CONCEPT AND USE OF HYDROGEN PERMEABLE CATALYSTS

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INTRODUCTION

The concept of a hydrogen-permeable catalyst has not previously been reduced to practice for any gaseous or liquid mixture of coal-derived compounds, including sulfur compounds. The only known instance of the use of this concept is that described in a U.S. Patent by Rudd (1). In his work hydrogen was diffused under pressure through a palladium coil into a vessel containing ethylene. The ethylene was readily reduced to ethane, presumably by reaction with the hydrogen at the palladium surface, the palladium acting as a catalyst. The hydrogen for this reaction was apparently limited to that which had diffused just to the surface of the palladium, and was present as atomic hydrogen. In another experiment, Rudd demonstrated that an oxide coating produced on one side of a Hastelloy B disc could be completely removed by diffusing hydrogen through the disc from the non-oxidized side. The self-cleaning effects of a hydrogen permeable catalyst are implied in this demonstration, although Rudd did not try to use Hastelloy B as a catalyst.

The successful implementation of the concept of hydrogen permeable catalysts to coal-derived gases or liquids, and even coal or coal/recycle oil slurries, may offer several technical and economic advantages. These could include the virtual absence of unused hydrogen that has to be purified, recompressed and recycled at considerable expense, because essentially all the hydrogen could be consumed at the catalyst surface, without forming hydrogen bubbles. Another advantage, as suggested by Rudd's work, is that the catalyst surface could be kept free of carbon deposits because, just as oxides were removed by reaction with hydrogen diffusing up through the metal, so coking precursors would be converted by hydrogenation, preventing the formation of carbonaceous deposits. Finally, it may be possible to prevent the buildup of mineral deposits when coal or coal slurries are used, because the presence of a monomolecular or monoatomic layer of hydrogen at the surface would prevent the adhesive forces between the mineral particles and the catalyst surface from being effective.

EXPERIMENTAL PROCEDURE

Reactor Design and Function

The general reactor design is briefly as follows. The shell of the hydrogen permeable catalyst reactor consisted of 3-inch O.D. schedule 80 stainless steel pipe, 4-feet and 7-inches in length. One end of the pipe was adapted to accept tubing from one inch to 3/8 inches in diameter. The other end was modifed to accept tubing from 1/2 to 3/8 inches in diameter. One quarter inch openings were made in the reactor walls to permit inlet and venting of gases. Catalyst tubes were connected at each end to short lengths of stainless steel tubing. The stainless steel tubing, holding the catalyst tube, was inserted into the reactor at the end containing the larger opening, and allowed to protrude from the lower end of the reactor for a length of about 8 inches. The reactor, containing the catalyst tube, was suspended vertically in a high temperature furnace. Connections were made to the walls of the shell to permit inlet and venting of gases. Connections were made to the stainless steel tubing at the bottom of the reactor to permit hydrogen sulfide and hydrogen

for presulfiding, and liquid feed to enter the tube, with appropriate valving. The upper end of the tube went directly into a product receiver (gas liquid separator). Lines from the gas-liquid separator were connected to a cold trap, and then into a wet test meter for measuring any gas flow.

Hydrogen Permeable Catalyst Tubes

The thin-wall nickel-200 tubing was composed of 99.5 wt. % Ni, with small amounts of iron and manganese. Dimensions of the tubes were 17-7/8 inch length by 3/8-inch O.D., with wall thickness reduced from 0.035-inch to 0.017-inch to a point approximately one inch from each end. Samples of finely porous nickel-molybdenum and cobalt-molybdenum tubing were fabricated at Oak Ridge National Laboratory from micron-range powders by flame spraying on a mandrel, followed by high-temperature sintering to densities in excess of 95% of the natural density. The dimensions after sintering were 16.5-inches length, 0.181-inches I.D., and 0.396-inches O.D. The total length was 21-inches after brazing on nickel tips for ease of mounting in the reactor.

Catalyst tube permeability measurements were made by determining the hydrogen flow from the shell side through the permeable tubing by the wet test meter connected to the tube side of the reactor.

The internal surfaces of all catalyst tubes were coated with a metal sulfide layer by passage of a 50% hydrogen sulfide and 50% hydrogen mixture through the tube for four hours at a catalyst tube temperature of 400°C. After sulfiding, the entire reactor system was cooled to 100°C, purged with nitrogen to remove all traces of hydrogen sulfide.

