

WATER-ASSISTED AND NONDONOR-VEHICLE-ASSISTED
COAL LIQUEFACTION

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In continuous coal liquefaction operations, the recycle vehicle has several functions. First, it serves as the medium in which to slurry the fresh coal feed and transport it through the preheater into the reactor. Second, it often acts as a source of hydrogen, i.e., it is a hydrogen donor. Much of the chemistry of coal liquefaction can be explained by reactions of hydrogen-donor vehicles with coal or the free radicals generated by thermolysis of coal. In the usual coal liquefaction process, much of the liquid product serves as recycle vehicle, since the slurry fed to the reactor is typically two parts recycle vehicle to one part coal. The throughput of coal for a given reactor might be increased if a lesser quantity of a readily available material could be substituted for the coal-derived recycle vehicle. One possible substitute would be water, at least as far as acting as a slurry medium for fresh coal feed.

Water has been used in the past in the liquefaction or the extraction of coal for a variety of reasons. When used in combination with carbon monoxide and a suitable catalyst, water was a source of hydrogen for the reduction of coal [1,2]. In this work, an organic solvent was frequently used in combination with water. Liquefaction under carbon monoxide has also been carried out with slurries composed of coal and either water or aqueous base without an organic solvent [3,4]. In some cases, water served to carry dissolved metal salts used as homogeneous catalysts as well as acting as the liquefaction medium [5]. Thus, the elimination of coal-derived recycle solvents commonly used in liquefaction in favor of water -- a simple, cheap, and readily available substitute -- has already been accomplished in the laboratory. In comparison with conventional organic liquefaction solvents, water has been shown to be quite effective when used in combination with H₂S, in particular under synthesis gas rather than hydrogen [6]. Aqueous liquefaction using impregnated catalysts has also been combined in a single operation with supercritical water distillation to separate the oil and asphaltene from the coal char residue [7]. The results clearly show that the liquids produced by hydrogenation can be extracted by supercritical water and transported away from insoluble coal residues. It has also been shown that the simple treatment of coal with supercritical water in the absence of hydrogen or catalysts renders a substantial portion of the treated coal extractable by tetrahydrofuran after the product was cooled and recovered from the autoclave [8]. The amount of extract obtained depended on the density of the supercritical water. Higher yields were obtained when coal was injected into supercritical water, thus providing a rapid heat-up of the coal, than when a coal-water slurry was heated to operating temperature. From these extraction studies, it is apparent that water is able to assist the diffusion and dispersal of liquefaction products and reactants. In addition to these roles, it has also been reported that water may directly participate as a reactant in the thermolytic chemistry of certain model

compounds. In the presence of water, dibenzyl ether decomposes at 400°C by both pyrolytic and hydrolytic pathways, the latter leading to the formation of benzyl alcohol [9]. The removal of nitrogen from heterocyclic compounds, such as isoquinoline, was also reported to be accelerated in the presence of supercritical water [10].

Taken together, these studies indicate that under various conditions, supercritical water may act as a good liquefaction medium, dissolve or extract coal-derived liquid products, promote the cleavage of certain bonds likely to be found in coal, provide hydrogen through the water-gas shift reaction, and possibly assist the contacting of coal with catalysts or hydrogen. It has also now been made clear by the successful preparation of coal-water mixtures for direct combustion that pumpable slurries can be made at ambient conditions using as little as 30% by weight of water. The present study is intended to evaluate further the role of water, near or above its critical temperature, in the conversion of coal to a liquefaction product. Specifically, we wish to determine whether it is possible, feasible, and, finally, advantageous to use water as a replacement for all or part of the recycle vehicle used for slurring coal in conventional liquefaction practice. Since water is not a hydrogen donor in the usual sense, the behavior of other nondonors was also examined. It should be pointed out that for coal hydrogenation alone, no vehicle is needed. Much of the previous work on coal hydrogenation was done by simply subjecting dry powdered coal in batch units to a high pressure of gaseous hydrogen, sometimes under the influence of an impregnated catalyst [11].

