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MAXIMIZING TAR YIELDS IN A TRANSPORT REACTOR

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INTRODUCTION

The objective of the Char Oil Energy Development (COED) project, sponsored by the Office of Coal Research, is to develop an economic process for converting coal to a gas, a liquid and a solid, and to upgrade the coal substance and decrease the delivered cost of coal energy. To achieve an economic process, a maximum amount of liquids and gases and a minimum amount of solid char had to be produced. One technique considered for possible scale up to a commercial process involved the transport of coal in a disperse phase through a hot-wall reactor. The transport reactor was consistent with our philosophy that we needed to heat coal rapidly to obtain maximum volatilization of coal. In addition, this type of reactor provided a ready means for removing pyrolysis products quickly from the hot zone.

The operation of a bench-scale transport reactor has already been described. (1) Those studies demonstrated that char yields decreased as reactor temperatures were raised to 2200°F. but increased at 2400°F. and higher temperatures. Investigation showed that the increased yield of char resulted from the decomposition of product tars and hydrocarbon gases to char and hydrogen. Because a maximum yield of tar was desired, the emphasis of these studies was changed from seeking maximum volatilization of coal at high heating rates to pyrolysis under conditions which avoided the loss of liquids to vapor-cracked carbon. Such operation involved pyrolysis with shorter residence times, so that tar vapors left the reactor before secondary cracking reactions occurred, or with lower temperatures and longer residence times. Most work was done with Elkol coal, a non-caking sub-bituminous C coal. However, some higher-rank coals were also processed to observe whether they would give larger tar yields on volatilization.

EXPERIMENTAL PROCEDURE AND RESULTS

1. Apparatus and Experimental Procedure

The first reactor used shown in Figure 1, had an 8-inch heating zone. This reactor has been discussed in detail. (1) Additional heating zones of one, two and four inches in length were attained with an induction furnace, the length of heating zone being controlled by the length of the inductor surrounding the ceramic reaction tube. The 12-foot reactor, shown in Figure 2, consisted of two 6-foot section of 1/4-inch stainless steel pipe. Each section was heated independently with 6-foot long electrical strip heaters. Coal could be introduced either at the middle or at the inlet of the reactor. When coal was charged at the center, the first half of the reactor was used to preheat the carrier gas. Unless stated otherwise, the carrier gas linear velocity at room temperature was 4. 0 ft. /sec.

Coking coals were processed in dilute phase in a 3-foot long, vertical 3-inch pipe. Coal was dropped into the reactor through an unheated, 1/4-inch ceramic tube. The sweep gas, either steam, helium, or nitrogen, was passed up the reactor at a linerar velocity of less than one foot per second. The velocity was sufficient to extend the coal's residence time within the hot zone, but low enough to prevent turbulence inside the reactor. This technique prevented plastic coal particles from striking each other or the hot walls of the furnace. Char was collected in an 8-inch, unheated bottom section of the reactor, and volatiles left the reactor 6 inches from the top. The recovery section was similar to that shown in Figure 1. Most char entrained in the carrier gas was collected in a cyclone, the balance in a settling vessel, along with tar, or on glass-wool filters. A cold trap after the filters removed moisture from the gas. The gas was metered and sampled for mass-spectrographic analysis.

Chars collected after the cyclone were treated in one of two ways. Some were washed with acetone to remove condensed tar. The recovered char was dried at 220°F., mixed with char from the cyclone and analyzed. Tar was recovered by evaporating the wash acetone. With other chars, the adsorbed tar was determined by the quinoline-solubility technique used for determining free carbon in coal-tar pitch. (5)

The analyses of coals used in these studies are shown in Table 1.

