

## EFFECT OF HYDROTREATING CONDITIONS ON HYDROCRACKING OF A COAL DERIVED LIQUID

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Keywords: Coal Liquid, Hydrotreating, Hydrocracking

### ABSTRACT

Several coal derived liquids produced using different hydrotreating severities were hydrocracked to naphtha over a presulfided commercial hydrocracking catalyst. The feeds had similar boiling range and molecular type distribution but different nitrogen content. Feed nitrogen content had a significant effect on the hydrocracking activity, activity maintenance, and selectivity. Rapid deactivation was observed for feeds with nitrogen content higher than 50 ppm. For the feed with 50 ppm N, the gas oil (+205°C) conversion to naphtha decreased observably in the initial 4 hours. An initial catalytic activity study indicated that first order kinetics can be used to describe the gas oil conversion to naphtha. The initial hydrocracking rate of gas oil was approximately inversely proportional to the feed nitrogen content. Related model compound studies showed that the hydrocracking of cumene and hexadecane was very dependent on feed N content.

### INTRODUCTION

Since it has been expected that total petroleum products demand will rise greatly before the end of this century, refiners are increasing the proportion of heavier, poorer quality crude or syncrude in their feedstocks. These feeds include less valuable petroleum stocks such as residua, and fuels derived from coal, shale, and tar sands. However, liquids derived from direct coal liquefaction still have low hydrogen to carbon ratio, high polyaromatic concentrations, and high sulfur and nitrogen concentrations. Upgrading of these liquids is required before they can be blended into refinery feeds. The primary upgrading process usually involves the hydrotreating of either the entire coal liquid or individual fractions obtained by distillation.

Although hydrogen content can be increased and heteroatoms reduced significantly in the hydrotreating process, the hydrotreated coal liquid still has a high boiling point because only minimal hydrocracking occurs in the hydrotreater. Further downstream treatment in the form of hydrocracking is necessary before fuels of high quality can be obtained. The hydrocracking process is required because coal liquids generally have a high content of polycyclic aromatic compounds, which are relatively unreactive in catalytic cracking.

Hydrocracking is a flexible refining process that allows conversion of feedstocks ranging from naphtha to residua into more valuable, lower boiling products. Hydrocracking catalysts are dual functional, consisting of hydrogenation metals on an acidic cracking base. There have been commercial hydrocracking processes using zeolite-based catalysts for converting petroleum distillates and residues.<sup>1</sup> The research on hydrocracking coal liquids is still very limited. In this work, we studied the activity and activity maintenance of a commercial hydrocracking catalyst using coal liquids with different hydrotreating conditions. The objective was to examine how hydrotreating conditions affect hydrocracking reactions. We also performed some model compound hydrocracking experiments to study the effect of N on hydrocracking rates.

### EXPERIMENTAL

**Model Compound Experiments.** Reactions were performed in tubing bomb microreactors (TBMRs) charged with 1000 psig ambient hydrogen pressure. Two solutions were used: (1) 5g of hexane solution containing 2 wt% cumene, (2) 6g of pure hexadecane. Different nitrogen contents were obtained using pyridine. Experiments were performed at 350°C for cumene reactions and at 400°C for hexadecane reactions; both for 20 min using 0.1g of a commercial NiMo/zeolite catalyst (Akzo KC2600, MoO<sub>3</sub> < 25%, NiO 1-10%, Al<sub>2</sub>O<sub>3</sub> 30-70%, SiO<sub>2</sub> 20-50%).

**Coal Liquid Experiments.** The coal liquid hydrocracking experiments were carried out in both an upflow continuous reactor and TBMRs to study the deactivation behavior and

initial activity of the catalyst. The feed reactants were hydrotreated coal liquids prepared with different hydrotreating severities in a continuous reactor<sup>2</sup>. Four hydrotreated liquids with similar boiling range distribution and molecular type distribution but with different nitrogen contents, as summarized in Table 1, were prepared as hydrocracking feeds to investigate the effect of hydrotreating conditions on the hydrocracking reaction.

