Devolatilization and Tar Production in a Bituminous Lump Coal

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INTRODUCTION

The devolatilization of coal in a fixed-bed gasifier is accompanied by the production of heavy liquid by-products (tars). To avoid the fouling of downstream equipment, these tars are condensed by scrubbing the hot raw gases with an aqueous liquor. This scrubbing and the subsequent aqueous/organic separations have several disadvantages: Heat recovery from the raw product gases is difficult, large quantities of phenolic wastes are generated, and the required chemical plant is complex, labor-intensive, and prone to operational problems. Scrubbing also precludes any benefits that might accrue from high-temperature desulfurization, for which processes are now being developed. The tars are difficult to market because of their complexity, variability, and solids content, and their production results in a loss of gas generation per tonne of coal.

Incentives therefore exist for changes in the design or operation of the gasifier that would reduce or eliminate tar production while still maintaining the basic features and advantages of the fixed-bed configuration. Such changes would require a clear understanding of the processes taking place within the devolatilization zone and, in particular, the conditions favoring tar production. Information on lump coal devolatilization also becomes more important as interest increases in the fixed-bed gasification of high-volatile and highly caking coals.

Little systematic information is available for tar production from fixed-bed gasifiers (Nakles, 1978; Desai and Wen, 1978). This is partly because the observed tar yield is the result of two overlapping effects within the gasifier: devolatilization within individual lumps and secondary reactivity of the volatiles after they have left the lump surface. Moreover, the focus of recent devolatilization research has primarily been on smaller particles, in which the chemical reaction process dominates (e.g., Anthony and Howard, 1976), rather than on lump coal in which physical processes are important. Few experimental data are available on the devolatilization of individual lumps under controlled conditions comparable to those in a fixed-bed gasifier. Early et al. (1980) heated a small number of lumps under simulated gasifier exit conditions, as part of the development of the Riley-Morgan fixed-bed gasifier. They examined the product coke as a function of gas temperature but did not collect the tars. Lurgi has apparently carried out similar tests (Rudolph, 1977), but no details have been published.

This paper summarizes experimental work on a captive-sample devolatilizer for lump coals that permits the quantitative recovery of tars. Data are presented for a highly caking Pittsburgh No. 8 coal (PSOC-1099), whose characteristics are given in Table 1. Complete details of this work can be found in Kalson (1981).

Although the original incentive for this work was the desire to *reduce* liquid production in a fixed-bed gasifier, the experimental approach may be equally useful for the solution of the converse problem, that is, that of *increasing* liquids production in processes for partial liquefaction by pyrolysis.

TABLE 1. MEASURED AND ESTIMATED PROPERTIES OF THE TEST COAL

Rank: High-volatile A bituminous
Source: Pittsburgh seam (PSOC-1099).

Measured Properties		Estimated Properties	
Proximate analysis		Thermogravimetric data	
(as-received basis)		(Kirov and Stephens, 1967)	
Moisture	1.77%	Initial decomposition	678 K
Ash	11.15%	Maximum decomposition rate	733 K
Volatile matter	33.65%	Completion primary devolatilization	803 K
Fixed carbon	54.45%	Rheological temperatures	
Carbon:	73.02% (83.9% maf)	(van Krevelen, in Jasienko, 1978)	
Hydrogen:	4.94%	Softening	613–638 K
Nitrogen:	1.34%	Start of swelling	688 K
Cal. value:	30,383 kJ/kg	Maximum fluidity	713 K
Free swelling index:	8	End of swelling	728 K
		Resolidification	733–748 K

Fixed-bed gasification tar yield: 2.4 MPa—4.0% tar, 1.4% light oil (Woodall-Duckham, 1974). 100 kPa—total tar/oil yield 6–9%.

