HOMOGENEOUS CATALYTIC HYDROGENATIONS
OF COMPLEX CARBONACEOUS SUBSTRATES

J. L. Cox, W. A. Wilcox, G. L. Roberts

BATTELLE
Pacific Northwest Laboratories
Richland, Washington 99352

Hydrogenation of unsaturated organic compounds with homogeneous catalysts has been known and practiced for some time. Such hydrogenations have been of both an academic and commercial interest. Some of the more extensively studied catalysts include $Co(CN)_5^{-3}$ (1), $RhCl(P\Phi_3)_3$ (2), $Ir(CO)Cl(P\Phi_3)_2$ (3,4), $IrH(CO)(P\Phi_3)_3$ (3,4), $OsHCl(CO)(P\Phi_3)_3$ (3,4) and Ziegler-type catalysts (5). These catalysts, with the exception of the Ziegler-type, have not been observed to hydrogenate aromatics. Infact, very few homogeneous catalysts have been reported that will hydrogenate aromatics. Wender, *et al.*(6) have shown that polynuclear aromatics are partially hydrogenated with $Co_2(CO)_8$. Efimov, *et al.*, (7,11) have observed rapid hydrogenation of polynuclear aromatics in the presence of a rhodium complex of N-phenylanthranilic acid (NPAA), formulated as $(RhNPAA)_2$. This rhodium catalyst is more active than the dicobalt octacarbonyl and shows a greater hydrogenation activity toward polynuclear aromatics than the Ziegler catalyst. Holly *et al.*(15) investigated the use of this rhodium complex and other homogeneous catalysts for coal liquefaction, concluding that such catalysts do not appear to offer a viable route to coal liquefaction.

Here we report the results of homogeneous catalytic hydrogenation of complex unsaturated substrates including coal and coal-derived materials.

HYDROGENATIONS

Using organic soluble molecular complexes as catalysts, a number of hydrogenations of various organic substrates were performed. These include a Hvab coal, solvent refined coal (SRC) and COED pyrolysate. The analysis of these feed materials are contained in Table 1. The hydrogenations were carried out in a 300 cc stirred autoclave by mixing coal with carrier solvent containing solubilized catalyst under prescribed conditions. Upon completion of the run the gases were measured and anlyzed. The solid carbonaceous residue was separated from carrier solvent by filtration, then thoroughly washed with benzene and finally dried in a vacuum oven.

TABLE I. Analysis of Feed Materials

	Coal (a)		SRC	COED	Hydrogenated Coal Run 25
	As Received	Vacuum Dried			
Moisture	1.1	0.0	0.0	0.0	1.8
Ash	14.5	14.7	0.3	0.1	27.0
H	4.8	4.6	5.6	7.3	4.4
C	68.8	68.3	87.7	85.0	55.0
O	6.0	6.1	4.0	7.2	5.9
N	1.2	1.2	2.2	1.1	0.2
S	4.6	4.6	0.5	1.3	4.0

(a) Both samples were -200 mesh.

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

All catalysts except the Ni-Ziegler are commercially available and were used as such without further purification. The Ni-Ziegler was prepared under a nitrogen atmosphere by reacting 4 moles of triethylaluminum with 1 mole nickel naphthenate in completely anhydrous n-heptane. The activity of this catalyst was first tested with benzene before proceeding to more complex substrates. Hence, 10 ml benzene were hydrogenated in 40 ml n-heptane containing 4×10^{-3} moles of the Ni-Ziegler catalyst for 1 hour at 150°C and 1000 psig H_2 (ambient temperature). Even though the hydrogenation covered a 1-hour period the autoclave pressure rapidly dropped to 650 psig once 150°C was reached, signaling rapid hydrogenation of the benzene. Liquid product analysis by gas chromatography revealed 99% conversion of the benzene to cyclohexane.

Hydrogenation conditions and results for coal and coal derived materials are summarized in Table II. The change in atomic hydrogen-carbon ratio (Δ) is the principal criterion for comparing catalyst activity and extent of hydrogenation. Since no attempt has been made to account for the lighter hydrocarbons that were removed with the carrier solvent by filtration the hydrogenation criterion is very conservative. This value has been obtained by subtracting the experimentally determined atomic hydrogen-carbon ratio of carbonaceous substrate from that of the product. The carbon-hydrogen analysis was performed on a Perkin Elmer model 240 elemental analyzer. Since a small amount of unremoved solvent in the product can seriously effect the interpretation of results, extreme precaution was taken to ensure its complete removal. This was accomplished by washing with a volatile solvent followed by vacuum drying with a nitrogen bleed at 110°C for at least 24 hours. In order to check thoroughness of solvent removal a dried sample showing H/C of 1.10 was further dried and reanalyzed. There was essentially no change in the H/C (i.e., 1.10 versus 1.09).

It is apparent from Table II that the Ni-Ziegler catalyst is more active than $Co_2(CO)_8$, $Ni[(PhO)_3P]_2(CO)_2$ and $Fe_3(CO)_{12}$. In Run 25 a Δ of 0.148 for the Hvab coal was observed over a 2-hour reaction time at 200°C and 2770 psig. This change in atomic H/C ratio from hydrogenation corresponds to a hydrogen usage of only 0.85% (w/w) of coal. Even in Run 36 where a Δ of 0.291 was effected at 200°C and 1300 psig H_2 after 22 hours only 1.7% (w/w) H_2 is consumed in the hydrogenation. These hydrogenations may be compared to Run 31 where a slight decrease in Δ, -0.003, was observed in the hydrogenation of the Hvab coal with no catalyst for 2 hours at 300°C and 2880 psig. In contrast to these hydrogen consumptions about 2% H_2 (w/w maf coal basis) is used in the SRC process, 2.5% in Synthoil and 4% for H-Coal.

