

LABORATORY STUDIES FOR SEPARATION OF
SOLIDS FROM SYNTHOIL GROSS PRODUCT*

by

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ABSTRACT

A variety of proprietary surfactants and agglomerating agents have been added to coal-liquefaction product (from the SYNTHOIL process) to determine the effectiveness of these agents in decreasing the viscosity of the product or inducing agglomeration of suspended solids in the product. More than two dozen additives were tested, but only two of the additives caused a reduction in the viscosity of the coal-liquefaction product. Two of the additives that reduced viscosity and five agglomerating agents were evaluated to determine if they could improve the settling of solids in the SYNTHOIL gross product. No improvement in solids settling was observed. In other tests, a number of organic solvents have been added to the SYNTHOIL gross product to determine their effectiveness in promoting the precipitation of suspended solids in the product. High-temperature settling of the product in the absence of a foreign solvent does not appear to be a promising mechanism for solids removal from this product. However, the promoter-solvent de-ashing scheme has been demonstrated to be a potentially attractive solids-liquid separation method, and kerosene had been found to be an effective promoter solvent for the SYNTHOIL gross product.

INTRODUCTION

A difficult technical problem encountered in the development of any coal liquefaction process is the removal of solids (carbonaceous solids and ash) from the product stream. This step is troublesome because coal-liquids are viscous and contain high concentrations of suspended solid residues; a substantial fraction are in the micrometer size range. This problem is particularly severe for those processes (such as the SYNTHOIL process under development by Pittsburgh Energy Research Center) aimed at producing boiler fuel with minimum hydrogenation, because with less hydrogenation, a more viscous product is produced. To meet the sulfur oxide and particulate emission standards for direct combustion of coal oil and to avoid fouling and poisoning of catalysts in further processing of coal oil, a substantial fraction of the solids in the oil must be removed.

*Work performed under the auspices of the United States Energy Research and Development Administration

A complete solids-liquid separation scheme generally involves four basic steps. They are pretreatment, solids concentration, solids separation, and post-treatment. To optimize a separation, all four steps must be carefully considered. Although it has been recognized that successful pretreatment or solids concentration can greatly simplify the entire separation operation, this type of approach has not been fully applied to coal-liquefaction studies. Most efforts on solid-liquid separation have addressed the solids-separation step only. A recent paper by Batchelor¹ indicated that the cost increment for removal of solid residues from coal-liquids was quite substantial, and research and development work in this area was necessary for successful commercialization of any liquefaction process.

In this paper, we present results from our laboratory studies for separation of solids from SYNTHOIL coal-liquefaction product. The studies consisted of two parts. In the first part, the use of commercially available additives (chemical pretreatment) to facilitate the removal of solid residues from the SYNTHOIL product stream was attempted. Our effort was aimed at either reducing the viscosity of the SYNTHOIL gross product or inducing settling of suspended solids in the gross product, by the addition of a small amount of chemicals. In the second part of our studies, the high-temperature settling and the promoter-solvent de-ashing schemes were explored for their effectiveness to the SYNTHOIL gross product. The organic solvents examined in the promoter-solvent de-ashing experiments ranged from solvents which dissolve only the heavy-oil fractions of the coal-liquids to solvents which dissolve all organic materials present.

EXPERIMENTAL

Materials

The SYNTHOIL gross product (uncentrifuged product), made from West Virginia coal (Pittsburgh seam of Ireland Mine), was supplied by the Pittsburgh Energy Research Center (PERC). This product oil was produced in a nominal 1/8 in. x 1/8 in. Pyrex glass cylinders; working conditions were 4,000 psig and 450°C; 35 percent solid slurry was fed on lined-out, coal-derived oil at 25 lb per hour. Table 1 gives the results of chemical property analyses of a sample of this product. Figure 1 shows the temperature-viscosity relationship, determined by using a Brookfield viscometer described below.

Chemical additives were provided by DuPont Chemical Company, Nalco Chemical Company, Emery Industrial, Inc., and the Tetrolite Division of the Petrolite Corporation. Three broad classifications of additives were studied; anionic, cationic, and non-ionic which had either amide or sulfonate functional groups.

