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SEPARATION OF SOLIDS FROM COAL LIQUEFACTION PRODUCTS VIA COUNTERCURRENT SOLVENT DEASPHALTING

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ABSTRACT

Counter-current deasphalting is a key unit operation in the Dow Liquefaction Process. The Dow developed deasphalter removes typically 99.8-99.9% of the ash and 94-95% of the toluene insoluble hydrocarbons from the coal liquefaction product.

The deasphalted oil, after separation from solvent, contains less than 0.05% ash. Deasphalted coal liquefaction product, a low sulfur, low residue, premium synthetic oil, constitutes 40% of the net liquefaction products. The deasphalter residue typically contains 40% ash and up to 25% hydrocarbonaceous coal solids. It has a heating value of approximately 9000 BTU/lb and is produced as a viscous pumpable fluid. These properties are important in the Dow Process where deasphalter residue is gasified to generate the hydrogen for the liquefaction step. The solvent used in the deasphalter is a paraffinic 50-75°C light oil cut from the liquefaction unit.

The counter-current deasphalting technology is based on the results from model and batch studies and results from the operation of two different 23 kg/hr continuous deasphalters. Operational parameters which have been studied include: extraction temperature and pressure, solvent to oil ratio, feedrate, coal oil composition and variations in column design.

The mass transfer which occurs during the deasphalting of coal liquefaction product is accompanied by interfacial tension gradients which develop naturally during the extraction process. The resulting interfacial convection (referred to as a Marangoni instability)

profoundly enhances the rate of the extraction process and greatly simplifies the design of the extraction column.

INTRODUCTION

The Dow Liquefaction Process, shown schematically in Fig. 1, is a relatively new development in the synthetic fuels area.(1-6) It has been developed, over a period of 6 years, incorporating results from a dozen small scale pilot plants. The Dow Process has been demonstrated at a 100 kg per day scale in recycle runs of up to 350 hours in the preferred operational mode. The three distinguishing features of the Dow Process are:

1) The use of a finely dispersed molybdenum based expendable catalyst which is added to the feed slurry in the form of a water in oil emulsion,
2) The use of hydroclones, and
3) The use of a counter-current solvent deasphalter.

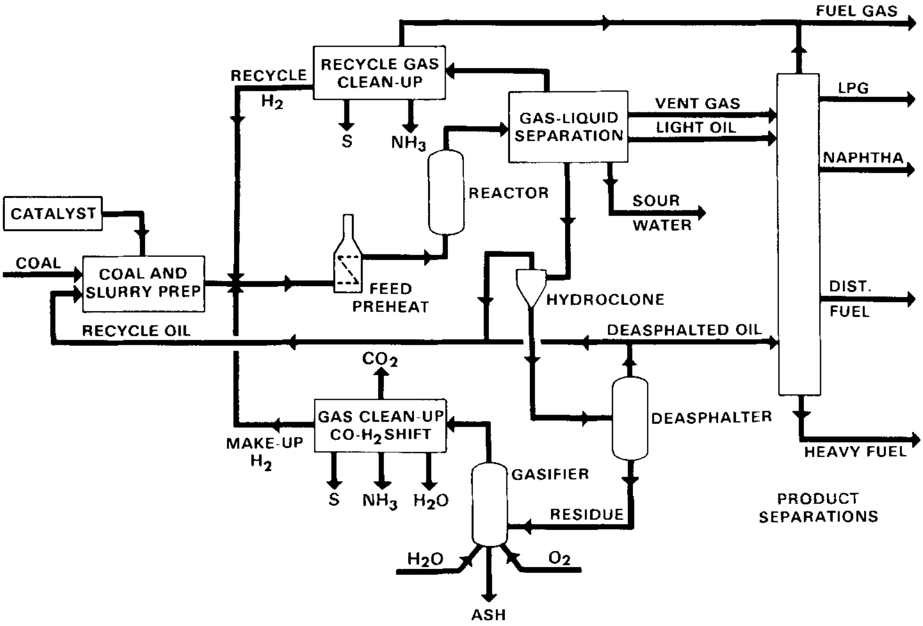

FIGURE 1. Dow coal liquefaction process.