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EXPERIMENT

Design Basis and Experimental Conditions

Design and operation of the experimental devolatilizer were governed by conditions within the upper zone of a full-scale, single-stage, fixed-bed gasifier. The exit gas temperature in such a gasifier, typically 811 K (1000°F), is above the plastic range of temperatures; the coal was thus subjected to a step change in temperature in the experimental devolatilizer. The data reported here cover a range of gas (exposure) temperatures of 703–823 K. The sample was a single lump, 15 g in weight and 2.75 cm in diameter. The data reported here were taken at 100 kPa (14.7 psia), although the design pressure of the apparatus was 1.7 MPa. At low pressures, the composition of the gas surrounding the coal has little effect on the devolatilization (Russel et al., 1979; Kalson, 1981); hence nitrogen was chosen in place of a synthetic gasification gas. Maximum superficial velocities reported for atmospheric air-fed gasifiers are approximately 1.4 m/s; the data reported here were taken at 0.28 and 2.4 m/s. Temperatures downstream of the sample were equal to or less than the sample temperature, and residence times were from 0.2 to 1.5 s; under these conditions, tar reactivity is negligible (Hesp and Waters, 1970; Serio et al., 1983).

Apparatus

The devolatilizer consisted of 5.25 cm I.D. (2-in. Schedule 40) stainless steel pipe. The coal sample was held in a 4.1-cm O.D. basket, made from 0.165 cm aperture stainless steel screen. The basket was suspended on a chain that was raised or lowered within the devolatilizer pipe by means of an electrically controlled winch. The winch resided in a cooled chamber above the devolatilizer pipe. Between the chamber and the inlet for the hot gas was a short spool section whose removal permitted insertion and removal of samples between runs.

The sample was heated by radiation from the hot walls and by convection from hot gas passing in downflow over the sample. The gas passed over the sample, picking up coal volatiles, then passed through a cooling coil immersed in an ice-water bath and was subsequently vented. The heavy liquid tars condensed in the cooling coil and were later washed from the coil by a solvent. Thus, tars are defined as those liquids that condense at the melting point of ice, as in low-temperature carbonization assay procedures (Goodman et al., 1953).

Pressure and gas flow within the devolatilizer were governed by regulating valves upstream of the devolatilizer and downstream of the cooling coils. Temperature, pressure, and flow were measured at various points thoughout the apparatus.

Operating Procedure

Upon achieving the desired temperature and flow conditions, a basket and coal sample were weighed. The flow was shut off, the apparatus opened, and the basket affixed to the end of the winch chain. The apparatus was then reclosed, and the flow reestablished. After the temperatures had again settled, the winch was activated to lower the sample basket into the hot devolatilizer pipe. Upon insertion of the cold sample, the wall temperature near the sample dipped about 10°C, but recovered to its original value within about 2 min. The progress of the devolatilization was observed through a sight glass. After passage of the desired devolatilization time, typically 20 min, the sample was raised, the flow stopped, and the sample basket removed. The coke-filled basket was reweighed with minimal delay so as to reduce the uptake of moisture from the air.

Tar Determination

For washing the tars from the coil, a strong solvent for these tars was chosen. Commercial tetrahydrofuran (THF), which had previously been distilled under nitrogen to remove its nonvolatile stabilizer, was poured into the coil. By a small nitrogen pressure, the solvent was then expelled as a brown-colored effluent into a collection jar. To remove the last traces of tar, the procedure was repeated, resulting in a total solvent volume of about 1000 cm^3.

The tar solution was passed through a coarse filter paper to remove any solids. Most of the THF was then removed by distillation under nitrogen; the last traces of solvent were removed by evaporation for 24 h in a ventilated hood. The recovered tar was weighed.

Reproducibility and Sources of Variability

Random variations in tar production may result from petrographic heterogeneity, from variations in sample shape between coal samples, or from minor random variations in run temperature between nominally identical runs. On occasion, a sample was found that exhibited unusually high or low swelling or tar yeild, due to unusual petrography, or to the inclusion of large chunks of mineral matter.

Systematic errors in the measurement of tar production due to incomplete collection of the tars within the coil, loss of tars during the tar determination, and incomplete solvent removal were all minimized by maintenance of appropriate temperature between the sample and the cooling coil and by control of the tar determination procedures.

The reproducibility of the experiment was demonstrated by a series of five runs under nominally identical conditions, performed early in the experimental program. The mean tar yield was 9.1% and the unbiased estimate of the standard deviation was 1.2% or 13% of the mean tar yield.