All hydrocarbon liquids, except kerosene and fuel oil, used in the promoter-solvent de-ashing tests were obtained from Fisher Scientific Company, and are at least technical grade. The kerosene and the fuel oil were purchased from a local vendor.

Table 1. Chemical Property Analyses of SYNTHOIL Gross Product.

Product	wt %
Benzene-Solubles	86.7
Heavy Oil	59.9
Asphaltenes	26.8
Benzene-Insolubles	13.3
Ash	4.9
Organics	8.4
Ultimate Analysis	
C	85.0
H	7.5
N	1.3
S	1.1

Table 2. Properties of DuPont Surfactants.

	Petrowet R	Alkanol WXN
Chemical type	Anionic	Anionic
Active ingredient	Sodium-dodecyl sulfonate	Sodium-dodecyl benzene sulfonate
Concentration of active ingredient	22%	30%
pH, 1% of sorbent in water	4.0 to 5.5	7.5 to 9.0
Flash point	91°C	100°C
Density, lb/gal	9.0	8.6
Solubility in H ₂ O	Miscible	Miscible
Stability		
Acid	Stable	Stable
Alkali	Stable	Stable

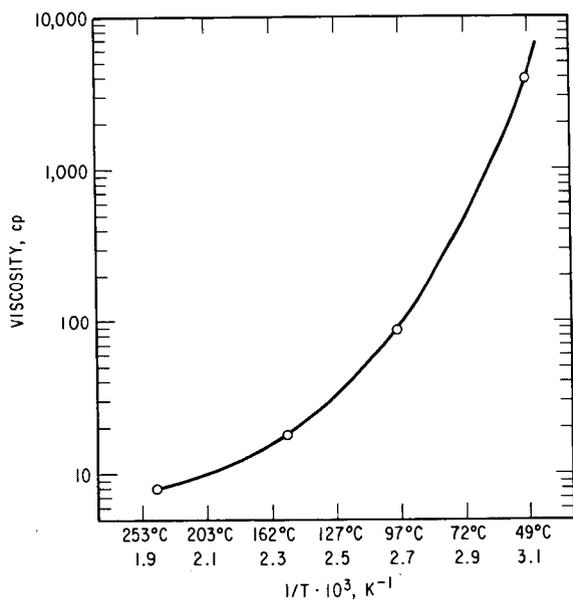


Figure 1. Viscosity-Temperature Behavior of SYNTHOIL Gross Products.

Procedures

Viscosity Reduction. A Brookfield Model LVT Synchro-lectric viscometer was used for the viscosity measurements of the SYNTHOIL products. This unit, along with a Brookfield Thermosel System to heat the sample, permitted us to obtain viscosities of liquid samples between 5 and 10,000 cp with a precision of 1%, at temperatures between ambient temperature and 260°C. Measurement of the temperature inside the liquid-sample container of the Thermosel was accomplished with a calibrated copper-constantan thermocouple; agreement with the set temperature on the controller was within 1%. To minimize the oxidation effect of the oil sample, the viscosity-measuring unit was confined in a Plexiglas enclosure that was continuously purged with nitrogen.

Additive-Induced Settling. In the settling tests, the effectiveness of each additive was judged by its effect on the extent of settling (for a chosen time) of suspended solids when the additive was added to SYNTHOIL gross product. Copper tubes, 3/4-in. OD (about 2 cm² in inner cross-sectional area) and 40 cm long, were used as settling columns. A measured amount of each chemical was added to a measured amount of SYNTHOIL gross product to make an approximate 65-ml mixture of the desired composition. The mixture was thoroughly stirred at 80°C for 10 min, and was then immediately transferred to the copper tube. The top of the tube was closed with a copper Gyrolok cap. The tube was then placed in a silicone oil bath for a prescribed time interval and the temperature was regulated with a Bayley Model 124 Precision temperature controller to within ±2°C of the set temperature (150-350°C). After careful removal from the oil bath, the tube was chilled in ice water and subsequently dipped in liquid nitrogen to quickly solidify the liquid sample; it took about 10 min to complete these two steps. The frozen sample was then divided into six fractions by cutting the copper tube with a tubing cutter into six 5-cm-long sections. Each fraction was analyzed for ash and sulfur contents by a standard ASTM method (D271) and a Leco technique, respectively.

