

COAL BENEFICIATION: PROCESS DEVELOPMENT FOR LIQUEFACTION

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ABSTRACT

Research was undertaken to evaluate techniques for removing mineral matter and unreactive components from coal for subsequent liquefaction. A sample of Burning Star Mine, Illinois No. 6 seam, bituminous coal was crushed, sieved, and gravity separated. The yields of fines (-60 mesh), float (1.40 gravity) and sink fractions were 30%, 46% and 24%, respectively. The ash levels were 14.9%, 6.5% and 18.3%, respectively. In the treatment of Martin Lake Texas lignite, the yield of fines was only 14%, but it contained 24% ash. To remove metal salts of organic acids in the lignite, the coarse fraction (+60 mesh) was treated with sulfurous acid and then gravity separated. The ash levels of the treated float and sink fractions were 5.6% and 39.3%, respectively. The overall recovery of the float fraction was 62%. Fractions of these coals were liquefied in a two-stage, bench-scale unit. The preferred feeds for high coal conversion were the float fractions. Both the sink and -60 mesh fine fractions should be rejected and used as fuel. However, in the case of Illinois No. 6 coal, the sink fraction gave a low-boiling product, presumably due to catalytic activity of the remaining mineral matter which had a high iron content.

INTRODUCTION

Several papers¹⁻⁵ have reported that coal liquefaction conversion is related to the concentration of macerals in the feed coal. Specifically, vitrinites convert well; liptinites liquefy well, but somewhat slowly; and inertinites liquefy only to a limited extent.

Coal beneficiation provides a means to separate the more reactive macerals from the mineral matter and less reactive macerals. Minerals can often be liberated by sufficient size reduction, and the unreactive maceral fusinite, which is charcoal-like, breaks into small particles during crushing and is concentrated in the fine fractions. Maceral density increases in the order liptinite < vitrinite < inertinite. Therefore, a portion of the inertinites along with minerals can be concentrated in the high-density fractions isolated by "sink/float" gravity separation.

In addition to mineral matter, low rank coals contain high levels of organic acids that bond cations. These consist of alkali and alkaline earth cations attached to carboxylates. Mochida et al.⁶ have shown that pretreatment of lignites with 0.4M HCl significantly increased conversion during liquefaction. We use sulfurous acid because of its low cost, easy recoverability, and less corrosive nature. Sulfurous acid hydrolyzes organic acid salts present as exchangeable ions in low rank coals. The resulting metal bisulfites are washed from the coal and subsequently precipitated.

The second aspect of this paper deals with the liquefaction of treated coal samples. These are liquefied at conditions that are representative of those in use at the Advanced Coal Liquefaction Facility located in Wilsonville, AL. Descriptions of this process have been published.⁷⁻⁹

In this facility, unconverted solids are separated from liquefaction product using the ROSE-SR process of Kerr-McGee Corp. The mineral-rich "ash concentrate" stream carries along a sizable amount of heavy liquefaction product¹⁰⁻¹¹ which is either lost, used as fuel, or gasified. If the level of mineral matter and unreactive coal in the liquefaction feed stream is low, organic losses also are low.

The objectives of our work were to prepare samples of beneficiated Illinois No. 6 bituminous coal and Martin Lake, Texas, lignite and to evaluate the liquefaction behavior of the various coal fractions using a two-stage, continuous flow unit.

EXPERIMENTAL

Fresh samples of Illinois No. 6 seam coal (Consolidation Coal Co. Burning Star Mine) and Martin Lake lignite (courtesy of Texas Utilities Electric, Dallas, TX) were obtained. Portions were pulverized under nitrogen and subsequently stored at 40°F.

Coal liquefaction solvents were obtained from the Wilsonville facility. They were derived from the liquefaction of similar coals (the same coal in the case of Illinois coal and Black Thunder subbituminous coal-derived product for the lignite runs.). Analyses are given in Table I.

Bulk samples of beneficiated coal were prepared at Hazen Research, Inc., Golden, CO. The Hazen facility includes coal crushing and wet screening units and a closed circuit sump-pump-cyclone unit. Water and magnetite media were added to the feed sump, the resulting slurry was pumped to the cyclone, and cyclone products were recycled to the sump. The specific gravity of each charge was determined and the amount of magnetite adjusted accordingly. The 8x60 mesh coal was added to the media at a ratio of about 1:5. When stable flow conditions were established, timed samples of the cyclone overflow and underflow were collected. The product samples were wet-screened at 60 mesh to remove the magnetite. Recovered coal was filter-pressed and dried under nitrogen at room temperature at Amoco.