The removal of micron and sub-micron size particles of ash and unconverted coal from the products of coal liquefaction is a technically challenging task. During the development of the Dow Process, a great deal of effort went into the task of defining the preferred approach to solids separations.

The solid separation technology employed in a coal liquefaction process must be capable of separating the reactor product into: (1) an ash rich residue stream; (2) a very low ash product oil stream; and (3) a slurry oil stream in which the ash level is kept to a reasonable value. Since, typically, two-thirds of the liquid reactor product must be recycled as slurry oil, the definition of an optimal solids separation strategy is crucial to the overall thermal and economic efficiency of the liquefaction process.

The solid separations technology which is used in the Dow Process is shown schematically in Fig. 2. The initial solid separation is performed using hydroclones, with the entire hydroclone overhead stream being recycled as slurry oil. The hydroclone split is adjusted so that the hydroclone overflow makes up typically 75% of the recycle slurry oil. The ash concentration in the hydroclone overflow is much lower than the ash level in the underflow, however, due to the fine dispersion of the catalyst, the catalyst is not effectively separated. Therefore, the hydroclone overflow contains a catalyst concentration essentially equal to that existing in the hydroclone feed. This catalyst recycle increases the catalyst concentration in the reactor by a factor of 2 or more over the catalyst level due to the fresh catalyst emulsion added to the feed.

The underflow from the hydroclones goes to the counter-current solvent deasphalter. In the deasphalter the more polar species form a second liquid phase which contains the solids in the

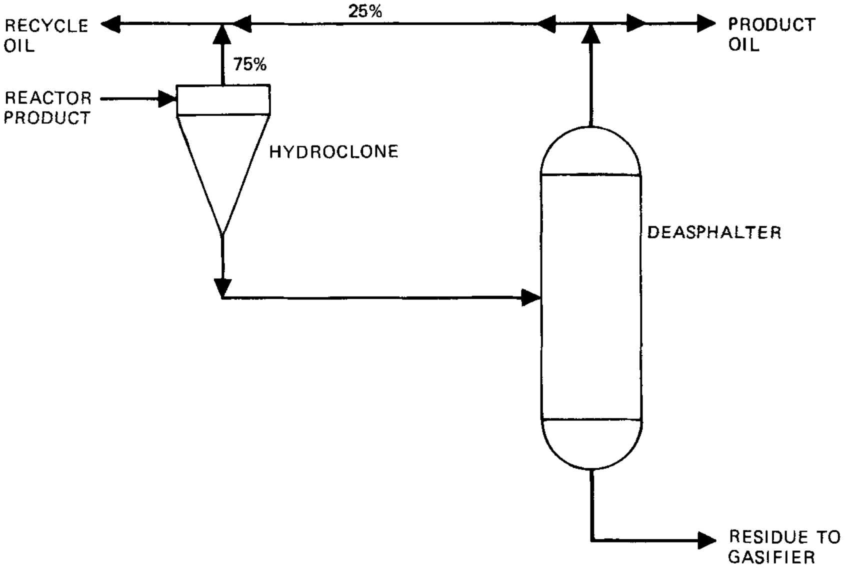

FIGURE 2. Solid separations used in the Dow liquefaction process.

oil feed. The agglomerated ash, unconverted coal, and a fraction of the asphaltenes are continuously removed from the bottom of the deasphalter column in the form of a very viscous liquid. The overflow stream from the deasphalter is flashed to recover process solvent. The resulting partially deasphalted product is an essentially solids-free, low-sulfur, premium oil. A portion of this oil is used to provide the remaining 25% of the recycle oil. The balance of the deasphalted oil is net product. The bottoms from the deasphalter are gasified with oxygen and steam to produce the hydrogen required for the liquefaction process.

With the above discussion as background, the remainder of this paper will describe the development and performance of the counter-current deasphalter which is used in the Dow Liquefaction Process.