TABLE I
ANALYSES OF COALS

Coal Mine	Elkol	Orient No. 3	Federal No. 1	Kopperston No. 2
Company	Kemmerer Coal Co.	Freeman Coal Mining Corp.	Eastern Associated	Coal Corp.
Seam	Adaville	Illinois No. 6	Pittsburgh	Campbells Creek
State	Wyoming	Illinois	W. Va.	W. Va.
County	Lincoln	Jefferson	Marion	Wyoming
Moisture, %, as-received	12.8	9.4	2.5	2.9
Proximate Analysis, %, dry basis				
Volatile Matter	40.7	34.6	37.7	31.6
Fixed Carbon	54.6	58.8	56.8	63.9
Ash	4.7	6.6	5.5	4.5
Ultimate Analysis, %, dry basis				
Carbon	70.6	75.0	78.4	85.1
Hydrogen	5.4	4.8	4.9	6.2
Nitrogen	1.2	1.6	1.5	1.5
Sulfur	1.0	1.5	1.9	0.7
Oxygen	17.1	9.7	7.8	2.0
Ash	4.7	7.4	5.5	4.5

2. Results

Using an induction heating furnace, 1-, 2-, and 4-inch hot zones were obtained. These studies were made with a downflow reactor, as opposed to the horizontal reactor used principally in the previous work. The first three runs in Table II show how product distribution varied with shortening of the hot zone.

TABLE II
INDUCTION FURNACE RUNS

Coal Mesh Size	100- x 200-mesh			Minus 5-Micron	
Run No.	26	23	21	24	25
Heating Zone, in.	4	2	1	1	1
Furnace Temp., °F.	2400	2400	2400	2400	3000
Coal Conversion, %, dry					
Char	54.5	67.1	87.5	87.0	65.0
Tar	3.4	6.0	4.7	2.4	4.0
Water	-	-	-	0.3	3.0
Gases	42.1	26.7	7.8	10.3	28.0
Gas Comp., Mol %					
H_2	13.6	42.4	-	12.2	37.6
CH_4	12.3	12.9	-	16.3	6.7
C_2's	16.4	13.7	-	17.0	6.7
CO	50.9	14.9	-	32.6	22.2
CO_2	6.8	12.9	-	16.2	26.8
Char V.M., %, dry	14.6	32.2	37.9	37.3	20.9