A portion of the 8X60 mesh lignite was agitated with sulfur dioxide saturated water. The liquid was decanted, and the resulting lignite was flushed with water. The lignite was then wet screened with additional water flush prior to sampling and gravity separation.

Pilot plant-scale liquefaction runs were made in a two-stage unit that operates in a once-through, continuous mode with regard to H₂, solvent, and coal, and in a batch mode with regard to catalyst. Each stage functions as a continuous, stirred-tank reactor (CSTR), as previously described.¹⁴

Presulfided Amocat-1C catalyst was used in both reactors. Operating temperatures in the two stages were 790°F and 740°F, and nominal residence times were 1.5 and 1 hour, respectively. Feed slurries with Illinois No. 6 coal were 33/67 coal/solvent, and those with Martin Lake lignite were 25/75.

Catalyst was lined out for about one week. Subsequent samples were run for about three days. A solvent only period was also included.

Coal conversion is defined in terms of tetrahydrofuran (THF), toluene, and hexane soluble material as determined by Millipore filtration. Modified ASTM distillations were carried out with subsequent to atmospheric pressure. Products were analyzed for C, H (Leco), N (AutoKjeldahl), S (X-ray fluorescence), metals (Inductively Coupled Plasma spectroscopy/ICP).

Because resid is present in the feed solvent and is generated from the liquefaction of the lignite, the yield of resid from the lignite is calculated as a difference between the measured level in the product and that observed in the reference solvent only period. A "negative" yield may result if less resid is recovered than determined in the solvent only run.

RESULTS

Coal Beneficiation:

Illinois No. 6 Coal: The results of the beneficiation of fresh Illinois No. 6 coal are summarized in Figure 1. Coal crushing and screening resulted in a 70% recovery of 8X60 mesh coal, designated "coarse". The "fines" (-60 mesh) could not be handled by heavy media beneficiation. A sample of the coarse coal was sink/float beneficiated at a specific gravity of 1.35. This resulted in a 66/34 (dry coal basis) split between the overflow and underflow of the cyclone. On the basis of coal feed, the product yields were: 30% fines, 46% overflow (float), and 24% underflow (sink).

Results of elemental analyses of the recovered fractions are shown in Table II. The feed coal contained about 12% ash. The levels of ash in the fines and sink fractions were high at about 15% and 18%, respectively. The float fraction contained 6.5% ash. This latter value is typical of that observed for such treatment of Illinois coal.¹² High levels of sulfur in the fines and sink fractions were likely due to high levels of pyrite in these fractions. The fines had a marginally low H/C ratio when compared to the other samples (0.79 vs. 0.82); this may have been due to a high level of inertinites.

Martin Lake Lignite: As shown in Figure 2, the yield of fines from crushing was only 14%. An additional 2% was generated during the sulfurous acid treatment step. Sink/float separation of the treated lignite was done at a gravity of 1.40. The resulting split between overflow and underflow was 76/24 on a dry coal basis. The overall product distribution was: 16% fines, 62% overflow (float), and 22% underflow (sink).

Analyses of lignite samples are given in Table III. The fines fraction had a very high ash level (24% vs. 15% in the feed); therefore, this fraction might better be used as fuel and not as a liquefaction feedstock. Sulfurous acid treatment of the coarse fraction resulted in about a 30% reduction of ash. From previous studies¹³ with this lignite, the 30% ash reduction was due primarily to the partial removal of alkali and alkaline earth metals. Gravity separation of the treated coarse fraction resulted in a sizable improvement in ash levels (5.6% vs. 39.3% for the float and sink fractions, respectively). However, further inspection of the sink fraction indicated that magnetite had not been effectively removed. The correct ash level in the sink fraction should be about 31%.

As also shown in Table III, there was an increase in sulfur and oxygen contents in the treated samples in comparison with the feed lignite. About 1 to 2% SO₂ was retained in the lignite as a result of treatment.

