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SMALL CONTINUOUS UNIT FOR FLUIDIZED COAL CARBONIZATION

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INTRODUCTION

Since the commercial development of the fluidized-bed technique in World War II, many individuals and groups have applied fluidization to low temperature carbonization of coal. (1-7, 9, 13, 14, 15) In addition to providing rapid heat transfer and good temperature control, the fluidized process produces much higher tar yields than a static carbonization in an oven or Fischer Assay. This is due to rapid heating and removal of vapors, minimizing secondary reactions to gas and coke. (10, 11)

A small-scale unit to study fluidized carbonization normally has two functions, one to determine yields and the other to define operability in a commercial unit. At constant temperature and residence time the yields, particularly of tar, are a function of the sweep gas rate used (volume of fluidizing gas per unit of coal fed), while operability is largely dictated by fluidizing velocity. To maintain both fluidizing velocity and sweep gas rate at commercial levels would require a bed of the same depth as a commercial unit. In a small unit, the resulting high depth-to-diameter ratio would result in severe slugging and a completely unrealistic simulation.

The dilemma was resolved here by designing a continuous unit with an internal stirrer so that it could be run at low gas rates corresponding to commercial sweep rates and still provide rapid heat transfer and mixing. This gives tar yields which match larger scale results and allows a study of tar yield as a function of sweep gas rate. It also permits tar yield information to be obtained from caking coals under conditions which cannot be used in a normal fluidized bed operation since operability is "forced" by the mechanical action of the stirrer.

Although high-volatile coking coals give the highest tar yields, they require preoxidation and/or thermal treatment to prevent agglomeration during normal fluidized carbonization. (3, 4, 5, 7, 9) When evaluating pretreated coals to determine their operability during carbonization (freedom from excessive size growth), it is desirable to match the commercial bed turbulence, i. e., the fluidizing velocity. This can be done with the carbonizer described here by removing the stirrer and operating with a normal fluidized bed. Thus, the unit can be operated either with normal fluidization (and high sweep gas rates) to test operability, or at normal sweep gas rates and sub-fluidization gas velocities, using the stirrer) to evaluate tar yields.

The use of a stirrer to simulate a fluidized bed has been reported by Lastovtsev, et al. (8) In mixing of pigments they report that at a critical blade tip velocity of 5 to 8 m/sec a bed motion similar to that obtained with flow of gases is produced. The blade tip speed used in the work reported here, however, was 0.9 m/sec and was combined with a low flow of gases.

DESCRIPTION OF CARBONIZATION UNIT

A flow sheet of the unit is given in Figure 1. Coal is picked up with recycle gas and conveyed into the side of the carbonizer. Additional recycle gas is fed to the bottom of the bed through a porous plate. Air may be added to either stream. The coal is carbonized and overflows the top of the bed into the char receiver. Gases and vapors pass overhead to either of two liquid recovery trains. The small quantity of char fines which do not settle out in the expanded section is caught by the filter. The clean gases from a recovery train pass through a back pressure control valve and to the inlet of the recycle compressor. Compressed gases are cleaned and sent to rotameters for return to the unit. Net make gases are removed between the pressure control valve and the compressor, either via a wet test meter or by automatic sampling.

The carbonizer itself is six inches in diameter and 20 inches deep in the lower bed section, increasing to 12 inches in diameter in the expanded section. The stirrer consists of a 7/8-inch