Hydrogenation of liquid feed was accomplished by pumping the feed at a predetermined rate up through the catalyst tube to react with hydrogen diffusing from the shell through the catalyst tube wall. Experimental runs were made at catalyst tube temperatures from 250°C to 450°C and shell side pressures of 655 psig hydrogen to 1510 psig hydrogen. Hydrogen pressures inside the tube varied from 650 psig to 1,495 psig. Temperatures inside the tube were determined with a thermocouple in an axially positioned well.

Analyses

The identities of the metal sulfides were determined by x-ray diffraction analysis, while the compositions of the liquid feeds and liquid products, and the composition of the gaseous products, were determined by gas chromatography/mass spectrometry, and gas chromatography. Other analyses were employed, as required. The hydrogen permeability values for nickel metal are known (2).

DISCUSSION OF RESULTS

Thin Wall Nickel Tubing Reactors

1. Runs with Tar Oil in Ni Tubes. X-ray diffraction analyses of the various samples of sulfided nickel tubing showed that in each instance the coating on the inner wall consisted of a mixture of Ni_3S_4 and Ni_3S_2. The latter compound, nickel subsulfide, was very likely the only form present soon after the start of each hydrogenation run. According to Weisser and Landa (3) all nickel sulfides are rapidly converted to the subsulfide by hydrogen in any use of the sulfides for hydrogenation reactions. In any event, a large amount of Ni_3S_2 was observed for both the fresh and used tubing. Weisser and Landa also describe the use of nickel subsulfide as a catalyst for hydrogenation, including the hydrogenolysis of thiophene-type compounds. That the Ni_3S_2

present was actually functioning as a catalyst was demonstrated by the decreases in the amounts of six major components of the feed, and the increases in the amounts of eleven probable product compounds, as shown in Table 2 for runs 1 through 5, according to the conditions shown in Table 1. The reactants, R, and probable products, P, are arranged into four groups, following the possible reaction mechanisms shown in Figure 1. The reaction intermediates, indicated in Figure 1 by brackets, were not detected. All other compounds shown were identified, and their amounts determined, by combined gas chromatography and mass spectrometry. The observed m/e values are given in Table 2, along with the number of millimoles of each compound per 100 g sample, and the change in millimoles per 100 g sample in going from the feed to the product. No benzothiophene was added to the feed in run 4.

Most of the possible reaction mechanisms shown in Figure 1 for the thin-wall nickel tubing reactors have been studied in depth by other researchers under various conditions other than with nickel subsulfide catalyst. Qader and Hill (4) have shown the sequence naphthalene → tetralin → methylindan → indan → alkylbenzene. Penninger and Slotboom (5) have further detailed the steps leading from tetralin to alkylbenzenes. Rollman (6) has defined the steps in the conversion of benzothiophene to alkylbenzene, as have Furinsky and Amberg (7). Oltay et al. (8) have shown the steps in the conversion of 2-methylnaphthalene to tetralin and alkylbenzene as have Qader et al. (9). The two conversion sequences: 1) phenanthrene → dihydrophenanthrene → ethylbiphenyl → biphenyl; 2) phenanthrene → tetrahydrophenanthrene → alkylnaphthalene → tetralin have been detailed by Wu and Haynes (10). The sequence fluorene → methylbiphenyl → biphenyl has been shown by Oltay et al. in a second paper (11), as well as Penninger and Slotboom (5).

The hydrogen permeable catalyst tube in run 2, which was regenerated with air oxidation after being used in run 1, and then resulfided, showed the greatest activity of the five tubes used. The lowest activity was shown for the tube in run 1, lower than the tubes used in runs 4 and 5, which were not presulfided with the $H_2 + H_2S$ mixture. In these latter two runs a more effective nickel subsulfide coating was obtained by the reaction of the organic sulfur compounds present in the tar oil (0.64 weight percent sulfur), and the reaction of the benzothiophene added to the tar oil feed. The small amount of sulfur in the tar oil was as effective in run 4 as was the much larger amount of benzothiophene added to the tar oil in run 5. The used tubes from all runs did not have any noticeable carbon deposits, even after 13 hours operation. The relatively low operating temperature of 400°C was probably helpful in this regard, and it seems reasonable to assume that the cleansing action of the diffusing hydrogen, as described by Rudd (1), was operative. Only small amounts of hydrocarbon gases were detected in the gas in the tubing, indicating that limited cracking has occurred, whether hydrocracking or thermal cracking. Typical concentrations observed were 0.14 volume percent methane and 0.03 volume percent ethane, the remainder being the hydrogen required to maintain the 1,000 psig tube-side pressure.

