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COAL DEASHING AND HIGH-PURITY COKE

Ward J. Bloomer , The Lummus Company, Newark, N. J. and  
F. L. Shea, Great Lakes Research Corp., Elizabethton, Tennessee

Introduction

In 1957, The Lummus Company and Great Lakes Carbon Corporation began a joint investigation into the use of coal as a source of high-purity coke. The process involved the production of a low-ash, low-sulfur deashed coal solution from high volatile bituminous coal, and the conversion of this coal solution into coke using a modification of the Lummus delayed coking operation. (1)

Experimental work on a bench scale was initiated in 1958 and completed in 1961. The experimental scope was expanded to include the production of deashed coal as well as the high-purity coke in either combined or alternate operations.

Bench programs were carried out on several scales of operation. A continuous (block operation) pilot plant was built and operated to confirm the bench work. This unit was capable of processing coal continuously at approximately 200 pounds per hour through the filtration step. At this point, the filtrate was stored for further continuous processing to either deashed coal product (performed in 150-200 pound quantities) or high-purity coke (500 pound quantities).

Summary

A process has been developed to upgrade the quality of coal to a low-ash, low-sulfur, low-chloride product. As a fuel, this material would result in reduced capital and operating costs for power stations. Investment costs would be reduced, due to the higher heating value and cleaner fuel. Operating costs would be reduced by charges associated with the transportation of ash, ash handling and disposal costs, lower maintenance costs, and fly ash removal costs. The substantial reduction in sulfur, ash, and volatile matter would greatly minimize air pollution.

Other potential applications are for use in gas turbines, as a reductant, as a raw material for synthesis gas, as an ingredient in preparing coal blends for metallurgical coke, or for high-purity coke.

The economic potential of the process in its present stage of development is covered in Table 5. The process has certain aspects requiring sustained demonstration efforts to obtain firm economic bases.

### Process Description

Figure 1 shows a schematic flowsheet for the production of either deashed coal or high-purity coke as investigated in this program.

Deashed Coal - Crushed, ground and dried raw coal is fed to agitated premix tanks where it is mixed with warm solvent. The slurry is pumped through an extraction heater and thence through either in-line reaction tubes or to agitated digestion tanks. Digestion was investigated over the temperature range of 650 to 850°F and over a pressure range of 75 to 135 psig. Residence times varied from three minutes to two hours. Solvent-to-coal ratios were varied from 1:1 to 4:1

From the digestion tanks, the coal dispersion is fed to a rotary pressure precoat filter designed for operating at 100 psig and 700°F. Washing provisions are included.

The filter cake (2) is discharged into a cake receiver. Filtrate and wash are collected and fed to the product and solvent recovery operations. Vapors from the filtrate receiver are compressed, heated and recycled to maintain pressure on the feed side of the filter drum.

Filtrate flows through the filtrate heaters into a vacuum product recovery unit. Vapors from this unit pass to a flash tower where the bottom stream is all solvent for recycle. A side stream is taken off and in part is used for solvent make-up with the remainder processed for by-product recovery.

Overhead vapors from the flash tower are condensed, and a low boiling fraction recovered as a by-product. Vapors flashing from the filtrate receiver are condensed and introduced as reflux into the bottom section of the flash tower.

Filter cake is calcined and the spent cake used as fuel for the process. Gas and distillate vapors from the kiln combined with gases from the filtrate receiver and flash tower overheads are passed into a light oil scrubber. The absorption oil -- the intermediates cut from the flash tower -- is stripped in the flash tower. Light oil fractions leave the system from a decanter on the flash tower overhead stream. Gas from the light oil scrubber is used for process heat.

High-Purity Coke - For coke product the same flow pattern prevails through the filtrate receiver. The filtrate is pumped to a coking heater and thence to coke drums. Overhead vapors from the coke drums pass to a combination tower where recycle solvent and by-product fractions are recovered. Overhead vapors from the tower pass

through a condenser, gas separator, and thence to a light oil scrubber.

The above operations were investigated on both a bench and pilot plant scale with the exception of cake calcining which was performed only on bench scale. Variables investigated are discussed in the following sections.

