Section 14

DOW COAL LIQUEFACTION PROCESS UPDATE

by

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INTRODUCTION

The Dow Coal Liquefaction Process has been developed in Dow research laboratories as part of a broad internal program to evaluate coal as an alternate feedstock to petroleum and natural gas products. This work now includes major Dow efforts in lignite gasification for power and synthesis gas generation; Fischer-Tropsch Synthesis to produce LPG's, olefins, and liquids; and coal liquefaction, the subject of this paper.

Dow research in coal liquefaction has spanned the time period from 1973 to the present. While the Dow Process today is clearly related to past historical developments, it incorporates novel features which comprise the main emphasis of this paper. Briefly these developments are:

1. An expendable catalyst, fed as a component of the coal slurry, which is effective at a 100 ppm addition level in the feed;

2. A mechanically simple catalytic reactor;

3. The use of hydroclones to provide partial solids removal from the major component of the recycle oil and to provide partial recycle of catalyst to the reactor;

4. The use of Dow developed solvent deasphalting technology to produce an essentially solids free, low sulfur product oil and a high solids concentrate, which is a suitable gasifier feedstock;

5. An integrated gasification scheme based in part on Dow developed gasification technology.

Together these features represent an advanced, versatile, and efficient process for coal conversion which combines simplicity of design with high thermal efficiency.

PLANS FOR DEVELOPMENT

We have elected to develop the patented Dow Process for licensing. This, we believe, will be in the best interest of the company as well as the public. In this way, the technology will gain an earlier demonstration. At the same time, the longer term interests of Dow will be served in that a viable technology will be available when a Dow commercial venture is deemed desirable. To coordinate this program, we have appointed Jim Leenhouts Venture Manager for coal liquefaction.

The action plan for achieving our goals includes several aspects:

1. Dow Process Demonstration Studies will be conducted in 1/10 ton/day scale facility. Replacing our previous development unit, a new 200 lb/day liquefaction mini-plant is scheduled for start-up in 8 weeks. Included in the unit are facilities for all the major liquefaction processing steps except coal preparation and gasification/hydrogen manufacture. A key feature of this facility is a state-of-the-art computerized process control system.

2. Scale-up and demonstration of the unique features of the Dow Process is planned. We are currently investigating and looking for opportunities for larger scale tests of the Dow emulsion catalyst and deasphalter.

3. Gasification studies based on deasphalter residue followed by molybdenum recovery studies on the slag are planned.

This work is aimed at defining scale-up parameters and demonstrating commercial viability in a relatively short time period. All of these activities are predicated on the strong conviction that the Dow technology embodies significant advances in the art.

EMULSION CATALYST SYSTEM

Since coal constituents include a variety of catalyst poisons, any catalyst system employed in coal liquefaction is in a certain sense expendable. Our approach to coal liquefaction has been to develop a finely divided catalyst which is active at very low concentrations, has a simple to implement preparation scheme, and utilizes readily available U.S. based raw materials. Because the catalyst residence time in the reactor is short, a few hours only, sustained long term catalyst activity is not a critical consideration.

The Dow expendable catalyst is prepared by solubilizing tech grade molybdenum trioxide with aqueous ammonium hydroxide then dispersing this solution in a suitable coal derived oil to form a water-in-oil emulsion. When this emulsion is mixed with the feed slurry, the molybdenum is effectively dispersed throughout the feed slurry in micron sized water droplets.

