

# LIQUEFACTION OF COAL WITHOUT CATALYST USING SELECTIVE HYDROGENATION

W. K. T. Gleim

University of Southern California  
Chemical Engineering Department  
Los Angeles, California 90007

## INTRODUCTION

Until recently refiners avoided the upgrading of residual fuels by catalytic hydrogenation. The difficulties experienced in the development of the catalytic desulfurization of residual fuels demonstrated the infeasibility of such a process. For example, heat sensitive asphaltenes (1) present in the residual fuels immediately deactivate the catalyst at the start of the process through excessive carbonization caused by the heats of hydrogenation and adsorption. Nevertheless, efforts are still made to upgrade coal extracts containing more asphaltenes than residual fuels, or even worse, components such as benzene insolubles or ash.

## EXPERIMENTAL CONSIDERATIONS

The most sensible approach is to selectively extract only the asphaltene free portion of the coal and use the remaining undissolved coal for the production of  $H_2$  and the energy necessary for processing. Approximately 40 to 50% of the coal will be needed to provide these essential services for the refining of coal. As an example, 100g moisture ashfree-maf-Illinois #6 coal contains: 81.0% C = 6.7 atoms; 5.2% H = 5.2 atoms; 9.5% O = 0.6 atoms; 2.9% S = 0.09 atoms; 1.4% N = 0.10 atoms. For every atom of C, approximately 0.8 atoms of H are present. This is less than 1H for 1C. In paraffins,  $H_2C-(CH_2)-CH_3$ , the ratio of  $H_2:C$  is 2:1 since the terminal  $CH_3$  groups do not affect this ratio very much. In reality, fuels which are saturated mixtures of paraffins and naphthenes like kerosene, do not achieve this ratio of 2:1 due to the presence of small amounts of benzene rings and condensed naphthenes. A more realistic ratio for a saturated fuel should be 1.8H:1C corresponding to 13.3% H.

If one wanted to upgrade 4 of the 6.7 carbons in the 100g maf coal by increasing the atomic H:C ratio from 0.8 to 1.8, this would require the addition of 2 moles of  $H_2$  to the 4C atoms, producing 55.2g of oil ( $4C = 48g$  and  $4 \times 1.8H = 7.2g$ ). Approximately 0.8 mole of  $H_2$  would also be necessary for the removal of the heteroatoms O, S, N. Therefore, 2.8 moles of  $H_2$  have to be produced from the 100g maf coal. Out of the 6.7 atoms of carbon, 4 are being hydrogenated to a hydrocarbon oil and 2.7 C are available to produce  $H_2$  via the water-gas and the subsequent shift reaction. The autothermic equation, coupling the maximum  $H_2$  production with a minimum C consumption,  $2.0C + 0.60 O_2 (+188 \text{ Kcal or } 2.0 \times 94) + 2.8 H_2O (-185 \text{ Kcal or } 2.8 \times 68) \longrightarrow 2.8 H_2 + 2.0 CO_2$  demonstrates that an absolute minimum of 2.0 carbon atoms of the remaining 2.7 C atoms is necessary for  $H_2$  production, 0.7 C, about 10% of the maf coal is available for the energy needed to run this reaction and the coal refinery.

This crude approximation demonstrates that it is only necessary to extract 55g oil from 100g maf coal, the remaining undissolved coal has to provide the  $H_2$  and the energy for the operation. If only 55% has to be dissolved it should be possible to extract selectively only heptane soluble oil, thereby avoiding all downstream refining difficulties caused by the presence of asphaltenes. Ideally, the solvent should do two things, dissolve 50-60% of the coal selectively, e.g., asphaltene free and thermo-hydrocrack using  $H_2$  from the  $H_2$  atmosphere to achieve a sufficiently low molecular weight to permit separation of the extract from the insoluble coal by distillation. The conditions under which the solvent must operate, i.e., the temperature and  $H_2$  pressure must also be established. Bituminous coal acts like a giant potential asphaltene. The coal is heat labile and begins to soften at about 380°C. At 400°C it starts coking, which produces gas, volatile liquids, tar, and coke. Increasing the temperature beyond 400°C produces additional coke from the tar. Coking can be repressed by the application of high  $H_2$  pressure. However, beyond 440°C the thermodynamic equilibrium favors complete aromatization. Obviously, it would be advanta-

geous to dissolve the coal below the coking temperature to keep coke and asphaltene production to a minimum. Yet the temperature should be sufficiently high for a reasonable rate of decomposition. It was found earlier that 400°C was a good compromise (2), and should probably not be exceeded. Increasing the temperature to 430°C yields undesirable extracts having a higher asphaltene content. High H<sub>2</sub> pressure is beneficial since it represses coking and stabilizes heat labile materials. However, for practical operating reasons, the pressure should not exceed 200 atm.