2. Runs with Pure Compounds in Ni Tubes. A series of six test runs (runs 6 through 11) on the hydrogen permeability of thin wall nickel-200 tubing at various temperatures and differential pressures, and on the degree of hydrogenation of four different pure polycyclic aromatic compounds used as model compounds was likewise conducted. The hydrogen diffusivities were measured from the shell side to the inner tubing side over the shell to tubing pressure differential range of 300 to 1,700 psig, and temperatures of 400° and 450°. At both temperatures the amount of hydrogen diffusing through the wall at a Δp of 300 psig was essentially zero. The H_2 flow through the wall increased rapidly with increasing Δp, leveling off at about 0.45 liters/hr at 400°C and 1,500 psig Δp, and about 0.65 liters/hr at 450 C°and 1,700 psig Δp.

The inside of the nickel tubing was sulfided by reacting at 400°C with about 8 cu. ft. of a 50-50 mixture of hydrogen sulfide and hydrogen. X-ray diffraction analysis showed the principal component to be nickel subsulfide. The inner surface was covered with a very rough texture of tiny, dark grey crystallites of this

material. There was no significant decrease in hydrogen permeability after sulfiding. Benzothiophene was added to all liquid feeds in order to ensure maintainance of this sulfided surface. SEM analysis gave 0.2 μm as a typical crystallite size.

Phenylcyclohexane was chosen as the solvent for the model compounds because of its presumed relative inertness and because it is a liquid at room temperature. Runs were made with about 5 to about 13 weight percent of each of the four model compounds dissolved in this solvent. The Δp was 700 or 750 psig, with the inner tube pressure about 1,000 psig. Temperatures of 290, 340, 400 and 450°C were used, generally with a feed residence time of about 1 hour, and usually somewhat less than the stoichiometric hydrogen required for complete hydrogenation of the components present. Table 3 shows the results for gas chromatographic analyses of the products. There was a general trend to greater hydrogenation with higher temperature and longer residence time, as would be expected.

Porous Nickel-Molybdenum Reactors

1. Runs with Pure Compounds in Ni-Mo Tubes. The run conditions are summarized in Table 4 for the Ni-Mo tubing reactors. The results for the gas chromatographic analysis of the receiver product for runs 12 and 13 with pure compounds are shown in Table 5. At low hydrogen pressure (650 psig) inside the tubing, with about 4.5 psig differential pressure for diffusing the hydrogen through the pores of the tubing from the shell side, there was substantial reaction of the phenanthrene (45% conversion) and the benzothiophene (27% conversion). Biphenyl in the product probably came from hydrogenolysis of dihydrophenanthrene. The alkylbenzenes came in part from the phenanthrene and benzothiophene but probably also from hydrogenolysis of the solvent, phenylcyclohexane. High yields of alkylbenzenes were obtained in the thin-wall nickel tube runs in the absence of phenylcyclohexane (Table 2). At the higher hydrogen pressure (1,350 psig) enough of the intermediate di- and tetrahydrophenanthrenes were produced to be detected, and the amount of biphenyl increased. The apparent increase in the amounts of phenanthrene and benzothiophene was due to loss of volatiles, probably mostly benzene, as shown by the unexpectedly low yield of this product. As will be seen for the results from the comparable runs at these pressures with tar oil as feed, the most reasonable estimate is that the amount of conversion was doubled upon doubling the pressure, as indicated by the yields of toluene, xylenes, and biphenyl.

In two runs with pure compounds, designated 13-S and 14-S, at the run conditions shown for runs 13 and 14 in Table 4, product from the top (exit) end of the catalyst tube drained down the outside of the tube into the cold lower portion of the pressurized shell, from which it was drained at the conclusion of the run, rather than from the product receiver. It was observed in these runs under these particular operating conditions there was even greater conversion to benzene, alkylbenzenes, and biphenyl. The dihydrophenanthrene was largely converted to biphenyl under these conditions, but in so doing the intermediate methylbiphenyl was produced in large enough amount for detection. The amount of conversion was increased upon decreasing the LHSV from 20.0 to 13.3, i.e., upon increasing the residence time from 3.0 to 4.5 minutes, as indicated by the yields of toluene, xylenes, and biphenyl. The production of naphthalene in this run would indicate the formation of the intermediate tetrahydrophenanthrene, but none could be detected.