The conversion of the catalyst precursor to the active catalyst is a critical step. Recent liquefaction studies, described below, have helped to elucidate this conversion. Electron micro-probe examinations of solids recovered from the liquefaction products indicates that the molybdenum is normally present as molybdenum disulfide. The catalyst activation is presumed to include the following transformations:

$$\text{Ammonium Heptamolybdate} \xrightarrow{\Delta} MoO_3 + NH_3 + H_2O$$

$$MoO_3 + H_2 + 2H_2S \longrightarrow MoS_2 + 3H_2O$$

EMULSION CATALYST STUDIES USING SUBBITUMINOUS COAL

Sulfiding of the catalyst is dependent on sulfur, as H_2S, being readily available in the reactor. The importance of accessible sulfur was shown in a series of single pass liquefaction studies on a Canadian subbituminous C coal. This is a low sulfur, low ash coal containing only small amounts of pyrite. Continuous bench scale liquefaction studies were made in a 200 cc autoclave at the conditions indicated in Table 1. Initial liquefaction attempts using the emulsion catalyst gave poor results as indicated (in Column 3 of Table 1) by the low hydrogen uptake and high yields of toluene and hexane insolubles. Since the absence of pyrite was a major difference from previously used coals, the experiment was repeated with FeS_2 added (Column 4 of Table 1). Conversion was now significantly better. Why? Was iron sulfide acting as a catalyst? Was there synergism between iron and molybdenum? Or was sulfur, released by the pyrite → pyrrhotite conversion, important for molybdenum activation? By performing several additional experiments it was conclusively demonstrated that sulfur was the critical element in obtaining good catalyst activity. Iron sulfide alone had little catalytic effect in the liquefaction, however, the H_2S formed in the conversion of pyrite to pyrrhotite was effective in sulfiding the molybdenum. Calculated H_2S partial pressures present in the reactor for the various experiments are shown. While thermodynamic calculations indicate that MoS_2 should be the stable form of molybdenum at very low H_2S partial pressures, it appears that the much higher H_2S pressures obtained with CS_2 are necessary for proper activation of the liquefaction catalyst. In larger scale operations, the necessary pressure could in most cases be achieved by selective H_2S recycle with the unconverted hydrogen.

SUBBITUMINOUS COAL PRODUCT YIELDS

The experiments with the subbituminous coal clearly demonstrated the compatibility of the Dow Process with this coal. In Table 2, results of a recycle liquefaction study on the Alberta subbituminous coal are tabulated. Note this data is for the liquefaction step only and does not include solid separations and residue processing for hydrogen manufacture. While coal reactivity was high and the yield of lighter products was greater than for typical bituminous coals, calculated thermal efficiency was somewhat lower. This is primarily due to the higher content of organic bound oxygen in the coal, 22.3% vs 9.6% for a typical high volatile bituminous coal. This high oxygen content is detrimental in several ways:

1. It increases hydrogen consumption in liquefaction with a corresponding increase in water yield;
2. It lowers gasifier efficiency for hydrogen manufacture;
3. Oxygen remaining in the product liquids lowers their heating value; and
4. It increases the hydrotreating hydrogen requirement if the oxygen must be removed from fuels or feedstocks.

Thus, the processing of subbituminous coals has advantages and disadvantages which must be weighed in a detailed economic analysis. Preliminary conceptual designs for commercial processing of Alberta subbituminous C coal and Pittsburgh No. 8 high volatile B bituminous coal have calculated thermal efficiencies of 68 and 75%, respectively. Cost of coal, transportation to markets, product values, and political questions are among many other areas to be considered.

DOW SOLIDS SEPARATION TECHNOLOGY

In addition to the catalyst system, Dow research has given major attention to the processing steps downstream from the reactor where solid-liquid separations are conducted. The objective here is to generate a suitable recycle oil, a solids rich residue stream for gasification, and a clean product oil. The unit operations employed for these separations strongly impact process efficiency, operability, and product quality. In the Dow Process, these key separations are achieved using a simple combination of hydroclone and deasphalting (Figure 1).

Hydroclones are used to achieve a significant reduction in the solids level of the major component of the recycle oil stream. The hydroclone feed is the liquefaction product slurry with lower boiling fractions removed in a series of flash tank separations. The hydroclone overflow-underflow split can be varied to fine tune the process. Normally, the hydroclones are operated with a 1:1 split so that the quantity of overflow is sufficient to provide 75% of the required recycle oil. MoS_2 catalyst particles, generated by the emulsion catalyst system, are too small to be removed by the hydroclone and are partially recycled with the hydroclone overflow. This raises the actual catalyst level in the reactor feed slurry at steady state to about 2.5 times the addition level.