Homogeneous catalytic hydrogenations were also conducted on solid products from the SRC and COED coal liquefaction processes. The analyses of these substrates are contained in Table I. Upon examination of the hydrogenation results summarized in Table II it becomes apparent that the ease of hydrogenation under these homogeneous catalytic conditions is SRC > COED > Hvab, although some reservation must be made since the hydrogenations were not made under identical conditions. That the coal-derived substrates are more readily hydrogenated than the coal is not too surprising since they are liquids at reaction temperatures (>200°C) and quite soluble in carrier solvent permitting effective catalyst-substrate interaction. Diffusional resistances to hydrogenation are also expected to be less for these materials than the solid coal.

TABLE II. Summary of Homogeneous Catalytic
Hydrogenations of Carbonaceous Substrates

Run No.	Catalyst/Feed[a]/Solvent	Temperature/ Pressure[d]/Time[b]	H	C	At.H/C	Δ(atomic H/C)[c]
31	No catalyst/15g C/decalin	300/2880/2	4.64	68.6	0.806	-0.003
17	14 mmole $Co_2(CO)_8$/30g C/decalin	200/2950[e]/2	4.69	67.4	0.829	0.020
21	7 mmole $Co_2(CO)_8$/15g C/decalin	300/3080[e]/2	5.16	69.0	0.891	0.082
20	7 mmole $Co_2(CO)_8$/15g C/decalin	400/3400[e]/2	5.26	71.8	0.873	0.064
18	13 mmole $Fe_3(CO)_{12}$/30g C/decalin	200/2830[e]/2	4.56	65.9	0.824	0.015
19	7 mmole $Ni[(PhO)_3P]_2(CO)_2$/15g C/ decalin	200/2720[e]/2	4.94	70.7	0.833	0.021
25	7 mmole Ni-Ziegler/15g C/decalin	200/2770/2	4.48	55.8	0.957	0.148
36	8 mmole Ni-Ziegler/15g C/heptane	200/1300/22	5.88	63.6	1.10	0.291
38	8 mmole Ni-Ziegler/10g SRC/THF	200/1200/23	7.29	77.1	1.13	0.377
40	5.7 mmole Ni-Ziegler/17.2g COED/THF	200/3850/21	8.28	74.8	1.32	0.290

a Feed materials include: Consolidation coal (C), 4.64%H, 68.3%C, At.H/C = 0.809; Solvent Refined Coal (SRC), 5.55%H, 87.7%C, At.H/C = 0.753; FMC pyrolysate (COED), 7.32%H_2, 85.0%C, At.H/C = 1.03.

b Variables temperature, pressure and time reported as $^\circ$C, psig and hr., respectively.

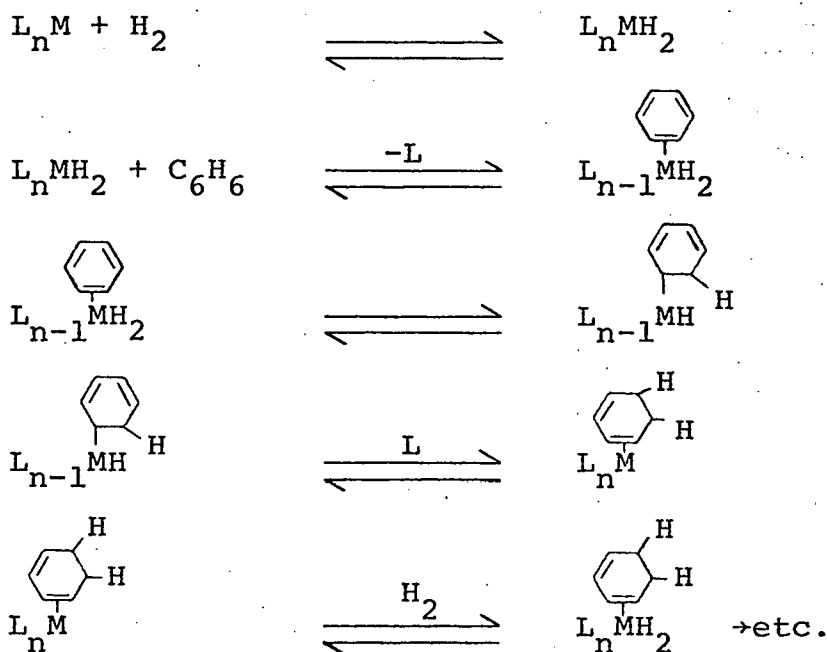c Δ, is the change in atomic H/C ratio between substrate and product.

d Pressures are those at reaction temperature and due to hydrogen and solvent unless otherwise stated.

e Gas composition of 25% CO, 75% H_2, used in hydrogenation.

Product gas analysis on each experimental hydrogenation run revealed predominantly reactant gases. In Runs 17, 18, 19, 20 and 21 the product gas consisted of $\geq 98\%$ H_2 and CO, while Runs 25, 31, 36, 38 and 40 showed at least as great a concentration of hydrogen. Except for Run 20, CO_2 and CH_4 contributed $\leq 0.2\%$ to the gas balance. The gas composition of Run 20 was different from the others in that low but noticeable concentrations of light hydrocarbons including CH_4, C_2H_6, and C_3H_8 were found. The observed light hydrocarbons in this run are undoubtedly due to the higher temperature (400°C versus ≤ 300°C) employed, which was high enough to affect hydrogenolysis. The gas analysis of Runs 25, 36, 38 and 40 employing the Ni-Ziegler catalyst were unique in that appreciable concentrations (1 to 2%) of ethane were observed. The ethane is attributed to loss of ethyl groups from the Ni-Ziegler catalyst or decomposition of excess triethylaluminum which was used in its preparation.