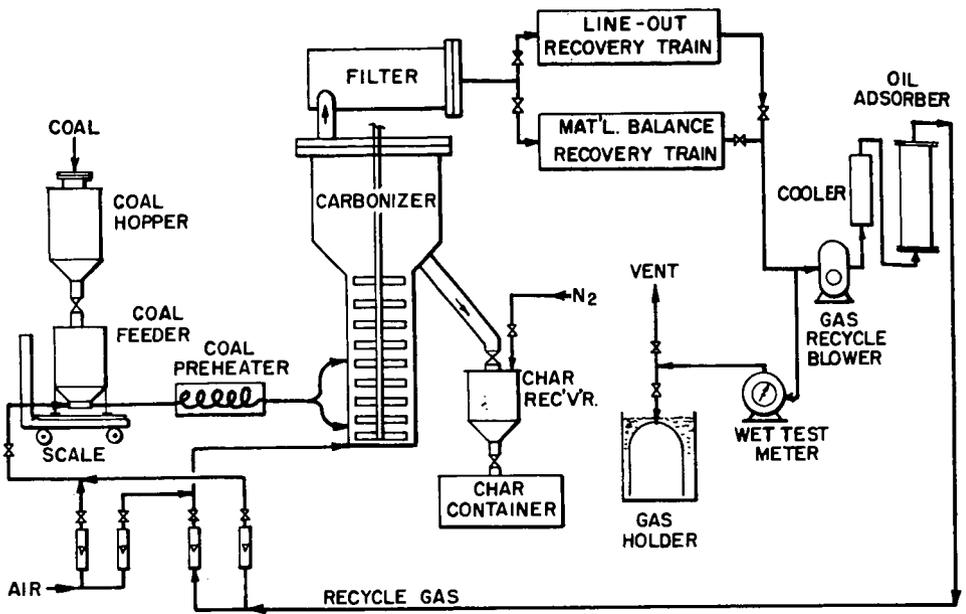
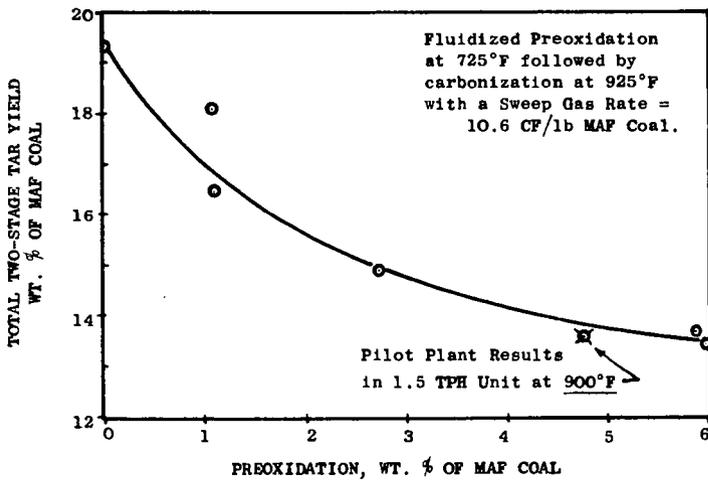


FIG. 1 STIRRED CARBONIZER UNIT

FIGURE 4

THE EFFECT OF PREOXIDATION ON TAR YIELD



shaft on which are mounted thirteen, three-bladed propellers with a left-hand helix. These blades were made from 8-inch blades machined to fit closely to the side walls and are mounted with a thermowell or other baffle extending two inches into the vessel between each blade. The stirrer is rotated at 112 rpm. Temperature is maintained by electrical windings on all sections of the carbonizer.

Coal is ground to pass a 28 mesh screen and charged to the lock-hopper above the feeder. The coal feeder is one developed by S. A. Jones in our laboratories and operates by squeezing coal between two rubber rolls. The rate is varied by changing roll speed and is measured by noting change in weight on a scale on which the feeder and lock hopper are mounted. After passing through the rolls, the coal is picked up by recycle carrier gas and transported through the pre-heater into the carbonizer. The coal preheater is a 16-foot coil of 1/4-inch O. D. tubing coiled to 3-inches O. D. and cast into an aluminum cylinder 5 inches in diameter and 15 inches long. The preheater is electrically wound and its temperature controlled to prevent coking in case the flow stops.