Hydroclone underflow is fed to the deasphalter where it is contacted with a 50-75°C boiling range process derived paraffinic solvent, nominally pentanes and hexanes. In the deasphalter column, extraction of soluble components from the feed slurry occurs nearly instantaneously due to the phenomena known as the Marangoni Effect, illustrated in Figure 2. Because solids contained in the deasphalter feed slurry remain in the insoluble portion of the oils, their settling rate is much higher than would be the case for the individual sub-micron particles in a similar medium. A deasphalter column design adequate for the removal of > 99.8% of the feed solids thus has a relatively short residence time. Operating conditions and typical separations obtained when processing Pittsburgh No. 8 coal liquids are shown in Table 3. The fraction of the feed oil which is insoluble is a strong function of the solvent to oil feed ratio and the extraction temperature. By adjusting these parameters the solids content of the residue phase is controlled at 60-65% which corresponds to an ash level of 40-43%. This level is just below the transition zone between a high solids content slurry and an oil-wet, granular solid.

Being pumpable, the deasphalter residue is a preferred feed for an entrained-flow slagging gasifier. Typically, the feed for entrained-flow gasifiers is in the form of a fuel in water slurry. Since it is pumpable, the deasphalter residue avoids a major gasifier thermal efficiency loss associated with the vaporization of the water used to prepare feed slurries.

The solvent soluble oil phase from the deasphalter is first distilled to recover solvent for recycle and is then separated into two streams either by distillation or physical means. One stream is recycled, representing 25% of the recycle oil. The other is net product. Typical properties of full range deasphalted oil and deasphalter residue are shown in Table 4.

The use of the Dow deasphalter completely eliminates the need for a vacuum still handling the high solids content feed. The solvent recovery step, because of the widely different boiling ranges of the solvent and deasphalted oil, is relatively simple. Similarly, the solvent can be recovered from the residue by a simple flash.

Further advantages for deasphalting result from differences in the separation obtained by extraction as compared to distillation. Since extraction separates on the basis of solubility, the more difficult to convert polar materials--preasphaltenes and asphaltenes--are selectively rejected. Thus, refractory materials are preferentially purged from the recycle oil stream improving the yield of premium soluble products. The polar materials in the deasphalter residue tend to be hydrogen deficient as shown by the low atomic H/C ratio in typical residue--actually only about 90% of that in the feed coal.

In the Dow Process, deasphalted oil takes the place of the vacuum distillate typically employed as a component of the recycle oil. Because of the complex nature of the coal dissolution process, it is not readily apparent which material should function best as a recycle oil component. In Table 5, net products are shown for two steady state recycle liquefaction studies with Pittsburgh No. 8 Coal. The emulsion catalyst was used at an addition level of 0.05 wt% $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ based on dry coal for both experiments. Operating parameters for the two runs were identical in all respects except for the recycle oil which in Run 97 consisted of 25% vacuum gas oil distilled from the liquefaction products and in Run 98 consisted of 25% deasphalted oil with an initial boiling point comparable to that of the vacuum gas oil. The remaining 75% of the recycle oil was hydroclone overflow obtained from the products produced in the respective runs. The significantly reduced asphaltenes obtained in Run 98 indicate that deasphalted oil has superior properties as a coal liquefaction solvent. Since deasphalted oil contains some 975°F+ residual material, the improved conversion observed in Experiment 98 was achieved in the face of higher residue levels in the feed and reactor with no reduction in throughput.

The presence of an ash free residue in the Dow product slate has led us to begin an evaluation of this material as a possible precursor for premium coke products. Again, the use of extraction as a means of separation is expected to exert a strong influence on the properties of this material.