Organic material proposed as coal solvents have ranged from paraffins (3) to hydroaromatics, to aromatics; and from coal tar fractions, to coal tar itself to dissolve the coal. Pott and Broche (4), proposed a coal solvent consisting of 80% tetralin and 20% coal tar cresol which could dissolve as much as 90-95% of the coal. Tetralin, without the cresols, is a little more discriminating. It will dissolve only 80-85% coal. Such an extract will contain around 30% heptane insolubles, but only a relatively small amount of benzene insolubles. Many investigators have shown that part of tetralin's ability to liquefy coal consists of transferring its H<sub>2</sub> to coal, thus becoming naphthalene. To our knowledge, no one has proven that tetralin can also transfer H<sub>2</sub> from the atmosphere to coal, i.e., carry out a catalyst-like reaction. This type of claim would be very difficult to substantiate since even if the H<sub>2</sub> material balance did show an uptake of H<sub>2</sub>, this uptake could always be attributed to the catalytic activity of the walls of the reactor and/or the catalytic activity of coal constituents. Secondly, one would not expect a large effect and correlations drawn from very small differences in the analytical hydrogen data raise grave doubts as to their reliability. However, there is another means of proving hydrogenation activity, namely to demonstrate different degrees of hydrogenation with different solvents in the same reactor vessel with the same coal under identical H<sub>2</sub> pressure and temperatures. In addition, a solvent should be employed which leaves no doubt as to its direct role in the promotion of hydrogenation. Such a solvent was found in a partially hydrogenated refinery stream (5) used by A.W. Langer and co-workers for the thermal hydrocracking of petroleum residues (6).

#### EXPERIMENTAL RESULTS AND DISCUSSION

Vacuum bottoms were hydrocracked using a typical Ni-Mo on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> desulfurization catalyst under rather severe conditions, i.e., (760°F and 300 psi H<sub>2</sub>). The results are shown in Table I under Run 4. An oil was obtained which consisted of 50% hydroaromatics and 40% saturates. Unfortunately, the oil also contained 10% polycyclic aromatics. For comparison the following solvents were used:

- Run 1 - tetralin
- Run 2 - cocracker slurry oil which is practically all aromatic
- Run 3 - raw, non-hydrogenated vacuum bottoms
- Run 4 - hydrocracked vacuum bottoms. This solvent had the highest H<sub>2</sub> content (12%) while the slurry oil had the lowest H<sub>2</sub> content (7.2%)

TABLE I

Solvent	Run	1	2	3	4
	I, BP		545°F		475°F
API				8.2	18.8
C <sub>7</sub> insol.			1.3	4.7	1.1
%H		9.1	7.2	10.5	12
% P + N					40
% HAR		100			50
% cond. polycycl. Ar					10

As can be seen, even the hydrocracked vacuum bottoms still contain some C<sub>7</sub> insolubles. Whether or not these figures are reliable is questionable. Very often, C<sub>7</sub> insolubles in hydrocracked vacuum bottoms are not asphaltenes but microcrystalline waxes soluble in warm oil but insoluble in C<sub>7</sub> at ambient temperatures (?).

200 g Illinois #6 raw coal was extracted in autoclaves with 200 g solvent at 400°C under 200 atm. H<sub>2</sub>. The coal had the following composition (moisture and ashfree - maf): C 81.0%, H 5.2%, O 9.5%, S 2.9%, N 1.4%. The raw coal contains 7.8% ash and 7.2% water.

The results (Table II.) confirm that the extraction with the hydrogenated vacuum bottoms is a selective process (See Run 4-56%); while tetralin (Run 1) and slurry oil (Run 2) yielded the same extraction result, namely 83%. Run 3 using raw, unhydrogenated vacuum bottoms extracted only 10% so the products from this run were not investigated any further.

TABLE II.