Even though there is no kinetic data to support a proposed mechanism for the observed homogeneous catalytic hydrogenation of aromatics the following mechanism is consistant with the chemistry of analogous systems. In this proposed mechanism L represents coordinated ligands and solvent and M is the transition metal. This proposed mechanism depicts that generally accepted for the hydrogenation of olefins (including cyclohexene) by a number of group VIII metal complexes.

$$L_nM + H_2 \quad \rightleftharpoons \quad L_nMH_2$$

$$L_nMH_2 + C_6H_6 \quad \xrightarrow{-L} \quad L_{n-1}MH_2$$

$$L_{n-1}MH_2 \quad \rightleftharpoons \quad L_{n-1}MH \cdot H$$

$$L_{n-1}MH \cdot H \quad \xrightarrow{L} \quad L_nM$$

$$L_nM \quad \xrightarrow{H_2} \quad L_nMH_2 \quad \rightarrow etc.$$

We know for instance that molecular hydrogen will undergo oxidative addition reactions with a number of transition metal complexes as shown in the first equation (12). The metal migrations during hydrogenation may occur through a π-allyl complex. Finally, intermediates similar to those postulated in this mechanism have been supported by chemical evidence and include the two following compounds (13):
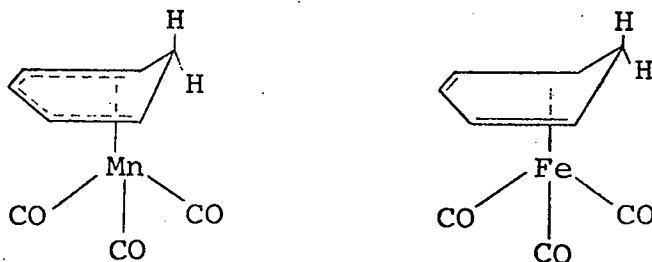
Even though the above mechanism has been written with benzene as the substrate it is relatively easy to write analogous mechanisms for yet more complex aromatic substrates.

PRODUCT CHARACTERIZATIONS

The products from the hydrogenation of the coal and coal derived materials were all solid glossy black materials at room temperature, except in Run 20 where the temperature reached $400^\circ C$ and a black viscous liquid was obtained. The carbon and hydrogen analyses of these hydrogenation products are contained in Table II. With respect to these complex carbonaceous substrates hydrogenation is often falsely taken to be synonymous with liquefaction. The polymeric structure of coal (8,9) implies that complete saturation with hydrogen would not alter its physical state. An appropriate analogy would be the hydrogenation of polystyrene to produce the solid saturated polymer

$$\left(-CH-CH_2-\right)_n + 5/2nH_2 \longrightarrow \left(-CH-CH_2-\right)_n$$
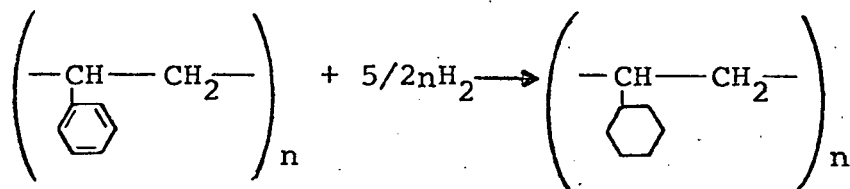
Even though polyethylene has an H/C ratio of 2.0, it is also solid. Hence with respect to coal liquefaction, undoubtedly the hydrogenolysis reactions and not hydrogenation are responsible for converting the solid to a liquid by conventional processing schemes. The liquefaction that occurred in Run 20 was undoubtedly due to hydrogenolysis as a consequence of the high temperature ($400^\circ C$) employed. Again using polystyrene for analogy, the hydrogenolysis may be represented by the following reaction in which the product ethyl benzene is clearly a liquid.

$$\left(-CH-CH_2-\right)_n + nH_2 \longrightarrow nCH_2CH_3$$
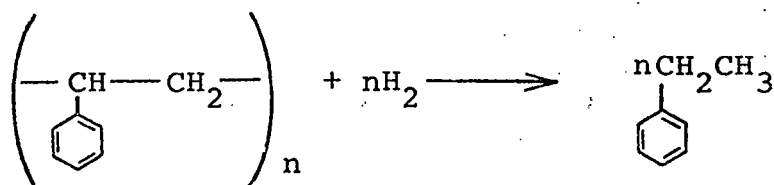
Coal hydrogenolysis has been contrasted with its hydrogenation by carrying out a material balance estimation on the Synthoil process as shown in Table III. These results show that one net result of catalytic hydrogenolysis is a decrease in the product (char + crude oil) H/C ratio (0.765 versus 0.883), despite the addition of 9000 scf H_2 per ton of coal (maf). The decrease in the H/C ratio is a direct consequence of the hydrogenolysis reaction which breaks structural bonds in the solid substrate and adds hydrogen to the fragments. Hence, a large hydrogen consumption is seen in removing oxygen and sulfur from the coal as H_2O and H_2S, respectively. Considerable hydrogen is also consumed by light hydrocarbon gases ($C_1 - C_3$) as a result of hydrogenolysis reactions. On the other hand, hydrogen consumed by hydrogenation goes directly to increase the substrate H/C ratio. This is why the H/C ratio is high for the amount of hydrogen consumed in the homogeneous catalytic hydrogenations. Of course, from a practical viewpoint it is highly desirable, if not necessary, to at least remove the sulfur which is invariably accompanied by oxygen removal and light hydrocarbon gas production.