Promoter-Solvent De-ashing. The same procedure described above in the additive-induced settling was used also in de-ashing tests to judge the effectiveness of each solvent. However, the mixing temperature was maintained at 60°C instead of 80°C.

RESULTS AND DISCUSSION

Viscosity Reduction

The following commercially available chemicals were tested for their abilities to reduce the viscosity of SYNTHOIL products: DuPont's Alkanol BG, Alkanol WXN, Alkanol 189-S, Duponol SP, Duponol WAQE, Petrowet R, Product BCO and Zonyl A, Nalco's 81C09, NALCOAL 8863 and NALCOLYTE 8861, Ivory soap, Emery's Emerest 2400, 2410 and Emsorb 2500, 2503, 2505, 2515, 6903, 6915, and Tretolite's TFL-313, TFL-330, TFL-366, 771-119, 772-238 and 771-139.

Of these chemicals, only two DuPont surfactants had a significant effect (>10% viscosity reduction) on the viscosity of the SYNTHOIL products;

they have been investigated in detail. The effective DuPont surfactants are Petrowet R and Alkanol WXN. Petrowet R is a solution of sodium dodecylsulfonate in water and isopropyl alcohol, and Alkanol WXN is a solution of sodium dedecyl benzene sulfonate in water. Their properties are listed in Table 2.

Viscosity measurements were made on SYNTHOIL gross product, to which had been added various amounts of Petrowet R or Alkanol WXN, as the samples were heated from 82°C to 120 or 140°C and again at the same temperature as the samples were cooled. The complete results are shown in Table 3. The estimated precision of the percent viscosity reduction values is about 2%.

As can be seen from the results for 0.91 wt % Petrowet R and 1.29 wt % Alkanol WXN in Table 3, when the sample was heated to 140°C, the percentage reduction in viscosity due to the additive was not reversible upon decreasing the temperature. The viscosities obtained at the lower temperature upon decreasing the temperature were equivalent to those obtained in the absence of additive. Reversibility was only partial when the temperature maximum had been 120°C.

At 82°C, the addition of 1 wt % "Petrowet" R reduced the viscosities of the gross product by 11%; the viscosity of the gross product was reduced by 14% by the addition of about the same amount of "Alkanol" WXN. However, the magnitude of the reduction in viscosity decreased as the temperature was increased, and there was essentially no reduction in viscosity at 140°C due to additive. Furthermore, if 1 wt % additive were used, the cost contribution of these two additives to the production cost of one barrel of oil would be approximately \$2.40, which is high from a practical viewpoint.

Additive-Induced Settling

Researchers at Oak Ridge National Laboratory, using small sedimentation tubes, have observed²⁻⁴ that certain liquid additives in low concentration (1,000 ppm) significantly increased the settling rate of suspended solids in the SRL* (Solvent Refined Liquid) of the SRC (Solvent Refined Coal) process. The most promising additive (Tretolite 771-119) appeared to provide at least a factor of five improvements in comparison to the settling rate of untreated SRC oil and to be valid over a wide (210 to 350°C) temperature range. Since the small amount of additives had a practically negligible effect on the viscosity of the SRC unfiltered oil, the improvement in settling is believed to be due to the agglomeration of solid residues, or the coprecipitation of asphaltene and ash. It was believed that if similar results could also be obtained for the SYNTHOIL gross product, the solids agglomeration induced by additives would greatly simplify subsequent separation steps.

*The solvent refined liquid is the unfiltered combination of dissolved coal and solvent.

Table 3. Effect of Additives on Viscosity of SYNTHOIL Gross Product.

For each concentration, viscosity measurements were taken with temperature increasing to the temperature maximum and then with temperature decreasing.