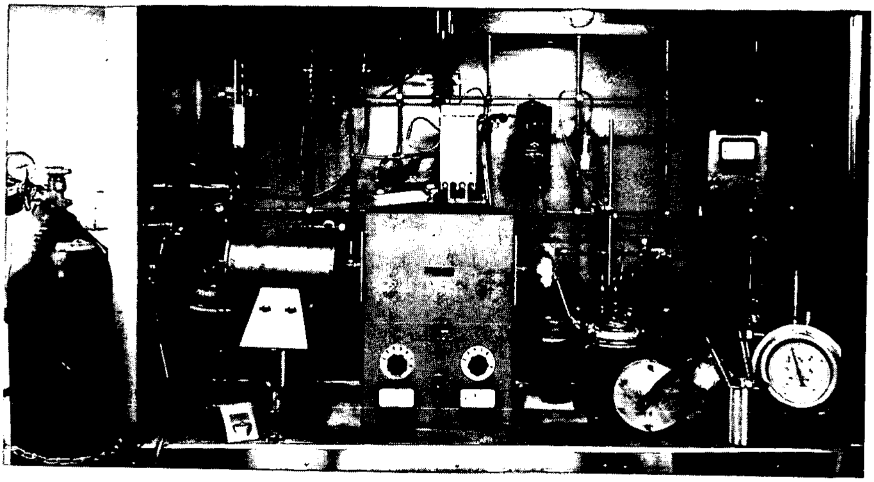


FIGURE 1

Transport Reactor Assembly - Original Reactor

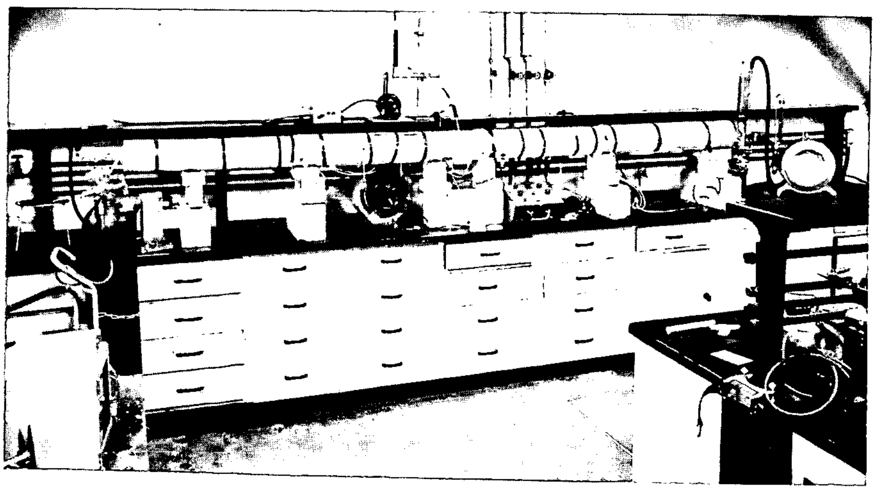


FIGURE 2

Twelve-Foot Transport Reactor

As the zone was shortened from 4 inches to 1 inch, at 2400°F. furnace temperature, the char yield rose from 54.5 to 87.5 percent, gas yields dropped from 42.1 to 7.8 percent, and the volatile-matter content of the char rose sharply. It is obvious that the maximum coal particle temperature was far lower than the indicated furnace temperature. The 6 percent tar yield in Run 23 with the 2-inch hot zone was especially interesting, since it was more than double that obtained at the same furnace temperature with an 8-inch hot zone. Note that some tar was recovered even at a 3000°F. furnace temperature with the 1-inch hot zone. All tars formed in these experiments appeared to be similar to low-temperature-carbonization tars, being brownish in color and quite sticky. Infrared analysis, however, indicated that these tars had a higher conjugated carbonyl-to-alkyl ratio than normal for LTC tar, and were virtually free of long methylene chains commonly found in low temperature tars. These data confirmed that with sufficiently short residence time, tar could be recovered from pyrolysis chambers operated at temperatures considerably higher than tar-cracking temperatures. Some vapor-cracked carbon was found in the run made with the 4-inch hot zone at 2400°F. furnace temperature, but none was found in the runs made with shorter heating zones. Use of the much finer coal in the last two runs did not increase the volatile products, nor was the product distribution different from that obtained with the coarser coal. This is also true when comparing these two differently sized coals in other work done using the 8-inch hot zone of the Lindberg furnace.

The 12-foot reactor gave residence times from 0.7 to 2.0 sec. at temperatures ranging from 500 to 1400°F. These compared with the 0.02 to 0.05 sec. residence times obtained using the 8-inch hot zone in the Lindberg furnace. Using preheated steam as the carrier gas and injecting the Elkol coal at the center of the reactor, tar yields of 16 weight percent of dry coal charge were obtained at temperatures ranging from 1100 to 1400°F. As the reactor temperatures were lowered, the char yields increased and the hydrogen content of the product gas dropped. These results are summarized in Table III. The residual volatile matter in these chars was much higher than in previous transport reactor studies cited, indicating that further processing would yield additional gas and perhaps some tar. Only 4 percent of tar was recovered at a reactor temperature of 825°F.

TABLE III

DEVOLATILIZATION OF ELKOL COAL IN TWELVE-FOOT REACTOR

100- x 200-Mesh Coal
Carrier Gas - Steam

				Vitrainoids
Run No.	104	93	99	107
Preheat Temp., °F.	1400	1100	1400	1500
Reactor Temp., °F.	1400	1100	825	1100
Coal Conv., %, dry				
Char	59.0	67.9	91.0	60.0
Tar	16.0	16.2	4.1	20.4
Gas	17.4	10.2	4.9	14.0
Total	92.4	94.3	100.0	94.4
Gas Anal., Mol %				
H_2	15.5	5.5	12.2	6.0
CH_4	21.8	23.6	6.1	23.8
C_2	15.7	12.2	2.2	11.4
C_3+	6.6	8.0	1.2	10.0
CO	27.6	19.9	18.3	24.9
CO_2	12.8	30.8	60.0	23.9
V.M. of Char, %, dry	21.0	27.4	37.5	27.3

The last column in Table III shows data obtained using a concentrate of vitranoids from the same Elkol coal which was prepared by Bituminous Coal Research, Inc. Over 20 weight percent of tar was recovered from this run--the highest yield obtained from Elkol coal. The product char contained 27.3 percent volatile matter, indicating that additional tar might have been obtained by reprocessing the char at a higher reactor temperature. This run has interesting implications, in that concentration of specific coal macerals offers a way of obtaining more tar from coals by pyrolysis.

