

## HYDROCRACKING OF AROMATIC COMPOUNDS

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### Abstract

Dualfunctional catalysts based on Cobalt, Molybdenum and Nickel were used for the hydrocracking of different types of hydrocarbons and heterocyclic compounds. The interfering effect of heterocyclic compounds on the hydrocracking of hydrocarbons was studied. The deactivation of the dualfunctional catalysts by some of the heterocyclic compounds was investigated.

### Introduction

Hydrocracking over dualfunctional catalysts is a versatile method for converting polynuclear aromatic hydrocarbons and heterocompounds to lower boiling compounds. Though hydrocracking has been widely employed for the processing of petroleum and synthetic oils<sup>1-3</sup>, the published data on the hydrocracking of pure aromatic hydrocarbons and heterocompounds are very meager. Flinn et. al.<sup>4</sup> studied the hydrocracking of n-butylbenzene and tetralin over a nickel sulfide on silica-alumina catalyst and found that the principal reactions occurring were ring opening, dealkylation and dehydrogenation. Sullivan et. al.<sup>5,6</sup> investigated the hydrocracking of different types of aromatic hydrocarbons over a nickel sulfide on silica-alumina catalyst and reported the occurrence of the 'paring reaction' which involves the removal of methyl groups attached to aromatic nuclei and their elimination as light isoparaffins with no loss of aromatic rings. They also reported the isomerization and cyclization of side chains to varying degrees forming indane type of structures. In this communication, the data on the hydrocracking of different types of polynuclear aromatic hydrocarbons over several dualfunctional catalysts are presented. The effect of the presence of sulfur, nitrogen and oxygen compounds on the conversion of aromatic hydrocarbons is reported.

### Experimental

Pure grade hydrocarbons and heterocompounds were used for hydrocracking. The catalysts contained 20% by weight of oxides of molybdenum, cobalt and nickel on silica-alumina. The quantity of the catalyst used was 25% by weight of the reactants unless otherwise mentioned.

Equipment: The hydrocracking work was done in a batch autoclave of 300 c.c. provided with all controlling and recording devices.

Hydrocracking procedure: Experiments were carried out with 10 gm of the hydrocarbon and heterocompound mixture with varying amounts of the catalyst at 475°C. The hydrogen to hydrocarbon mole ratio was maintained

at 15.51 and 21.57 in case of naphthalene and anthracene respectively. The starting (cold) pressure was kept constant at 1000 p.s.i. and the final pressure varied between 1700-1800 p.s.i.

### Results and Discussion

Synthetic crude oils produced from coal contain large quantities of aromatic hydrocarbons and heterocyclic compounds. The processing of these crudes mainly involves the conversion of aromatic hydrocarbons in admixture with aliphatic hydrocarbons and heterocompounds. A better understanding of the conversion of polynuclear aromatic hydrocarbons alone and in admixture with heterocyclic compounds to lighter products will be very useful in the development of efficient processes for the processing of synthetic crudes. The conversion of polynuclear aromatic hydrocarbons to lower boiling products can best be done by hydrocracking over dualfunctional catalysts. The aromatics have to be either partially or completely hydrogenated before they can crack to lighter products. Therefore, the temperature, hydrogen pressure or concentration and the activity and selectivity of the catalyst control the product distribution of the hydrocracking reaction. The data in Table I shows that the conversion of naphthalene increased with reaction time up to 2 hours. The yields of gas and coke and hydrogen consumption increased with naphthalene conversion. Alkylation of naphthalene took place during hydrocracking to a significant extent. The low concentration of decalins and saturated C<sub>5</sub>-C<sub>6</sub> hydrocarbons in the liquid product indicates that naphthalene was mainly hydrogenated to tetralin but only to a small extent to decalin.