2. Runs with Tar Oil Feed in Ni-Mo Tubes. The results for the gas chromatographic analysis of the receiver product for runs 15 and 16 with coal tar creosote oil feeds are shown in Table 6. In run 15 considerable total hydrogen sulfide was evolved, showing that the 0.6 wt. % sulfur in the feed was insufficient to maintain a heavy sulfide coating inside the nickel-molybdenum tubing. This was probably because the hydrogen permeability of the Ni-Mo tubing was so high as indicated by the pressure differentials of only 5 to 10 psig (Table 4), compared to 700 psig for the thin-wall nickel tubing (Table 1). Nevertheless, a significant conversion of various feed components was observed. MoS_2, molybdenum disulfide, a known hydrogenation catalyst,

was present in the Ni-Mo tube, as well as Ni_3S_2. The presence of $MoNi_4$ alloy was also shown.

Analysis of the product gas from run 15 showed 0.29 vol. % hydrogen sulfide, whereas the gas from run 16 had no detectable H_2S, showing that the metal sulfide layer had stabilized with the small sulfur content of the feed. The hydrocarbon in largest quantity in the gas from run 15 was propane at 0.14 vol. %. This would seem to indicate hydrocracking of the saturated rings of hexahydropyrene to yield propane and naphthalene, or propane, ethane, and methylnaphthalene. Table 6 shows that the primary product was methylnaphthalene in run 15. The product gas from run 16 showed methane at 2.67 vol. %, and ethane at 0.26 vol. % to be the hydrocarbon gases in the largest quantities. This would seem to indicate hydrocracking of the saturated rings of tetrahydroacenaphthene to produce these gases and alkylbenzenes. Table 6 shows that the primary reactant was acenaphthene, with tetrahydroacenaphthene and alkylbenzene the major products.

These possible reaction mechanisms, and others, are shown in Figure 2. The hydrogenated derivatives of pyrene and fluoranthene could not be detected, and so are shown in brackets. However, tetrahydroacenaphthene (Table 6), dihydrophenanthrene (Table 5), and tetrahydrophenanthrene (Table 5) were all found in significant quantities when using the porous nickel-molybdenum tubing reactors. The only reasonable source for the pentane found by GC would be the hydrocracking of phenylcyclohexane. Qader and Hill (4) have shown the sequence pyrene → hydropyrenes → naphthalenes → tetralin → benzenes. As mentioned previously, Wu and Haynes (10) have outlined the two conversion sequences for phenanthrene. Fluoranthene also has the sequence leading to tetrahydrofluoranthene and then, by hydrocracking, to methylbiphenyl.

Porous Cobalt-Molybdenum Reactors

Runs were made using the porous cobalt-molybdenum tubing fabricated at ORNL and pure compounds (phenanthrene and benzothiophene) dissolved in phenylcyclohexane. The inner surface of the tubing was sulfided before use in the same manner as for the nickel-molybdenum tubing. The operating conditions and the results for gas chromatographic analysis of the products, are summarized in Table 7.

The respective run numbers, weight of feed material (g), pump rate (g/hr), and total run time (hr) were: 17, 32.82, 45, 2.00; 18, 189.4, 50.49, 2.25; 19, 239.2, 26.3, 2.50. The hydrogen flows for the Co-Mo reactors were very similar to those for the Ni-Mo reactors, the respective run numbers, average hydrogen flow (l/hr), and total hydrogen flow (l) being: 17, 4.7, 9.4; 18, 7.2, 16.3; 19, 5.64, 14.1.

A comparison of the results for the porous Ni-Mo reactors in Table 5 with those for the porous Co-Mo reactors in Table 7 shows that the reactions of the pure compounds were similar, but the sulfided Co-Mo appeared to have a little greater activity than the sulfided Ni-Mo, at the same approximate temperature and pressure, for the production of dihydrophenanthrene and its hydrocracking products, dimethylbiphenyl, methylbiphenyl, and biphenyl, and the production of tetrahydrophenanthrene, and its cracking product, naphthalene.