Additive Weight (wt %)	Viscosity ^a (cp)						
	82°C	100°C	120°C	140°C	120°C	100°C	82°C
0	241.	82.8	37.0	21.3	37.2	85.2	275.
0	242.	83.0	37.4		37.4	83.8	247.
<u>Petrowet R</u>							
0.06	240. (0.8)	82.7 (0.4)	36.8 (1.6)		36.8 (1.6)	83.0 (1.0)	244. (1.2)
0.16	232. (4.1)	80.2 (3.4)	36.2 (3.2)		36.2 (3.2)	81.5 (2.7)	234. (5.3)
0.45	221. (8.7)	76.5 (7.8)	35.7 (4.5)		35.7 (4.5)	80.5 (3.9)	240. (2.8)
0.91	218. (9.5)	75.0 (9.4)	35.4 (4.3)	21.2 (0.5)	37.2 (0.0)	85.4 (0.0)	276. (0.0)
1.47	216. (10.8)	75.0 (9.6)	35.5 (5.1)		35.5 (5.1)	80.5 (3.9)	233. (5.7)
<u>Alkanol WXN</u>							
0.39	228. (5.8)	79.0 (4.8)	36.2 (3.2)		36.2 (3.2)	80.4 (4.1)	240. (2.8)
0.63	211. (12.8)	74.5 (10.2)	35.0 (6.4)		35.0 (6.4)	76.4 (8.8)	228. (7.7)
1.13	209. (13.6)	73.2 (11.8)	34.8 (7.0)		34.8 (7.0)	76.6 (8.6)	228. (7.7)
1.29	208. (13.7)	72.5 (12.4)	34.7 (6.2)	21.0 (1.4)	37.0 (0.5)	84.5 (0.8)	274. (0.4)

^aPercentage reductions in viscosity

$(100 \times \frac{\text{Viscosity of Gross Product} - \text{Viscosity of Gross Product with Additive}}{\text{Viscosity of Gross Product}})$
are in parentheses.

Seven chemicals have been evaluated using the settling test. They are: Nalco's 81C09, NALCOAL 8863 and NALCOLYTE 8861, DuPont's Petrowet R, and Alkanol WXN, and Tretolite's 771-119 and 772-238. Experiments with the first five additives were conducted at 200°C and with the last two additives at 250°C; settling time was 4 hr. Comparison of the results with the results for blank tests showed no significant additional settling of solid residues. The disparity of the effect of Tretolite's 771-119 on SYNTHOIL gross product with the results obtained for SRL at ORNL is not surprising because SRL differs considerably from the SYNTHOIL gross product.*

High-Temperature Settling

Scouting studies by research workers at Oak Ridge National Laboratory (ORNL)⁵ also showed that high-temperature settling is a promising mechanism for solids separation from SRC (Solvent Refined Coal) unfilter oil. They also noticed that during the course of settling at elevated temperatures, suspended solid residues agglomerated, probably due to softening of high-molecular-weight hydrocarbons coated on the surface of the solid residues; consequently, the solids stuck together upon collision.

Table 4 gives representative settling results for SYNTHOIL gross product at 200 and 250°C. Unlike the results observed by Oak Ridge workers for SRC unfiltered oil, no great settling of the SYNTHOIL gross product occurred in 4 hr. Even after settling for the impractical time interval of 24 hr, the top fraction was not clear. Also, settling was only slightly improved when the settling temperature was increased from 200°C to 250°C.

Using the Stoke's equation and the viscosity results from Fig. 1, we calculated the settling velocities of a 6- μ m spherical solid particle at 200°C and 250°C; they are 0.7 cm/hr and 1 cm/hr, respectively.⁶ Because it fails to take the shape effect of suspended particles and the interactions between individual particles into account, the Stoke's equation does not provide accurate predictions of the settling velocities for a complex system of high solid concentration and wide particle-size range. Nevertheless, this equation can be used to calculate an upper limit for settling velocity. Since about 30 wt % of solid particles in the SYNTHOIL gross product are in the size range under 6 μ m, the smallness of the calculated value of settling velocities, in conjunction with the preceding experimental results, suggest that in the absence of a second solvent, high-temperature settling is unlikely to be a practical separation scheme for the SYNTHOIL process stream.

