

CARBONIZATION REACTIONS IN THE GRAND FORKS  
FIXED-BED SLAGGING GASIFIER

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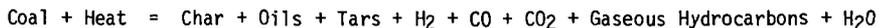
A coal gasification pilot plant using a fixed-bed slagging gasifier is being operated at the Grand Forks Energy Research Center of the U.S. Department of Energy. The gasifier has a nominal maximum coal feed rate of 1 ton/hour and operates at pressures to 400 psig. Current gasification studies have focused on Western lignite and subbituminous coals; plant modifications are underway to extend operating capability to Eastern caking coals.

The slagging gasification pilot plant was installed during 1958-59, when GFERC was a part of the U.S. Bureau of Mines. The original program was conducted through 1965, to determine operability and maximum capacity. Details of the construction of the gasifier and test results obtained during the 1958-65 period have been reported (1). Operation of the pilot plant was resumed in 1976, and these later results have been reported by Ellman and co-workers (2).

A cross-sectional view of the gasifier is shown in Figure 1. The reactor chamber is about 16-1/2 inches in diameter and has a maximum fuel bed depth of approximately 15 feet. The test coal (nominally sized 3/4 x 1/4 inch) flows by gravity from the coal lock into the gasifier shaft. As the coal descends, drying and devolatilization is accomplished by the countercurrent flow of hot gases from the gasification reactions in the lower section of the gasifier. Gasification occurs at temperatures of 2800-3100° F and is sustained by an oxygen-steam mixture injected through four tuyeres at the bottom of the fuel bed. During the gasification reaction the coal is completely consumed, leaving only the molten ash. The molten ash (slag) drains continuously through a taphole into a water quench bath.

As the coal descends through the gasifier, various reactions occur. A previous publication (3) has shown that a slagging fixed-bed gasifier could be thought to consist of four reaction zones at steady state operation, as shown in Figure 2. This figure is an idealized example, since in actual practice the locations and relative lengths of the indicated zones will vary and overlap depending on the operating conditions and the characteristics of the coal being gasified. Similar conceptual schemes have been given for other gasifiers (4,5).

In the drying zone the incoming coal is heated by the ascending gases to the temperature at which the moisture in the coal is vaporized. After being dried, the coal descends through the devolatilization zone where the tars and oils are vaporized and some product gas is formed. The reaction



indicates the changes taking place in this zone. The devolatilized coal (char) then enters a zone in which little carbon is consumed but some gas reactions take place; this has been termed (3) the quasiquiescent zone. Finally, the coal enters the gasification/combustion zone.

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One of the major components of the current GFERC gasification pilot plant program is the sampling, analysis, and characterization of effluents produced during the gasification process. The GFERC effluent program has been treated in extensive detail in a recent publication by Paulson and co-workers (6), which describes sampling and analytical methods, and summarizes results on effluent composition. One aspect of this study is the development of mathematical and conceptual relationships between the effluent characteristics and the gasifier operating conditions and coal type.

From a consideration of the gas and coal tar characteristics, the production of organics in the devolatilization zone can be shown to be very similar to a high-pressure, low-temperature carbonization process. The similarity is important since it is then possible to draw on the extensive literature of coal carbonization to help interpret and understand the factors governing the production of tar and volatiles in the GFERC gasifier.

The product gas from the GFERC gasifier contains small quantities of C<sub>2-4</sub> hydrocarbons; these gases typically being less than 1 pct (by volume) of the total. Analytical methods and production information have been discussed previously by Olson and Schobert (7). Formation of these gases during a carbonization process is considered to be due to thermal cleavage of the peripheral aliphatic and alicyclic portions of the coal "molecule." The relative proportions of the C<sub>2-4</sub> hydrocarbons in the GFERC product gas is compared in Table 1 to gas from carbonization. The data from the three sources has been normalized to a basis of C<sub>2</sub>H<sub>6</sub> = 1. The GFERC data represent average values from two 200 psi pilot plant tests using Baukol-Noonan lignite. Except for ethylene, good agreements exist for the relative quantities of the gases produced.