In the continuous reactor, liquid feed and hydrogen were mixed to produce a dispersive stream entering the bottom of the externally heated reactor tube. The catalyst (5 g) was crushed to 16-25 mesh, diluted with 1.0 mm glass beads (20 g), and then placed in the center of the reactor. The reactor was operated at 400°C and 9.7 MPa with a pressure drop across the reactor bed of about 0.1 MPa. Prior to the start of a run the catalyst was presulfided using 5 wt% CS<sub>2</sub> in cyclohexane at a liquid flow rate of 0.05 ccm and hydrogen at 100 sccm.

The TBMR runs were performed at 400°C and 6.9 MPa cold H<sub>2</sub> pressure. For the deactivation runs in TBMR, 4 g of liquid reactant was used with 1 g catalyst for 2 hours. The catalyst was recovered, washed in THF, and dried in air over night. This catalyst was then used for the next run with fresh feed and the same procedure was repeated for five times, so that the total time the catalyst exposed to the reaction environment was 10 hours. Prior to the first reaction, the catalyst was presulfided in the same type of TBMR using 0.5 g CS<sub>2</sub> for two hours at 400°C and 6.9 MPa cold H<sub>2</sub> pressure. For the kinetic experiments, approximately 4 g of liquid reactant was charged to the TBMR with different loadings of catalyst ranging from 0.1 g to 1 g. The reaction time was from 20 to 120 min. The liquid product was collected and analyzed using GC simulated distillation according to ASTM test method D2887. While the detailed GC boiling curve was obtained, for simplicity of discussion, the product boiling range distribution in this study was grouped into three cuts only: gas, naphtha (-205 °C), and gas oil (+205 °C). The gas make was obtained by difference using the weights of feed and liquid products. The percentage of gas make was defined as

$$\text{Gas Make} = \frac{\text{wt. of gases after RXN} - \text{wt. of Initial H}_2}{\text{wt. of liquid feed}} \quad (1)$$

## RESULTS AND DISCUSSION

**Model Compounds Experiments.** The effect of feed nitrogen content on cumene and hexadecane conversion is shown in Figure 1. Cumene conversion without nitrogen was 96%. It is relatively easy to crack cumene into benzene and propylene due to the tertiary carbon of cumene which can form very stable tertiary carbonium ions on acid sites. The reactions of hexadecane, a straight-chain paraffin, showed about 51% conversion in the absence of nitrogen. In this reaction (0 ppm N), 5% gas, 41% naphtha, and 54% of gas oil were obtained and 82% of the hexadecane converted was in the naphtha fraction. KC2600 catalyst with hexadecane in the absence of nitrogen has very good selectivity for naphtha. Little conversion was observed above 100 ppm N in both reactions. These results show that the hydrocracking activity of KC2600 is completely poisoned by amounts of nitrogen around 100 ppm and nitrogen removal from the high nitrogen containing feeds such as coal derived liquids is required prior to the hydrocracking process. The catalytic cracking and hydrogenation functions of KC2600 (NiMo/zeolite) can be examined by two reaction pathways of cumene hydrocracking.

- 1: cumene → benzene + propylene → other products
- 2: cumene → iso-propylcyclohexane → other products

Pathway 1 is cumene cracking to benzene (B) and propylene (PP) by acid sites mainly on the zeolite. In pathway 2, cumene is hydrogenated to iso-propylcyclohexane (IPCH) by metal sites (Ni and Mo) followed by cracking to other compounds such as cyclohexane (CH), PP, etc. From these experiments, the concentrations of cumene, B, and IPCH from cumene reactions as a function of nitrogen content are shown in Figure 2. The concentration of B was about 0.7% at 0 ppm N and decreased to 0 at about 33 ppm N. IPCH was observed to appear at about 13 ppm N. Below 13 ppm, IPCH is probably cracked to form CH and PP. The IPCH concentration increased to a maximum around 33 ppm N and decreased to about 0 above 100 ppm N. These observations show the following. Below 10 ppm N, cracking reactions by acid sites are dominant. As nitrogen content increases from 10 ppm, however, acid sites are poisoned. On the other hand, metal sites have substantial activity in the range of 10-100 ppm N with IPCH being the main product identified. This activity was also poisoned above 100 ppm N. It can be concluded that the acid function for reaction pathway 1 is severely poisoned around 33 ppm N, while the hydrogenation function (Ni and Mo) still has some activity up to

about 100 ppm N.