The data that will be presented have been obtained during model and batch studies and from the operation of two different 23 kg/hr continuous deasphalters.

The present continuous deasphalter, Fig. 3 and Fig. 4, consists of feed systems for solvent and coal oil, a Dowtherm jacketed extraction column with a gamma-ray level controller, a thermosiphon still for recovery of solvent, and associated tankage and instrumentation. The unit is capable of operating at temperatures up to 300°C and pressures up to 35 atmospheres.

Mass Transfer Mechanism

The operation of the deasphalter is best understood from a room temperature model study in which coal derived oil was introduced dropwise into paraffinic solvent. The interaction between the coal oil and the solvent was recorded photographically.

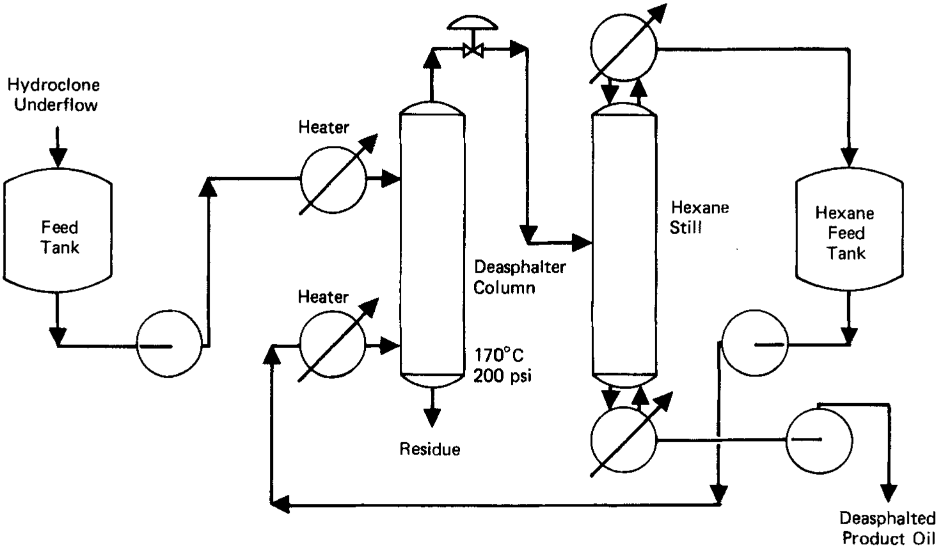

FIGURE 3. Dow deasphalter development unit.