Complete hydrogenation of the unsaturated carbon-carbon bonds in the complex carbonaceous substrates is estimated to result in an H/C

ratio of at least 1.5. The maximum value we have obtained is 1.32 for the COED pyrolysate. The failure to obtain more extensive hydrogenation may be due to the catalyst's inability to activate the more complex aromatics. Also, a portion of the substrate's unsaturation is undoubtedly very facile and a portion is very inert toward hydrogenation. As noted earlier, the Ni-Ziegler very rapidly hydrogenates mononuclear aromatics but is much more sluggish toward the polynuclear aromatics. For example, at 1000 psig H_2, phenol is 92% converted to cyclohexanol in 0.2 hours at 150°C in the presence of 5 mole % Ni-Ziegler catalyst, while only 12.5% naphthalene is converted to decalin in 18 hours at 210°C in the presence of 2.5 mole % Ni-Ziegler (5). The more complex polynuclear aromatics, such as phenanthrene and pyrene that are contained in coal along with the heteropolynuclear aromatics such as indoles and dibenzothiphenes will undoubtedly be even more sluggish toward hydrogenation.

TABLE III. Synthoil Material Balance

Materials Charged	lb-moles	lb
Coal[a] (atomic H/C = 0.883)		2000
C	1117.90	1416
H	104.20	105
O	22.50	360
S	3.00	96
N	7.50	105
Hydrogen[b] (H)	50.04	50.5
		2050.5
Materials Out		
C_1-C_3 Hydrocarbons[c]		100
C	6.52	78.3
H	21.53	21.7
Heteroatoms		467.8
H_2O[d]	21.25	382.8
H_2S[e]	2.5	85.0
Product[f] (atomic H/C = 0.765)		1482
C	111.4	1338
H	85.3	86
O	1.2	20
S	0.5	16
N	1.6	22
		2049.8

(a) maf basis.
(b) 50.04 lb-moles H equivalent to 9000 scf H_2.
(c) Amount to 5 wt% of maf coal charged with estimated composition of 60% C_1, 30% C_2 and 10% C_3.
(d) 340 lb O + 42.8 lb H.
(e) 80 lb S + 5.04 lb H.
(f) Crude oil + char.

Another possible cause of low hydrogenation levels is the inaccessibility of catalyst to substrate. This is anticipated to be more of a problem for coal than for coal-derived products, due to their differences in physical properties, particulary pore size distributions and solubility in carrier solvent. The moderate to high solubility of the coal-derived materials will undoubtedly enhance catalytic hydrogenation over the relatively insoluble coal in a carrier solvent. The coal itself having an extensive pore structure will undoubtedly contain a significant number of micropores that are too small for access of the catalyst (14).

To obtain information on the reactivity of the solid hydrogenated product, thermogravimetric analyses were run and compared to those of the unhydrogenated coal. The results are shown in Fugure 1 for hydrogenation products of Runs 25 and 36 as well as the parent coal. These differential thermograms were all recorded with a duPont model 900 analyzer on 19-23 mg samples under a high-purity argon atmosphere at 20°C/min heating rate, from ambient to 800°C. Although the sample from Run 25 had an H/C of 0.148, greater than the parent coal, there is no qualitative difference in their differential thermograms except for the small amount of moisture devolatilized from the parent coal at about 125°C. This type of thermogram is typical of many that have been reported for different ranks of coal (10). In sharp contrast, the sample from Run 36 which had an H/C increase of 0.291 over the parent coal reveals considerable structure in its differential thermogram. In addition to the major peak at about 475°C which was also observed for the coal and sample from Run 25, two additional peaks were observed at considerably lower temperatures--one at 360°C and the other at 275°C. The volatile matter from this sample was 54% (ash-free basis) while that from Run 25 and the parent coal was 42% and 37% respectively (ash-free basis).

It is not surprising that the sample from Run 36 showed more structure in its thermogram and a larger amount of volatile matter production than the parent coal since it does have a significantly greater hydrogen content than the parent coal. What is somewhat surprising is that the sample from Run 25 acted very similar to the parent coal during thermolysis even though its H/C ratio lies between that of product from Run 36 and the parent coal. The hydrogenation in Run 36 is apparently extensive enough to saturate key unsaturated groups in coal leading to decreased thermal stability. It is generally recognized that cleavage of saturated groups is much more facile than unsaturated groups under thermolysis conditions.

To project the yield of liquid product from the thermogravimetric analysis we have assumed that a linear relationship exists between the percent volatile matter and liquid yield. This implies that if a coal is 25% volatilized and yields 10% oil then 35% devolatilization of this coal after pretreatment such as hydrogenation will yield 0.35/0.25 x 10% = 14% oil. Using this approximation one can readily estimate that prehydrogenation of the coal in Run 36 has increased yield of oil by 46% over the unhydrogenated coal upon pyrolysis. In practical terms this means that prehydrogenation could be used to significantly increase the yield of liquids from coal by pyrolysis. For instance, the oil yield from the COED process (16) which uses multiple stage pyrolysis to produce gases, liquids and char would be increased from 1.5 bbl/ton to about 2.2 bbl/ton.

A hydrogenolysis experiment was conducted with the Hvab coal and its hydrogenated product under indentical experimental conditions. The analysis of these -200 mesh feed materials was reported in Table 1. Hydrogenolysis was carried out in the previously described 300 cc magnedrive autoclave. In the hydrogenolysis of Hvab, 10.0 g were charged to the autoclave along with 30.0 g (32 ml) tetralin and 0.5 g -100 mesh Co-Mo catalyst (Harshaw HT-400 containing 3% cobalt oxide and 15% molybdenum dioxide on alumina). In the hydrogenolysis of the prehydrogenated coal from Run 25 the same quantity of carbonaceous feed and tetralin were charged, but no catalyst was added. After materials were charged, the autoclave was purged twice with high-purity hydrogen and then pressurized with hydrogen to 1500 psig. Experimental hydrogenolysis conditions were 0.5 hour at 400°C, 2700 psig (1500 psig H_2 ambient) and 300 rpm. The autoclave was brought up to reaction temperature and cooled after the designated reaction time as rapidly as possible. It required about 30 minutes to reach 400°C from ambient and 10 minutes to cool from 400°C to 60°C. However, the time required to heat from 200°C to 400°C and cool from 400°C to 200°C was only about 2 minutes; i.e., the time spent at temperatures sufficiently high to potentially contribute to hydrogenolysis was significantly shorter than the overall heat-up and cool-down time.