Liquefaction of Illinois No. 6 Coal Samples:

Differences were observed in conversion, resid yield, and hydrogen consumption from the liquefaction of the coal fractions, as shown in Table IV. The sink fraction produced low conversion to THF solubles, indicative of a high inertinite content. However, liquid product from the sink fraction was of very high quality, containing virtually no resid. Conversely, product from the float fraction was heavy, containing twice as much resid as product from the reference coarse coal. Therefore, sink/float beneficiation of Illinois No. 6 coal apparently does more than just change the level of unconverted coal and ash. The removal of some of the mineral components, which probably had catalytic properties, affected the upgrading aspects of liquefaction.

The effect of beneficiation is also indicated by the level of hydrogen consumption. An internal catalyst was present in the sink fraction, as indicated by hydrogen consumptions of 6.0% for the sink fraction and 4.7% for the float fraction. Iron was the likely internal catalyst as shown from the metals analyses in the unconverted coal solids (Table V). The sink sample was enriched in Fe, and to a lesser extent Ca.

Liquefaction of Martin Lake Lignite Samples:

Conversion of sulfurous acid-treated lignite to THF solubles was higher than that of the untreated lignite (Table VI), but the product contained much more resid. The second lignite liquefaction run was made only with samples of sulfurous acid treated lignite. Surprisingly, conversions of both the sink and float samples were lower than that of the coarse treated material that was used as their feedstock; see Table VII. The treated sink fraction gave only 69% conversion, which is consistent with a high inertinite level, as found in analogous laboratory-scale samples.¹²

The yield of resid from sulfurous acid-treated lignite was significantly higher than from untreated lignite, 12% vs. -6%, respectively. The difference between resid yields is not as great as shown, because contributions from solvent conversion changed throughout the run. However, there was at least 10% more resid produced from the treated lignite.

High yields of distillable product, defined as 975°F- liquids, were obtained from the treated float and sink fractions. In fact, no resid was recovered from processing the treated float fraction. There was a negative yield in the case of the sink fraction, indicating that some of the resid present in the feed solvent was being converted in addition to that generated from the lignite. The sink fraction was heavily contaminated with magnetite, which apparently acted as an upgrading catalyst.

CONCLUSIONS

Beneficiation of Illinois No. 6 coal using sequential size selection and gravity separation was effective in obtaining an improved coal liquefaction feedstock. However, there were both positive and negative effects. Ash and inertinite removal by rejection of the sink fraction would decrease liquid losses in the solids separation step. Offsetting this, internal mineral matter catalyst is also rejected thereby resulting in heavier liquefaction products. Sulfurous acid treatment and sink/float beneficiation of Martin Lake lignite is clearly beneficial. Ash levels in the lignite were reduced, conversion was slightly increased, and an all-distillate product was generated.

ACKNOWLEDGMENTS

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FIGURE 1

IL NO. 6 BENEFICIATION PROCEDURE

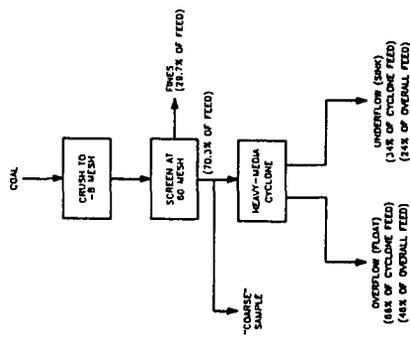


FIGURE 2

LIGNITE BENEFICIATION PROCEDURE

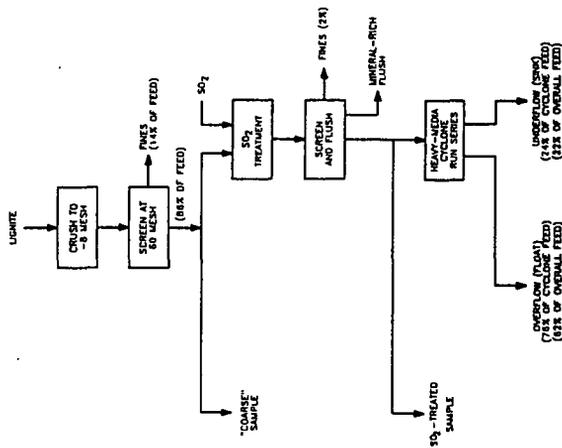


TABLE I
SOLVENT ANALYSES

WILSONVILLE RUN 257 258
WILSONVILLE COAL IL. No. 6 BLACK THUNDER

ELEMENTAL ANALYSES, Wt%	
C	89.26
H	8.83
H	0.57
S	.08
O	1.26
DISTILLATION, Wt%	
IBP-650°F	0.36
650-975°F	55.78
975°F	43.86
SOLUBILITY, Wt%	
THF INSOLUBLES	0.12
TOLUENE INSOLUBLES	1.07
HEXANE INSOLUBLES	7.96

