

EFFECT OF CARRIER GAS ON TAR YIELD AND
QUALITY OF OCCIDENTAL FLASH PYROLYSIS

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ABSTRACT

Occidental Flash Pyrolysis employs recycled heated char as heat carrier to supply the heat of pyrolysis. When nitrogen was used, as transport gas, tar yield decreased due to char-catalyzed tar cracking reactions. When low surface area heat carrier was used, tar cracking reactions was prevented and the tar yield was raised back to the expected level.

The tar was lighter with lower average molecular weight. The improvement of tar yield and quality was attributed to the stabilization of reactive coal fragments by nascent hydrogen produced by char gasification (by CO₂ and steam) and water-gas shift reactions.

INTRODUCTION

Flash Pyrolysis of coal employs very rapid heating to devolatilize pulverized coal in the absence of air to partition the coal into hydrogen-rich tar and carbon-rich char residue. It has been studied in both batch and continuous reactors. (1-5)

Occidental Research Corporation (ORC) developed this concept in a novel entrained flow reactor in which hot recycled char provides the heat to pyrolyze the coal. The typical tar yields are approximately twice that obtained from Fischer Assay test from the same coal. The detailed description of ORC process has been provided elsewhere. (6)

During the operation of a 3-ton-per-day process development unit (PDU), tar loss by char-catalyzed tar cracking reactions was uncovered. A smaller scale unit, 1 kg-per-hour bench scale reactor (BSR), was used to study the effects of transport gas and heat carrier on tar yield. Reactive gases such as CO₂ and H₂O instead of nitrogen were used to transport the char. Tar loss was prevented when the high surface area of char was covered by reactive gases. The tar yield was increased to the same level as that predicted by the electrical heating cases. When low surface area aluminum was used as heat carrier tar loss was also prevented. These results and the mechanism to prevent the tar loss were discussed by Duraiswamy et.al. (7)

This paper presents the effect of carrier gas and heat carrier on the tar quality.

EXPERIMENTAL

The experiments for pyrolysis of coal were carried out in a 1 kg-per-hour bench scale reactor as shown in Figure 1. Coal was metered by a screw feeder and carried by transport gas into the reactor. Char was metered by a second screw feeder and carried by nitrogen or desired transport gas. The char was preheated to the desired temperature before it mixed with the coal. Coal particles were brought to the pyrolysis reaction temperature in a few milliseconds.

Coal disproportionated into hydrogen-rich volatiles and carbon-rich char. The char was separated in a series of cyclones and the vapors and gases were cooled to collect the liquid products. The effluent gases were analyzed by gas chromatographs. The condensed liquid product is dissolved in acetone for easy removal from the collection vessels. After evaporation of the acetone under vacuum, tar and water are separated by distillation.

Each of the fractions, namely acetone, water and tar, are analyzed separately to determine water, light oil and tar ($110^{\circ}\text{C}+$). Tar in condensed water, tar left in char, if any, as determined by pyridine solubility and tar adsorbed in the activated charcoal, as determined by Fischer Assay are all included in the total tar yield.

For the purpose of this study, the characterization of tar properties was only carried out on the $110^{\circ}\text{C}+$ fraction material which is usually over 90% of the "tar".

The analyses of coal and char are given in Table 1. The molecular weight distribution profiles were determined by using gel permeation chromatography performed on tar samples using a Waters 244 ALC/GPC Liquid Chromatograph equipped with a refractive index detector. The columns employed were Waters styragel-columns 30 cm x 7.8 mm ID consisting of 1-1000A, 1-500A and 3-100A pore size packings. Tetrahydrofuran, THF from Burdick and Jackson, was used as the solvent at a pressure of 1000 psig. Calibration of the instrument used the polystyrene standards ranging in molecular weight from 100 to 33,000 AMU. Therefore, the molecular weight labeling of GPC chromatograms was for reference and comparison purpose.

GPC samples were prepared by adding 8 drops of 15% solution of tar in THF to 5 ml THF and filtering through a 0.65 micron filter sample sizes were 125 μl .

The tar was subjected to a solvent fractionation procedure to yield oils, asphaltenes and preasphaltenes. The solubility classes were defined as: oils (hexane soluble), asphaltenes (hexane insoluble/toluene soluble) and preasphaltenes (toluene insoluble/pyridine soluble). Separation was obtained according to the procedure described in Ref. (6).

RESULTS AND DISCUSSIONS

For the purpose of this study, the initial pyrolysis experiments were performed using subbituminous coal, nitrogen carrier gas and electrical heating; i.e., no preheated char was used. A series of runs ranging from 1000°F to 1400°F was carried out. The yields and properties of tar for these runs are given in Table 2.