Gas component	Source		
	GFERC	Reference (8)	Reference (9)
Ethane.....	1.00	1.00	1.00
Propane.....	0.18	0.23	0.35
Butane.....	0.02	0.00	0.10
Ethylene.....	0.74	0.43	0.24
Propylene.....	0.30	0.23	0.23
Butylene.....	0.00	0.07	0.03

Total alkene production decreases with increasing pressure, as suggested (9) for high pressure carbonization processes. Data from pilot plant tests at 125, 200, and 400 psi with Indian Head lignite show alkenes (the sum of ethylene, propylene, and butylene) decreasing from 0.26 + 0.01 pct at 125 psi to 0.23 ± 0.02 pct at 200 psi and then to 0.16 + 0.03 pct at 400 psi.

The aromatization index has been proposed (10) as a convenient method for classifying coal tars. The aromatization index, N, is calculated from the relationship

$$N = C_w/3 H_w$$

C<sub>w</sub> and H<sub>w</sub> are the weight percent of carbon and hydrogen in the tar. Tar samples are obtained both from an end-of-run composite sample and from side stream samplers described in previous publications (2,6). Analyses were done using the classic combustion train method or a Coleman model 33 carbon-hydrogen analyzer. Data from 17 pilot plant tests were used to calculate average values of N for 12 sets of operating conditions.

Coal	Rank	Pressure psi	Oxygen rate scfh	O <sub>2</sub> /Steam ratio	N
Baukol-Noonan	Lignite	200	4,000	1.0	3.20
Do.....	..do.....	200	5,000	1.0	3.25
Do.....	..do.....	400	4,000	1.0	3.27
Indian Head	Lignite	100	4,000	1.0	3.83
Do.....	..do.....	125	4,000	1.0	4.18
Do.....	..do.....	200	4,000	0.9	3.16
Do.....	..do.....	200	4,000	1.0	3.13
Do.....	..do.....	400	4,000	1.0	3.26
Do.....	..do.....	400	6,000	1.0	3.25
Kemmerer	Subbituminous	200	4,000	1.0	2.97
Rosebud	Subbituminous	200	4,000	1.1	3.18
Do.....	..do.....	200	5,000	1.1	3.19

Nine of the 12 values are between 3.13-3.27 and a tenth is 2.97. This agrees reasonably well with a value of 3.05 suggested by Jurkiewicz et al (11) for low temperature carbonization tar from European brown coals.

Increasing pressure has been shown (9) to decrease the concentration of phenol and increase the concentration of high molecular weight aromatics in carbonization tar. Coal tar composition is determined at GFERC by mass spectrometry. For two pilot plant tests at 200 psi the average phenol content of the tar was 18.4 pct; for two other tests in which only the pressure was changed -- to 400 psi -- the phenol content averaged 13.0 pct. The lignite gasified in these tests was Indian Head.

The effect of pressure on the formation of higher molecular weight compounds in the tar was evaluated for five compounds: fluorene, phenanthrene, pyrene, chrysene, and benzopyrene. The same pilot plant data used to determine the effect of pressure on phenol concentration was also used for this comparison. Results are summarized as follows:

Tar component	Gasification pressure, pct	
	200 psi	400 psi
Fluorene.....	3.4	4.0
Phenanthrene.....	3.0	4.6
Pyrene.....	2.0	2.8
Chrysene.....	2.1	2.1
Benzopyrene.....	2.4	2.2

The quantities of three of the five compounds agree well with the high pressure carbonization model (9), in that the amount of these compounds increased with increasing pressure.

Increasing residence time in the reactor should decrease the yield of tar (9). Two mechanisms are available for changing residence time in the GFERC gasifier. At constant pressure, an increase in the oxygen-steam feed rate will decrease residence time; at identical oxygen-steam rates, increasing operating pressure will increase residence time. Previously published GFERC data (6) show that at 400 psi, tar production at a 6,000 scfh oxygen rate is 71.9 lb/ton maf lignite. Tar production drops to 55.5 lb/ton maf lignite at an oxygen feed rate of 4,000 scfh. At an oxygen rate of 4,000 scfh, tar production, decreases 92.4 lb/ton maf lignite in 100 psi tests to 70.1 at 200 psi and to 55.5 at 400 psi. These results were from tests using Indian Head lignite at a 1.0 oxygen/steam mole ratio.