Hydrogen Permeability

It was not possible to measure hydrogen permeability of thin-wall nickel tubing during a run, because of the relatively low rate of hydrogen flow, and permeabilities had to be measured beforehand with the empty tubing, making hydrogen stoichiometry calculations difficult. However, direct hydrogen flow measurements could be made during the runs with the porous nickel-molybdenum tubing (Table 4) for comparison with the amounts required for any presumed set of hydrogenation reactions. Neglecting certain reactions, such as the hydrocracking of the phenylcyclohexane solvent, from 54 to 89% of the available hydrogen was consumed in the pure compound runs, and 85

to 90% in the tar oil runs. When estimations are allowed for these neglected reactions, it appears that essentially all hydrogen was consumed except that required to maintain pressure on the inside of the tubing. The high hydrogen flow rates with the porous Ni-Mo tubing allowed economically low feed residence times of only 3.0 to 12.6 minutes. A similar situation existed for the Co-Mo tubing.

As long as hydrogen flow was maintained through the tubing wall, there was never any indication of carbon deposits, even after many hours use on successive runs. However, in one instance, at the termination of run 16 at 400°C, the pressure differential of 10 psig H_2 from the shell-side to the tubing-side was lost, allowing the tar oil feed to penetrate the pores under conditions of poor contact with hydrogen. A heavy carbonaceous deposit was produced, typical of extensive cracking.

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TABLE 1. Operating Conditions for Thin-Wall Nickel Tubing Hydrogen Permeable Catalyst Reactors

Hydrogenation Run No.	1	2	3	4	5
H_2 Permeability of Cat. Tube - 700 psig Diff. & 400°C, cc/min	0.77	0.72	0.68	1.83	1.83
Dry Air Oxidation of Catalyst Surface	Non Oxidized	Oxidized 4 Hrs. @ 400°C	Non Oxidized	Non Oxidized	Non Oxidized
Sulfiding Conditions - Internal Surface of Tube	50% H_2 + 50% H_2S 4 Hrs. @ 400°C	50% H_2 + 50% H_2S 4 Hrs. @ 400°C	50% H_2 + 50% H_2S 4 Hrs. @ 400°C	Non Sulfided Sulfided by Feed Oil	Non Sulfided at Start of Run
H_2 Permeability of Cat. Tube - 700 psig, 400°C after sulfiding, cc/min	0.79	0.93	0.57	1.83	1.83
Feed Raw Material	Clean Reilly Tar Oil + Benzothiophene	Clean Reilly Tar Oil + Benzothiophene	Clean Reilly Tar Oil + Benzothiophene	Clean Reilly Tar Oil	Benzothiophene Modified Reilly Tar Oil
Wt. of Feed Material, g	151.80	131.89	146.76	142.00	187
Pump Rate, cc/hr	7.04	10.65	8.90	15.33	11.49
Catalyst Tube Temperature °C	400	400	400	400	400
Pressure Differential (shell to tube) psig - H_2	700	700	700	700	700
Tube Side Pressure, psig	1,000	1,000	1,000	1,000	1,000
Residence Time in Catalyst Tube, Hrs.	2.87	1.90	2.27	1.32	1.62
LHSV	0.35	0.53	0.44	0.76	0.62
Total Run Time, Hrs.	12.27	9.0	12.0	9.33	13.08

TABLE 2. Amounts of Reactant and Product Compounds in Feed Oil and Product from Ni Hydrogen Permeable Catalyst Tube; 400°C; 1,000 psig Tube Side