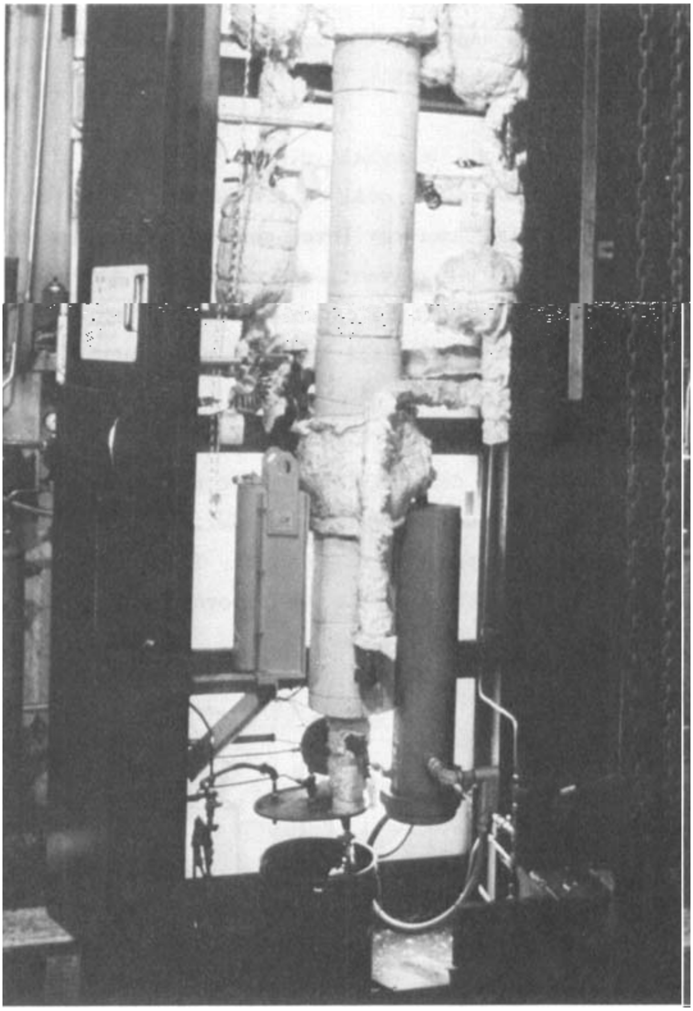

FIGURE 4. Developmental scale deasphalter pilot plant.

The series of high speed photographs presented in Fig. 5 shows that as soon as a drop of coal oil enters the solvent it literally explodes. This occurrence is the result of a phenomenon known as the Marangoni instability. When the drop enters the solvent an interfacial tension exists at the drop interface. Non-polar species