High-Temperature Settling with Solvent

Promoter-solvent de-ashing has been demonstrated to be a promising scheme of removing suspended solid residues from the product stream for a variety of coal-liquefaction processes;⁷⁻¹⁰ however, the mechanism behind

*In their recent progress report (ORNL-5208), however, ORNL researchers indicated that the significant improvement (at least a factor of 5) observed with small sedimentation tubes could not be found with their bench-scale settler.

Table 4. Analyses of Settling Fractions of SYNTHOIL Gross Product (4.9 wt % Ash, 1.1 wt % S).

Settling Temperature (°C)	Settling Time (hr)	Fraction ^a No.	Ash (wt %)	Sulfur (wt %) ^b
200	4	1	4.1	1.1
		2	4.1	1.0
		3	4.1	1.0
		4	4.2	1.1
		5	4.2	1.3
		6	5.4	1.3
200	24	1	0.54	0.67
		2	1.6	0.67
		3	3.0	0.87
		4	6.9	1.2
		5	7.9	1.3
		6	9.6	1.5
250	4	1	4.0	
		2	4.0	
		3	4.0	
		4	4.0	
		5	4.0	
		6	8.1	

^aEach fraction is 5 cm long; fraction numbers are in order from the top to the bottom of a sample.

^bThe estimated precisions are 5% for ash and 10% for sulfur.

its success is still not fully understood. It has been suggested that the presence of a second liquid phase causes the heavier asphaltic materials to precipitate by lowering their solubility limit to the heavy-oil phase. It is also very possible that some of the solid particles would act as sites for the initiation of precipitation and that, as the precipitation process continues, some of the solid particles would stick together, forming large aggregates.

The selection of effective promoter solvents for different liquefaction products is, nevertheless, largely an art. Some controversy exists between investigators on the effectiveness of a promoter liquid. For instance, Gorin and coworkers⁸ stated that, on a weight basis, n-paraffins from n-butane to n-decane, cyclohexane, and decalin were approximately equally effective in de-asphalting and reducing the ash content of a CSF (Consol Synthetic Fuel) product stream. However, Sze and Snell¹⁰ concluded that hexane, being a paraffinic liquid, is not an effective promoter solvent for a Lummus liquefaction product.

In our study, the following organic liquids were tested: n-hexane, n-octane, No. 2 fuel oil, kerosene, toluene, tetralin, and tetrahydrofuran. The n-hexane is believed to dissolve only the heavy-oil fractions of the coal-liquefaction product; the tetrahydrofuran is able to dissolve nearly all of the organics. The rest of the solvents have intermediate solvent powers. N-octane has a solvent power close to that of n-hexane; the solvent powers of tetralin and toluene are close to that for tetrahydrofuran. Because of the complex nature of the coal-liquefaction product, the true solvent power of each solvent to the product could not be accurately estimated.

Representative results for settling runs with toluene, n-octane, and kerosene are tabulated in Table 5. Tetralin and tetrahydrofuran gave results similar to those for the toluene, and the results for n-hexane and No. 2 fuel oil were slightly inferior to those for the n-octane. These results clearly support Sze and Snell's finding^{9,10} that, of the solvents we have tested, kerosene is the most effective and promising promoter solvent for the SYNTHOIL gross product. The settling efficiency of solid particles appears to increase as the concentration of the promoter solvent increases. The results for settling runs using 30 wt % kerosene are especially good, resulting in three top fractions of almost ash-free oil. When the settling temperature was increased from 200°C to 250°C, the settling time required to obtain three clear oil fractions was reduced from 6 hr to 4 hr, indicating that temperature also plays an important role in the settling process.