		Millimoles/100 GRAMS											
COMPOUND	m/e	Feed Oil + Benzothiophene	Run 1 Product 0.35[4]	Change[2]	Run 2 Product 0.53[4]	Change	Run 3 Product 0.44[4]	Change	Run[3] 4 Product 0.76[4]	Change	Run 5 Product 0.62[4]	Change
Naphthalene (R)[1]	128	46.8	37.5	- 9.1	34.06	-12.74	35.00	-11.8	34.37	-18.47	32.19	-14.61
1-Benzothiophene (R)	134	90.3	8.95	-81.3	8.13	-82.17	8.20	-82.10	0.0	0.0	7.68	-82.62
Benzene (P)	78	0.0	0.26	+ 0.26	3.46	+ 3.46	0.89	+ 0.89	1.41	+ 1.41	1.79	+ 1.79
Toluene (P)	92	0.54	2.06	+ 1.52	13.47	+12.93	3.04	+ 2.50	5.65	+ 5.11	7.17	+ 6.63
Xylenes & Ethylbenzene (P)	106	0.0	2.17	+ 2.17	2.73	+ 2.73	3.11	+ 3.11	2.83	+ 2.83	2.45	+ 2.45
Trimethylbenzenes (P)	120	0.08	2.75	+ 2.67	1.83	+ 1.75	1.91	+ 1.83	1.83	+ 1.74	1.58	+ 1.50
2-Methylnaphthalene (R)	142	37.6	25.5	-12.1	24.64	-12.96	22.11	-15.49	21.05	-21.34	22.60	-15.00
Ethylindan (P)	146	0.0	2.39	+ 2.39	2.19	+ 2.19	2.53	+ 2.53	2.67	+ 2.67	2.26	+ 2.26
Indan (P)	118	2.54	3.60	+ 1.06	4.41	+ 1.87	3.05	+ 0.51	3.64	+ 0.77	3.64	+ 1.10
Acenaphthene (R)	154	49.0	33.11	-15.9	30.84	-18.16	27.53	-21.47	29.09	-26.28	29.67	-19.33
Ethylnaphthalenes (P)	156	4.67	9.20	+ 4.53	10.77	+ 6.1	10.12	+ 5.45	9.23	+ 3.96	10.00	+ 5.33
Dimethylnaphthalenes (P)	156	17.1	22.8	+ 5.70	25.32	+ 8.22	26.79	+ 9.69	25.00	+ 5.68	23.78	+ 6.68
Fluorene (R)	166	36.9	28.2	- 8.70	26.44	-10.46	24.39	-12.51	24.75	-16.94	25.96	-10.94
Phenanthrene (R)	178	90.7	47.8	-42.9	41.23	-49.47	35.88	-54.82	37.75	-64.74	40.56	+50.14
Methylbiphenyls (P)	168	3.33	13.1	+ 9.77	17.79	+14.46	17.62	+14.29	14.46	+10.7	16.72	+13.39
Biphenyl (P)	154	8.31	12.3	+ 3.99	13.31	+ 5.0	13.11	+ 4.8	12.46	+ 3.07	12.59	+ 4.28

[1]R = Reactant, P = Product
[2]+ = Increase, Feed to Product; - = Decrease, Feed to Product
[3]1-Benzothiophene Free Reilly Tar Oil Feed Used In Run 4
[4]LHSV (Liquid Hourly Space Velocity)

TABLE 3. Reaction of Diffused Hydrogen with Pure Compounds in Thin Wall Ni Tubing with Ni_3S_2 Coating, about 1,000 PSIG

Solvent = Phenylcyclohexane

Run No.	Temp., °C	LHSV	Compound	Weight % Feed	Weight % Product	Weight % Hydrogenated
6	290	1.0	Benzothiophene	5.74	4.68	19
7	290	1.0	Phenanthrene	7.58	6.36	16
			Benzothiophene	6.22	5.11	18
8	290	1.0	Acenaphthene	7.67	4.98	35
			Benzothiophene	6.25	5.63	10
9	340	1.0	Fluorene	7.79	5.13	21
			Benzothiophene	6.09	5.30	13
10	400	1.2	Phenanthrene	12.97	7.70	41
			Benzothiophene	7.06	4.79	32
11	450	0.51	Phenanthrene	5.21	2.62	50
			Benzothiophene	5.10	2.23	56

TABLE 4. Operating Conditions for Porous Nickel-Molybdenum Tubing Hydrogen Permeable Catalyst Reactors at 400°C

Run No.	12	13	14	15	16
Sulfiding Conditions, Internal Surface	50% H_2 + 50% H_2S, 4 hours at 400°C, total gas flow = 8 feet^3				
Feed Material	Phenylcyclohexane, Phenanthrene Benzothiophene (various proportions)			Filtered Reilly Tar Oil	
Wt. of Feed Material, g	150.0	160.1	205.2	267.7	114.4
Pump Rate, g/hr	56.2	64.0	41.0	48.6	57.2
Total Run Time, hrs	1.63	1.25	1.5	1.9	2.0
Residence Time in Catalyst Tubing, min	3.0	3.0	4.5	12.6	10.2
Pressure Inside Tubing, psig	650	1,350	1,350	767	1,380
Pressure Differential (shell to tubing), psig	4.5	10.0	10.0	8.5	10.0
Hydrogen Flow, liters/hr	6.26	5.56	4.50	5.40	5.10

