Coal Gasification

Lester G. Massey

ADVANCES IN CHEMISTRY SERIES

131

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Lester G. Massey, *Editor*

A symposium sponsored by
the Division of Fuel
Chemistry at the 165th
Meeting of the
American Chemical Society
Dallas, Texas,
April 9-10, 1973.

ADVANCES IN CHEMISTRY SERIES **131**

AMERICAN CHEMICAL SOCIETY
WASHINGTON, D. C. 1974

ADCSAJ 131 1-266 (1974)

Library of Congress Catalog Card 74-78009

ISBN 8412-0195-1

PRINTED IN THE UNITED STATES OF AMERICA

Advances in Chemistry Series

Robert F. Gould, *Editor*

FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

Until recently, interest in coal and other hydrocarbon gasification in the United States was limited mostly to a few technically trained people in a few research departments and institutions, and to the U. S. Department of the Interior's Bureau of Mines and Office of Coal Research. Projections of serious shortages of natural gas and other forms of energy during the 1950's and 1960's failed to spawn a positive response from the public and business communities. Even at this writing, in the face of severe fuel oil shortages and with the threat of gasoline rationing, many people believe the "energy crisis" to be fabricated and controlled by oil and natural gas interests.

Although the Arab oil embargo of 1973 sharpened the focus of public attention on the general energy situation of the United States, the energy problem was destined to be recognized. The United States is running out of reserves of oil and gas while it has enormous reserves of coal and oil shale. Undoubtedly we must turn to these solid fossil fuels as a major source of non-polluting energy while developing geothermal, solar, and nuclear forms of energy.

Evidence has emerged in the last two years to show an acute awareness of the need for clean gaseous fuels from coal on the part of the gas, petroleum, and electric power industries and on the part of the governments. A good example is the $120 million process development program sponsored jointly by the American Gas Association and the U.S. Department of the Interior's Office of Coal Research. Its goal is to have adequate information by 1976 to design and construct a coal gasification demonstration plant. Other large scale efforts are being launched by private companies and by new U.S. Government proposals for energy research, development, and, ultimately, demonstration plants.

Such extensive change in public and private attitudes toward energy and its efficient use is reflected in the scientific and technological communities where a much expanded and intense interest has developed rapidly. This is easily observed and, to a certain extent measured, by strongly increasing attendance at coal gasification symposia and the increasing volume of pertinent technical literature.

The need for fundamental information such as reaction mechanisms, catalysis, and kinetics and for new approaches such as the plasma arc for gasification studies has been clearly established. In partial satisfaction of this need, this volume presents 14 papers by distinguished authors, all aimed at providing fundamental scientific information of permanent value in the arduous search for substitute natural gas from coal.

L. G. MASSEY

Cleveland, Ohio
December 1973

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Devolatilization of Coal by Rapid Heating

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Coals were devolatilized at rates comparable with those encountered in combustion and gasification processes. Rapid pyrolysis was attained with pulse-heating equipment developed for this purpose. This technique permitted control of the heating time and the final temperature of the coal samples. Subbituminous A to low volatile bituminous coals were studied. All bituminous coals exhibited devolatilization curves which were characteristically similar, but devolatilization curves of subbituminous A coal differed markedly. The products of devolatilization were gases, condensable material or tar, and residual char. Mass spectrometric analysis showed the gas to consist principally of H_2, CH_4, *and CO. Higher hydrocarbons, up to* C_6, *were present in small quantities.*

Coal has been used mainly for the generation of electric power. Now that there are critical shortages of natural gas for residential heating and industrial use, industry and government are developing processes for gasifying coal (*1*, *2*). When these processes are fully developed, the will represent a second major outlet for coal utilization.