The activity and selectivity of the dualfunctional catalyst depend upon the relative amounts of the hydrogenation and cracking components. The data in Table II shows that a MoO<sub>3</sub> content of 20 to 25% is optimum to get maximum hydrogenation and cracking functions. The total conversion also depends upon the hydrocarbon to catalyst ratio as shown by the data in Table III. Maximum hydrogenation activity was obtained at 25% of catalyst whereas cracking reached a maximum at 15%. Hydrogen concentration also plays an important part in the hydrogenation-cracking system as shown in Table IV. Both the hydrogenation and cracking increased with hydrogen concentration. The gas yield increased while the coke yield decreased slightly. Higher hydrogen concentration also increased the formation of decalin from naphthalene as can be seen from the higher concentrations of decalins and saturated C<sub>5</sub>-C<sub>6</sub> hydrocarbons in the liquid product.

As mentioned earlier, synthetic crudes contain large quantities of oxygen, sulfur and nitrogen containing compounds and it is of interest to know the effect of their concentration on hydrocarbon conversion. The effect of phenol on the conversion of naphthalene is shown by the data in Table V. The conversion of naphthalene increased with the phenol content up to 20%. However, the cracking activity was not affected even at 30% phenol though the hydrogenation activity decreased to some extent. The yields of gas and coke decreased and the yield of liquid product increased. The data indicates that the presence of phenol up to about 30% improves the hydrocarbon conversion. On the contrary, the presence of carbazole and

quinoline reduced naphthalene conversion (Tables VI and VII) to a significant extent. The effect was more pronounced at higher nitrogen contents. However, the yields of gas and coke decreased at higher nitrogen concentrations. The effect of the presence of dibenzothiophene on naphthalene conversion is shown by the data in Table VIII. 1% sulfur improved naphthalene conversion but a sulfur content of 2% and above, decreased the conversion significantly. The gas yield decreased while the coke yield increased. Like dibenzothiophene, n-hexyl mercaptan and diethyl sulfide also improved naphthalene conversion (Table IX) when they were present to the extent of 1% sulfur.

Anthracene was hydrocracked under similar conditions as naphthalene and the effect of reaction time on conversion is shown by data in Table X. Hydrogenation of anthracene reached a maximum of 95% at one hour while the cracking increased with reaction time up to 3 hours. In contrast to naphthalene hydrocracking, anthracene cracking produced more coke but less gas. The main products were the partially hydrogenated anthracenes and naphthalenes. Small amounts of tetralins and decalins present in the product indicate that either more hydrogenation activity is necessary for converting anthracene to monoring compounds as compared to naphthalene or anthracene hydrocracking has to be carried out in several stages.

The hydrocracking product distribution depends upon the type of catalyst used. Naphthalene and anthracene were hydrocracked over catalysts containing oxides of cobalt, molybdenum and nickel and the data are given in Tables XI and XII. In case of naphthalene hydrocracking, all the three catalysts affected similar naphthalene conversions of about 74 to 75%. However, cobalt and nickel exhibited slightly more hydrogenation and cracking activities and yielded more gas. The coke yield was more in case of molybdenum. Almost similar results were obtained with anthracene except cobalt exhibited more hydrogenation and cracking activity when compared to molybdenum and nickel, the latter exhibiting similar activities. Molybdenum yielded more coke.

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TABLE I  
EFFECT OF REACTION TIME ON NAPHTHALENE CONVERSION

Catalyst: MoO<sub>3</sub> on Silica-alumina

<u>Reaction Time, Minutes</u>	<u>30</u>	<u>60</u>	<u>120</u>
Product Distribution, wt, %			
Gas	6.1	10.4	12.9
Coke	3.8	5.8	7.6
Naphthalene	49.6	16.7	15.5
Alkyl naphthalenes	6.3	16.7	10.3
Tetralin	11.7	9.6	7.8
Alkyl tetralins	8.1	5.1	4.2
Decalins	Traces	1.3	1.3
Saturated hydrocarbons (C <sub>5</sub> -C <sub>6</sub> )	1.4	6.1	1.7
Alkyl benzenes	13.0	28.3	38.7
Hydrogen Consumption	3.1	4.1	4.5
Naphthalene Conversion	44.1	66.6	74.2
Hydrogenation	44.1	66.6	74.2
Hydrocracking	24.3	50.6	60.9

