason for the difficulty of completely hydrogenating the maltene fraction of Synthoil is indicated by results obtained from hydrogenation of model compounds, e.g. phenanthrene and pyrene(11,12) using commercial hydrogenation catalysts (Ni-Mo/Al<sub>2</sub>O<sub>3</sub>, Ni-W/Al<sub>2</sub>O<sub>3</sub>, etc.). It was found that hydrogenation of the outer rings in phenanthrene is a fast reaction. But, once the two outer rings are saturated, the subsequent step of hydrogenating the sterically hindered inner ring is much slower. It should be expected in the case of condensed polycyclic compounds present in the maltene fraction, at least a part of the inner rings become sterically hindered by adjacent hydroaromatic rings during the step-wise hydrogenation process. This would be more probable in tetracyclic and pentacyclic systems, e.g., triphenylene. In the latter compound, for instance, there is one inner ring which is fully substituted by three terminal benzene rings which upon hydrogenation form a steric barrier around the residual inner benzene ring. Examination of molecular models show that flatwise adsorption of this inner benzene ring on the catalyst surface is very difficult while edgewise adsorption is excluded. The residual 8.1% of H-aromaticity in the hydrogenated maltene fraction corresponds roughly to 15-20% of residual non-hydrogenated aromatic rings, *viz.* approximately one residual aromatic ring per 5-6 hydroaromatic rings, in line with the above suggested model. The relatively higher resistance to hydrogenation shown by the asphaltene-preasphaltene fraction (Table 2; expt. 2, 3, and 4) may be due to the higher complexity and proportionally higher concentration of sterically hindered inner rings in the polycyclic systems present in this fraction. For instance, in 1,2,3,4,5,6,7,8-tetrabenzonaphthalene which is a hexacyclic system, the completely substituted rings represent 33% (one out of three) of the condensed system.

The products of hydrogenation of the asphaltene-preasphaltene fraction (expts. 2,3, and 4) were analyzed for cyclohexane solubility. Results obtained are plotted in Figure 5. As seen, solubility increases sharply with gradual decrease in the H-aromaticity of the asphaltene fraction, reaching a level of about 85% at a point of 31% decrease in H-aromaticity. This important result can be rationalized by considering three possible factors affecting solubility: (a) polar compounds such as O, S, and N-containing compounds undergo heteroatom removal (Table 2) making the product less polar, *viz.*, more soluble in a non-polar solvent, e.g., cyclohexane, (b) decrease in the complexity and molecular weight of the asphaltene molecules resulting from splitting reactions, (c) the partial hydrogenation of the polycyclic aromatic system could also contribute to the observed increase in solubility.

#### CONCLUSIONS

Results obtained from this study of hydrogenation of Synthoil and its fractions indicate the following:

(i) Even under severe hydrogenation conditions where the aromatic saturation equilibria favor in the direction of complete saturation, coal-derived liquids show marked resistance to complete hydrogenation. It is concluded, in line with the results obtained with model compounds, that the resistance to complete hydrogenation may be due to sterically hindered aromatic rings.

(ii) Hydrodenitrogenation is relatively more difficult when compared to hydrodesulfurization in coal-derived liquids.

(iii) The rate and depth of hydrodenitrogenation and hydrodesulfurization of coal-derived liquids may strongly depend on the steric characteristics of condensed N and S heterocyclic aromatic feed components, or of partially hydrogenated intermediates.

(iv) The asphaltene-preasphaltene fraction of Synthoil shows higher resistance to hydrogenation than the maltene fraction of Synthoil.

(v) The solubility of the hydrogenated product of asphaltene-preasphaltene fraction of Synthoil in cyclohexane increases with decrease in H-aromaticity and heteroatom content.

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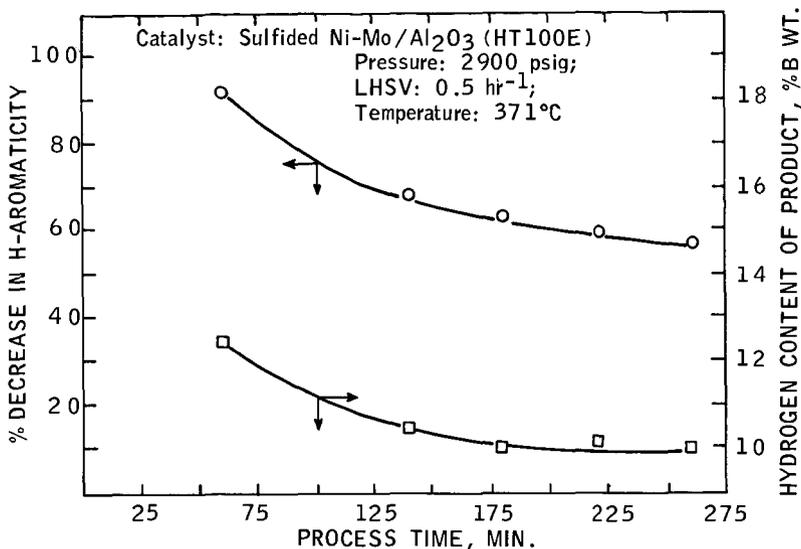


Fig. 1. Change in hydrogen content and H-aromaticity of the product from hydrogenation of Synthoil as a function of process time.