TABLE II
ANALYSES OF BENEFICIATED IL NO. 6 COAL SAMPLES

ULTIMATE ANALYSES (DRY BASIS)			
FEED	FINES COARSE OVERFLOW (FLY)	UNDERFLOW (SINK)	
CARBON	69.0	66.8	70.0
HYDROGEN	4.7	4.4	4.8
NITROGEN	1.5	1.5	1.4
SULFUR	3.5	3.8	3.4
ASH	11.9	14.9	10.7
OXYGEN (DIFF)	9.4	8.6	9.7

TABLE III

ANALYSES OF BENEFICIATED
MARTIN LAKE LIGNITE SAMPLES

ULTIMATE ANALYSES
(DRY BASIS)

FEED	FINES COARSE	SO ₂ TREATED COARSE	FLY	FLY	SINK
CARBON	63.3	56.8	64.4	63.4	68.3
HYDROGEN	4.5	4.0	4.6	4.3	4.9
NITROGEN	1.2	1.2	1.2	1.3	1.4
SULFUR	1.5	1.6	1.5	2.4	1.5
ASH	14.6	23.6	13.1	10.0	5.6
OXYGEN (DIFF)	14.9	12.8	15.2	18.6	18.3

TABLE IV

LIQUEFACTION OF DENSITY BENEFICIATED
IL. NO. 6 COAL

COAL SAMPLE	COARSE	FLY	SINK
CONVERSION	94.6	94.7	92.7
C ₁ -C ₃ HYDROCARBON	3.2	6.5	6.0
C ₄ -360°F	9.5	5.4	12.5
360-650°F	38.4	29.5	35.8
650-975°F	23.6	26.5	27.7
975°F RESID	9.3	18.6	0.5
HYDROGEN CONSUMPTION	5.6	4.7	6.0

TABLE V

METALS IN UNCONVERTED COAL
(WEIGHTS ARE REPORTED RELATIVE TO ALUMINUM)

COAL	COARSE	FLOAT	SINK
Ca	0.33	0.14	0.39
Fe	2.07	1.57	2.72
Hg	0.08	0.07	0.08
Na	0.05	0.05	0.04
K	0.22	0.23	0.23
Ti	0.05	0.05	0.04
V	0.00	0.01	0.00
Zn	0.01	0.01	0.02
Mn	0.00	0.01	0.00
Cr	0.01	0.01	0.01
Ni	0.00	0.01	0.00

TABLE VII
COMBINED WATER/SO₂-BENEFICIATION AND DENSITY
BENEFICIATION

LIGNITE SAMPLE	WATER/SO ₂ -BENEFICIATED		SINK
	TREATED FEED	FLOAT	
CONVERSION	91.0	86.4	68.9
C ₁ -C ₃ HYDROCARBON	8.6	10.2	7.3
C ₄ -360°F	9.6	7.9	9.6
360-650°F	29.5	37.9	40.0
650-975°F	9.7	14.7	13.3
975+°F RESID	16.5	0	-23.0
HYDROGEN CONSUMPTION	6.4	6.4	8.4

TABLE VI

WATER/SO₂-BENEFICIATED MARTIN LAKE LIGNITE

LIGNITE SAMPLE	WATER/SO ₂ -BENEFICIATED	
	UNTREATED	BENEFICIATED
CONVERSION	84.7	91.3
C ₁ -C ₃ HYDROCARBON	7.3	6.2
C ₄ -360°F	13.2	14.1
360-650°F	33.5	33.1
650-975°F	24.7	9.6
975+°F	-6.3	12.0
HYDROGEN CONSUMPTION	7.4	7.4

RESULTS FROM UNTREATED FINES WERE INCONCLUSIVE BECAUSE THE PILOT PLANT OPERATED AT 0.5 RELATIVE SPACE VELOCITY DUE TO PUMPING DIFFICULTIES.