#### Process and Operating Variables for Deashed Coal

A review of our work on solvent deashing indicated the operating conditions necessary to optimize the process. These may be briefly summarized:

1. The development of a stable, high-extractive-efficiency solvent capable of essentially complete recovery in the vacuum recovery unit to yield deashed coal was accomplished by special treatment of a high-boiling coal tar distillate. The required solvent having excellent temperature stability and high solvent power was attained by refractorizing the high-boiling coal tar distillate, employing recycle thermal decomposition and fractionation to eliminate the less refractory and low-boiling constituents. Gratuitously, these are the less effective extraction components.
2. Recovery of from 88 to 95 weight percent of the available carbonaceous matter at extractor pressures in the range of 5 to 8 atmospheres and with solvent-to-coal ratios in the range of 2 or 3:1 was achieved using the refractorized solvent with a boiling range of 600 to 900°F. Typical extraction conditions were 750°F, 75 psig, at a solvent-to-coal ratio of 3:1.
3. Extraction at residence times of 5 to 20 minutes in a stirred solutizer vessel or, preferably, in continuous in-line solution heating coils which would permit a direct circuit from the solvent-coal mixing tank through a conventional heater with a discharge to either a rotary pressure precoat filter or a suitable hydroclone.<sup>(3)</sup> Bench extractions were successfully conducted at holding times of as low as 3 minutes. These were duplicated in a pilot furnace heater coil discharging the hot coal solution continuously through an expanded section of the transfer line to the filter charge tank.
4. Ash removal from the coal solution was accomplished at filtration rates of 200 to 300 lbs/hr/sq. ft. of filter surface. Preliminary rates of 200 to 250 were secured in the pilot rotary precoat pressure filter at low pressure differentials. Small-scale runs on cake washing and calcining were performed to obtain closed-cycle data on solvent and distillate distribution. It was anticipated that the filter cake would be washed with a light oil, calcined and the spent cake used as steam fuel for the process in a full-scale plant.

The bench and pilot plant operations in general closely approached the goals set at the start of the work for the deashed coal production phase of the program. In Table I, there are provided examples of the data relative to the composition of the raw coal, coal-to-solvent ratios, temperatures and pressures and analyses of the coal extract solutions. Yields are shown on the basis of both raw and ash-free coals. Typical coal deashing results are shown in Table 2.

#### Available Coal Charge Stocks

Extraction of coal with phenanthrene by earlier workers related the degree of extraction to the rank of the coal.<sup>(4)</sup> Thus, about 95 percent of the organic material in bituminous coal was dispersed as compared to 27 percent for subbituminous coal and 23 percent for lignite. Bench studies using a preprocessed coal tar distillate solvent matched these extraction efficiencies for the bituminous coal and lignite studied.

The coals extracted ranged in ash content from 5 to 20 weight percent and in sulfur values from 1 to over 4 percent. In each case, it was possible to secure excellent removal of the ash and a substantial portion of the sulfur, chlorides and other contaminants.

Sulfate and pyritic sulfur were fully eliminated with the ash and the organic sulfur forms were noticeably reduced. It was also possible to reduce the volatile matter contents from original values of near 40 percent to around 15 to 25 percent by distillation or by solvent precipitation<sup>(5)</sup> of the deashed coal solution.

#### Improvement of Solvent for Coal Deashing

The wide-range heavy anthracene oil fraction originally used in the coal solution studies boiled between 600°F and 1050°F. Bench delayed coking of the deashed coal solutions gave solvent losses ranging as high as 30 to 60 volume percent through polymerization of the heavy ends and decomposition of the less refractory components of the solvent.

Accordingly, studies were initiated to produce a more stable solvent. As a result, the efficiency of the coal solvent was improved to a point where 85 to better than 90% solution is achieved of the total extractable carbonaceous material of the coal (i.e., excluding the nonsoluble fusain).

This preferred solvent, freed of easily polymerizable material, is capable of essentially complete recovery from either the coal solution by vacuum stripping or from the delayed coking operation at reduced pressure.

Solvent upgrading is the result of two important factors. First, the solvent boiling range has been narrowed and, secondly, the solvent has been stabilized by removal of its less refractory (readily cracked) components. Continued use and recycle of this solvent improve its stability.

A brief discussion of the variables in coal solution and coking of its deashed solution will outline the reasons for the improvements secured by the changes in solvent boiling range and composition noted above:

It is known that the effective solvents for coal are those that have an angular configuration of the rings, and that boil above 300°C (572°F).<sup>(4)</sup> Nonangular, or linear, condensed ring systems have a greatly reduced selective solvent action on the constituents of coal that act as binding agents for the micellar portion of the coal. It is this removal of the binding material that leads to the complete disintegration of the colloidal nature of the coal, and peptization of the micelles in the solvent.

Because of the temperatures at which coal dissolution and subsequent recovery of deashed products are effected, it was found that certain high boiling fractions polymerized and were lost from the original solvent. These viscous fractions also decreased filtration rates. They were, therefore, helpfully removed in the course of refractorizing the solvent.