TABLE II  
EFFECT OF MoO<sub>3</sub> CONTENT ON NAPHTHALENE CONVERSION

Catalyst: 10% by Weight of Naphthalene

Reaction Time: 120 Minutes

MoO <sub>3</sub> Content, Wt. %	15	20	25	35
Product Distribution, Wt. %				
Gas	10.0	11.0	11.7	10.5
Coke	5.1	5.2	5.0	4.9
Naphthalene	21.6	21.2	20.9	20.7
Alkyl naphthalenes	10.8	10.5	8.9	12.0
Tetralin	12.1	11.7	13.5	10.7
Alkyl tetralins	1.0	1.1	1.4	2.6
Decalins	0.5	1.0	1.3	0.5
Saturated Hydrocarbons (C <sub>5</sub> -C <sub>6</sub> )	1.0	1.2	1.3	1.0
Alkylbenzenes	37.9	37.1	36.0	37.1
Hydrogen Consumption	4.1	4.0	4.2	4.1
Naphthalene Conversion	67.6	68.3	70.2	67.3
Hydrogenation	67.6	68.3	70.2	67.3
Hydrocracking	54.0	54.5	54.0	53.5

TABLE III  
EFFECT OF CATALYST CONCENTRATION ON NAPHTHALENE CONVERSION

Reaction Time: 120 Minutes

Catalyst: MoO<sub>3</sub> on Silica-alumina

<u>Catalyst Wt. % of Naphthalene</u>	<u>10</u>	<u>15</u>	<u>20</u>	<u>25</u>
Product Distribution, Wt. %				
Gas	10.5	13.0	12.8	12.9
Coke	5.2	5.7	5.9	7.6
Naphthalene	21.2	19.2	16.1	15.5
Alkyl naphthalenes	11.0	8.5	11.4	10.3
Tetralin	11.7	9.6	8.7	7.8
Alkyl tetralins	1.1	1.4	2.0	4.2
Decalins	1.0	1.1	0.7	1.3
Saturated Hydrocarbons (C <sub>5</sub> -C <sub>6</sub> )	1.2	0.8	1.8	1.7
Alkylbenzenes	37.1	40.7	40.6	38.7
Hydrogen Consumption	4.1	4.2	4.3	4.5
Naphthalene Conversion	67.8	72.3	72.5	74.2
Hydrogenation	67.8	72.3	72.5	74.2
Hydrocracking	54.0	60.2	61.1	60.9

TABLE IV  
EFFECT OF HYDROGEN CONCENTRATION ON NAPHTHALENE CONVERSION

Catalyst: MoO<sub>3</sub> on Silica-alumina

<u>Hydrogen/Naphthalene Mole Ratio</u>	<u>15.51</u>	<u>20.68</u>
Product Distribution, Wt. %		
Gas	12.8	15.0
Coke	5.9	4.8
Naphthalene	16.1	15.2
Alkyl naphthalenes	11.4	5.7
Tetralin	8.7	8.2
Alkyl tetralins	2.0	0.8
Decalins	0.7	1.5
Saturated Hydrocarbons (C <sub>5</sub> -C <sub>6</sub> )	1.8	3.1
Alkyl benzenes	40.6	45.7
Hydrogen Consumption	4.3	4.6
Naphthalene Conversion	72.5	79.1
Hydrogenation	72.5	79.1
Hydrocracking	61.1	69.6