The solid product from carbonization (char) overflows and is lock-hoppered out. The small amount of very fine char elutriated with the gases is removed by a filter maintained at carbonization temperature. This filter is housed in a separate 6-inch vessel above the carbonizer and consists of a 3-1/2-inch O. D. cylinder of expanded metal, 18 inches long, on which about one-half inch of Pyrex wool is wrapped.

In order to provide accurate material balances in two shifts of operation, tar recovery is provided for via two similar trains--one to be used during line-out and the other for a material balance period. The latter train is constructed of aluminum and is taken down completely and weighed before washing out the tar. Both trains include: a) a bare 1-inch pipe cooler, b) an electrostatic precipitator, c) a water-cooled condenser, d) an electrostatic precipitator, and e) a silica gel trap to absorb light oil and water. The electrostatic precipitators consist of 0.0007-inch diameter tungsten wires centered in 2 or 2-1/2-inch pipes by means of spark plugs in the top flanges and weighted glass spiders near the bottom. The power supply is a Trion modified Type B Power Pack supplying up to 20,000 volts D. C.

PROCEDURE

The general procedure for a run is to charge the carbonizer with a start-up bed of char and turn on gas flows, using prepurified nitrogen for start-up. After adjusting pressure and flows, the heats are turned on and the reactor and lines brought up to operating temperature. The coal flow is started with products passing through the line-out recovery train. After the carbonizer has been at the desired temperature long enough to replace the bed three times, flows are switched to the material balance train and the char receiver emptied. At the end of the balance period (at least three inventory changes), the char receiver is again emptied and the flows switched back through the line-out train. Gas samples are taken at the beginning and end of the balance period as well as an integrated sample collected over the whole period. After switching from the balance period, the coal feed is normally stopped, but temperatures and flows maintained for another hour to complete carbonization of the bed inventory. Gas flows are continued as the unit cools down.

After a balance, the recovery train is removed, weighed, and cleaned with benzene. The benzene plus tar plus water is placed in a 5-liter flask and water removed by modified Dean-Stark azeotropic distillation. The recovery train pieces are then further cleaned with methyl ethyl ketone and the effluent combined with the water-free benzene solution. Solvents are then distilled off and the tar analyzed. Light products are recovered from the absorber by heating the trap while it is connected to a vacuum pump through a dry ice-acetone cold trap.

The amount of preoxidation is defined as the weight percent of oxygen consumed, based on moisture- and ash-free coal. All oxygen fed to the carbonizer was completely consumed. In preoxidation, a small breakthrough (ca. 1%) was obtained at lower temperatures and detected with a continuous Beckman Oxygen Analyzer operating on a side stream of overhead gas.

EXPERIMENTAL RESULTS

To illustrate the use of the 6-inch stirred carbonizer, a few results are given from the 1950-54 development of the Consolidation Fluidized Carbonization Process. (1, 13) The coals used were high volatile bituminous coals from the Montour No. 10 and Arkwright mines operating in the Pittsburgh Seam of Western Pennsylvania. Properties of these coals are given in Table 1. All of the results reported here except in Table 4 were obtained with Montour No. 10 coal.

The sweep gas rate as used here is the volume of all gases entering the carbonizer bed at reaction conditions (usually 925°F, 10 psig) per pound of moisture- and ash-free coal fed.