RESULTS AND DISCUSSION

Total Product Yields

The total yields of coke and tar over a period of 20 min were measured at 100 kPa and a superficial velocity of 0.28 m/s. Coke and tar weights were measured directly, and total volatiles were calculated from the difference between the dmmf coal and coke weights. The difference between tar and volatiles was attributed to gas production.

Results from a series of experiments over the range of 724 to 831 K are shown in Figure 1. With one exception (indicated by a triangle), each point represents the collective tars from two separate devolatilizations. The exceptional point represents a single coal sample that exhibited unusually low swelling, probably due to a

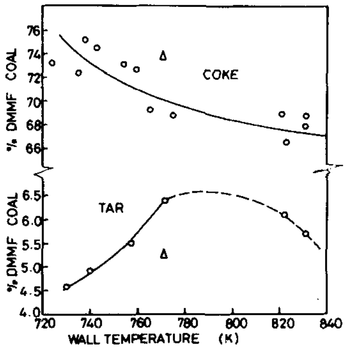

Figure 1. The effect of temperature on coke and tar yields.

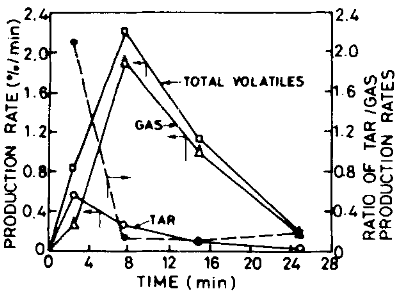

Figure 2. Production rates vs. time.

large mineral inclusion. The coke yield decreases with increasing temperature. Assuming a reproducibility of 13% in tar yield, as noted earlier, there is a statistically significant increase in tar yeild over the first portion of the temperature range. The tar yield thus achieves a maximum value at about 780 K. Within experimental error, other curves indicating a constant or decreasing tar yield could have been drawn over the second portion of the temperature range. The tar yield would be expected to decline to negligible values at lower temperatures, as well as at sufficiently high temperatures with the onset of tar destruction reactions on the coal surface.

Product Distribution as a Function of Time

Several samples were devolatilized under identical conditions but for various periods of time. The average yields of tar, coke, and, by difference, gas obtained over various time intervals are plotted in Figure 2.

Tar production peaks soon after the lump is introduced into the hot environment and falls gradually thereafter. Gas production peaks somewhat later. That the tar and gas production peaks are distinguishable suggests that the holdup of volatiles within the lump is not so great as to mask the difference in timing. The implication for modeling is that the first Damkohler number (the ratio of rates of reaction and bulk flow) is small. The ratio of tar production to gas production dropped from a high initial value (over 2) to a value of 0.1–0.2, which prevailed over the major portion of the devolatilization. The maximum gaseous production rate is approximately 2 wt%/min or 1 $cm^3/g{\cdot}s$.

The maximum efflux took place over the period between 5 and 10 min after the start of the test, during which the average efflux velocity, assuming uniform efflux over the lump surface, was 0.67 cm/s. This is only an order of magnitude smaller than the surface velocity estimated by Suuberg (1977) for particles smaller by several orders of magnitude. Over this same time period, the average Peclet number, $Pe(h) = (u\rho c_p \lambda)_g/R_p$ was 0.18. Murty (1969) also found values for $Pe(h)$ in wood pyrolysis that were mainly fractional. Physical argument suggests that a Peclet ratio of the order of unity is a maximum, obtainable when all the heat transferred is balanced by that leaving in the product gases; reaction heat and the sensible heating of the solid are small. In the absence of data, therefore, an upper limit for the devolatilization rate might be estimated by assuming a Peclet ratio of unity or, more precisely, of the order of the fractional volatiles yield, here, 0.25. More data are required to test this theory. In any case, for the Biot and Peclet ratio conditions of these lump-heating experiments, the reduction in convective heat transfer due to volatiles efflux is negligible (Kalson, 1981).