Once the run was completed and the temperature had cooled to ambient the experiment was worked up according to the diagram in Figure 2. The gas volume was measured with a wet test meter and its composition determined by gas chromatography. The liquid and solid products were emptied into a tared extraction thimble whence the filtrate from the thimble was collected and saved. The autoclave was rinsed with benzene into the same extraction thimble. The solids were then extracted with the rinse benzene for 8 hours in a soxhlet apparatus whence the extraction thimble was vacuum dried and weighed. The benezene solution from the extraction was combined with the previously saved tetralin-laden filtrate. To this solution was added a three-fold excess of pentane, to precipitate asphaltenes which were then separated by filtration and vacuum dried. This filtrate was then vacuum distilled (∿25 mm Hg, 40-80°C) to remove the pentane and benezene from the tetralin soluble product (light oil). The yields of the various fractions obtained by following this procedure are all summarized on a maf charge basis in Table IV for the Hvab coal and the prehydrogenated coal.

The tabulated results (Table IV) for the hydrogenolysis of the coal and hydrogenated coal clearly indicate a significant difference in their product yields. The yield of gas and light oil was greater for the hydrogenated than the nonhydrogenated coal (38% and 49.0% versus 31% and 48.6%). Perhaps even more significant is the lower asphaltene yield observed for the hydrogenated sample (3.0% versus 10.3%). The overall conversion was essentially the same for both samples (90 versus 89%) and there was little difference in their product gas compositions.

In examining the differences between these two hydrogenolysis experiments one is reminded that while a Co-Mo catalyst was used with the coal, there was no addition of catalyst to the hydrogenated coal. However, the hydrogenated coal did contain nickel that was apparently deposited on the coal from the Ni-Ziegler catalyst during the homogeneous catalytic hydrogenation. This nickel undoubtedly participated as a catalyst in the hydrogenolysis of the sample. So in essence, we are comparing the hydrogenolysis of this hydrogenated sample containing

nickel with the Hvab coal to which was added a conventional Co-Mo catalyst. An analysis* of the nickel content in the hydrogenated coal revealed 1.2% Ni which can be compared to 5% Co-Mo catalyst in the Hvab coal. Since the nickel catalyst was apparently decomposed on the hydrogenated coal sample it almost certainly had better catalyst-substrate contacting than the Co-Mo which was mixed with the Hvab coal. This in itself could account for the higher hydrogenolysis yields of gas and light oil and lower asphaltenes than with the Co-Mo catalyst. In addition, nickel catalysts generally show higher gas yields under

TABLE IV. Hydrogenolysis Experimental Results

	Hvab Coal	Hydrogenated Coal Run 25
Reaction Conditions		
feed, g	10.0	10.0
tetralin, g	30.0	30.0
catalyst, g	0.5	none
temperature, °C	400	400
pressure, psig	2660	2770
time, hr	1/2	1/2
Conversion, %	90.0	88.9
Product Yields, %		
gas	30.8	38.0
oil	58.8	52.1
light oil	48.6	49.0
asphaltenes	10.2	3.0
char	10.3	9.9
Gas Composition, mole %		
H_2	91.2	87.7
CO_2	0.5	0.4
C_2H_4	trace	trace
C_2H_6	2.4	2.6
O_2	trace	0.3
N_2	0.5	2.5
CH_4	4.1	3.9
CO	0.1	0.2
C_3H_8	1.3	2.3
C_4H_{10}	0.2	0.1

hydrogenolysis than supported Co-Mo catalysts. Finally, the hydrogenated sample is expected to produce higher yields of gases and light oils and lower asphaltenes under hydrogenolysis simply because it has been hydrogenated.

---

* The analysis of the hydrogenated sample was performed by first ashing the sample at 850°C in a muffle furnace. This revealed 27.0% ash. The ash was then digested in hot aqua regia solution and filtered. The filtrate was then diluted with water and analyzed for nickel by atomic adsorption spectroscopy to give 1.2% Ni in the hydrogenated sample.

In an attempt to better define the nature of the liquid product from the hydrogenolysis of these two samples their light oil fractions were subjected to gas chromatographic-mass spectral analysis. The more prominent components of the tetralin soluble fraction (light oil) from hydrogenolysis of the two samples were analyzed on a Hewlett-Packard (HP) 5980A quadruple mass spectrometer with a HP 5710A GC and HP 5934A data system. Chromatography was performed on a 6-foot SP 2250 column temperature programmed from 80 to 250°C at 8°C/min using He carrier at 40 ml/min. Mass spectrometry was conducted with electron impact at 60 electron volts. Additional chromatography of the light oil from each sample was performed on an HP 5830A GC equipped with an HP 18850A terminal at the previously described run conditions.

A typical chromatogram of these samples is shown in Figure 3 along with retention times while Table V contains the mass spectral identification of the more prominent components of both samples. Upon comparing the chromatograph data their similarity is particularly striking. When the solvent (tetralin) is subtracted from both samples as has been done in tabulating the area percent in Table VI we quickly realize that only a few of the more than 22 integrated peaks account