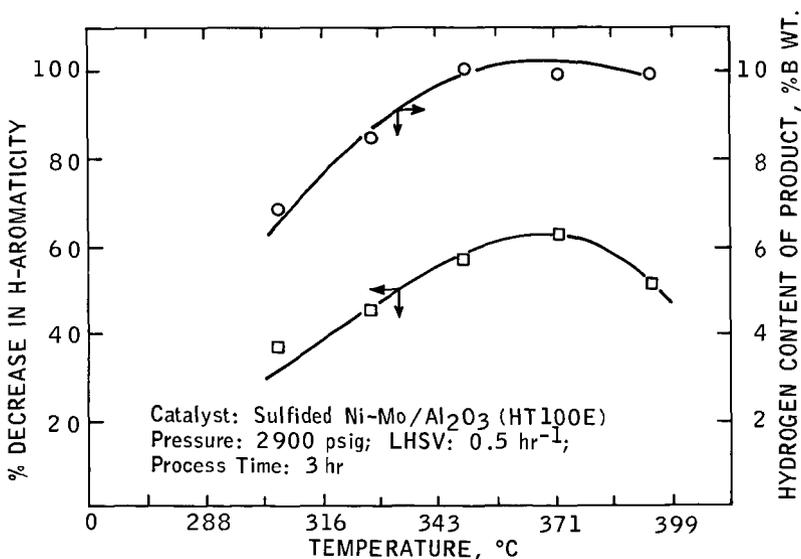


Fig. 2. Change in hydrogen content and H-aromaticity of the products from hydrogenation of Synthoil as a function of temperature.

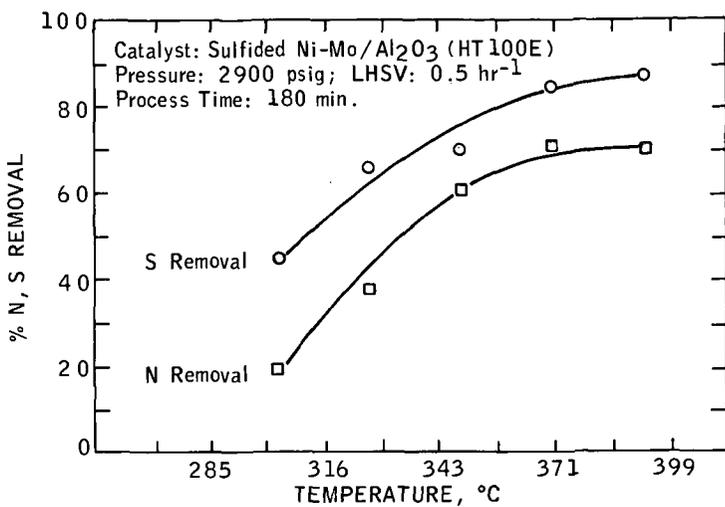


Fig. 3. Change in nitrogen and sulfur content of the product from hydrogenation of Synthoil as a function of temperature.

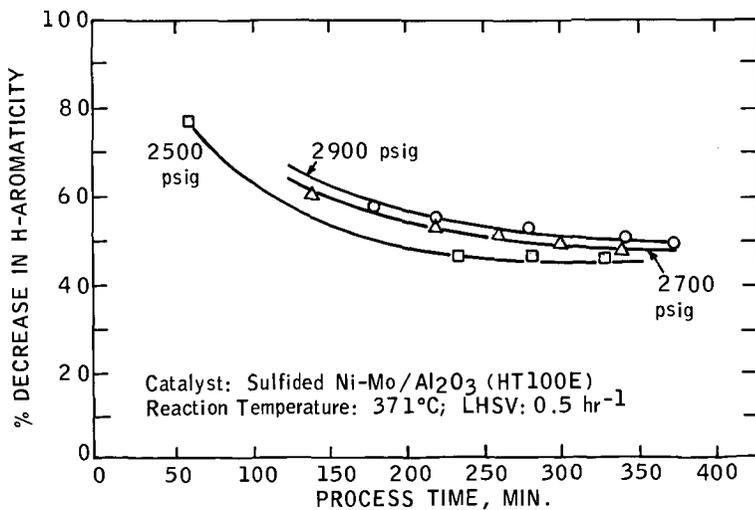


Fig. 4. Change in H-aromaticity of the product from hydrogenation of Synthoil as a function of pressure.

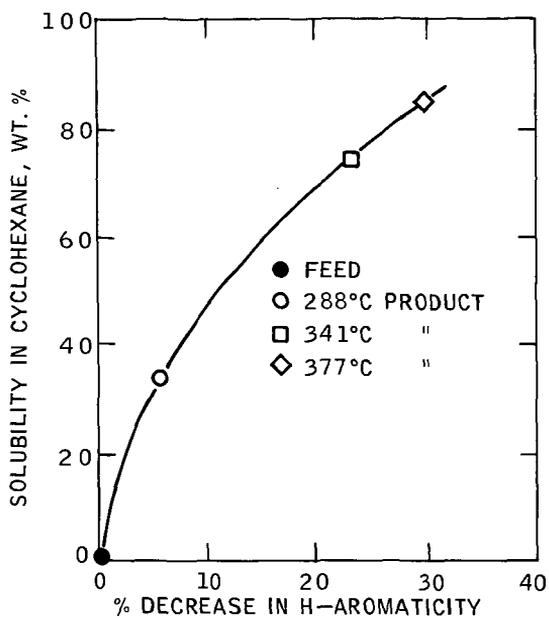


Fig. 5. Change in solubility of asphaltene fraction in cyclohexane as a function of decrease in H-aromaticity.

Pressure: 2900 psig  
 Reaction time in each run, 7 hr.  
 Catalyst: Sulfided Ni-W/ $\text{Al}_2\text{O}_3$