If thermal cracking destroyed tars, improved tar yields should result if tars were quenched before decomposition set in. This was the case in some 12-foot studies, as demonstrated in Runs C-970-97 and 98 in Table IV. The coal was introduced with helium as the carrier gas at the beginning of the reactor and steam was introduced at the mid-point of the reactor as the quenching medium. To reduce tar residence time within the hot zone, the helium velocity was raised to 8 ft./sec., twice the normal rate. A temperature profile showed that the steam cooled the center of the reactor 200 to 300°F., but the end of the reactor approached the prequench temperature. The indicated tar yields from these runs, 13.9 and 17.2 percent, respectively, were the highest obtained with helium as the carrier gas. Although sought in several ways, no quenching effects were found in any short reactor, high-temperature studies.

TABLE IV
INCREASE IN TAR YIELDS VIA QUENCHING
100- x 200-Mesh Coal

Run No.	90	97	91	98
Reactor Temp., °F.	1400	1400	1100	1100
Carrier Gas	He	He	He	He
Quench	None	Steam	None	Steam
Coal Conv., %, dry				
Char	48.5[a]	56.9	57.0	69.5
Tar	11.2	13.9	11.0	17.2[b]
Gas	21.5	24.2	26.4	6.0
Total	81.2	95.0	94.4	92.7
Gas Anal., Mol %				
H_2	22.2	10.1	25.6	2.0
CH_4	29.6	26.6	33.9	18.8
C_2	15.4	15.0	8.8	15.8
C_3+	5.1	7.2	5.2	4.5
CO	15.4	24.3	10.5	18.8
CO_2	12.3	16.8	16.0	40.1
V.M. of Char, %, dry	15.6	19.4	23.1	28.0

[a]Some solids lost.
[b]2% moisture may be included.

In the gas analyses presented in Tables III and IV, the CO:CO_2 ratio was less than 1.0 in runs made at or below 1100°F., but was over 1.0 in runs made at higher temperatures. Since this was the case when both steam and helium were used as carrier gas, this phenomenon must have been due to some temperature-dependent decomposition characteristic of this coal, rather than to a water-gas reaction.

Higher-rank coals were devolatilized in a 3-inch diameter vertical reactor. The coal-charging gas to the Syntron feeder was nitrogen, and steam was passed up the reactor to slow the rate at which the coal dropped and to entrain evolved volatiles. Some typical data for Federal coal are shown in Table V. These runs gave tar yields of between 28.5 and 31.5 weight percent of dry coal charged. These were the highest tar yields found throughout these studies. This mode of operation was the only one found suitable for handling strongly coking coals and this is believed to be the first time such coals were devolatilized in this manner.

The Syntron coal feeder was operated in Run 130 employing a minimum quantity of air as the coal-charging gas, about 0.1 cubic foot per minute. Although this amount of air caused the concentration of CO to double and that of CO_2 to increase by a factor of 5 to 10, it had no apparent effect of the yield of tar.

TABLE V

DEVOLATILIZATION OF FEDERAL COAL AT 1100°F.