An optional processing scheme in which the deasphalted oil is topped in a vacuum still to an end point such that the residue provides 25% of the recycle oil has several advantages: The net deasphalted product is all distillate with an end point of ∿ 700°F. The net product is totally ash free since traces of ash in the deasphalted oil are now recycled. Continuous, steady operation of our previous 200 lb/day mini-plant in this mode gave superior results as shown in Table 6.

SUMMARY

In this paper we have described a number of the unique features of the Dow Coal Liquefaction Process. Parts of this technology may be of specific interest to developers of other liquefaction processes. Taken as a whole, the Dow technology fits together to provide an integrated efficient process. Our primary objective is to provide test results at larger scale to prove the usefulness of the integrated process as well as the component parts. We would welcome the opportunity to talk with any interested parties regarding this technology.

We look forward to contributing significantly to the growth of our newborn US Synfuel Industry.

Further descriptions of the Dow Process are contained in the Bibliography which follows.

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TABLE 1

COAL LIQUEFACTION

CATALYST COMPARISON STUDY

COAL ANALYSIS

Type: Subbituminous C

Source: Forestburg, Alberta, Canada

Proximate Analysis, Wt%

Moisture	26.09
Ash	4.45
Volatile Matter	35.96
Fixed Carbon	33.50

Ultimate Analysis, Wt% of Dry Coal

Carbon	65.10
Hydrogen	4.58
Nitrogen	1.39
Sulfur	.50
Oxygen (Organic)	22.30
Ash	6.12

Miscellaneous Analysis

Gross Heating Value BTU/Lb Dry Coal	11,836
Iron (Present as Pyrite in Dry Coal)	.36%

EXPERIMENTAL CONDITIONS

Reactor Type	Continuously fed stirred autoclave
Reactor Volume	200 cm^3
Reactor Pressure	2000 psig
Temperature	460°C
Agitator, RPM	1500
Slurry Feedrate	200 gm/hr 23.3 lb dry coal/hr-ft^3
H_2 Feedrate, SCFH	6.3
Slurry Oil	Deasphalted coal derived oil

TABLE 1, CONTINUED

LIQUEFACTION RESULTS

Basis: 100 Lb MAF Coal

Catalyst	None	Pyrite(1)	Moly Emulsion(2)	Pyrite(1) + Moly Emulsion(2)	CS_2(3) + Moly Emulsion(2)
Net Products					
Gases	21.6	24.3	25.4	27.7	28.5
Aqueous	17.5	16.5	16.4	18.8	16.6
Naphtha, 350°F-	11.5	8.6	10.3	13.4	13.6
Hexane Soluble Oil, 350°F+	-.6	-9.7	-18.0	14.9	19.1
Asphaltenes	4.2	-.9	25.6	7.8	1.8
Pre-asphaltenes	18.5	38.1	22.1	7.8	10.6
Unconverted	30.2	25.0	22.0	15.7	16.7
Hydrogen Usage lb/100 lb MAF Coal	2.9	3.6	3.8	6.1	6.7
H_2S Pressure, psi	.04	8.5	1.9	9.5	25.0

NOTES:

(1) Pyrite added = 2.0 lb/100 lb dry coal

(2) Molybdenum added = 0.10 lb $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$/100 lb dry coal

(3) Carbon disulfide added = 2.0 lb/100 lb dry coal

TABLE 2

LIQUEFACTION OF ALBERTA SUBBITUMINOUS C COAL

Experimental Conditions

Reaction Pressure, psig	2000
Temperature, °C	460
Slurry Concentration, %	37.3
Volumetric Feedrate, lb coal/hr-ft^3	33
Hydrogen Feedrate, SCFH/lb coal	35

Net Product Composition

Component (lb/100 lb dry coal)