The Effect of Gas Velocity on the Tar Yield

An increase in the gas velocity from 0.28 to 2.4 m/s increased the tar yield from 9.1 to 13.3%. A decrease in coke yield from 76.2 to 72.8% accounted for the major portion (76.2–72.8)/(13.3–9.1), or 81% of the difference; only 19% of the difference was attributable to a decrease in gas yield. As noted earlier, and as confirmed experimentally, downstream cracking is negligible for the conditions of these tests; the effect of increased velocity cannot be through decreased residence time for downstream cracking. Furthermore, since the decrease in tar yield at low velocities goes largely to coke, the dominant process must be one that takes place within the lump rather than beyond it.

Nor can the observed effect be due to heat transfer. For a lump concurrently devolatilizing and rising in temperature, an increase in external heat transfer coefficient due to increased velocity shifts the peak reaction rate to higher temperatures (Juntgen and van Heek, 1970). Given the expected relative temperature sensitivities of tar distillation and tar destruction, a decrease rather than an increase in tar yield would be expected. In any case, the overall heating rate of the lump is dominated by the internal resistance (Kalson, 1981), and the effect of external velocity should therefore be small.

The effect of velocity on tar yield must therefore be due to an increased rate of removal from the lump surface, either through an increase in the mass transfer coefficient, hence greater distillation, or through increased shearing of liquids from the surface. The former is most likely, as tar distillation is the dominant process for tar removal (Unger and Suuberg, 1983).

Secondary Tar Reactivity

The velocity variation data also reveal an important feature of secondary reactivity. The tar destruction reaction is primarily one of polymerization to coke, with little gas production. Taking hydrogen contents of the char, liquid, and gas of 3.6% (Lowry et al., 1942), 6% (Woodall-Duckham, 1974), and 0.13–0.19% (Yancey et al., 1932, coal #28), mass balance on hydrogen dictates a gas yield in the range of 16–26% of the tar. This agrees well with the experimental value of 19%.

General Reaction Pattern

Approximately 1.5 min after insertion of the sample, wetting of the surface with tars was observed on edges and protrusions near the top of the lump where heat transfer was greatest. The plasticized area gradually increased until the whole surface was affected. When sufficient plasticity occurred, the lump, originally placed tightly in the mesh near the top of the basket, would slide down into the basket.

Swelling took place as a flowering of portions of the structure, rather than as a uniform expansion. The lump was free to swell along the length of the basket, but was partially constrained radially by the double layer of mesh forming the basket. The tars typically oozed through the basket in several places. As the devolatilization proceeded, the surface resolidified, first at the top, then on the lower portions of the lump, following the order of plasticization. Most of the swelling took place between 5 and 10 min into the devolatilization, which was also the period of highest gas production.

At an exposure temperature of 763 K, i.e., slightly above the plastic range, the lump swelled and formed a coke uniformly composed of large cells. When the exposure temperature was much higher than the plastic range (823 K), the lump swelled less, and a distinct two-zone structure was exhibited by the coke: a hard, dense outer layer 0.8 cm in width, surrounding an open cellular core approximately 2 cm across. Simple heat transfer calculations suggest that the surface resolidified before significant devolatilization of the interior had taken place (Kalson, 1981). Less swelling was also observed when the exposure temperature was 723 K, i.e., within the plastic range.

SUMMARY

An apparatus was built for step-heating single lumps of coal, and for quantitative collection of the tars produced. Tar yields were obtained for a highly caking bituminous coal. Experiments of this type can be used to determine the ratio of tar to gas production, the sensitivity to parameters such as temperature and velocity, and the general reaction pattern. Information can also be derived concerning the nature of the tar destruction reaction and the relative importance of various physical and chemical processes. Such information should be of use in addressing the problem of tar production in fixed-bed gasifiers, in the development of more realistic fixed-bed gasifier models, and in the extension of fixed-bed gasification to highly caking tar-producing coals. The heating of lump coal in an apparatus such as this may also be useful in assessing the behavior of coals in processes designed for the production of coal liquids by pyrolysis.

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NOTATION

c_p = heat capacity at constant pressure
dmmf = dry mineral-matter-free basis
maf = moisture- and ash-free basis
$Pe(h)$ = Peclet ratio for heat transfer
R_p = particle (lump) radius
u = velocity
λ = thermal conductivity
ρ = density

Subscript

g = gas

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