In both combustion and gasification, coal is heated to elevated temperatures therefore sustaining some degree of decomposition prior to or concurrently with other chemical reactions. In the Synthane process of the Bureau of Mines (*3*, *4*), for example, pretreated coal enters the upper, carbonizing section of the gasifier where it undergoes extensive thermal degradation to form char. The reaction products formed at this stage in the process make an important contribution to the overall performance of the gasifier. For these reasons, research on the devolatilization of coal by rapid heating has been a part of our program on gasification. The results presented in this paper represent a continuation of preliminary work that was reported earlier (*5*).

Experimental

Single pulses of electrical current provide high-speed heating that is needed to measure the thermophysical properties of solids (metals in particular) (*6, 7*) at elevated temperatures (*8*). This technique, termed pulse heating, was adopted for devolatilizing coal in the present study. Coal samples were decomposed *in vacuo* in order to collect and identify the gaseous products. Quantitative measurements of the resultant weight loss of sample after rapid heating served as a measure of the total volatiles evolved from the coal.

The reaction vessel was essentially a 29/42-tapered, ground-glass joint sealed to a pumping system. Suitable vacuum gauges, manometers, and gas sampling and storage bulbs were attached to the reactor. Total volume of the reactor, including the sampling bulb, was 418 cm^3. No. 10 copper wires entered the reactor through Kovar-borosilicate glass seals. These copper electrodes terminated in spring clamps which supported the heating element containing the coal sample. Resistive heating elements were made into long, thin cylinders by wrapping 400-mesh stainless steel screen on a mandril. The cylinders were 6 cm long and 1.2 mm in diameter. In preparation for pulsing, the open ends of the cylinder were completely closed, and the flattened ends were inserted into the jaws of the spring clamps.

Current was supplied to the wire-screen heating elements by a current controller. This device was an electronic circuit designed to set the initial current flow at a desired value and to allow the current to increase in a predetermined way. Shaping of the current pulse was necessary to compensate for increase in electrical resistance of the wire and also for radiant heat losses at high temperatures. Typical current values were in the range 15–20 amps. The current controller was triggered by a preselected pulse coming from a General Radio unit-pulse generator, and current flow continued only for the duration of the timing pulse. Pulse times extended from 65 to 155 msec. A 0.1 Ω resistor in the current controller converted the current pulse to a voltage pulse which was displayed on a storage-type oscilloscope. Precise values of current and time were measured from the oscilloscope trace.

Coal samples were prepared by cutting vitrains from lumps of coal. The vitrains were further upgraded by microscopic examination in which coal particles with adhering mineral matter were discarded. Vitrains were chosen for study because they constitute the most abundant and homogeneous component of coal and because they are also low in min-

Table I. Proximate Analyses of Vitrains

		Proximate Analysis, % (mf)		
Coal Source	*Rank*	*Fixed Carbon*	*Volatile Matter*	*Ash*
Pocahontas No. 3, W. Va.	lvb	82.4	16.8	0.8
Lower Kittanning, Pa.	mvb	73.8	25.3	0.9
Pittsburgh, Pa.	hvAb	63.1	35.1	1.8
Colchester Illinois No. 2, Ill.	hvCb	51.1	48.0	0.9
Rock Springs No. 7½, Wyo.	Sub A	61.7	37.7	0.6

eral matter (9). The ash content was less than 2% in the Pittsburgh coal and less than 1% in the other coals used (Table I). A low mineral-matter content in the vitrains was desired to avoid ambiguities in the data from possible pyrolysis of mineral matter. The vitrains were ground to 44–53 μm particle size for the experiments.

Coals were selected to encompass a range of rank and volatile matter. Bituminous coals ranged from hvCb to lvb; one subbituminous coal was also studied. Their proximate analyses are given in Table I.

The temperature attained by the wire-screen heating elements was related to the time of current flow by a calibration method. Times required to melt pure metal powders of like particle size and amounts as the coal were determined by trial and error. A number of calibration points were thus established, and the temperature at the end of the current pulse was proportional to the time of current flow in the region to 1450°C. The heating rate was therefore a constant 8250°C/sec.