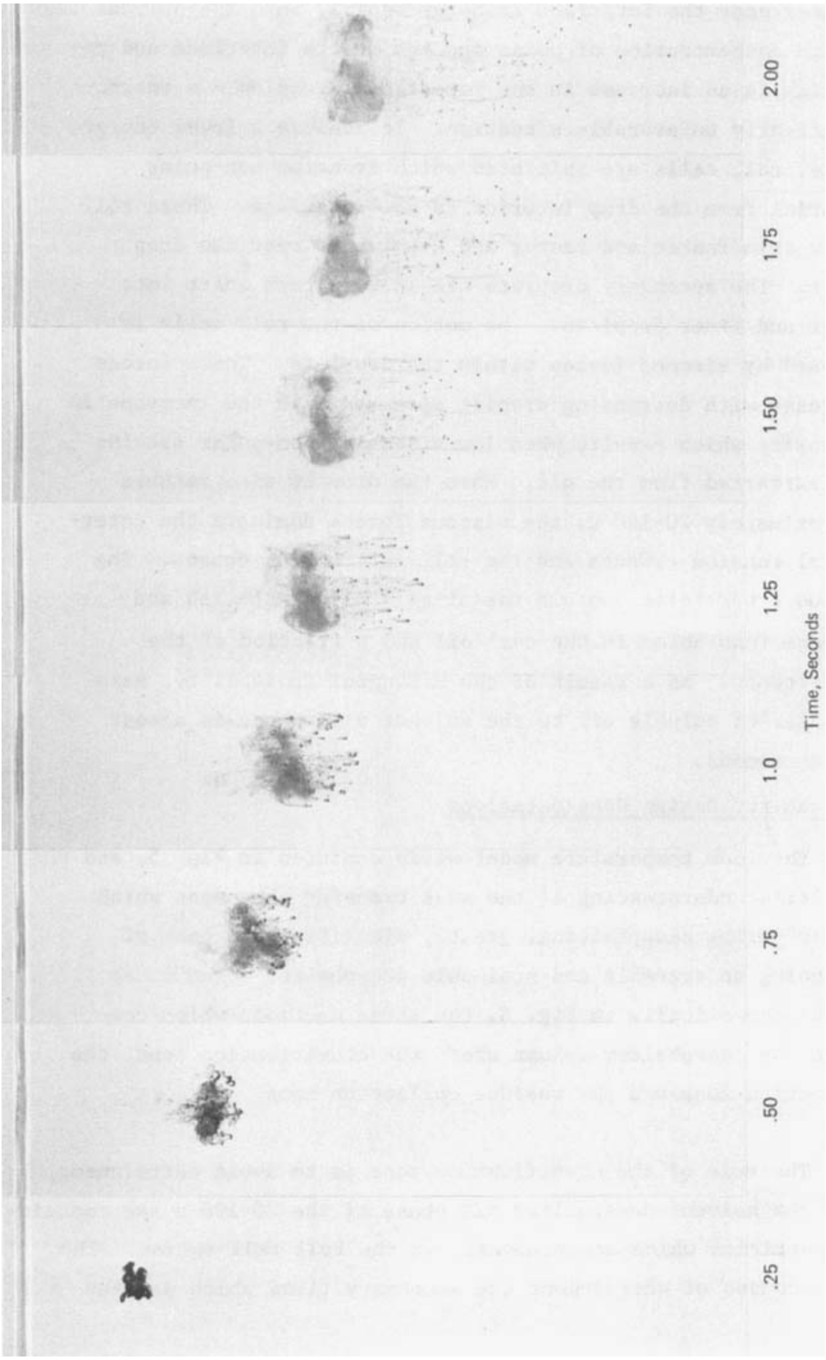

FIGURE 5. Photographs showing droplet break-up due to the Marangoni effect.

located near the interface transfer rapidly into the solvent leaving a high concentration of polar species at the interface and resulting in an increase in the interfacial tension - a thermodynamically unfavorable situation. To achieve a lower energy state, roll cells are initiated which transfer non-polar material from the drop interior to the interface. These roll cells spin faster and faster and eventually tear the drop apart. The secondary droplets are in turn torn apart into finer and finer droplets. The motion of the roll cells is opposed by viscous forces within the droplets. These forces increase with decreasing droplet size and with the increase in viscosity which results when low viscosity non-polar species are extracted from the oil. When the droplet size reaches approximately 20-100 μ, the viscous forces dominate the interfacial tension effects and the roll cell motion ceases. The 20-100 μ particles contain essentially all of the ash and toluene insolubles in the coal oil and a fraction of the asphaltenes. As a result of the Marangoni instability, mass transfer of soluble oil to the solvent rich phase is almost instantaneous.

Deasphalter Design Considerations

The room temperature model study depicted in Fig. 5, and the resulting understanding of the mass transfer phenomena which occurs during deasphalting, greatly simplified the task of designing an operable and scaleable deasphalter column. As shown schematically in Fig. 6, the three sections which comprise the deasphalter column are: the clarification zone, the extraction zone and the residue collection zone.

The role of the clarification zone is to avoid entrainment with the solvent-deasphalted oil phase of the 20-100 μ ash containing particles which are produced via the roll cell motion. The major causes of entrainment are secondary flows which are in-

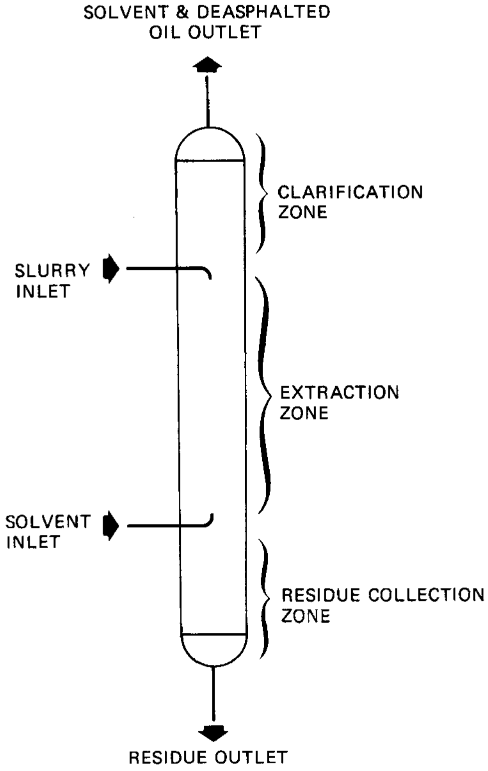

FIGURE 6. Dow deasphalter column schematic.

duced by the flow field existing in the extraction zone or which result from thermal gradients along the length of the clarification zone. At the 23 kg/hr scale, induced flows are not a problem and jacketing the clarification zone with a heat transfer medium such as Dowtherm® effectively eliminates thermal gradients. At larger scale vertical baffles would be used to eliminate secondary flows. Based on quiescent upward flow of the solvent-deasphalted oil phase, the 23 kg/hr deasphalter has been designed to recover droplets larger than approximately 8 μ.