Effect of Residence Time

Tar produced at the longer residence time contained a higher proportion of oil, and was also characterized by a lower specific gravity, lower viscosity and lower sulfur content than that produced at the lower residence time. These improved tar properties were attributed to the additional cracking that occurs at the longer residence time.

The evidence of the additional tar cracking due to longer residence time is provided by GPC chromatograms, Figure 2. They show that at longer residence times, the concentrations of high molecular weight species decreased while the concentrations of lower molecular species increased.

The oil content of tar was relatively independent of the pyrolysis temperature but was affected by the residence time as shown in Figure 3. The oil content increased from an average value of 43% to 54% when the residence time increased from 1.5 to 3 seconds with a corresponding decrease in the preasphaltenes content. The data suggested that asphaltenes and preasphaltenes underwent cracking at longer residence times and thus the proportion of oil increased. These results indicate that chemical transformations of the tar which occurred during the process enhanced its properties without suffering significant loss in yields. More importantly, these reactions apparently occurred over a practical and controllable range of residence times.

Effect of Heat Carrier: Char and Alumina

When preheated char was used as heat carrier, the tar yields decreased as the ratio of char-to-coal increased, as shown in Figure 4. This effect has been attributed to the char-catalyzed tar cracking reaction by DuraiSwamy et. al.⁽⁷⁾ Due to the secondary cracking reactions, the tar is lighter compared to the tar produced in the electrical heating mode as shown in Table 3. The higher atomic hydrogen-to-carbon ratio and oil content were indications of tar cracking.

When the low surface area (0.23 m²/g) alumina was used as heat carrier, the tar yield was higher than the case which used char as heat carrier. The tar is lightest among the three as shown in GPC of Figure 5. The tar loss reaction by char-catalyzed cracking was prevented when alumina was used as heat carrier. However, a different catalytic reaction might have taken place on the surface of alumina to improve the tar quality, as shown by the GPC.

GPC of tar from the alumina run showed significant reduction of heavy species. This could be attributed to a second possibility that the tar could not lay down on the surface of heat carrier polymerization or condensation to form heavy tar was prevented. The effect on tar yield and quality can be summarized in the following:

Tar Yield: Electrical > Alumina > Char

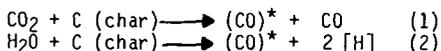
Tar Quality: Alumina > Char > Electrical

Petroleum fluid coke was used in PDU tests instead of alumina and it was found to be in between alumina and char for improving the tar yield and quality.

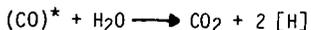
Effect of Reactive Carrier Gases

When different kinds of carrier gases such as CO, CO₂ and steam were used, the tar produced were lighter. The properties are summarized in Table 4. The molecular weights of tars were reduced as shown by vapor phase osmometric analysis and GPC profiles of Figure 6. The high polymeric species such as asphaltenes and preasphaltenes also decreased.

The tar yields were as high as the electrical heating case. The improvement of tar yield and quality were due to the adsorption of reactive gases on the char. When the surface area of char is occupied, tar vapor will not get adsorbed and get cracked on the surface of char to form coke and gases. Additionally by CO₂ and steam char gasification takes place producing CO and [H].



Where (CO)* is surface adsorbed carbon oxides. Nascent hydrogen can be formed on the surface of char by water-gas-shift reaction.



When the primary pyrolysis fragments (free radicals) are formed, they are seeking for stabilization by either reacting with the nascent hydrogen in the gas phase or on the char surface or recombining (polymerizing) stabilization of reactive fragments by nascent hydrogen prevents polymerization reaction to form heavy molecular weight species and coke.

CONCLUSION

Both carrier gas and heat carrier were found to affect the tar yield and tar quality in the Flash Pyrolysis of coal. Preheated char of high surface area provided adsorption sites for tar vapor. Tar either polymerized or cracked on the char to form gases and coke thus lowering the tar yield. When low surface area heat carrier were used, tar loss was reduced significantly. When the active sites of preheated char were occupied by reactive gases such as CO₂ and tar loss was prevented, and the tar quality was also improved. This improvement was attributed to the stabilization of pyrolysis free radicals by the nascent hydrogen produced from carbon gasification between char and reactive gases.

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7. K. Duraiswamy, S.C. Che, E.W. Knell, N.W. Green and R. Zahradnik, "Tar Yields in ORC Flash Pyrolysis Process", presented in Fuel Chemistry Symp. ACS Nat'l meeting. Honolulu, Hawaii, April, 1979.