Run	1	2	3	4
<u>Liquid Product</u>				
% Coal MAF (dissolved)	83	83	10	56
API			15.8	18.6
% C <sub>7</sub> insol. (of solution)	14	20	4	2
% C <sub>7</sub> insol. (of extract)	34	43		3.8
% Bz insol. (of solution)	2.5	5.7		
% Bz insol. (of extract)	6	14		
% H <sub>2</sub> (of solution)	8.4	7.1	10.6	11.4
% H <sub>2</sub> (of extract)	7.4	7.0		9.0
<u>Unconverted Solids</u>				
% H	2.8	1.7		3.8
mols H <sub>2</sub> added to 100 g MAF coal	0.8	0.5		1.35

The percentages in the extract (Table II.) were calculated from the percentages in the solvent and in the solution; % in extract = % in solution - % in solvent. In the case of % H<sub>2</sub>, the H<sub>2</sub> in the unconverted coal solids was used to arrive at the H<sub>2</sub> material balance.

In examining the extract figures, note that the C<sub>7</sub> insolubles of Run 4 are still too high, 3.8%, for easy refining, but remarkably low compared to the asphaltenes in the tetralin extract, 34%, Run 1. This is most likely due to the 10% polycyclic aromatics in the solvent of Run 4. That effect is especially apparent in Run 2, where the whole solvent, slurry oil, is polycyclic aromatic. The extract contained 43% C<sub>7</sub> insolubles and an additional 14% benzene insolubles, which leaves 43% of the extract soluble in C<sub>7</sub>. Such a product could not be refined economically since it would have to be de-asphalted first, a very expensive process yielding only 43% C<sub>7</sub> solubles. The tetralin extract (Run 1) does not look much better; 34% C<sub>7</sub> insolubles and 6% benzene insolubles. The last horizontal line in Table II indicates the values of H<sub>2</sub> consumption for 100 g of maf coal. According to this table, the hydrogenated vacuum bottoms (Run 4) are not only more selective solvents, but much better H<sub>2</sub> transfer agents or if you wish, catalysts. The absolute accuracy of these figures is questionable due to the increasing error in arriving at the smaller absolute H<sub>2</sub> values. However, even though the values are not very accurate, they still show real differences (i.e. 1/2 or 1/3 as much, etc.). The figures also establish that organic compounds cannot only transfer H<sub>2</sub> from themselves to another organic compound, but also molecular H<sub>2</sub> from the surrounding atmosphere.

A repeat of these experiments with another hydrocracked vacuum bottom containing only 4% polycyclic aromatics showed a much greater selectivity (Table III.). Notice that the tetralin contains 1% C<sub>7</sub> insolubles and the resulting coal solution

had the same percentage. Thus, the extract itself also contained 1% C<sub>7</sub> insolubles. The total coal solution can be distilled by vacuum distillation and thereby facilitate the separation of the undissolved coal. In addition, these solvents actually upgrade the undissolved solids also.

TABLE III.

W.K.T. Gleim and M. J. O'Hara	U. S. 3,867,275	February 18, 1975
Hydrocracked VB's	Solvent	Coal Solution
I. BP	475°F	
API	18.8	20.5
C <sub>7</sub> insol.	1.1	1.2
% P + N	46	
% HAR	49	
% cond. polycycl. Ar	4	
% H in solids		5.9
% extract of MAF coal		58.1
% Bz extract		18.6

Furthermore, the upgrading of this residue was demonstrated by the fact that additional material was extracted from the residue by boiling benzene at atmospheric pressure. This second extract yielded 18.6% and consisted of 50% C<sub>7</sub> insolubles and 50% solubles.

In reference to the first extract, by reusing it over and over again without removing the dissolved coal, it is possible to slowly increase the dissolved coal content of the solvent thereby increasing its hydroaromaticity. Thus, the solvent would dissolve more coal, thereby losing its selectivity, meaning that the % C<sub>7</sub> insolubles would increase with the number of extractions. Rehydrogenating the coal solution between extractions will not totally reconstitute the selectivity of the original coal solvent. The paraffins in the original solvent derived from petroleum, contribute to its selectivity. These paraffins would be diluted by the additional of dissolved coal. In order to maintain this selectivity, a continuous fresh stream of solvent from a petroleum refinery would be necessary. This is a good argument for combining coal liquefaction with petroleum refining.