The hydroclone underflow and solvent are fed to the top and bottom of the extraction zone respectively. As a result of the difference in specific gravity between the two feeds, the extraction zone is well mixed by gravity driven flows. Mass transfer occurs nearly instantaneously via the Marangoni instability. As a result of these naturally occurring phenomena agitation is not required during extraction and the design of the extraction zone is relatively simple.

The residue which is recovered from the extraction column is a viscous material containing a high concentration of solids. A potential problem in the operation of the residue collection zone is that a low viscosity solvent phase rests on top of the high viscosity residue. During early experiments there was a tendency for the solvent-extracted oil phase to penetrate or "finger" through the residue phase and exit with the residue with a resultant loss of separating efficiency. The solution to this problem was to maintain the wall temperature of the residue collection zone somewhat above the temperature of the extraction column.

EXPERIMENTAL RESULTS

General Discussion

The deasphalter pilot plant has been operated using commercial grade hexane as the solvent. It has been operated at temperatures in the range 110°C- 225°C with the operational pressure maintained at a level sufficient to avoid the formation of a vapor phase. In addition to temperature, the operational parameters which have been studied include: solvent to oil ratio, feedrate, coal oil composition, and feedport geometry. The designs of the three sections which comprise the extraction column have been modified to maximize performance.

Product Quality

The product quality definitions that were used in the present study are the following:

Ash - Noncombustible solid residue.
Toluene Insolubles - Combustibles; insoluble in toluene.
Asphaltenes - Oil; soluble in toluene and insoluble in hexane.
Hexane Soluble Oil - Oil which is soluble in hexane.

The solubility determinations were made using a 4 to 1 weight ratio of solvent to sample. It should be noted that the analytical results obtained by this procedure differ somewhat from results which are obtained by Soxhlet extractions.

Feed Port Design

Since the Marangoni phenomenon causes extensive dispersion of the oil phase in the solvent rich phase, it would be expected that the feed port design for the deasphalter column would not be a critical consideration.

To test this hypothesis, three different oil feed tube designs were investigated. Each design introduced the feed into the column in the downward direction near the center of the deasphalter column. Feed port dimensions are tabulated below:

Feedport Designation	No. of Openings	Diameter of Opening, mm
A	1	4.9
B	3	0.8
C	2	1.6

Except for a modest variation in the S/O ratio, experimental conditions were constant throughout the series of experiments. Performance data in which these feed tubes were used are shown in Table 1. Ash removals and toluene insolubles removals were practically invariant. The differences in asphaltenes removal which were observed were mostly due to differences in S/O ratio. These results confirm that feedport design is not a critical aspect of the overall deasphalter design.

Deasphalter Feedrate

The effect of total flowrate of solvent and coal derived oil on deasphalter performance was examined during a study of process variables. Representative data from this study is presented in Table 2. As the data indicates, over the range of feedrates examined, total flowrate had little or no effect on deasphalter performance.

TABLE 1

Results of Oil Feed Tube Experiments

Conditions: 190°C - 18.7 atm

Feedrate: 19.9 kg/hr

Run No.	Feed Tube Designation	Solvent/Oil Ratio	Performance Data, % Removals TI	Ash	Asphaltenes
B-25	A	0.80	96.1	99.96	42.2
B-28	B	0.86	94.6	99.94	39.5
B-30	C	0.77	97.2	99.88	36.7

The deasphalter pilot plant has a maximum throughput of approximately 23 kg/hr. At this feedrate, with a S/O ratio of 0.8:1, the average residence time in the extraction zone is slightly more than 5 min. It is probable that if the total flowrate were increased to the point where the upwards flow velocity in the clarification zone exceeded the terminal velocity of the smaller droplets generated by the Marangoni phenomenon, poorer solid separation would result. Unfortunately the pilot plant could not be operated with sufficiently high throughputs to determine the flowrate at which ash would be entrained in the deasphalter overhead stream.