TABLE V  
EFFECT OF PHENOL ON NAPHTHALENE CONVERSION

Reaction Time: 60 Minutes

Catalyst:  $\text{MoO}_3$  on Silica-Alumina

<u>Phenol Content, Wt. %</u>	<u>0.0</u>	<u>10.0</u>	<u>20.0</u>	<u>30.0</u>
Product Distribution, Wt. %				
Gas	10.4	9.0	8.5	7.6
Coke	5.8	4.2	4.0	4.0
Naphthalene	16.7	16.6	15.6	14.3
Alkyl naphthalenes	16.7	13.6	9.5	14.3
Tetralin	9.6	9.5	9.9	10.2
Alkyl tetralins	5.1	3.0	5.8	2.6
Decalins	1.3	1.1	1.8	0.9
Saturated Hydrocarbons ( $\text{C}_5\text{-C}_6$ )	0.7	4.0	5.4	6.6
Alkylbenzenes	33.7	39.0	39.5	39.5
Naphthalene Conversion	66.6	69.8	74.9	71.4
Hydrogenation	66.6	69.8	74.9	71.4
Hydrocracking	50.6	56.2	57.4	57.7

TABLE VI  
EFFECT OF CARBAZOLE ON NAPHTHALENE CONVERSION

Catalyst:  $MnO_3$  on Silica-alumina

<u>Nitrogen Content, Wt. % Naphthalene</u>	<u>0.0</u>	<u>1.0</u>	<u>2.0</u>
Product Distribution, Wt. %			
Gas	10.4	7.1	5.1
Coke	5.8	3.0	2.6
Naphthalene	16.7	38.2	41.6
Alkyl naphthalenes	16.7	7.2	5.9
Tetralin	9.6	26.9	28.7
Alkyl tetralins	5.1	0.4	0.2
Decalins	1.3	Traces	0.1
Saturated Hydrocarbons ( $C_5-C_6$ )	0.7	1.0	0.3
Alkyl benzenes	33.7	16.2	15.5
Naphthalene Conversion	66.6	54.6	52.5
Hydrogenation	66.6	54.6	52.5
Hydrocracking	50.6	27.3	23.5

TABLE VII  
EFFECT OF QUINOLINE ON NAPHTHALENE CONVERSION

Catalyst: MoO<sub>3</sub> on Silica-alumina

<u>Nitrogen Content, Wt. % of Naphthalene</u>	<u>0.0</u>	<u>1.0</u>	<u>2.0</u>
Product Distribution, Wt. %			
Gas	10.4	8.8	7.4
Coke	5.8	2.7	2.6
Naphthalene	16.7	33.4	36.0
Alkyl naphthalenes	16.7	7.3	20.0
Tetralin	9.6	20.0	15.9
Alkyl tetralins	5.1	2.1	0.9
Decalins	1.3	Traces	0.5
Saturated Hydrocarbons (C <sub>5</sub> -C <sub>6</sub> )	0.7	1.7	1.0
Alkyl benzenes	33.7	24.0	15.7
Naphthalene Conversion	66.6	59.3	44.0
Hydrogenation	66.6	59.3	44.0
Hydrocracking	50.6	37.2	26.7

TABLE VIII  
EFFECT OF DIBENZOTHIOPHENE ON NAPHTHALENE CONVERSION

Reaction Time: 60 Minutes

Catalyst: MoO<sub>3</sub> on Silica-Alumina

Sulfur Content: Wt. % of Naphthalene	<u>0.0</u>	<u>1.0</u>	<u>2.0</u>	<u>3.0</u>
Product Distribution, Wt. %				
Gas	10.4	9.0	8.9	8.2
Coke	5.8	6.1	6.4	6.2
Naphthalene	16.7	14.8	17.4	15.0
Alkyl naphthalenes	16.7	16.6	16.6	24.4
Tetralin	9.6	11.5	11.4	11.1
Alkyl tetralins	5.1	2.9	3.8	2.7
Decalins	1.3	1.5	1.0	0.7
Saturated Hydrocarbons (C <sub>5</sub> -C <sub>6</sub> )	0.7	1.9	1.2	1.2
Alkyl benzenes	33.7	35.7	33.3	30.5
Naphthalene Conversion	66.6	68.6	66.0	60.6
Hydrogenation	66.6	68.6	66.0	60.6
Hydrocracking	50.6	52.7	49.8	46.1