TABLE 1
ANALYSES OF FEED COAL AND CHAR

	<u>Feed Coal</u>	<u>Feed Char</u>	<u>Product Char</u>
<u>Proximate Analysis, Wt.%</u>			
Moisture	11.59	1.18	0.7
Ash	5.00	11.40	10.00
Volatile Matter	37.01	7.02	7.88
Fixed Carbon	46.40	80.40	81.42
<u>Ultimate Analysis (Dry), Wt.%</u>			
Carbon	69.12	82.27	82.63
Hydrogen	4.95	1.87	2.13
Oxygen	18.32	2.52	3.29
Nitrogen	1.29	1.14	1.11
Sulfur	0.66	0.66	0.57
Ash	5.66	11.54	10.27
<u>Fischer Assay, Wt.%</u>			
Char	60.4	-	-
Water	21.4	-	-
Tar	9.3	-	-
Gas	8.9	-	-

Table 2
YIELDS AND PROPERTIES OF SUBBITUMINOUS COAL TAR

<u>Pyrolysis Conditions</u>		1.5		3.0	
Residence time, seconds					
Run Number	132	130	134	135	131
Temperature, °F	1000	1200	1400	1000	1400
Tar Yield, wt % MAF	8.7	17.3	15.2	15.2	14.7
					9.7
<u>Tar Properties</u>					
I. Physical Data:					
Specific Gravity, (80/80°F)	1.170	1.171	1.250	1.097	1.090
Viscosity, Centipoises (@ 415°F and extrapolated to)	45	54	23	16	12
0 sec-1 shear)					18
Melting Point, °F	230-265	194-230	-	-	68
					86-104
II. Ultimate Analysis, wt% (Dry Basis)					
Ash	0.7	0.15	0.05	0.02	0.04
Carbon	79.34	80.41	80.86	79.41	79.46
Hydrogen	7.44	7.47	6.35	7.75	6.73
Sulfur	0.51	0.65	0.49	0.39	0.51
Nitrogen	1.25	1.42	1.45	1.04	1.41
Oxygen (by difference)	11.39	9.90	10.80	11.39	11.85
Atomic H/C	1.13	1.11	0.95	1.17	1.02
III. Solubility Classification, wt%					
Oil	43	42	44	56	53
Asphaltenes	29	30	28	27	30
Preasphaltenes	28	28	28	16	17
					21
					24

TABLE 3
COMPARISON OF TAR PROPERTIES
EFFECT OF CHAR HEAT CARRIER

Run No.	<u>175</u>	<u>139</u>	<u>141</u>
Carrier Gas	N ₂	N ₂	N ₂
Preheater Temp °F	----	1200	1200
Pyrolysis Temp. °F	1200	1255	1255
Residence Time, Sec.	2.0	1.2	1.5
Char/Coal Ratio	0 (electric)	3.3	5 (Alumina)
Tar Yield (wt.%)MAF	18.0	9.7	14.1
Sp. Gravity, 60/60°F			
g/cc	1.218	1.191	-
Ultimate Analysis %Wt.			
C	81.47	80.00	76.81
H	6.32	6.68	6.75
N	1.14	1.48	1.12
S	0.55	0.43	0.38
O	10.52	11.40	14.94
Atomic H/C	0.93	1.00	1.05
VPO MW	285	--	--
Solubility Classification, Wt.%			
Pre-asphaltenes	25.6	17.1	--
Asphaltenes	33.0	24.6	--
Oil	41.4	58.3	--

TABLE 4
PROPERTIES OF TARS USING REACTIVE CARRIER GASES

BSR Run	176	177	178
Temperatures, °F char preheater	1500	1500	1500
Reactor	1191	1200	1200
Char/Coal Ratio	3	3	3.3
Carrier Gas	Steam (50%) CO (50%)	Steam (10%) CO ₂ (90%)	CO ₂
Residence Time, sec	1.9	1.94	2.0
Tar Yield, %MAF coal	15.2	19.2	18.3
Ultimate Analysis, % Wt			
C	80.78	81.22	80.15
H	6.25	6.48	6.34
N	1.47	1.43	1.58
S	0.66	0.56	0.61
O (by diff)	10.77	10.31	11.39
Ash	0.07	-	-
Atomic H/C	0.928	0.957	0.949
Sp. Gravity, 60/60°F			
g/cc	1.195	1.183	1.183
°API	-13.1	-11.9	-11.9
VPO MW	275	254	245
Solubility Classification, Wt%			
Preasphaltenes	16.9	16.3	17.4
Asphaltenes	28.6	28.4	27.2
Oil (by diff)	54.5	55.3	55.4