EXPERIMENTAL

A multireactor consisting of five individual microautoclaves, each of approximately 45-ml capacity and attached to a single yoke, was used to study these reactions [12]. The entire assembly was immersed rapidly into a preheated, fluidized sand bath, allowing heat-up to reaction temperature in 4-6 minutes. Immersion in a second fluidized sand bath held at room temperature provided rapid quenching. The autoclaves were agitated by a rapid horizontal-shaking motion, assuring good mixing of heterogeneous, multiphase mixtures. Individual thermocouples allowed continuous temperature monitoring of each microautoclave. For all experiments reported here, the reactors, once pressurized, were isolated from the gas-handling manifold by a valve and a short length of tubing of negligible volume. This prevented loss of water from the reaction zone due to condensation in the unheated portion of the system. Separate experiments using different reactors, in which it was possible for water to migrate to unheated regions of the system, indicated that such water loss had a profound but erratic effect on measured values for pressure and coal conversion, and generally led to misleading data.

The pressure at reaction temperature was not measured directly in these experiments. Using van der Waal's equation, the partial pressure of water was estimated as 1700 psi at 385°C in those cases where 1.7 g of water was charged. When 3.4 g was charged, the partial pressure was estimated at 2670 psi. At this temperature, the partial pressure due to hydrogen is estimated to be about 2600 psi. Total pressures are thus about 4300 psi or 5300 psi. The density of supercritical water was 0.05 g/mL when 1.7 g was charged and 0.11 g/mL when 3.4 g was charged.

Table 1 gives the analyses of the Illinois No. 6 (River King Mine) bituminous coal and the vehicles used in these experiments.

Most of the conversion values were obtained by the centrifugation method given below. Conversions for run 13 and the three series HD2, HD3, and HD4 were determined by a somewhat different method based on filtration of the insolubles.

TABLE 1. Elemental Analyses of Coal and Vehicles.^a

<u>Material</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>O</u>	<u>S</u>
Illinois No. 6 Coal, River King Mine ^b	73.7	5.6	1.5	14.8	4.5
SRC-II Distillate	87.1	8.0	1.4	3.0	0.4
Lummus Vehicle ^c	89.8	6.8	1.0	1.8	0.5

^a wt.%, daf basis, Huffman Labs, Wheatridge, Colo.

^b Moisture-free ash content was determined to be 13.6 wt.% for the River King Coal. As used, the coal contained 3 wt.% water.

^c Obtained from operations of the integrated two-stage Lummus liquefaction plant at Bloomfield, N.J., on Illinois No. 6 coal.

Separate experiments established that similar values were obtained by both methods.

Following gas collection and measurement via water displacement, the reactors were washed out with tetrahydrofuran (THF) together with physical scraping of the reactor walls. The THF was distilled before use to remove the inhibitor. The reactor and contents were sonicated to aid the dissolution and/or dispersion of the products in THF. This was repeated until the THF solution was clear and the reactor tare weights before and after reaction agreed to within ± 0.01 gram. The total volume of THF so accumulated (~300 mL) was evaporated in a hood to a volume of about 50 mL and transferred to a tared 250 mL centrifuge bottle. Additional THF was added to bring each volume up to ~150 mL, and the bottles were centrifuged at 3500 rpm for 20 minutes. The THF solution was then decanted and an additional 150 mL of THF was added to each residue in the bottle with stirring. This centrifugation/decantation/solvent addition sequence was repeated until the opaque solution became amber and opalescent. Experience indicated that such a process was necessary twice in the higher conversion runs and up to 5 times with lower conversions. The residues (THF-insolubles) were then dried overnight in their bottles in a vacuum oven at 110°C under an aspirator-maintained vacuum. The oven was purged with nitrogen until the temperature was below 60°C, and the bottles with residues were allowed to cool in air and were then weighed. The percent conversion was equal to

$$100 - \frac{\text{wt. THF-insoluble residue} - \text{wt. ash}}{\text{wt. moisture, ash-free coal}} \times 100$$

The reproducibility was usually within 1-2%.