Gases	20.6
Aqueous	19.1
Liquid Product Oil	66.2

Hydrogen Consumption

Lb H_2/100 Lb Dry Coal	5.9

Gas Analysis, Wt% of Total

N_2	1.2
CO	7.4
CO_2	20.1
H_2S	3.5
CH_4	20.2
C_2H_4, C_2H_6	15.3
C_3H_6, C_3H_8	15.5
C_4's	9.1
C_5's	3.4
C_6's, C_7's	4.3

BOILING CURVE OF NET LIQUID OIL PRODUCT

Temperature Interval	Wt% Boiling In Interval
< 75°C	1.8
75-125	5.2
125-175	7.5
175-225	5.9
225-275	12.4
275-325	10.8
325-375	13.1
375+ Hydrocarbons	34.1
Ash	9.2

FIGURE 1

DOW SOLID SEPARATIONS SCHEME

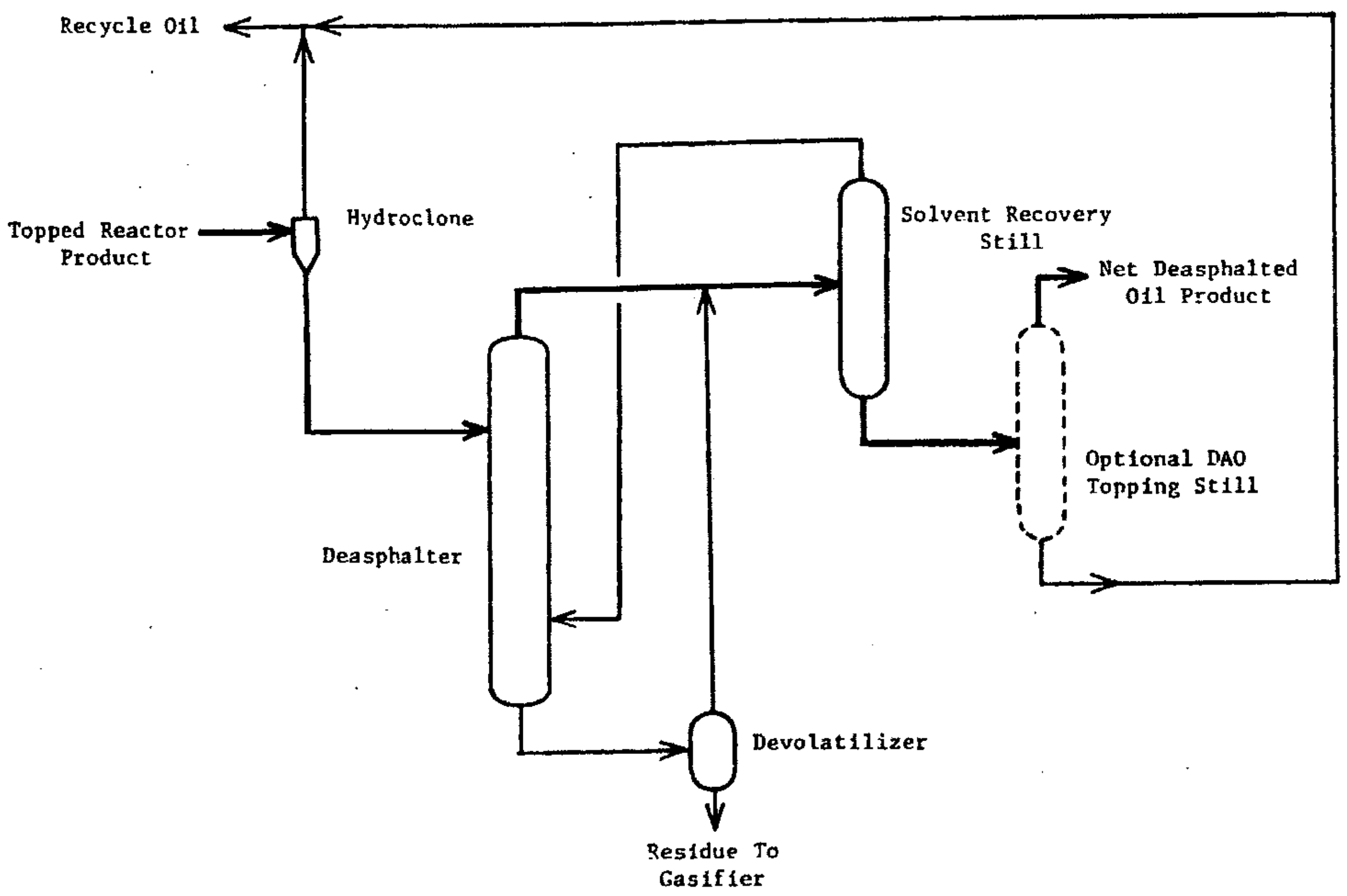

FIGURE 2

PHOTOGRAPHS SHOWING DROPLET BREAK-UP
DUE TO THE MARANGONI EFFECT

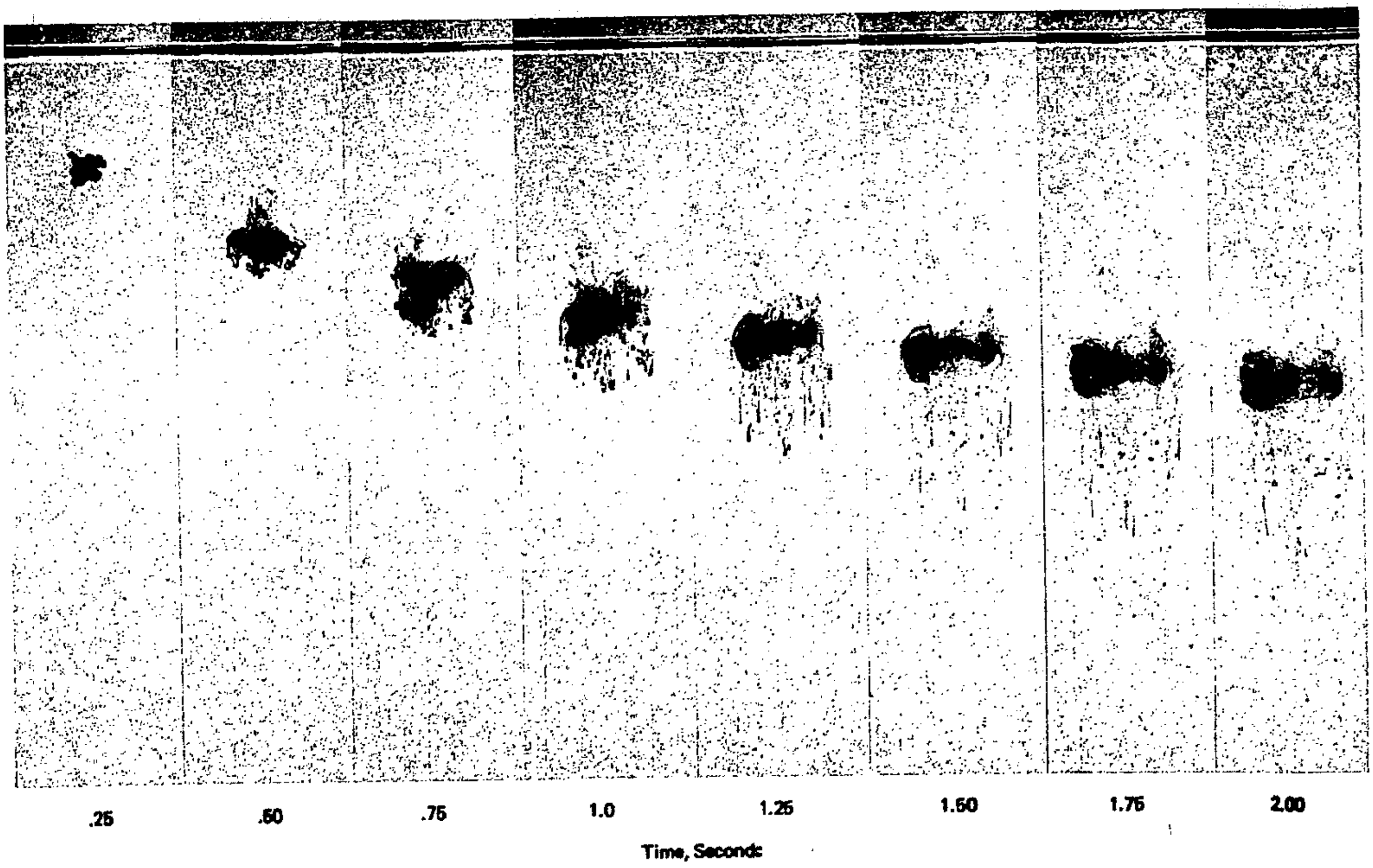

TABLE 3

DOW DEASPHALTER

Operating Conditions

	Typical	Range
Temperature	200°C	160-210°C
Pressure	220 psig	200-350 psig
Solvent	50-75°C mixed C_5-C_6's	---
Solvent/Oil Wt Ratio	.8	0.5-1.0
Liquid Residence Time	10 minutes	---