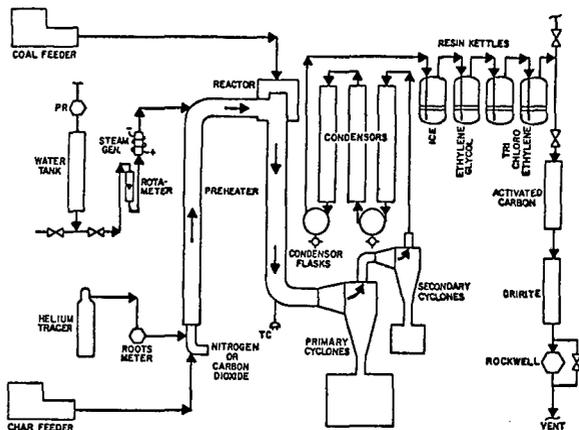


FIGURE 1 FLOW DIAGRAM OF 1 Kg-PER HOUR BENCH SCALE REACTOR

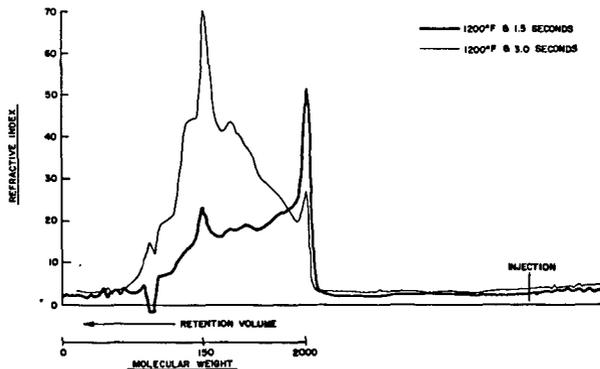
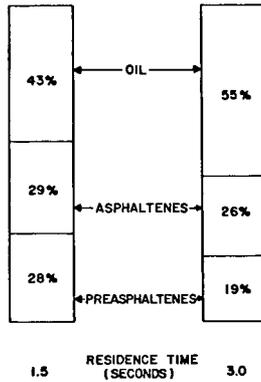


FIGURE 2 GEL PERMEATION CHROMATOGRAMS OF SUBBITUMINOUS COAL TARS PRODUCED AT 1200°F.



YIELDS, RELATIVELY TEMPERATURE INDEPENDENT,
WERE AVERAGED FROM RUNS AT 1000-1200-1400°F

FIGURE 3 SOLUBILITY CLASSIFICATION OF
SUBBITUMINOUS COAL TARS AS A
FUNCTION OF RESIDENCE TIME.

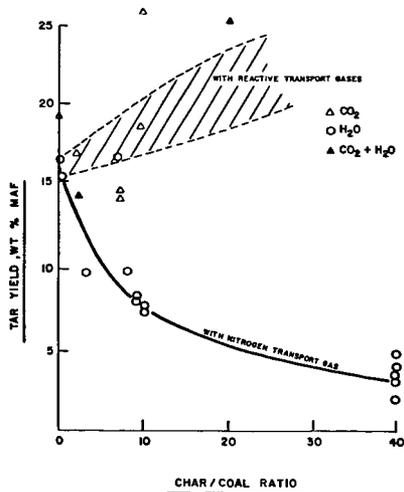


FIGURE 4 EFFECT OF RECYCLED CHAR ON
TAR YIELD

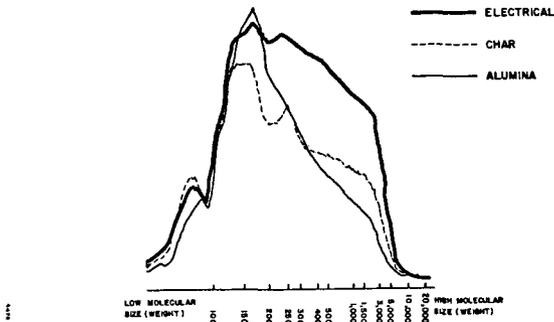


FIGURE 5 EFFECT OF SOLID HEAT CARRIER ON THE MOLECULAR SIZE DISTRIBUTION OF TARS.

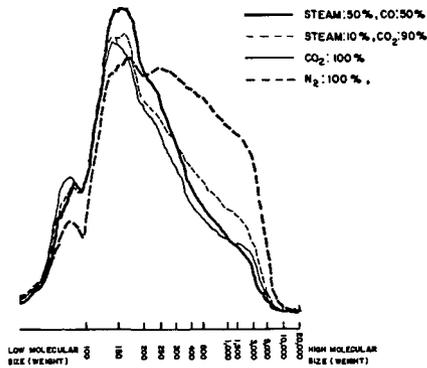


FIGURE 6 EFFECT OF CARRIER GASES ON THE MOLECULAR SIZE DISTRIBUTION OF TARS.