**Coal Liquids Experiments.** Figure 3 shows the lumped boiling range distribution of the hydrocracking liquid products from continuous reactor. The feed had a nitrogen content of 230 ppm (Feed B in Table 1), and the reaction conditions have been described previously. It is seen that there is a significant deactivation of the catalyst, and it is completely deactivated in 24 hours on stream, as reflected by the gas oil content. However, very high hydrocracking activity was observed in a TBMR run with fresh catalyst, which is also shown in Figure 3. It is probable that, during the first few hours in the continuous reactor, the liquid produced might contain low gas oil fraction (high naphtha fraction) because of initially high cracking activity. The gas oil content then increased gradually due to catalyst deactivation. As a result, the sample collected in the first 24 hours, which is actually a mixture produced during this period, exhibited some gas oil conversion, but not as high as that in TBMR in which the reaction time was only 2 hours. The rapid deactivation of the catalyst is speculated to be due to nitrogen or polyaromatics in the feed. Therefore, as a follow on to this study, several deactivation runs were performed in TBMRs with different feed nitrogen contents.

Figure 4 shows the experimental runs made to examine the effect of feed hydrotreating conditions on the hydrocracking reactions. In the following, the feed N content is used as a measure of hydrotreating severity, although other feed characteristics, e.g. polyaromatics content, are also important in catalyst activity behavior. Figure 4 shows that the gas oil conversion decreases with the increase of nitrogen in the feed. The deactivation rate also increases with the increase of nitrogen content, except for the 1800 ppm N feed, where gas oil conversion was low. This is consistent with previous results in the literature. Yan<sup>3</sup> reported that for the hydrocracking of heavy gas oil over NiW/REX-NiW/silica-alumina, when the nitrogen content was increased from 1 ppm to 12 ppm, the reactor temperature had to be increased by 16.7°C to maintain the same catalyst activity. Bouchy et al<sup>4</sup> studied the hydrocracking of a model light cycle oil with 480 ppm N in the feed. They found that the inhibiting effect of nitrogen led to a decrease of the reaction rate of about 30%. It is generally agreed that nitrogen compounds will irreversibly adsorb on acidic sites of hydrocracking catalysts and thus reduce their effectiveness and activity maintenance. It thus appears that a more active hydrotreating catalyst must be developed or more severe hydrotreating conditions should be employed for HDN to reduce the nitrogen content to even lower levels. Another option lies in the development of new hydrocracking catalysts which are more resistant to nitrogen poisoning. Yet it should be noticed that the yield of desired product, e.g., naphtha formation, also might be greatly affected by the catalyst activity and reaction conditions, as is seen in Figure 5 where considerable gas formation was accompanied with gas oil conversion. It seems that some nitrogen in the feed may function to temper the catalyst activity towards gas formation. Therefore, it appears that quantitative determination of the hydrocracking rate constant and the nitrogen effect would be meaningful for the optimal design of hydrocracker for the coal liquid.

To quantify the effect of N content on the initial hydrocracking rate, an empirical power-law kinetic model, as shown in equation (2) was used to describe the gas oil conversion.

$$-\frac{dy_A}{dt} = \frac{W_{cat}}{W_{liq}} k y_A^a p_H^b \quad (2)$$

In equation (2),  $y_A$  is the weight fraction of gas oil,  $p_H$  is the partial pressure of hydrogen which is directly proportional to the weight fraction of dissolved hydrogen,  $W_{cat}$  is the weight of catalyst, and  $W_{liq}$  is the weight of liquid feed. The term  $W_{cat}/W_{liq}$  is equivalent to the reciprocal of WHSV generally used in flow reactors.