Deasphalted Oil/Residue Wt Ratio	3.1	2.3-5

Separation Efficiencies

Ash	99.8+%	---
Toluene Insolubles	95%	92-96%
Asphaltenes	40%	25-45%

Feed Composition

	Demonstrated Ranges
Ash Level	3-15.3%
Estimated Total Solids	4-25%
Viscosity at 25°C	150-30,000 cps

TABLE 4

TYPICAL DEASPHALTER PRODUCT PROPERTIES*

	Deasphalted Oil	Deasphalter Residue
Elemental Analysis, Wt%		
Carbon	88.8	48.9
Hydrogen	7.95	3.19
Nitrogen	1.02	1.20
Sulfur	.44	4.10
Oxygen	1.74	--
Hydrogen:Carbon Atomic Ratio	1.07	.78
Ash Level	.02	41.2
Heating Value, BTU/Lb	17,000	9,078
Ramsbottom Carbon Residue, %	∿ 11	79

Simulated Distillation

Boiling Range	Wt% In Interval
IBP-200°C	10.5
200-300°C	37.5
300-400°C	28.2
400-500°C	14.6
500°C+	9.2

*Products produced in the liquefaction of Pittsburgh No. 8 Coal.

TABLE 5

EFFECT OF RECYCLE OIL CONSTITUENTS ON LIQUEFACTION YIELDS