FIGURE 2
THE EFFECT OF SWEEP GAS ON YIELDS FROM
UNTREATED COAL

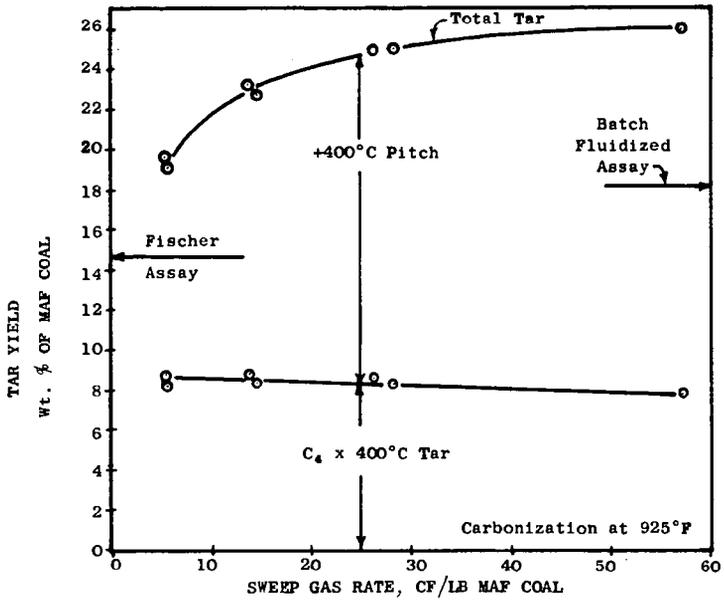
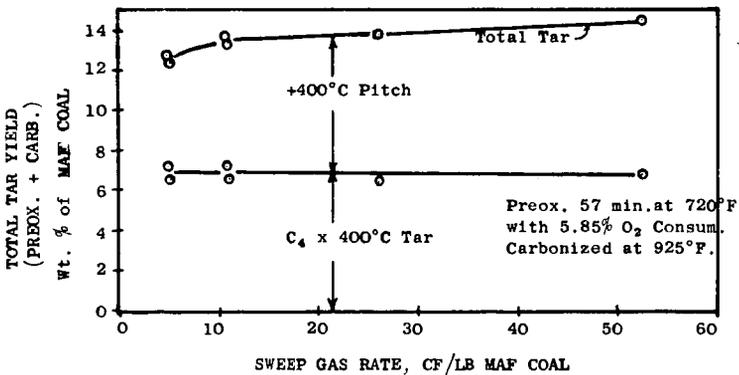


FIGURE 3
THE EFFECT OF SWEEP GAS ON YIELDS WITH
PREOXIDIZED COAL



The exit gas volume is larger by 3 to 5 CF/lb due to gases and water produced. The sweep gas rate in a commercial carbonizer is determined by the coal feed rate per unit of cross-sectional area, the operating pressure and temperature, and the fluidizing velocity (usually 0.8-1.5 ft/sec). The designer thus has some latitude in choosing sweep rate. Generally, they will fall in the range of 5 to 15 CF/lb of coal fed. The effect of sweep gas rate on tar yield was therefore studied over the range of 5 to 60 CF/lb.

The effect of sweep gas rate on tar yield from carbonization of untreated coal at 925°F is shown in Figure 2. The retort pressure was held constant at 10 psig throughout this series of runs, and the solids residence times were long enough so that essentially all available tar was evolved (45-120 minutes).

It can be seen that the total tar yield increased with sweep gas rate, particularly at low sweep gas rates. Note, however, that the increased tar is entirely in the +400°C pitch fraction, and the incentive to increase its yield would depend upon an economic balance between increased value and increased cost. It is clear, therefore, that the major effect of higher sweep gas rates is to aid in the evaporation of high molecular weight pitch molecules. The pitch yield apparently is controlled by saturation of the gas with pitch vapor. On this basis the controlling variable at constant temperature would be the sweep rate as defined above.

Results of two batch carbonization assays are also shown on Figure 1. One is the familiar Fischer Assay in which coal is heated without gas injection in a static retort. The fluidized assay is a method developed by G. P. Curran of our laboratories to assay coals for fluidized carbonization. A 400 gram charge of coal or coal diluted with coke is fluidized in a 2-inch diameter retort at 0.3 ft/sec with nitrogen. Both assays heat to a final temperature of 932°F (500°C) and the heating rates over the last 80°F are similar (4°F/min.). It will be noted that these two assays represent opposite extremes in sweep gas rate. Thus, the difference between them must be a measure of the effect of increased sweep gas rate for batch carbonization. The fluidized assay gives about 24 percent higher tar yield than the Fischer Assay (18.2 vs. 14.7%) with this coal. The tar yield from the continuous unit is, however, 42% higher than the fluidized assay yield (25.9 vs. 18.2%). This represents the effect of rapid heating in the continuous unit. It is obvious, moreover, that the increase due to rapid heating is also some function of sweep gas rate since the upper curve as it approaches zero sweep rate will fall considerably below the Fischer Assay value plus 42 percent. The ratio of yield in continuous carbonization to that from batch Fluidized Assay varies with the coal used. Table 4 shows that for coals from the same seam this effect is small, but much larger variations can be expected from widely different coals. (11b)