TABLE V. G. C. Mass Spectral Analysis of Light Oil

G. C. Retention Time, Area %				Mass Spec Assignments
Hvab Coal		H_2-Hvab Coal		
0.59 , 18.59		0.58 , 16.02		benzene
0.93 , 0.44		0.93 , 0.52		toluene
1.19 , 0.15		1.19 , 0.20		
1.60 , 0.67		1.59 , 1.32		xylene
2.15 , 0.35		2.17 , 0.52		xylene
2.99 , 0.46		2.97 , 0.68		C_3-benzene
4.41 , 2.06		4.39 , 2.03		decalin
5.73 , 8.10		5.78 , 10.37		C_4-benzene
7.44 , 20.47		7.51 , 22.74		1-methylindane
8.38 , 0.93		8.41 , 1.04		
12.32 , 40.54		12.35 , 40.61		naphthalene
13.15 , 0.80		13.17 , 0.49		Methyl-tetrahydronaphthalene
14.07 , 0.50		14.12 , 0.14		
14.65 , 0.82		14.67 , 0.60		
15.30 , 0.65		15.33 , 0.29		methyl-naphthalene
16.13 , 0.42		16.17 , 0.05		
17.38 , 1.17		17.18 , 0.54		C_2-tetralin
17.87 , 0.32		17.88 , 0.08		
18.51 , 0.68		18.53 , 0.10		
--- , ---		18.95 , 0.03		
19.54 , 0.31		19.47 , 0.10		
20.34 , 0.04		20.40 , 0.12		
20.90 , 0.04		20.93 , 0.12		
21.86 , 0.05		21.87 , 0.07		
22.87 , 0.29		22.89 , 0.28		Methyl-biphenyl
24.25 , 0.12		24.28 , 0.27		
25.15 , 0.66		25.20 , 0.52		
26.12 , 0.00		26.19 , 0.02		
28.00 , 0.18		28.07 , 0.12		

for the majority of the sample. In fact, there are only five compounds, all with two or greater area percent, that account for greater than 90 area percent of the entire sample. These compounds are common to each sample and include the following in descending order of abundance: naphthalene (⬡⬡) >methyl indan (⬡⬠—CH$_3$) >benzene (⬡), C$_4$-benzene (⬡—C$_4$H$_9$) >decalin (⬡⬡). Of these five compounds the first three account for a least 80% of the light oil in each sample. The broadness of many of the chromatogram peaks, particularly those at the longer retention time, is a good indication that they consist of more than one component. Hence, the number of chemical compounds actually in the light oil sample is probably at least twice the number of integrated GC peaks.

UTILITY

Even though homogeneous catalytic hydrogenation has had considerable practical utility in the hydrogenation of specialized chemicals such as certain fats, oils and pharmaceuticals, its economic and technical utility in processing carbonaceous feedstocks such as coal, oil or their derived intermediates is very uncertain. We have seen that prehydrogenation of coal can significantly increase the amount of liquids obtained by pyrolysis compared to the unhydrogenated coal. It has also been shown that the hydrogenolysis of prehydrogenated coal produces less asphaltenes and more light oil and gas than the catalytic hydrogenolysis of the parent coal. Finally it was shown that homogeneous catalytic hydrogenation can effectively increase the atomic hydrogen to carbon ratio of the carbonaceous materials including coal and materials derived from coal by pyrolysis and solvent refining.

Although the amount of experimental data generated here in support of homogeneous catalytic hydrogenation is infinitesimal in regard to that needed for a sound technical judgment concerning its utility in the area of fuels processing, there is a clear indication that the approach has merit. The extrapolation of the experimental data indicates that homogeneous catalytic hydrogenation has considerable potential as a preliminary processing step for carbonaceous materials such as coal, and possibly oil shale and tar sands for increasing the atomic H/C ratio over conventional methods. The derived benefit from such a unit operation aside from the addition of hydrogen to these hydrogen-deficient materials is to increase the yield and quality of the products over what is now obtainable by conventional processing techniques at such mild conditions. Yet another potential application of homogeneous catalytic hydrogenation is as an intermediate step in fuel processing or conversion schemes in which the H/C ratio is increased to produce a superior quality product. Finally, potential applications of homogeneous catalytic hydrogenation are foreseen in the area of basic research studies where it is used as an anlytical tool or technique for investigating complex carbonaceous substrates.

Much of the impetus behind contemplating the use of homogeneous catalysts lies in the prospects of reducing temperature and pressure required for conversion, increasing reaction specificity and obtaining the most efficient use possible of the active metal component. In some instances of homogeneous catalytic hydrogenation, all these prospects have been realized. I think that it is reasonable to expect that homogeneous catalysts will eventually be developed that are capable and effective in hydrogenolysis reactions of carbon-carbon bonds. This indeed would be an extremely significant break-through with respect to coal liquefaction.

The major technical drawback to the use of homogeneous as well as heterogeneous catalysts is connected to their recovery from processing streams and poisoning. Since catalysts are extremely expensive, processing materials as a result of their manufacturing costs and cost of their component constituents only small losses can be economically tolerated. In homogeneous catalytic hydrogenation Run 25 where 7 mmole of Ni-Ziegler catalyst was employed per 15 g coal, the cost of nickel alone at zero recovery (i.e., 54.8 lb/ton coal) would amount to about $110/ton coal hydrogenated. If the cost of the triethylaluminum and the carboxylate of nickel are taken into consideration the cost of catalyst materials alone is estimated to exceed $150/ton coal hydrogenated. Clearly, in order to contemplate such a use of these catalysts, they must either be recovered or used in a much reduced concentration or preferably both. Even though no attempts were made at catalyst recovery or use of reduced amounts in this study it was found that the hydrogenated coal in Run 25 contained 1.2% Ni. This figures to be 31% of the nickel used in the homogeneous catalytic hydrogenation. The remaining 69% of the nickel catalyst apparently remained in the carrier solvent, which in practice would be recycled. Obviously, even higher catalyst recovery is necessary to promulgate its economic viability.

That catalysts can be used effectively and economically in bulk chemical processes is amply demonstrated in the hydrocarbon processing industries. Although these catalysts have been for the most part heterogeneous, homogeneous catalysts have found a home in at least two notable areas. One is the use of Ziegler catalysts in coordination polymerization and the other is in the hydroformylation process. These two examples show that the technical and economic problems so often associated with the use of homogeneous catalysts in industrial processes can be overcome.