The narrow range solvent first prepared by distillation and employed for solution yielded 83.9 percent of the original ash-free coal. However, by successive heatings of the recovered solvent and redistillations to the original narrow boiling range, the extractive efficiency was increased to 89 to 93% in subsequent extractions.

#### Use of Other Refractory Aromatic Solvents

Numerous refinery stream fractions such as, for example, thermal-cracked, cat-cracked heavy cycle oils are rich in condensed ring aromatic compounds and their alkylated homologues. For example, a 700° to 1000°F clarified slurry oil has been reported as containing in excess of 70% condensed ring aromatics. Further, thermal cracking of this clarified oil increased the concentration of these aromatics to over 90% and these are predominantly condensed ring types. It is considered that these cracked refinery tars, after further refractorizing, could provide a low-cost coal solvent of high solution efficiency comparable to that of the coal tar solvents.

#### Removal of Ash

The efficiency of coal solution deashing has been a function of ash particle size distribution rather than of total

ash content of the initial high volatile bituminous coal. Thus, it has been repeatedly demonstrated in the bench and pilot solvent deashing studies on coal samples with ash contents varying from 5 to 20 weight percent that final ash values of 0.1 to 0.3 could be obtained in the treated coal extracts.

Likewise, inorganic chlorides have been largely eliminated with the ash. Coals containing 0.25 and 0.15 weight percent chlorine were reduced to values of 0.004 to 0.003, respectively. It is assumed that coals of considerably higher inorganic chloride contents could be reduced to similar low values. The harmful corrosive effects of ash and chlorides on furnace operation are well known and their effective reduction is obviously very desirable.

#### Sulfur Reduction

The degree of bituminous coal desulfurization by solvent deashing has proven to be a function of the original ratio of inorganic sulfate and pyritic sulfur to the organic forms. Original total sulfur contents of 1 to 4 percent are reduced to values of 0.4 to 1 weight percent in the extracts.

It is known that this ratio increases with coals of increasing total sulfur content, i.e., in the lower grade coals of correspondingly higher ash. The final sulfur of the deashed coal therefore relates to the original organic sulfur which is only partially removed in the process, whereas the inorganic sulfur is removed substantially quantitatively.

Thus, in Table 1, complete elimination of the pyritic and sulfate sulfurs has been achieved with an accompanying 26 percent reduction in organic sulfur, for an overall sulfur reduction of about 50 percent.

#### Delayed Coking

The original 1957 concept of the coal deashing process was to prepare a coal solution which, after filtration for removal of its ash, sulfur and other contaminants, would be charged to the conventional Lummus delayed petroleum coking process. The coke drum vapor would pass to the combination fractionation tower for separation of gas and light and medium distillate from a tower bottom cycle oil which would be re-used for fresh coal solution.

The bench and pilot coking of the deashed coal solution proved to be almost routine. This charge stock resembled in many of its characteristics a low temperature carbonization pitch. Lummus had previously in bench scale and pilot plant delayed coking apparatus successfully coked both low and high temperature carbonization pitches as well as Gilsonite and Athabasca tar sand pitches.

The range of temperatures and general operating characteristics proved similar to those employed for the stocks noted above. Reduced pressure is necessary for high solvent (600-900°F) recovery. Thus, it is anticipated that full scale plant operation would produce cokes with volatile matter contents approaching those normally encountered with petroleum stocks. Such cokes would be of low ash and satisfactory sulfur contents and would be secured at high yields.

The product distribution on coal solution and on coal are summarized in Table 3, based on a 2:1 solvent to coal ratio. It was found on examination of the coker total liquid products that the extraction solvent had been recovered without significant change. The properties of the coker feed and product coke are listed in Table 4.

An alternate method of producing high purity coke utilizes the pure coal extract as the raw material. This may be pulverized in a ball and ring or ring roller type mill, such as is used for powdered coal burners. The milled pure coal is then used to form a slurry with a refractory recycle stock, having a boiling range of about 500-700°F. The boiling range of this stock will vary somewhat, depending upon conditions in the heater, the coke drum, and the ratio of solids to liquid, but is selected so that sufficient liquid phase remains in the heater coils so as to convey the milled pure coal without coke build-up in the heater.

A third method of pure coke production considered, particularly where production of pure coke from coal would be conducted in conjunction with the operation of a refinery, involves utilization of petroleum coker feedstock as the liquid in which the slurry of pure coal is formed. Where a low coke yield feedstock is used, the coke produced would be predominantly from pure coal. However, the proportion might be varied, depending upon the type of coker feedstock employed and the ratio of solids to liquid in the slurry charged to the delayed coker.