TABLE 5. Reaction of Pure Compounds at 400°C with Hydrogen Diffusing Through Porous Nickel-Molybdenum Tubing with a Sulfided Inner Wall

Feed: 4.52 wt. % benzothiophene
10.17 wt. % phenanthrene
(solvent: phenylcyclohexane)

	Receiver Product, Wt. %	
Run No.	12	13
Pressure, psig	650	1350
LHSV	20.0	20.0
Benzene	16.56	0.69
Toluene	0.63	1.49
Xylenes	1.77	3.33
Trimethylbenzenes	0.06	0.97
Biphenyl	0.58	1.28
Dihydrophenanthrene	0.00	2.26
Tetrahydrophenanthrene	0.00	1.09
Phenanthrene	5.60	12.03[1]
Benzothiophene	3.29	7.97[1]

[1]High, due to loss of volatiles, mostly benzene.

TABLE 6. Reaction of Coal Tar Creosote Oil at 400°C with Hydrogen Diffusing Through Porous Nickel-Molybdenum Tubing with Sulfided Inner Wall

	Composition, Weight %					
Run No.	15			16		
LHSV	4.8			5.9		
Pressure, psig	767			1,380		
Reactants	Feed	Receiver Product	Decrease	Feed	Receiver Product	Decrease
Acenaphthene	8.61	8.45	0.16	8.23	4.03	4.20
Phenanthrenes[1]	20.01	19.06	0.95	20.77	18.44	2.33
Pyrene	6.68	4.30	2.38	5.59	3.52	2.07
Fluoranthene	5.83	4.81	1.02	5.99	4.09	1.90
Total			4.51			10.50
Products			Increase			Increase
Benzene	0.00	0.21	0.21	0.00	1.52	1.52
Toluene	0.10	0.10	0.00	0.33	2.22	1.89
Xylenes	0.16	0.20	0.04	0.21	2.03	1.82
Indan	1.23	1.57	0.34	1.99	3.06	1.07
Tetralin	1.15	1.60	0.45	1.45	2.15	0.70
Methylnaphthalenes	11.70	14.56	2.86	9.29	10.91	1.62
Tetrahydroacenaphthene	0.00	0.34	0.34	0.00	1.85	1.85
Total			4.24			10.47

[1]Phenanthrene plus methylphenanthrenes.

TABLE 7. Reaction of Pure Compounds with Hydrogen Diffusing Through Porous Cobalt-Molybdenum Tubing with Sulfided Inner Wall

Solvent = Phenylcyclohexane

Run No.	17	18	19
Temp., °C	350	400	400
Pressure inside tube, psig	750	728	1,495
Pressure, differential, psig	20	9.0	7.0
Residence time, min.	11.4	10.2	19.2
LHSV	5.3	5.9	3.1

	Composition, Weight %					
	Feed	Product	Feed	Product	Feed	Product
Pentane	0.00	0.00	0.00	2.73	0.00	0.00
Benzene	0.64	6.91	0.60	7.54	1.75	0.03
Toluene	0.00	0.02	0.00	4.73	0.00	0.08
Xylenes	0.00	1.93	0.00	6.36	0.00	1.74
Trimethylbenzenes	0.00	0.00	0.00	1.13	0.00	0.59
Naphthalene	0.00	0.62	0.00	4.68	0.00	2.20
Biphenyl	0.00	0.00	0.00	3.46	0.00	4.49
Methylbiphenyl	0.00	0.00	0.00	0.00	0.00	0.99
Dimethylbiphenyl	0.00	0.00	0.00	0.00	0.00	1.12
Dihydrophenanthrene	0.00	0.00	0.00	0.05	0.00	5.97
Tetrahydrophenanthrene	0.00	0.00	0.00	0.00	0.00	2.08
Phenanthrene	11.82	5.05[1]	12.12	5.70[1]	13.28	23.74[1]
Benzothiophene	4.42	4.42[1]	4.51	5.40[1]	5.27	5.28[1]

[1]High, due to loss of volatiles, primarily pentane and benzene.