A new (unheated) screen cylinder containing no coal was pulsed to 900°C in the reactor which had previously been evacuated. Prefiring of the screen cylinders is essential because they undergo significant weight losses when they are heated for the first time. Such losses would interfere with measurements made on the coals. However, after the initial heating of a screen cylinder, its weight remains demonstrably constant in further tests. A prefired screen was weighed precisely on a Cahn RG microbalance, approximately 250 μg of coal was inserted into the cylinder, and the combined weight of the screen cylinder and coal sample was again determined precisely on the balance. The weighed coal sample and heating element were placed in the reactor and pumped until the system pressure was reduced to 10^{-3} torr. When this reduced pressure was attained, the coal sample was pulse-heated to a given temperature. After devolatilization occurred, the coal residue and screen were removed from the reactor and reweighed.

The volume of gases generated during devolatilization was determined from the pressure increase in the reactor. Mass spectrometric analyses of the gases were made at many, but not all, of the different test conditions. In this way, the weight of the gases produced by rapid devolatilization of coal was ascertained.

Results and Discussion

The devolatilization behavior of bituminous coals under rapid heating conditions is shown in Figure 1. This figure presents the weight-loss curves of four bituminous coals of different rank over temperatures from 400° to 1150°C. All of the weight-loss curves have a characteristic shape in common, although they differ in detail. For most of the coals the reaction threshold occurs at 400°C, followed by very rapid decomposition to 600°C. Production of volatile reaction products reaches a peak at relatively low temperatures of 700°–900°C, a finding that should be of considerable importance to those engaged in design of coal-gasification equipment. At still higher temperatures the declining trend in the forma-

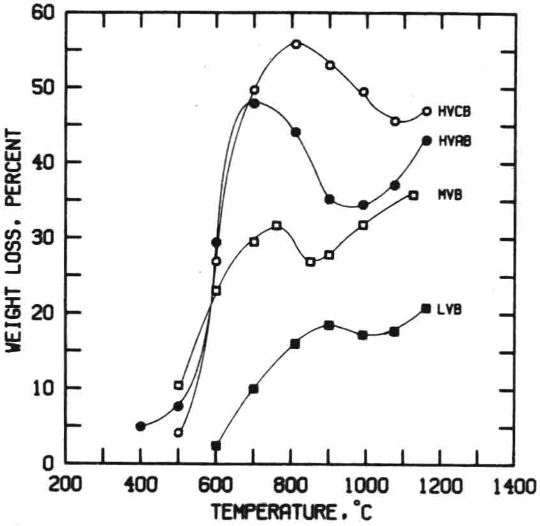

Figure 1. Devolatilization of bituminous coals by rapid heating

tion of volatiles reverses and starts to increase again at the highest temperatures of this study.

Some discussion of the low temperature peak in volatile production from bituminous coals is merited because this phenomenon does not occur during slow heating. In the latter case the weight loss increases monotonically with temperature (*10*). The broadest peak is exhibited by the Illinois hvCb coal which has the highest volatile-matter content of the coals studied (*see* Table I). For the higher rank bituminous coals, the peaks become progressively less intense with increase in rank, and the peak position shifts to higher temperatures. In all instances the volatile yield corresponding to the peak in the weight-loss curves was greater than the volatile matter in the coal determined by the ASTM standard method of analysis. These results are demonstrated by the data in Table II which show that the yield of total volatiles may be increased

Table II. Increased Volatiles from Rapid Pyrolysis

	Volatile Matter Content, %		
Coal Source	*By ASTM Analysis*	*From Peak Weight Loss*	*Increase Factor*
Pocahontas No. 3	16.8	18.5	1.10
Lower Kittanning	25.3	30.8	1.22
Pittsburgh	35.1	47.9	1.36
Colchester Ill. No. 2	48.0	55.8	1.16
Rock Springs No. 7½	37.7	42.4 (plateau)	1.12

as much as 36% by rapid heating. Supportive evidence for increased yields of volatiles is found in other rapid heating studies (*11*, *12*).