ACKNOWLEDGMENT

REFERENCES

1. J. Kwiatek, I. L. Mador and J. K. Seyler, Adv. in Chem. Ser. No. 37, 1963, pp. 201-215.

2. J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkerson, J. Chem. Soc., A, 1711-32 (1966).

3. L. Vaska and R. E. Rhodes, JACS, 87, 4970 (1965).

4. L. Vaska, Inorg. Nuclear Chem. Letters, 1, 89 (1965).

5. S. J. Lapporte, Annales N. Y. Acad. Sci., 158 (2), 510 (1969).

6. S. Friedman, S. Metlin, A. Svedi and I. Wender, J. Org. Chem., 24, 1287-89 (1959).

7. O. N. Efimov, et al., J. Gen. Chem., USSR, 38 (12), 2581 (1968).

8. L. A. Heredy and M. B. Neuworth, Fuel, Lond., 41, 221 (1962).

9. K. Ouchi, K. Imuta and Y. Yamashita, Fuel, Lond., 44, 29 (1965).

10. H. C. Howard in "Chemistry of Coal Utilization Supplemental Volume," H. H. Lowry, ed., John Wiley & Sons, New York, 1963, pp 363-70.

11. O. N. Efimov, et al., Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, 855-8 (1969).

12. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd edition, Interscience Publishers, New York, 1972, pp 772-6.

13. G. E. Coates, M. L. H. Green, P. Powell and K. Wade, Principles of Organometallic Chemistry, Methuen & Co., Ltd., London, 1968, pp 197-8.

14. H. Gan, S. P. Nandi and P. L. Walker, Jr., Fuel, 51 (10), 272-77 (1972).

15. N. Holy, T. Nalesnik and S. McClanahan, Fuel, 56 (1), 47-8, (1977).

16. J. F. Jones, "Project COED", Clean Fuels from Coal Symposium, IGT, Chicago, Ill., September 10-14, 1973.
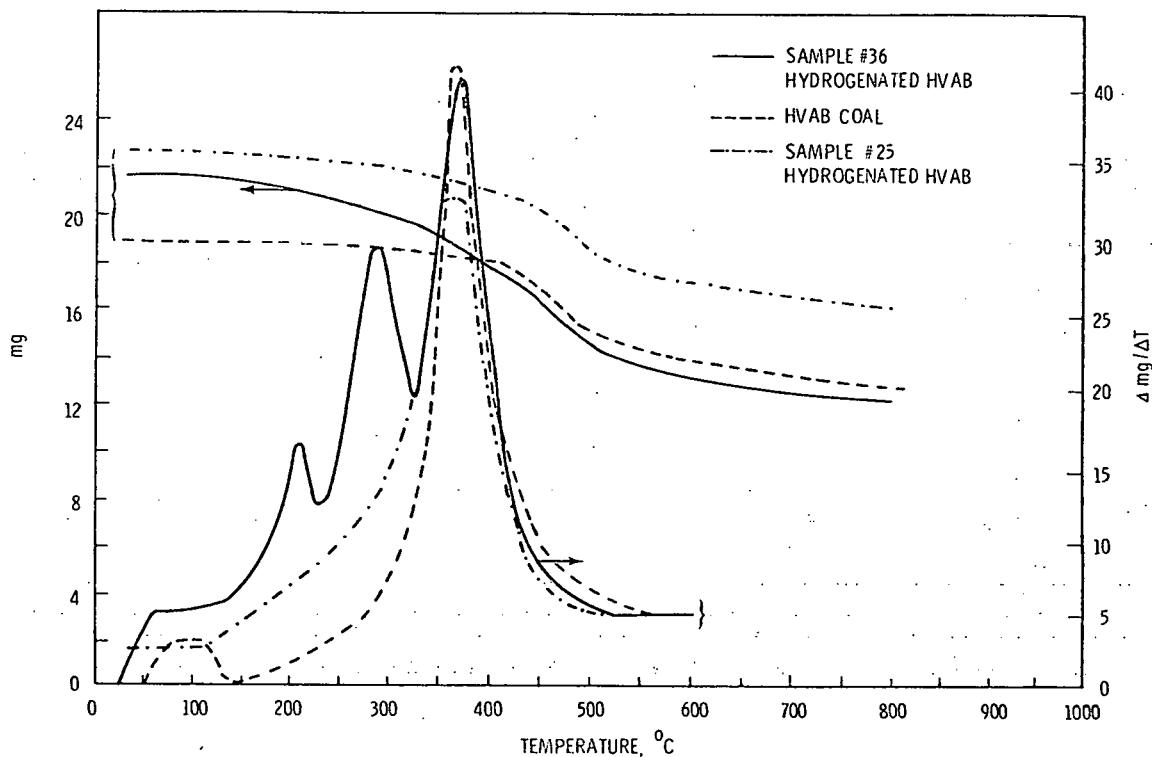
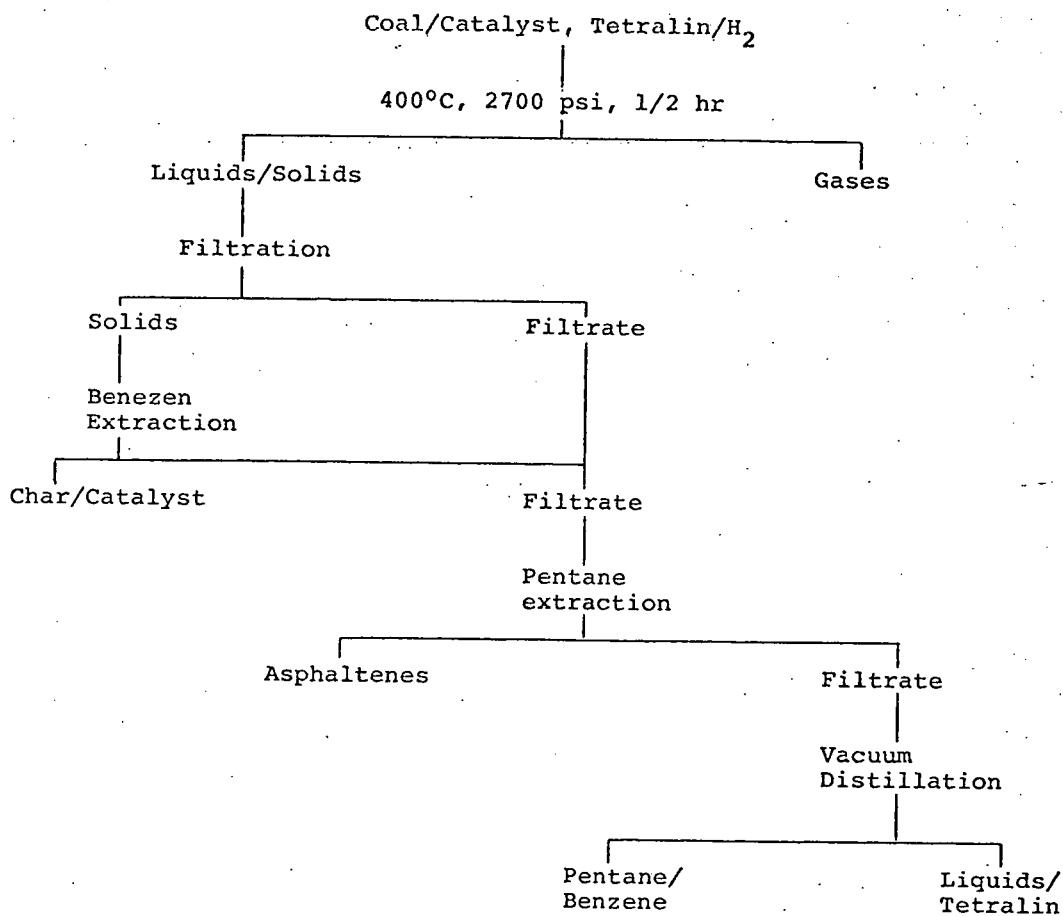FIGURE 1. Thermograms and DTG of Coal and Hydrogenated Coal