The THF solutions obtained from the above procedure were roto-evaporated under an aspirator vacuum in tared, 250-mL round-bottom flasks. When no more solvent was seen to condense, the flasks were dried and the THF-soluble products were thus obtained. In some cases, cyclohexane solubles were isolated using a similar procedure. The THF extracts were transferred to 250-mL centrifuge tubes with 25.0 ± 1 mL of hot THF with the aid of sonication. To these solutions, 125 mL of cyclohexane was added and the centrifugation process employed, followed

by a second extraction with an additional 150 mL of pure cyclohexane. The extracts were recovered by roto-evaporation of the solutions and drying in the vacuum oven at 110° overnight.

For a typical run, the gas analysis showed CO₂ and H₂S were the major gases produced, along with the much lesser amounts of methane, ethane, and propane. The yields for one run were 4.2 wt.% for CO₂, and 0.3 wt.% each for methane, ethane, and propane, on a daf coal basis.

In experiments 6E and 6F of Table 3, where a coal/water/catalyst slurry was used, the procedure was as follows. Catalyst was added to 8.5 mL of solution of 200 ppm Aerosol OT surfactant (American Cyanamid) in water in a round-bottom flask, and the mixture slowly added to 10 g coal with physical mixing, followed by immersion in a sonic bath for 5 minutes, followed by rotation on a roto-evaporator at atmospheric pressure while submerged in a ice bath for 15 minutes. This slurry did not appear to settle with time. The slurry was mixed by hand again just prior to transfer of 7.4 g to the microautoclave. In experiment 6D, an aqueous solution of catalyst was added to the coal in the autoclave; and in 6G, 6H, and 6J, a solution of catalyst containing 200 ppm Aerosol OT was added. In experiment 6K, a slurry made as in 6E and 6F above was dried in a vacuum oven before use. In experiment 6I, such a dried slurry was added to the autoclave with fresh water.

RESULTS AND DISCUSSION

Table 2 shows the results of runs made to measure conversion of Illinois No. 6 (River King Mine) bituminous coal under a variety of conditions selected to uncover effects of water addition. Since this work was directed toward replacing or reducing the amount of organic recycle vehicle normally employed, all of the experiments reported here were conducted with the relatively low vehicle-to-coal ratios of 0.5 or less. Experiments with higher ratios showed no better conversions. As may be seen, without addition of water, conversions for these high coal-content slurries are quite low at the very moderate reaction temperatures employed. The addition of 0.42 parts water based on coal (the amount contained in a 70/30 coal/water slurry) increases conversion significantly. Evidently, reasonable conversions can be obtained using this minimal amount of water provided the loading of recycle vehicle is not too low, that is 1.6 g or above in the case of HD3-1, -2, and -3. We also note that under these mild, non-catalytic conditions the nature of the reducing gas had little effect, since in one experiment (HD4-2), the substitution of carbon monoxide for hydrogen had little effect on the conversion. The use of the more severe conditions of 1200 psi hydrogen (cold) and 427°C produced a small increase in conversion as expected (13 and HD2-3). However, variables other than reaction severity may have more significant effects, since still higher conversions were obtained at 385°C by appropriate choice of the organic vehicle, as discussed later.

A second series of experiments was run under conditions chosen to reveal the effect of the nature of the organic vehicle used in noncatalytic aqueous liquefaction. In a general way, conversions increased moderately as the organic vehicle was changed from one usually considered to be a poor hydrogen donor (1-methylnaphthalene) to vehicles considered to be better hydrogen donors (tetralin and 9,10-dihydroanthracene). Thus, the usual concepts of hydrogen-donor liquefaction chemistry may also be applied usefully to this series of less conventional liquefaction systems.

If good conversion in a noncatalytic system requires a minimal amount of an organic vehicle and also benefits from the addition of some water, it is reasonable to ask if the combination of organic vehicle and water is superior to either used separately. The final set of experiments in Table 2 indicates that this is the case. Conversion was poor without either (HD29-4), much improved with water alone (HD29-3), and still better with SRC-II distillate vehicle alone

(HD19-3,4). A combination of SRC-II distillate and water (HD18-3,4) produced a conversion better than either used separately.

Cyclododecane is a high-boiling hydrocarbon expected to be a poor hydrogen donor. When it was used as a nondonor vehicle, the conversion fell between the value for water and that for SRC-II distillate used in a lesser amount. When used in combination with SRC-II distillate, the conversion was not improved over that of SRC-II distillate alone. This stands in contrast to the result obtained for the combination of SRC-II distillate plus water. This different behavior indicates that addition of the second component to SRC-II distillate is not acting simply to dilute the relatively small amount of the recycle vehicle used in these experiments.