Run No., C-970	130[a]	139	144[c]	149
Coal	Federal (Pittsburgh-Seam)			
Mesh Size	-100	-100	-100	-200
Coal Charged, gm.	43.6	53.0	52.5	148.9
Charge Rate, gm./hr.	101	206.0	105	270
Product Recovery, wt. %, dry coal basis				
Tar-free Solids	48.5	49.7	38.5	57.3
Tar	29.5	29.5	31.5	28.5
Gas	21.2	-[b]	22.0	11.0
Total	99.2		92.0	96.8
Gas Composition, Mol %				
H_2	5.0	18.6	17.1	28.6
CH_4	10.0	40.3	42.9	35.1
C_2H_2	0.0	0.0	0.0	0.0
C_2	4.4	15.5	14.1	13.2
CO	20.2	12.4	9.5	6.6
CO_2	58.5	6.2	9.5	8.8
C_6H_6	0.0	6.2	2.3	0.0
C_3+	1.9	0.8	2.6	7.7
% Ash in Char, dry basis	8.5	9.7	11.4	10.6

[a] Air used as coal charging gas.
[b] Gas leak due to plug in feed line.
[c] Coal, steam and N_2 passed in bottom of reactor.

Data in Table VI show results obtained from the pyrolysis of Orient No. 3 and Kopperston No. 2 coals in the 3-inch downflow reactor. Both coals gave less tar than the Pittsburgh-seam coal from Federal. Raising the reactor temperature to 1300°F. in Run 40 caused some lowering of tar yields. This was also the case with Federal coal.

Because it contained more hydrogen and much less oxygen than any other coal investigated, it was thought that Kopperston No. 2 coal might give high yields of tar. Data for Run 42 in Table V showed no particular advantage for this low-oxygen coal as far as the tar yield was concerned.

TABLE VI

DEVOLATILIZATION OF ORIENT NO. 3 AND KOPPERSTON NO. 2 COALS

Run No.	39	40	42
Coal	Orient No. 3		Kopperston
Reactor Temp., °F.	1100	1300	1100
Coal Charged, gm.	104	77.5	140.4
Charge Rate, gm./hr.	147	86	210
Product Recovery, wt. %, dry coal basis			
Tar-free Solids	56.1	51.5	73.0
Tar	19.6	17.2	18.7
Gas	13.9[a]	26.7	1.8[a]
Total	89.6	95.4	93.5
Gas Composition, Mol %			
H_2	23.0	47.0	19.4
CH_4	40.7	31.8	24.7
C_2H_2	0.0	0.0	0.0
C_2	17.1	10.7	38.0
CO	0.0	0.0	3.6
CO_2	11.7	7.0	9.2
C_6H_6	0.0	0.2	0.0
C_3+	7.5	2.3	5.1
% Ash in Char, dry basis	11.0	13.9	5.3

[a]Some gas lost.

DISCUSSION

Throughout these studies it was obvious that chars were not heated to the indicated furnace temperatures. Based on a devolatilization correlation described previously (1), we estimated the temperatures to which chars were heated in the various reactors described. These data are summarized in Figure 3. According to this figure, char pyrolyzed in the 12-foot reactor almost reached the reactor temperature at 825°F., but only reached 1100°F. when the reactor temperature was 1400°F. As the furnace temperature was raised and the heating zone was shortened, the disparity between calculated particle temperatures and furnace temperatures grew. Thus, particle temperatures in a short transport reactor were far below the furnace temperatures, and the difference became greater as the residence time was cut. Increasing the furnace temperature gave sharper heating rates, as indicated by the slopes of the lines for runs made at 2000-2400°F.

No significant amount of vapor-cracked carbon was found in any char having an indicated char temperature of less than 1200°F. in this figure. No. vapor-cracked carbon was found in chars from the 12-foot reactor and, as stated above, none was found in runs at 2000°F. in the Lindberg furnace. All these runs, according to Figure 3, had a maximum char temperature of only 1100°F. This temperature might seem low for the amount of volatilization which was obtained. However, other investigators (2, 3) indicated that in the rapid heating of coal, devolatilization was essentially completed at 600°C., or 1112°F.

The existence of a time-temperature relationship in the shock-heated Elkol coal pyrolysis experiments became apparent. Thus, a hot zone of 4 inches at 2400°F. was roughly comparable to 8 inches at 2000°F., and a 1 inch zone at 3000°F. was about as effective as 2 inches at 2400°F. in volatilizing coal. For a carrier gas velocity of 4 ft./sec. calculated at room temperature, an approximate expression for this relationship is

$$Y = 0.0084t + 3.75L$$

where

Y = percent volatilized
t = furnace temperature in degrees R
L = length of hot zone in inches.