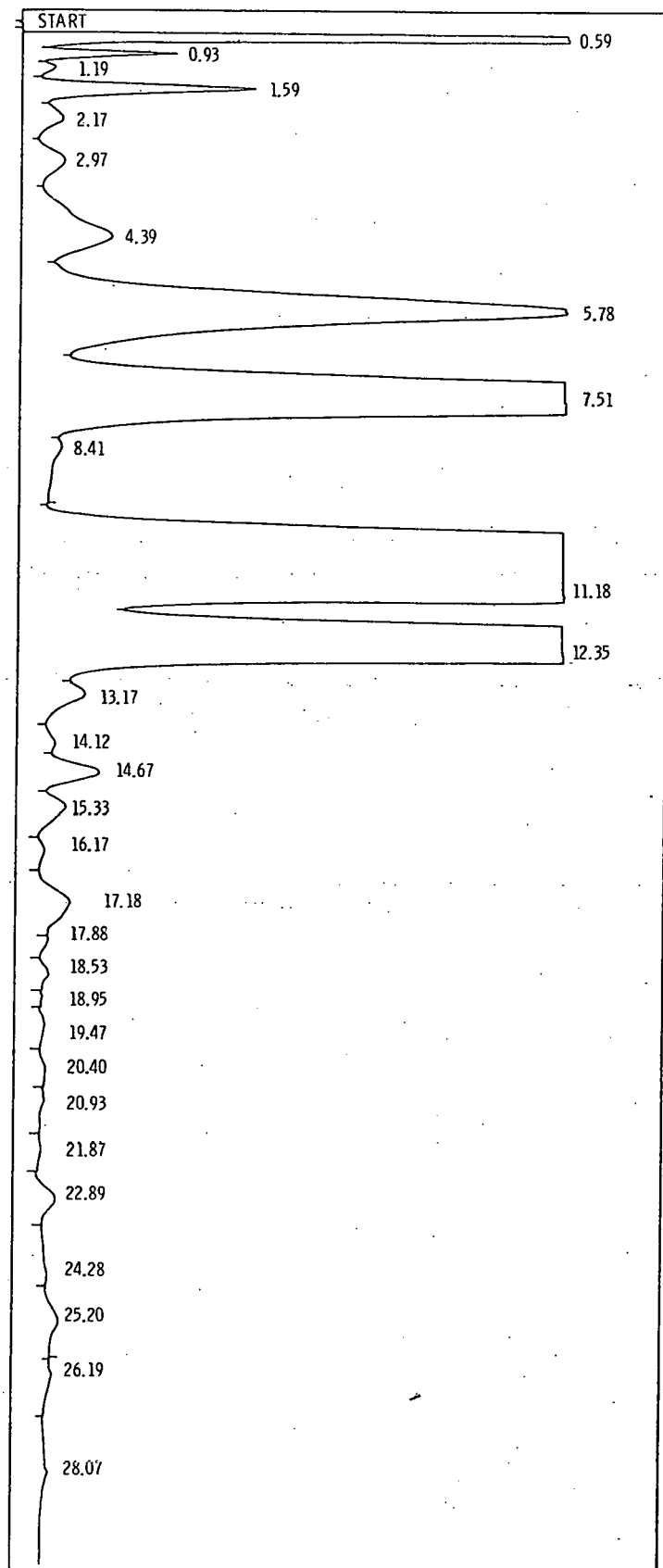FIGURE 2. Schematic for Workup of Hydrogenolysis Experiments

FIGURE 3.   Gas Chromatogram of Light Oil from Hydrogenolysis
of Hydrogenated Hvab Coal