Figure 6, plotted as weight fraction vs. reaction time, suggests that the reactions can be adequately described using the following consecutive reaction scheme, because the initial rate of gas formation is zero, and the reaction rate of naphtha to gases is much slower than that of gas oil to naphtha.



In Figure 6, the data were obtained with catalyst loading from 0.1 to 1g, three particle sizes (16-25, 60-80, 80-200), and reaction time from 20 to 120 min. There was no discernable effect of catalyst loading, particle size, or reaction time, therefore, it is believed that, in our experiments, there is neither internal nor external mass transfer limitation and the data represent the results of reaction kinetics. At  $W_{cat}/W_{liq}$  larger than 0.15 hour, the percentage of naphtha

is essentially stable, but more gas was generated with time at the expense of gas oil. Thus, it appears that a value of  $W_{cat}/W_{in}$  of no more than 0.15 (or WHSV in flow reactor larger than 6) would be appropriate for the hydrocracking of coal liquid, if the desired product is naphtha. In practice, the value of WHSV in a flow reactor is typically less than 6 because the catalyst will be deactivated somewhat in the initial reaction period.

Since the TBMR is a batch reactor, the hydrogen partial pressure decreases with gas oil conversion. For this reason, the rate constant was evaluated using the low gas oil conversion data. The hydrogen concentration in the liquid, which is approximately directly proportional to its partial pressure, was also assumed constant during this initial stage. Therefore equation (2) is reduced to equation (3).

$$-\frac{dy_A}{d\left(\frac{W_{cat}}{W_{liq}}t\right)} = k'y_A^a \quad (3)$$

The linear plots of Figure 7,  $\ln(y_{A0}/y_A)$  vs.  $W_{cat}/W_{in}$ , according to equation 3, indicate that gas oil hydrocracking can be described as a first order reaction. The effect of feed nitrogen content is significant. The reaction rate is approximately inversely proportional to nitrogen content. Since this study considered only the initial reaction rate of gas oil conversion, no quantitative effect of feed nitrogen content on catalyst activity towards gas formation was determined as it was generally less than 1%.

#### REFERENCES

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Table 1. Properties of Feeds for Hydrocracking

Feed	A	B	C	D
Nitrogen Content (ppm)	50	230	820	1800
Naphtha (-205°C) (wt %)	14.1	11.3	10.5	10.3
Gas Oil (+205°C) (wt %)	85.9	88.7	89.5	89.7
Molecular Type Distribution (wt%)				
Paraffins	17.3	15.3	14.4	11.4
Naphthenes	26.2	24.0	22.6	21.1
Monoaromatics	34.8	37.4	39.3	42.3
Polyaromatics	21.7	23.3	23.7	25.2

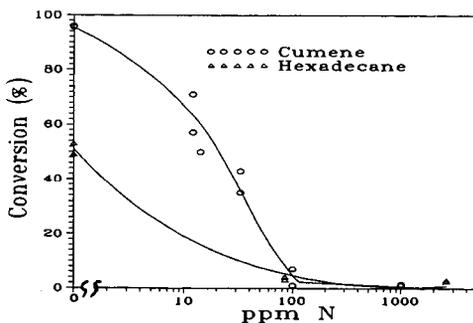


Figure 1 Effect of Nitrogen Content on Cumene and Hexadecane Conversion.

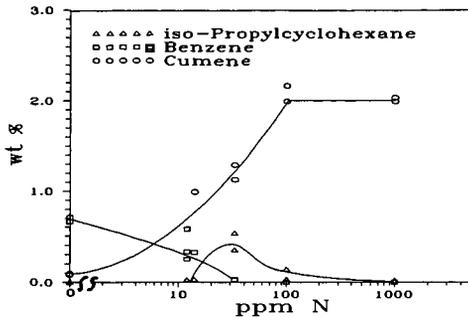


Figure 2 Product Distribution of Cumene Reactions as a Function of Nitrogen Content.