The quenching experiments showed that quenching was effective only when it initiated the cooling of the product vapors. This was the case inside the 12-foot reactor. In the Lindberg furnace, however, the volatilization products were cooled at the end of the furnace in the 5 to 20 milliseconds that elapsed between the time the particles left the hot zone and reached the quench zone. Further quenching at this point, however severe, had no effect on either the product yields or on the distribution of products. The initial cooling at the end of the furnace had already quenched the decomposition reactions.

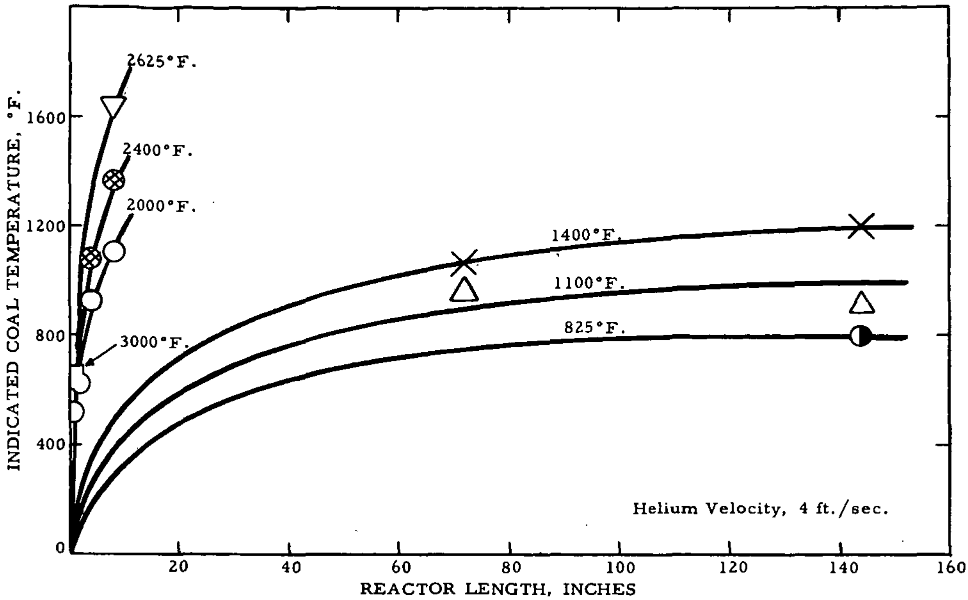
The transport reactor was designed to permit scaling up to a commercial unit. The alternate approach to achieving the COED objectives employed a 3-inch multistage fluidized-bed system to process coals. (4) Data in Table VII compare transport reactor tar yields with those from the 3-inch fluidized-bed unit. (4) Tar yields from the transport reactor were only slightly lower than those from the fluidized-bed unit. The difference was attributed to the much shorter residence time for vapors in the transport reactor.

TABLE VII
COMPARISON OF TAR YIELDS FROM TRANSPORT AND FLUIDIZED BED REACTORS

Coal Feed	Transport Reactor	Fluidized-Bed Reactor
Elkol	16.5%	17%
Illinois No. 6	19.6	23
Federal	28.5-31.5	32
Av. Residence Time		
Coal	2 sec.	20 min.
Vapors	0.01-0.7 sec.	1-2 sec.

FIGURE 3

Estimated Elkol Char Temperatures at Various Furnace Temperatures



SUMMARY

Transport reactors proved to be effective laboratory devices for shock-heating coals at rates in excess of 2000°F./sec. At such heating rates more coal was volatilized than was predicted from standard ASTM volatile matter determinations. Both coking and non-coking coals were processed in transport reactors. By controlling heating rates and residence times, yields of tars, chars and gases were varied over fairly wide limits. Highest yields of tars were achieved at reactor temperatures of about 1100°F. and relatively long (0.5 to 2.0 seconds) residence times.

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