Consideration of the cited studies in conjunction with our own leads to the conclusion that the ratio of total volatiles from rapid heating to ASTM volatile content depends not only on the rank of coal, as shown in Table II, but also on the magnitude of the heating rate. One suggested explanation for the appearance of maxima in the weight-loss curves is that of competitive reactions. For example, the bond-breaking reactions that occur in the coal structure and give rise to initial decomposition fragments may well have different temperature dependencies from those of recombination reactions that may form molecules more stable than the parent coal.

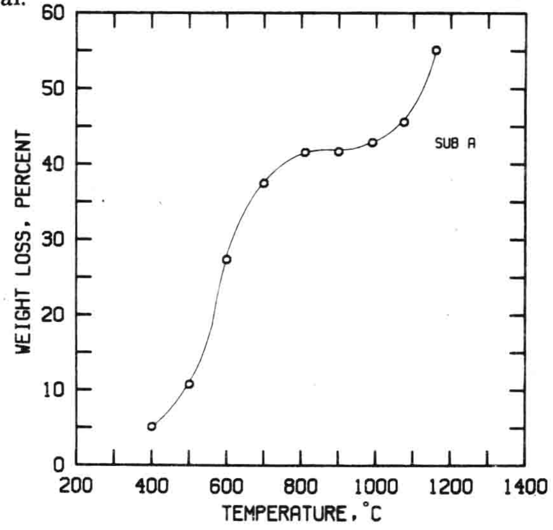

Figure 2. Devolatilization of subbituminous coal by rapid heating

In contrast to the results obtained with bituminous coals, the weight-loss curve of subbituminous coal exhibited no peak; instead, it reached a plateau in Figure 2. From 800° to 1000°C the volatile yield remained level at about 42 wt % of the coal. Beyond this region the production of volatiles increased sharply. The fact that the devolatilization curve of subbituminous A coal differs distinctly from those of bituminous coals indicates a need for further study of other subbituminous coals and lignites. Low rank materials such as these are of interest in coal gasification because their reserves are abundant and because they are situated in deposits with shallow ground cover.

The gases arising from rapid pyrolysis of coal vitrains have been examined by mass spectrometric analysis. The major components in the gas are H_2, CH_4, and CO. Lesser amounts of CO_2 and the higher molecular weight hydrocarbons (up to C_6) are also present. Hydrocarbons are present as both saturates and unsaturates with the notable exception of acetylene. Traces of aromatics such as benzene, toluene, and xylene are found as well as sulfur in the form of H_2S. The absence of acetylene, which has been found in appreciable quantity in some rapid heating processes (*13, 14*), is most likely attributable to the lower temperatures and lower heating rate employed in our experiments.

Temperature profiles of the individual gases from pyrolysis of Pittsburgh vitrain are shown in Figure 3. The molar percentages of CO_2, CH_4, and the C_2–C_4 hydrocarbons decrease with increasing reaction temperature. The functional dependence of H_2 and CO on temperature is more complex. H_2 production starts at 31.5 mole % at 700°C and increases to a maximum of 67.0 mole % at 990°C. Further increase in temperature causes a small but real decrease in its concentration. CO concentration changes in an opposite manner to H_2. A minimum CO value of 12.0 mole % is achieved at about the same temperature at which the maximum H_2 concentration occurred. The gas composition data are given on a H_2O–O_2–N_2-free basis.

In addition to the gases produced by rapid devolatilization of coal, heavier products, referred to as tar, also form. This material condenses on the walls of the reactor and is visible as a brown stain on the glass.