#### Alternate Processes for Coal Extract Recovery

As an alternate to the recovery of coal extracts of original or decreased volatile matter contents by distillation, as noted in Tables 1 and 3, it was determined that these products could be recovered readily from solution by precipitation with hydrocarbon solvents. Thus, a paraffinic solvent yielded the complete deashed coal extract, whereas it was possible to recover a deashed coal with a volatile matter content 60 weight percent below that of the original coal with control of intermediate product values by manipulation of the aromaticity of the solvent blends.

References

1. Bloomer, W. J., and Martin, S. W., U. S. Patent 3,109,803 (November 5, 1963).
2. Dicalite 40, General Refractories Company, used for bench and pilot filtrations.
3. Patent pending.
4. Orchin, M., Golumbic, C., Anderson, J. E., and Storch, H. H., U. S. Bur. Mines Bull. 505, 1951.
5. Patent pending.

COAL SOLUTION DEASHING USING A SOLVENT AND NARROW RANGE COAL TAR DISTILLATE AND NARROW RANGE COAL TAR SOLVENT

Coal Source	I		II Illinois		III Illinois		IV Penna.		V Illinois		VI Penna.		Lignite
	Raw	Deashed	Raw	Deashed	Raw	Deashed	Raw	Deashed	Raw	Deashed	Raw	Deashed	
Coal Proximate Analysis, Percent by Weight													
Moisture	2.69		Moisture-free basis				1.4		2.75		1.4		1.9
Volatile Matter	37.7	33.6	32.6	33.5	37.2	36.6	36.6	38.90	36.6	36.6	45.2		45.2
Fixed Carbon	38.9	56.6	67.1	52.5	62.5	56.6	56.6	53.99	56.6	56.6	38.0		38.0
Ash	19.66	9.8	0.3	14.0	0.3	5.4	5.4	7.11	5.4	5.4	15.1		15.1
Sulfur	3.72	4.0	1.0	4.3	0.9	1.46	1.46	1.18(1)	1.46				
Chlorine		0.15	0.003	0.25	0.004								
Solvent													
	Wide Range	Narrow Range	Wide Range	Narrow Range	Wide Range	Narrow Range	Wide Range	Narrow Range	Wide Range	Narrow Range	Wide Range	Narrow Range	Wide Range
Refractorized	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No
Deashed Coal Recovery													
On crushed coal	67.3	83.6		75.4		67.5		85.3		90.0			21.3
On ash-free coal	83.8	92.7		89.8		71.3		91.8		95.2			25.2

(continued on next page)

TABLE I (cont'd)

COAL SOLUTION DEASHING USING AS-RECEIVED WIDE-RANGE COAL TAR DISTILLATE  
AND NARROW RANGE REFRACTORIZED SOLVENT

Coal Source	I		II		III		IV		V		VI	
	Illinois		Illinois		Illinois		Penna.		Illinois		Penna.	
Filtrate	Raw	Deashed	Raw	Deashed	Raw	Deashed	Raw	Deashed	Raw	Deashed	Raw	Lignite
Sp. Gravity(100°/100°F)	1.2516	1.2250	1.2208		1.2523		1.2140		1.2355		1.2140	1.2355
Softening Point, °F(B&R)	147	131.5	111.0		212				121.5			121.5
Sulfur, Wt. %	0.63				0.44		0.51				0.51	0.57
Carbon Residue, Wt. %	32.7						23.9				23.9	28.0
Ramsbottom Conradson					35.9							
CS <sub>2</sub> Solubility, Wt. %												
Bitumen	76.81	78.56	80.71		68.35		81.01		85.13		81.01	85.13
Ash	0.06	0.08	0.03		0.07		0.05		0.02		0.05	0.02
Difference	23.13	21.36	19.26		31.58		18.93		14.85		18.93	14.85

(1)	Raw Coal		Coal Extract	
	Raw Coal	Coal Extract	Raw Coal	Coal Extract
Organic S. %	0.799	0.593		
Pyritic S. %	0.370	Not Detected		
Sulfate S. %	0.012	Not Detected		
Total	1.181	0.593		

TABLE 2

TYPICAL COAL DEASHING RESULTS

Coal Source:	Pennsylvania		Illinois		Pennsylvania	
	As Charged	Product	As Charged	Product	As Charged	Product
<b>Bench Scale</b>						
Proximate Analysis						
Moisture	1.4					
Volatile Matter	36.6	22.3-30.3	33.62	25.2	33.53	37.3
Fixed Carbon	56.6	77.4-69.4	56.56	74.5	52.54	62.5
Ash	5.4	0.02-0.5	9.79	0.3	13.93	0.3
Sulfur	1.46	0.3 - 0.6	3.95	1.0	4.32	0.9
Chlorine			0.15	0.003	0.25	0.004