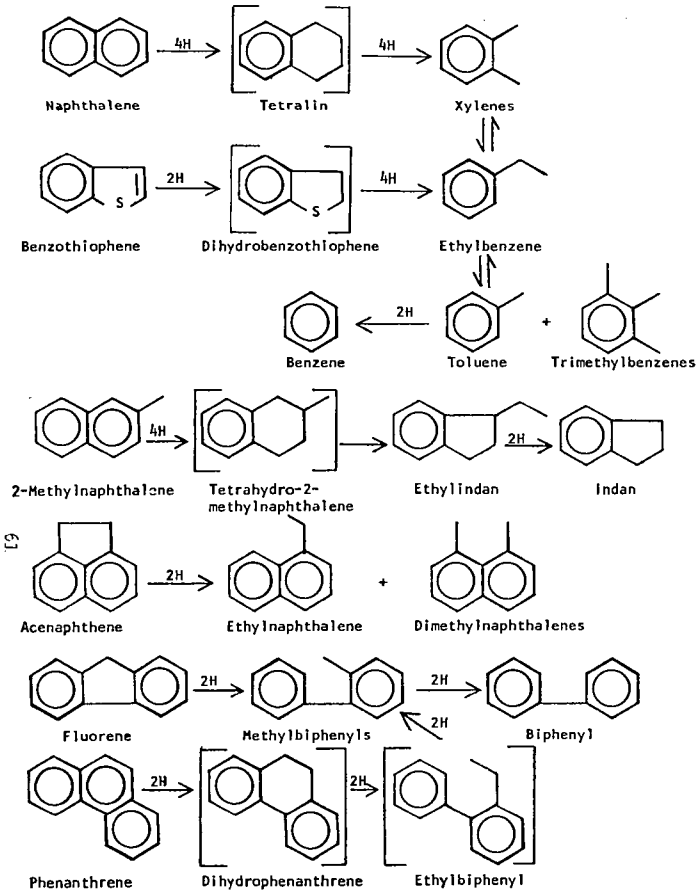

Figure 1. Possible Reaction Mechanisms Involved in Hydrogenation of Tar Oil with Nickel Subsulfide Catalyst at 1,000 psig and 400°C

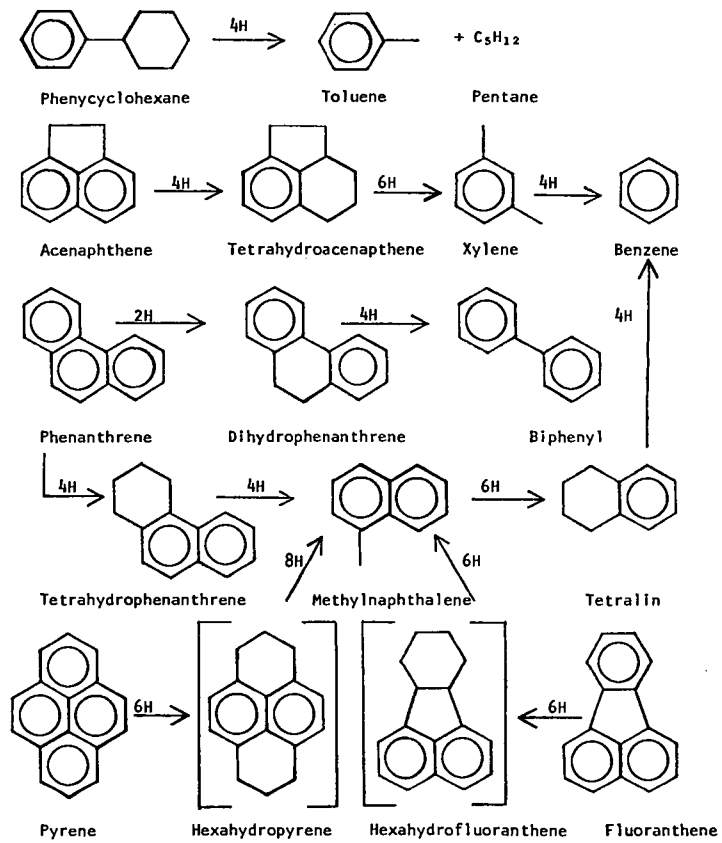

Figure 2. Possible Reaction Mechanisms Involved in Hydrogenation with Sulfided Nickel-Molybdenum at 400°C and 650 to 1,400 psig