It is interesting to note that Peters (11b) reported about the same tar yield at 1112°F (600°C) in the Lurgi-Ruhrgas unit with no sweep gas as was obtained here at 925°F (496°C) at high sweep rates. Although different coals were used, they had the same Fischer Assay values.

Figure 3 shows the effect of sweep gas rate on tar yield from a coal which was preoxidized before carbonization. Preoxidation and carbonization were conducted separately to provide accurate balances, but the tar yields shown are the sums for both steps. The sweep rate is slightly distorted since preoxidation products did not pass through the carbonizer, but the effect is very minor since the preoxidation tar yield is less than 2 percent absolute.

The effect of sweep rate on tar yield is less pronounced with the preoxidized coal, due to the lower tar yield. Note that the percentage yield loss in the case of distillate is considerably less than the loss in the pitch fraction.

The decrease in tar yield with extent of preoxidation is illustrated in Figure 4. The shape of this curve is typical, but the extent of loss of tar varies widely with the coal used, the preoxidation temperature and residence time, coal size and oxygen partial pressure as well as sweep rate. The amount of preoxidation required to result in an operable carbonizer also varies greatly with the feed coal—for Montour 10 coal it is approximately 4 percent for an unstirred fluidized carbonizer. The fact that preoxidation decreases tar yield has been reported previously (3, 5, 7, 14), but it is difficult to find such a curve as Figure 4. It should be noted that the tar yield of 19.3% at zero oxidation takes into account the reduction in tar yield due to thermal treatment at 725°F without added oxygen. With no pretreatment at 725°F, the yield at this sweep rate is 22 percent as shown in Figure 2.

Also shown in Figure 4 is the result of a run with Montour 10 coal in the pilot plant operating at 1.5 tons/hour feed rate. The point falls below the line for the 6-inch unit since the pilot plant was carbonizing at 900°F instead of 925°F. This and later work with other coals confirm that the 6-inch stirred unit gives a reliable assay of tar yields when sweep gas rates are equal.

TABLE 1
TYPICAL COAL PROPERTIES

Source:	Montour No. 10 Mine Library, Pa.	Arkwright Mine Morgantown, W. Va.
<u>Proximate Analysis (MF)</u>		
Volatile Matter	38.70	38.26
Fixed Carbon	56.00	53.69
Ash	5.30	8.05
<u>Ultimate Analysis</u>		
Hydrogen	5.31	5.17
Carbon	78.96	77.29
Nitrogen	1.60	1.55
Oxygen (By Diff.)	7.57	5.29
Sulfur	1.26	2.65
BTU/LB (Gross)	13,900	14,000

TABLE 2
EFFECT OF AIR INJECTION POINT ON TAR YIELD

Results of a Number of Runs with 5.8 to 6.1% Oxygen Consumed and Carbonized at 925°F with Sweep Gas Rate of 10.5 CF/LB MAF Coal

	Loss of Tar Yield, Lb. Tar/Lb. Oxygen
<u>With Preoxidation</u>	
at 725°F, 1 hr. residence time.	
Loss due to preoxidation.	1.0*
<u>Without Preoxidation</u>	
Air and Coal Enter Carbonizer Together	1.2
Air Enters Above Bed - Sees Vapors Only	0.94
Air Enters Bed Above Coal Feed Point	0.36
Air Enters Bed 4" Below Coal Feed Point	0.0

*With preoxidation, there is a loss due to thermal treatment at 725°F in addition to the loss due to oxidation.