Pilot Plant

Coal Source:	Illinois	
	As Charged	Product
<b>Sample</b>		
Proximate Analysis		
Moisture	2.75	
Volatile Matter (Dry Basis)	38.90	20.9+
Fixed Carbon (Dry Basis)	53.99	78.4+
Ash	7.11	0.65
Sulfur	1.18	0.593

TABLE 3  
DELAYED COALING RUN - PRODUCT DISTRIBUTION

Basis: Run PF-15  
 2000 lbs. Southern Illinois Coal (Moisture Free)  
 4000 lbs. Coker Recycle 500-700°F

<u>Product</u>	<u>Solution Basis</u>		<u>Solvent-free Basis</u>	
	<u>Wt. lbs.</u>	<u>Wt. %</u>	<u>Wt. %</u>	
Gas	134	2.2	6.7	
Liquor & Lt. Oil	60	1.0	3.0	
Coke	1256	20.9	62.8	
Solvent	4000	66.7		
Distillate	46	0.8	2.3	
Spent Cake	<u>504</u>	<u>8.4</u>	<u>25.2</u>	
Total	6000	100.0	100.0	

TABLE 4

DELAYED COKING OF DEASHED COAL SOLUTIONRESULTS OF COKER TEST RUN DC-13

Properties of Feed (1)	Coke Drum No. 1	Coke Drum No. 2
Specific Gravity, 100/60°F	1.1928	1.1811
Softening Point, °F (R&B)	158	108.5
Benzene Insoluble, Wt. %	22.2	19.6
Properties of Coke		
Wt. Percent of Feed	25.7	22.3
Density, lbs/ft <sup>3</sup>		
By Weight of Volume Occupied in Coke Drum	50.1	38.5
By Weight of Water Displaced by Sample	66.7	51.3
Volatile Matter, Wt. %	9.17	10.06
Fixed Carbon, Wt. %	90.22	89.28
Ash, Wt. %	0.61	0.66
Sulfur, Wt. %	0.37	0.38
Heating Value, BTU/lb.	14,520	
(1) Weight percent coal extract		-26.2
Benzene insoluble, weight percent-		21.0

TABLE 5

ECONOMIC STUDY - DEASHED COAL PRODUCT

Plant Capacity, Tons/year	750,000		1,500,000	
Plant Cost	\$13,400,000		\$24,000,000	
	<u>Cost/Ton Product</u>	<u>¢/MM BTU</u>	<u>Cost/Ton Product</u>	<u>¢/MM BTU</u>
Raw Material (Coal)	\$6.50	21.6	\$6.50	21.6
Labor, Supervision, & Overhead	1.14	3.8	.98	3.2
Utilities	1.30	4.3	1.30	4.3
Depreciation	1.19	3.9	1.06	3.5
Maintenance	.54	1.8	.48	1.6
Insurance & Interest	.89	2.9	.80	2.7
Sales Costs	<u>.15</u>	<u>.5</u>	<u>.15</u>	<u>.5</u>
Gross Operating Costs	\$11.71	38.8	\$11.27	37.4
By-Product Credits	<u>(2.60)</u>	<u>(8.6)</u>	<u>(2.60)</u>	<u>(8.6)</u>
Net Operating Costs	\$9.11	30.2	\$8.67	28.8
Pre-tax Investment Return	<u>2.24</u>	<u>7.4</u>	<u>2.00</u>	<u>6.6</u>
Sales Price, (Coal @ \$4.00/ton)	\$11.35	37.6	\$10.66	35.3
Sales Price, (Coal @ \$3.00/ton)	\$9.72	31.9	\$9.03	29.6

- Notes: 1. Plant is a 'grass-roots' facility capable of handling run-of-mine coal from stockpile.
2. Labor - \$5.00/man hour including supervision and overhead.
3. Utilities - Electricity @ \$.006/KWH  
Steam @ \$.50/M lbs.  
Cooling Water @\$ .02/M Gallons
4. Depreciation - Straight Line over 15 year period.
5. Maintenance - 3% of investment.
6. Insurance & Interest - 5% of Plant cost.
7. By-Product Credits - \$.01/pound average for net excess distillate.
8. Pay-Out - 8 Years.

FIGURE 1  
SCHEMATIC FLOW DIAGRAM  
DEASHED COAL OR HIGH PURITY COKE