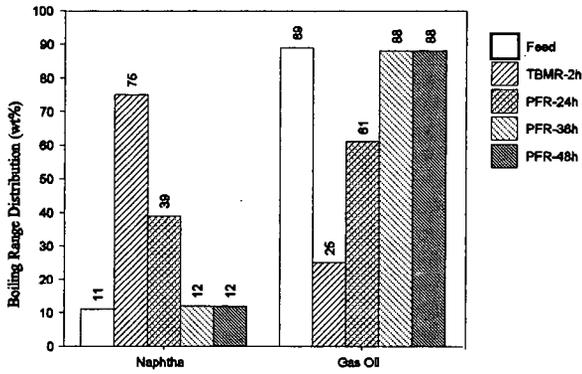


Figure 3 Hydrocracking Catalyst Deactivation in Continuous Reactor with Feed Nitrogen Content of 230 ppm.

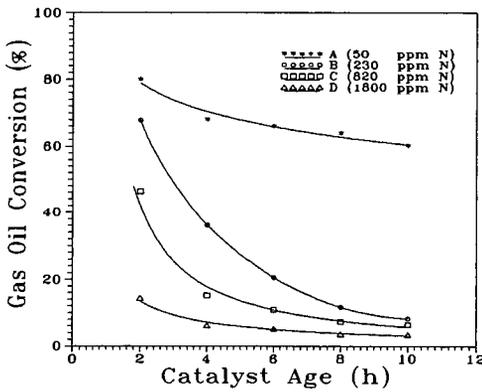


Figure 4 Effect of Feed Nitrogen Content on the Catalyst Deactivation Behavior and Gas Oil Conversion in Successive 2h TBMR Experiments.

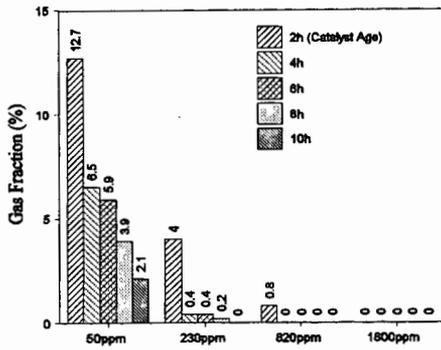


Figure 5 Effect of Feed Nitrogen Content on the Gas Make for Hydrocracking Reactions in TBMR

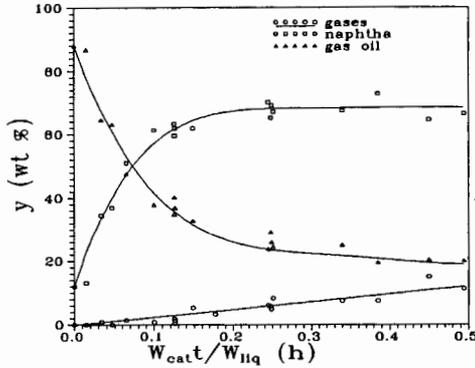


Figure 6 Hydrocracking Product Distribution at 400°C with Feed Nitrogen Content of 230 ppm

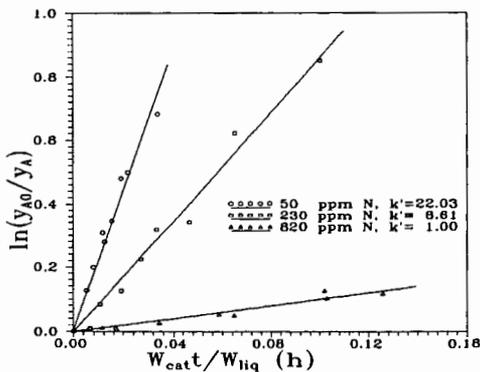


Figure 7 First Order Plots of Gas Oil Conversion with Different Feed Nitrogen Contents