Table 3 contains data for the catalytic liquefaction of coal in the presence of water. When various forms of molybdenum are added to the coal, conversions are substantially increased. Clearly, high temperatures are not required for these molybdenum catalysts to influence liquefaction. More important, with catalyst present, the organic vehicle may be totally replaced by water without loss in conversion. As was seen in Table 2, this result was not obtained in the absence of catalyst. The important function of water is also underscored by the rather low conversion obtained with added catalyst but with no vehicle of any kind, i.e., a dry hydrogenation (6K).

Conversion increases continually with catalyst loading up to at least 1000 ppm molybdenum on coal (6A, HD30-1, -2, -3). Of the several methods used for application of the catalyst, none seemed to give notably superior results insofar as THF conversion values are concerned. However, there are indications now under study that the yield of lighter products may change significantly according to the method of catalyst application.

The surfactant, Aerosol OT, used to assist the preparation of coal/water/catalyst feed slurries had a small beneficial effect on conversion in both the presence of catalyst (HD30-4 vs. HD30-1) and the absence of catalyst (HD29-3 vs. 6A). At this point, it is only possible to speculate that the surfactant enhances the action of the water by improving the wetting of the coal.

In one case (6F), a low-boiling ether, THF, was substituted for water. The conversion was unexpectedly high, albeit the catalyst loading was twice that used with water. Tetrahydrofuran is quite effective in swelling River King coal at room temperature. The connection between this property and the liquefaction result is presently unclear, but investigation of a series of lower molecular weight vehicles may shed more light on the structural requirements for superior performance. These and related experiments are in progress.

Table 4 gives the data for analyses of the THF-solubles isolated from runs HD19-1,2 in which 1000 ppm Mo was used as catalyst in conjunction with surfactant. Except for the higher-than-usual oxygen content, these are typical analyses for a coal liquefaction product. The infrared spectrum of the cyclohexane solubles obtained from a dilute CH_2Cl_2 solution shows that about 2.1 wt.% of oxygen is in phenolic OH and the remaining 5% is presumably in ethers. The carbon aromaticity of the THF solubles was determined by ^{13}C -CP/MAS NMR to be 0.72, which is virtually identical to that of the feed coal. The data for characterization of the products in hand so far are in accord with the rather mild conditions used to bring about the conversions.

The preliminary results obtained so far form a basis for an encouraging outlook on liquefaction with water or other nondonor vehicles. High coal conversions were obtained at modest temperatures with use of little or no organic recycle vehicle. Thus, it is possible and feasible to use water as a substitute liquefaction medium. The advantage in doing so in continuous units is still to be

TABLE 4. Elemental Analyses and Molecular Weights of HD19-1,2 Product Fractions.^a

<u>Elemental Analysis (wt.%)^b</u>	<u>Cyclohexane Solubles</u>	<u>Tetrahydrofuran Solubles^c</u>	<u>Tetrahydrofuran Insolubles^c</u>
C	82.9	81.8	24.5
H	7.3	5.9	1.4
O	7.1	7.3	7.5
N	1.2	1.9	0.5
S	1.8	1.9	6.9
<u>Ash (wt.%), 750°C</u>	---	---	66.2
<u>Molecular Weight, \bar{M}_n</u>		1300 ^d	

a Huffman Laboratories, Wheatridge, Colo.

b Average of duplicate microanalyses.

c Dried to constant weight @ 30°C under vacuum before analysis.

d VPO in pyridine at 90°C.

demonstrated. At the least, a different line of investigation is now open whereby important questions regarding the mechanism of liquefaction may be addressed. Since no organic vehicle need be used, the coal-derived products of liquefaction may be analyzed without interference. At the same time, the presence of a fluid medium provides better heat transfer and better dispersion of the reactants than possible with dry hydrogenations. It is expected that further work will be fruitful by determining how the course of liquefaction is affected by the chemical and physical properties of water or other nondonors and by uncovering the important variables associated with the use of dispersed catalysts at mild liquefaction temperatures.