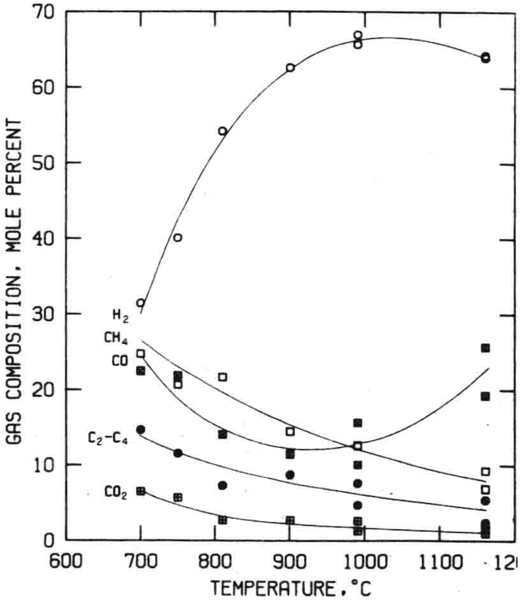

Figure 3. Composition of gas from devolatilization of Pittsburgh hvAb coal

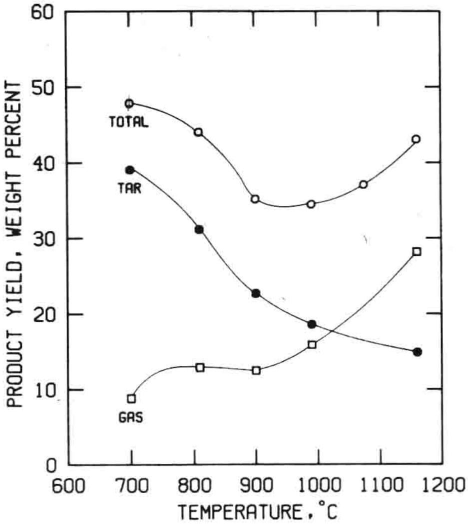

Figure 4. Yields of tar and gas from devolatilization of Pittsburgh hvAb coal

Because the quantity of tar from a single experiment is so small, it has not been measured nor has it been chemically analyzed. However, the quantity of tar can be obtained indirectly by subtracting the weight of the gases from the total volatiles, *i.e.*, the weight loss of the coal. Results of such calculations for Pittsburgh vitrain are shown in Figure 4 in which the experimentally determined curves for total volatiles and for gas have first been drawn. The curve for tar is of course determined by the difference calculation. The curves show that tar formation is favored by low decomposition temperatures and that tar is in fact the main product at all temperatures up to 1000°C. Above 1000°C the amount of gas exceeds the amount of tar even though the total volatile yield is still below the peak yield obtained at 700°C. Further correlations of product yields with rank and temperature parameters have been made and will be published later.

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RECEIVED May 25, 1973.

2

Production of Low Btu Gas Involving Coal Pyrolysis and Gasification

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Experiments involving the pyrolysis of bituminous coal, sawdust, and other carbonaceous feed materials have been performed in a 15-inch diameter, atmospheric, fluidized bed. Data from the pyrolysis experiments are analyzed to generate kinetic and heat-transfer information and to formulate a coal pyrolysis model useful in the design of commercial-sized processes. The model is then applied in forming a conceptual flowscheme for a relatively low pressure (5-13 atm) electrical-power generation plant. In the conceptual flowscheme, the low Btu gas is produced in two units, a pyrolyzer and a pyrolysis-char gasifier. The gas is then purified and fed into a combustion chamber; the electricity is generated in an advanced design gas turbine and steam turbine power cycle.

The demand for electrical power in the United States is predicted to quadruple in the next 20 years, with fossil fuels expected to be the energy source for at least half of this fourfold increase. Coal, because it represents over 95% of the untapped fossil fuel reserves, will certainly serve as the primary domestic energy source for most of these additional power requirements. However, uncontrolled coal burning is a dirty process with solid flyash particulates, sulfur dioxide, and nitrogen oxides as the major pollution culprits (*1*). The combined efforts of industry and government agencies are urgently needed to develop economical, efficient, and environmentally acceptable methods to convert coal into clean electrical power.

In this chapter, we describe a scheme to pyrolyze caking coal in a fluidized bed, present experimental data, devise a pyrolysis-gasification reaction model, and offer a conceptual flowscheme to convert coal to