Slurry Oil Composition: 75% Hydroclone Overflow Plus 25% of	Vacuum Gas Oil	Topped Deasphalted Oil
<u>Run Number:</u>	97	98
<u>Conditions:</u>		
Reaction Temp, °C	460	460
Reaction Pressure, psig	2000	2000
Slurry Feedrate, lb/hr	15.0	15.0
Feedrate, lb coal/hr-ft^3	22.6	22.7
Fresh Hydrogen, SCF/lb coal	20.8	20.6
<u>Product Distribution:</u>		
Gases	23.3	26.7
Light Oil	6.9	9.3
Hexane Soluble Oil	38.3	40.0
Asphaltenes	20.6	11.5
Pre-asphaltenes	9.1	9.3
Aqueous	6.9	8.4
<u>Hydrogen Consumption:</u>		
Lb H_2/100 Lb Dry Coal	5.15	5.21

TABLE 6

NET PRODUCT DISTRIBUTION
DOW LIQUEFACTION PROCESS RUN 98

Component	Wt
C_1	6.9
C_2, C_3	11.6
C_4, C_5	4.6
C_6-200°C	11.3
200-400°C	28.6
400°C+*	.3
$CO + CO_2$	1.4
H_2S	2.2
Aqueous	8.4
H_2 Consumption, Lb/100 Lb MAF Coal	5.24

*Products boiling above 400°C are recycled to be either converted to 400°C- or rejected as deasphalter bottoms and then gasified.