TABLE 2. Liquefaction of Illinois No. 6 (River King Mine) Bituminous Coal.^a

Run Number(s)	H ₂ Pressure cold, psig	Temp., °C	Time at Temp., min.	Vehicle		H ₂ O g.	Conv. %	Notes
				g.	Type			
HD3-5	800	370	60	1.62	LUM	0	55	Lummus vehicle
HD3-4	800	370	60	2.00	LUM	0	67	
HD3-3	800	370	60	1.29	LUM	1.70	61	
HD3-2	800	370	60	1.60	LUM	1.70	80	
HD3-1	800	370	60	2.00	LUM	1.70	79	
HD4-2	800(CO)	370	60	1.60	LUM	1.72	82	
13, HD2-3, 4	1185	427	60	1.98	LUM	1.70	86, 87	
HD10-3, 4	1200	385	40	1.50	MEN	1.70	77, 79	1-Methylnaphthalene
HD10-1, 2	1200	385	40	1.50	LUM	1.70	82, 84	
HD12-3, 4	1200	385	40	1.50	SRC-II	1.70	85, 87	SRC distillate
HD12-1, 2	1200	385	40	1.50	TET	1.70	88, 90	Tetralin
HD15-1, 2	1200	385	40	1.50	DHA	1.70	91, 93	9, 10-Dihydroanthracene
HD29-4	1200	385	30	0	---	0	25	
HD29-3	1200	385	30	0	---	3.4	52	
HD19-3, 4	1200	385	30	1.50	SRC-II	0	72, 74	
HD18-3, 4	1200	385	30	1.50	SRC-II	1.7	86, 88	
HD29-2	1200	385	30	3.4	CDOD	---	67	Cyclododecane
HD29-1	1200	385	30	1.50	SRC-II	1.7 CDOD	72	Cyclododecane

^aCoal charge in each case was 4.0 g.

^bBased on THF extractions.

TABLE 3. Catalytic Experiments and Associated Base Cases in Water-Assisted Liquefaction of Illinois No. 6 Coal.^a

Ex. #	Vehicle	Water, g.	Catalyst ^b	Precursor/Application ^c	THF Conv.
6C	SRC II	1.7	----		86, 88
6D	SRC II	1.7	1000 ppm Mo	aqueous sol. MoS ₄ ⁻	90, 92
6E	SRC II	1.7	1000 ppm Mo	NH ₄ molybdate/sol. slurry	89, 91
6F	SRC II	1.7, THF	2000 ppm Mo	Mo ₂ (OAc) ₄ /sol. slurry	90
6A	--	3.4	----	surfactant	67
6G	--	3.4	1000 ppm Mo	MoS ₄ ⁻ /surfact. soln.	86, 90
6H	--	3.4	1000 ppm Mo	NH ₄ molybdate/surfact. soln.	85, 87
6I	--	3.4	1000 ppm Mo	MoS ₄ ⁻ impreg. coal, then water	91
6J	--	3.4	1000 ppm Mo	MoS ₄ ⁻ /surfact. soln.	89, 91
6K	--	---	1000 ppm Mo	NH ₄ molybdate impreg. coal	76, 78
HD30-1	--	3.4	1000 ppm Mo	NH ₄ molybdate/surfact. soln.	87
HD30-2	--	3.4	250 ppm Mo	NH ₄ molybdate/surfact. soln.	80
HD30-3	--	3.4	100 ppm Mo	NH ₄ molybdate/surfact. soln.	73
HD30-4	--	3.4	1000 ppm Mo	NH ₄ molybdate/aqueous soln.	84

^a Reaction conditions: 4.00 g River King coal; 385°C; 30 minutes at temperature; 1200 psig (cold) hydrogen, using 1.50 g SRC-II distillate where indicated.

^b ppm metal on coal. See Experimental Section for details.

^c When the use of a surfactant is indicated, aerosol OT was employed at ≈200 ppm in water.

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ACKNOWLEDGMENT

M.A. Mikita was a Faculty Research Participant for the summer of 1984 and was appointed to the Pittsburgh Energy Technology Center by Oak Ridge Associated Universities. The authors wish to thank the personnel from the PETC Division of Coal Science for careful analyses of the various materials and products.

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