Temperature and Solvent to Oil Ratio (S/O)

The three dependent variables which are measured routinely during deasphalter operation are the fractional removals of ash, toluene insolubles and asphaltenes. The first two of these are essentially invariant with respect to wide variations in the independent variables, i.e.

Ash Removal = 99.8 - 99.9%

Toluene Insolubles Removal = 94-95%

TABLE 2

Effect of Feedrate on Deasphalter Performance

				Wt.% Removals		
Run No.	Temp,°C	Feedrate,kg/hr	S/O Ratio	Ash	TI	Asphaltenes
B-35	189	19.7	0.79	99.95	97.7	35.9
B-45	190	11.1	0.84	99.93	93.0	41.6

The remaining dependent variable, asphaltenes removal, is sensitive to operational parameters and can be varied over a wide range depending upon processing needs.

The control variables which have the most influence on asphaltenes removal are temperature and S/O ratio. Data showing these effects is presented in Fig. 7. As shown the temperature and the S/O ratio can be chosen to vary the fractional asphaltene removal over the range 25-50%. Deasphalter operating conditions are selected such that:

1) There is sufficient residue to generate the hydrogen required by the liquefaction process, and/or such that
2) The solids level in the residue is kept to a reasonable value.

When the ash level in the residue exceeds 42-43% (approx. 65% total solids), the residue becomes granular and loses its fluidity. Deasphalter operating conditions are generally selected which give an ash level of approximately 40% in the residue stream.

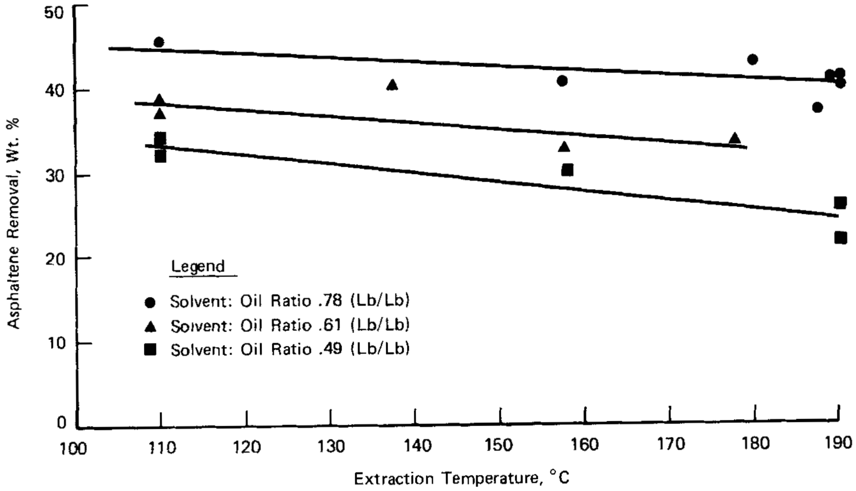

FIGURE 7. The effect of temperature and solvent/oil ratio on asphaltene removal.

The minimum S/O ratio which is required for reliable operation is approximately 0.5:1 (w/w). For S/O ratios below 0.5:1, phase separation is incomplete and significant amounts of oil are lost with the underflow.

Solvent Composition

The solvent used during the deasphalting studies was nominally commercial grade hexane. This material was recycled through the deasphalter many times. The componential analysis of recycled solvent is presented in Table 3. For comparison, the componential analysis of the 50-75°C cut of light oil from the liquefaction unit is also tabulated. At larger scale this fraction would yield deasphalter performance identical to the results which were achieved with commercial grade hexane.

Typical Deasphalter Performance

A typical set of deasphalter data is presented in Table 4.

An elemental balance has been completed around the deasphalter. The balance suggests that the deasphalter separates molecular

TABLE 3

Composition of Recycled Commercial Grade Hexane
and of Coal Liquefaction Light Oil (50-75°C Cut)

Description	Hexane Feed	Liquefaction Light Oil (50-75°C cut)
Component, wt%		
D-M-Butanes	.96	3.67
M-Pentanes	34.70	41.83
N-Hexane	49.58	42.02
M-Cy-Pentane	9.50	12.48
Benzene	1.27	--
Cy-Hexane	.92	--
C7+	3.06	--

species on the basis of hydrogen content and perhaps on the basis of nitrogen content. Somewhat surprisingly the sulfur and oxygen levels in the organic portions of the overflow and underflow are nearly identical.