VanKrevelen and Schuyer (12) provide a detailed kinetic treatment of carbonization processes. Production of char (or devolatilized lignite in the quasi-quiescent zone before gasification/combustion zone) can be determined for the slagging gasifier by sampling the bed after shutdown. Char sampling and analysis have been discussed previously (3). Using data from a 200 psi run, at 4000 scfh oxygen rate and 1.0 oxygen/steam mole ratio with Indian Head lignite, the first-order rate constant for char production was calculated to be  $0.014 \text{ min}^{-1}$ . The amount of volatile material produced was determined by summing the gaseous hydrocarbon, tar, and aqueous organic material. The first-order rate constant calculated for volatile production for the same run is  $0.011 \text{ min}^{-1}$ . The good agreement of the two rate constants suggests that the char and volatiles are indeed being produced in a reaction following VanKrevelen's kinetic model of a carbonization process.

The agreement of GFERC pilot plant data on gas, tar, char production with carbonization models shows that it is possible to regard the devolatilization zone in the gasifier as a region of typical coal carbonization reactions. As research continues at GFERC further understanding of devolatilization in the gasifier can be derived from carbonization models.

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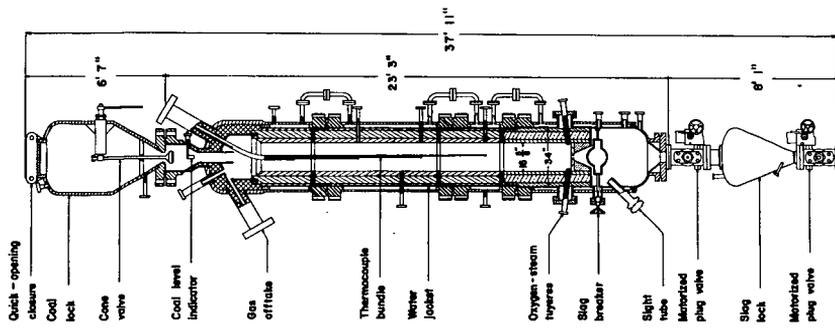


Figure 1

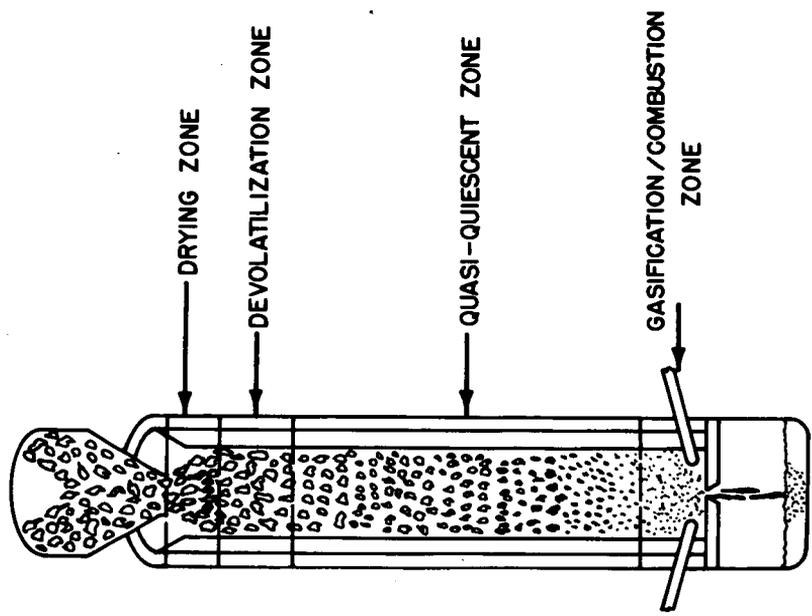


Figure 2