As shown in Table III., 58% of the maf coal can be dissolved, which means 50% of the raw coal. Assuming that all of the refined crude boiling above 500°F, can be used as coal solvent means that 70% of the total crude can serve as solvent in a coal-to-solvent ratio of 1:1.

#### CONCLUSIONS

How much additional distillate could such a scheme provide for the United States? Right now the U. S. produces  $8.5 \times 10^6$  bbls/day crude; in 5-6 years with Prudhoe Bay, the U. S. will be producing about  $10 \times 10^6$  tons/day. With  $6.5 \times 10^6$  bbls/day ( $\sim 1 \times 10^6$  tons/day),  $1 \times 10^6$  tons/day of raw coal can be extracted yielding 500,000 tons/day of coal extract, i.e.,  $3.25 \times 10^6$  bbls/day. At present, the U. S. uses approximately  $11 \times 10^6$  bbls/day of distillate. In ten years it will probably be at least  $13 \times 10^6$  bbls/day. This deficit could be balanced by  $3.25 \times 10^6$  bbls/day oil taken from coal in addition to the  $10 \times 10^6$  bbls/day from petroleum production. This means the yearly requirement will be  $365 \times 10^6$  tons of coal. Substituting coal for the  $3.3 \times 10^6$  bbls of residual oils that the U.S. uses daily would require another  $0.5 \times 10^6$  tons of coal/day, or  $182 \times 10^6$  tons/year. Therefore, a total of  $550 \times 10^6$  tons of coal per year will be needed to substitute for imported oil.

The present U. S. coal production is about  $600 \times 10^6$  tons per year. That means

that the U. S. coal industry would have to double their output in ten years. I do not believe that this can be achieved in the current political climate. The ideal conditions for these concepts I have expressed, exist in the Midwest. Oil, coal, and refineries are situated close together, with sufficient H<sub>2</sub>O available. One would begin with the total conversion of oil, including asphaltenes, to distillate. For this, coal would serve as the refinery fuel and H<sub>2</sub> source. When this is achieved, the second step, namely the selective extraction of coal is undertaken, leaving the undissolved coal to serve as a source of energy to power the refining of crude and coal.

To summarize, the better part of coal, that is the heptane soluble fraction, can be extracted selectively and thermohydrocracked to distillate with a petroleum derived solvent in an high pressure H<sub>2</sub> atmosphere without the help of an external hydrogenation catalyst.

#### REFERENCES

1. J. P. Dickie, M. N. Haller, and T. F. Yen, "Electron Microscopic Investigations of the Nature of Petroleum Asphaltics," *J. Coll. & Interface Sci.* 29, 475 (1969).  
J. P. Dickie and T. F. Yen, "Macrostructures of the Asphaltic Fractions by Various Instrumental Methods," *Anal. Chem.* 39, 1847 (1967).
2. M. Pier, "Production of Hydrocarbons of High Boiling Point Range," U. S. Patent 1,988,019, Jan. 15, 1935.
3. Scharmann, et al., "Method of Production of Motor Fuels," U. S. Patent 2,436,938, March 2, 1948.
4. A. Pott, H. Broche, H. Nedelmann, H. Scheer and H. Schmitz, *Glueckauf* 69, 903 (1933)  
Fuel 13, 91 (1934)  
13, 125 (1934)  
13, 154 (1934)  
U. S. Patent 2,123,380  
U. S. Patent 2,241,615
5. W. K. T. Gleim and M. J. O'Hara, "Coal Liquefaction Process," U. S. Patent 3,849,287, Nov. 19, 1974.  
W. K. T. Gleim and M. J. O'Hara, "Coal Liquefaction Process," U. S. Patent 3,867,275, Feb. 18, 1975.
6. A. W. Langer, et al., "Thermal Hydrogenation," *I & EC* 50, 1067 (1958).  
A. W. Langer, et al., "Thermal Hydrogenation of Crude Residua," *I & EC* 53, 27 (1961).  
A. W. Langer, et al., "Hydrogen Donor Diluent Visbreaking of Residua," *I & EC Process Design and Development* 1, 309 (1962).
7. J. Knotnerus and C. J. Krow, *Bitumen-Teere-Asphalte-Peche und verwandte Stoffe* 16, 299 (1965).