Typical residue properties are presented in Table 5. At the conditions existing at the deasphalter outlet, the residue viscosity has been measured to be 100,000 - 200,000 centipoise. In the Dow Process the residue generated during deasphalting is gasified to generate the hydrogen required for the liquefaction reactor. Although viscous, the residue is produced as a pumpable fluid - a fact which simplifies introducing it into a pressurized gasifier and which can increase the thermal efficiency of the gasification process.

Typical analytical data on deasphalted oil are presented in Table 6. Deasphalted oil is a high quality, full range product. In the Dow Process, a portion of the deasphalted oil is used as slurry oil and is recycled to the liquefaction reactor where, by purging difficult-to-convert polar liquids and refractory solids from the recycle oil, it serves a vital role in controlling reactor performance. The rest of the

TABLE 4

Typical Deasphalter Operations

Conditions

Temperature	160°C
Pressure	21.4 atm
Solvent/Oil Ratio	0.80
Underflow	23.5% of Feed

Results, wt%

Stream	Ash	Toluene Insolubles	Asphaltenes
Feed	9.12	10.78	19.82
Overflow	.02	.72	15.09
Underflow	40.68	---	---
Calculated Removals	99.83	94.82	40.90

TABLE 5

Typical Deasphalter Residue Properties

Ash Level	41.2%
Heating Value	9078 BTU/lb (21115 KJ/KG)
Ramsbottom Carbon Residue	72.7%
Elemental Analyses; wt%	
Carbon	48.88
Hydrogen	3.19
Nitrogen	1.20 (approx)
Sulfur	4.10
H:C Atomic Ratio	.78

TABLE 6

Typical Deasphalted Oil Properties

Elemental Analyses:

Carbon	88.83
Hydrogen	7.95
Nitrogen	1.02
Sulfur	.44
Oxygen(difference)	1.74
Ash	.02
	100.00

Solubility Analysis:

Hexane Soluble Oil	81.61
Asphaltenes	17.36
Toluene Insolubles	1.01
Ash	.02
	100.00

Simulated Distillation: (wt% in Interval)

IBP - 150°C	3.1
150 - 200°C	7.4
200 - 250°C	19.2
250 - 300°C	18.3
300 - 350°C	15.6
350 - 400°C	12.6
400 - 450°C	10.5
450 - 500°C	4.1
500°C+	9.2
	100.0

deasphalted oil is a net product from the liquefaction process.

In a slightly modified version of the Dow Process, the deasphalted oil is topped via distillation at approximately 300°C. The $300°C^+$ fraction is recycled as a component of the slurry oil while the $300°C^-$ fraction is a net product from the liquefaction process. In this configuration, the Dow Process produces a totally distillate net product slate.

Summary and Conclusions

This paper has described the development of a solvent deasphalter which is applicable to coal derived materials containing up to 15-16% ash. The deasphalter, operating at high throughput, produces a pumpable residue containing up to 65% total solids, and an extremely low ash, partially deasphalted, low sulfur product oil.

The deasphalter technology has been demonstrated at 23 kg/hr scale in continuous pilot plants. The parameters which control deasphalter performance have been identified and criteria have been established for scaleup of the deasphalter. A solvent deasphalter is incorporated into the Dow Liquefaction Process where it serves the dual function of producing high quality product and of purging difficult-to-convert refractory materials from the slurry oil recycle loop.

Utilizing the Marangoni effect, the Dow solvent deasphalter effectively solves a very difficult solid separations problem in a relatively simple and energy efficient manner. The economics of the Dow Liquefaction Process will be described in a subsequent publication,(6) however, it can be mentioned that the economics of the Dow deasphalter are superior to the economics of the competitive technologies.

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