TABLE 3
EFFECT OF VAPOR RESIDENCE TIME ON TAR YIELD AT 925°F.

Run Number	Vapor Residence Time, Seconds			Solids Residence Time (Min.)	Sweep Gas CF/LB MAF	Tar Yield Wt. % of MAF Coal
	In Bed	Above Bed	Total			
29	3	19	22	121	28	25.1
14	7	45	52	44.5	26	24.9
17	5	34	39	58	15	22.7
16	11	73	84	127	14	23.2

TABLE 4
RATIO OF TAR YIELDS FOR DIFFERENT PITTSBURGH SEAM COALS
AT 925°F.

Coal	Continuous Unit		Fluid Assay Tar Yield Wt. % MAF Coal	Yield Ratio Continuous Assay
	Sweep Rate CF/LB MAF	Tar Yield Wt. % MAF Coal		
Montour 10 Mine	28	25.1	18.2	1.38
Arkwright Mine	27	26.2	20.7	1.27

Effect of Carbonizer Air on Tar Yield

The 6-inch stirred unit with its flexibility and accurate material balances proved to be useful for a study of where the carbonizer air should be added for maximum tar yield. Tar yields were determined for runs in which the air was injected: (1) directly above the porous support plate, (2) 4 inches higher, entering with the coal, (3) in the upper part of the bed, and (4) above the bed where it contacted tar vapors only. The results of these runs feeding untreated coal to 925°F carbonization are compared in Table 2 with normal preoxidation plus carbonization with no additional air. All runs consumed approximately 6% oxygen with carbonization at a sweep gas rate of 10.6 CF/lb.

When preoxidation is conducted within the plastic range of the coal, there is a decrease in tar producing molecules due to thermal reactions in addition to the effect of oxygen. The thermal effect varies with temperature and residence time and can be as much as that produced by the oxidation. The loss due to oxygen alone is about 1 lb. tar/lb. oxygen consumed.

The loss due to preoxidation is similar to that obtained in direct carbonization of untreated coal with oxygen injected with the coal. This loss is apparently due to reaction of oxygen with tar or tar producing molecules since injection of oxygen above the carbonizer bed results in approximately the same tar loss. The decreased tar yield when the air is injected into the carbonizer along with the coal has been reported by several investigators. (2, 6)

When oxygen is introduced into the carbonizer bed at some distance above the coal feed point, the loss of tar is considerably reduced. This confirms the report by Lang, et al. (7) that oxygen preferentially attacks char rather than tar vapors where both are present. The best situation occurs where the oxygen is introduced sufficiently below the coal feed point to be largely consumed before it encounters tar vapors. In this stirred unit tar loss was reduced to zero when oxygen was injected four inches below the coal feed point. In a normal fluidized bed with its greater degree of solids and gas backmixing, tar loss is not reduced so completely unless baffles are used to promote it.

Vapor Residence Time

A few runs showing the effect of vapor residence time on tar yield at 925°F are shown in Table 3. Separate control could not be effected over solids and vapor residence times. Work not reported here, however, showed that tar yields were independent of solids residence time within the range given in Table 3. The first two runs shown, at a sweep rate of 27 CF/lb show similar tar yields even though the total residence time of tar vapors varied from 22 to 52 seconds. Similarly the last two runs at a sweep rate of about 14 SCF/lb show similar tar yields with residence times of 39 and 84 seconds. Since commercial vapor residence times would be less, one can be confident that there would be no influence on tar yield at 925°F.

Other work has shown that vapor residence time in the stirred carbonizer can reduce tar yield at higher temperatures. The maximum tar yield from this unit is therefore obtained in the range of 900-950°F. In the Lurgi-Ruhrgas unit where very short residence times prevail, the maximum tar yield is achieved at temperatures as high as 1150-1220°F. (11)

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