TABLE IX  
EFFECT OF DIFFERENT SULFUR COMPOUNDS ON NAPHTHALENE CONVERSION

Sulfur Content: 1.0% by Weight of Naphthalene

Catalyst: MoO<sub>3</sub> on Silica-alumina

<u>Sulfur Compound</u>	<u>Dibenzo- thiophene</u>	<u>n-Hexyl mercaptan</u>	<u>Diethyl Sulfide</u>
Product Distribution, Wt. %			
Gas	9.0	9.8	10.5
Coke	6.1	4.2	5.0
Naphthalene	14.8	16.4	16.3
Alkyl naphthalenes	16.6	14.0	12.6
Tetralin	11.5	10.6	11.9
Alkyl tetralins	2.9	3.4	6.0
Decalins	1.5	1.7	1.2
Saturated Hydrocarbons (C <sub>5</sub> -C <sub>6</sub> )	1.9	1.7	1.0
Alkyl benzenes	35.7	38.2	35.5
Naphthalene Conversion	68.6	69.6	71.1
Hydrogenation	68.6	69.6	71.1
Hydrocracking	52.7	53.9	52.0

TABLE X  
EFFECT OF REACTION TIME ON ANTHRACENE CONVERSION

Catalyst: MoO<sub>3</sub> on Silica-alumina

<u>Reaction Time, Minutes</u>	<u>60</u>	<u>120</u>	<u>180</u>
Product Distribution, Wt. %			
Gas	5.1	5.8	6.8
Coke	13.5	14.1	15.2
Anthracene	4.9	5.5	5.4
Hydroanthracenes	34.8	30.2	23.6
Naphthalenes	31.1	30.5	30.6
Tetralins and Decalins	2.2	3.1	5.3
Alkylbenzenes	8.4	10.8	13.1
Anthracene Conversion	95.1	94.5	94.6
Hydrogenation	95.1	94.5	94.6
Hydrocracking	60.3	64.3	71.0

TABLE XI  
NAPHTHALENE CONVERSION WITH DIFFERENT CATALYSTS

Reaction Time, 120 Minutes

<u>Catalyst</u>	<u>Cobalt Oxide (CoO)</u>	<u>Molybdenum Oxide (MoO<sub>3</sub>)</u>	<u>Nickel Oxide (NiO)</u>
Product Distribution, Wt. %			
Gas	16.2	12.9	15.4
Coke	5.6	7.6	7.0
Naphthalene	13.5	15.5	13.1
Alkyl naphthalenes	11.3	10.3	11.5
Tetralin	4.9	7.8	6.6
Alkyl tetralins	2.0	4.2	1.7
Decalins	4.9	1.3	3.3
Saturated Hydrocarbons (C <sub>5</sub> -C <sub>6</sub> )	3.0	1.7	2.0
Alkyl benzenes	38.6	38.7	39.4
Naphthalene Conversion	75.2	74.2	75.4
Hydrogenation	75.2	74.2	75.4
Hydrocracking	63.4	60.9	63.8

TABLE XII

ANTHRACENE CONVERSION ON DIFFERENT CATALYSTS

Reaction Time: 120 Minutes

<u>Catalyst</u>	<u>Cobalt Oxide</u>	<u>Molybdenum Oxide</u>	<u>Nickel Oxide</u>
Product Distribution, Wt. %			
Gas	7.2	5.8	6.2
Coke	11.0	14.1	12.2
Anthracene	4.8	5.5	4.7
Hydroanthracenes	26.0	30.2	30.9
Naphthalenes	32.1	30.5	32.3
Tetralins and Decalins	4.0	3.1	2.8
Alkylbenzenes	14.9	10.8	10.9
Anthracene Conversion	95.2	94.5	95.3
Hydrogenation	95.2	94.5	95.3
Hydrocracking	69.2	64.3	64.4