In an attempt to partially verify the speculation that the function of the added promoter solvent is to induce the precipitation of heavy asphaltenes, we measured the viscosity of each fraction from the 200°C settling run with 30 wt % kerosene. The results are presented in Table 6. Also shown in the table are viscosities of the SYNTHOIL gross product-kerosene mixture at several temperatures. The viscosity results for the bottom two fractions (5 and 6) are much greater than those for other four fractions, and a clear viscosity gradient exists from the top to the bottom. It is well known that the viscosity of the coal liquefaction product increases greatly with increasing asphaltene content.¹¹ The viscosity results thus support the suggestion that most of the heavy asphaltenes precipitated and settled in the bottom fractions during the course of settling.

One point regarding the promoter-solvent de-ashing method that should be emphasized is that although the major advantage of this method is elimination of the troublesome rotational equipment associated with filters and centrifuges, its economic justification is highly dependent on recovery and recycling of the promoter solvent. To facilitate recovery, it is desirable that a boiling point gap exists between the promoter solvent and the front end of the coal-liquefaction product treated. It has been suggested⁹ that the low-boiling fractions of the coal-derived complex first be driven off to provide the boiling point gap. However, for the SYNTHOIL process, the primary goal is to produce nondistillable boiler fuels, and the boiling-point gap desired is naturally built in.¹² Consequently, the promoter-solvent de-ashing scheme should be particularly useful in the SYNTHOIL process.

Table 5. Analyses of Settling Fractions of SYNTHOIL Cross-Solvent Mixtures.

Solvent	Settling Temperature (°C)	Settling Time (hr)	Fraction No.	Ash (wt %)	Sulfur (wt %)
20 wt % toluene	200	4	1	2.1	0.91
			2	2.5	0.94
			3	2.6	0.96
			4	2.7	0.95
			5	2.5	0.98
			6	4.6	1.32
25 wt % n-octane	200	4	1	1.5	0.76
			2	2.1	0.70
			3	2.5	0.64
			4	2.7	0.78
			5	2.8	0.85
			6	7.8	1.37
25 wt % kerosene	200	3	1	0.91	0.44
			2	1.0	0.56
			3	0.8	0.55
			4	1.7	0.67
			5	5.5	1.1
			6	8.7	1.4
30 wt % kerosene	200	6	1	0.03	
			2	0.02	
			3	0.03	
			4	1.5	
			5	6.7	
			6	11.8	
30 wt % kerosene	250	4	1	0.07	
			2	0.06	
			3	0.05	
			4	1.51	
			5	6.9	
			6	11.0	

Table 6. Viscosities of 200°C Settling Fractions of SYNTHOIL Gross Product-30 wt % Kerosene Mixture.

T (°C)	SYNTHOIL-Kerosene Mixture	Fraction No.					
		1	2	3	4	5	6
50	72.4	18.8	30.6	40.8	41.5	405	>10,000
100	11.5	9.0	10.1	9.8	11.2	42	372
150	7.5	6.7	6.8	6.2	6.4	18	127
200	5.0	3.8	3.6	4.6	4.2	12.6	47.9

CONCLUSIONS

Tests of more than two dozen commercially available additives indicate that the use of additives to reduce the viscosity of coal-liquefaction product streams is not productive. The greatest reduction in viscosity observed for SYNTHOIL products is 14% at low temperature (82°C); further decreases in viscosity become smaller as the temperature increases. Such relatively small reductions in viscosity could be realized by a small increase in temperature in the absence of an additive. Furthermore, cost figures do not support the use of additives as a potential pretreatment step to reduce the viscosity of coal-liquefaction product streams.

Although additive-settling tests did not yield positive results for the SYNTHOIL gross product, chemical pretreatment has been widely applied and desirable agglomeration has been experienced in the waste water treatment area. This pretreatment step is potentially attractive and warrants more investigation.

High-temperature settling with no second solvent added is unlikely to be a practical solids-liquid separation scheme for the SYNTHOIL process stream.

The attractive promoter-solvent de-ashing method for removing solid residues from product stream has been demonstrated to be applicable to the SYNTHOIL gross product. Selection of suitable promoter solvents is the key to the success of this method, and we have found that kerosene is an effective promoter solvent for the SYNTHOIL gross product.

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