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CRITICAL STUDIES OF THE RAPID PYROLYSIS AND HYDROPYROLYSIS OF COAL

Quarterly Progress Report for the
Period February 10, 1979 - June 30, 1979

Jack B. Howard, Patrick C. Bigot, Ted W. Bush, Richard Caron,
Raymond Casaprima*, Howard Franklin, Michael A. Serio, Robert M. Steinberg,
Mark Zacharias, and William A. Peters

Energy Laboratory and Department of Chemical Engineering
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

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Critical Studies of the Rapid Pyrolysis and Hydropyrolysis of Coal

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1. Objective and Scope of Work

The objective of this research is to perform systematic studies of the effects of operating conditions on product yields, compositions and rates of formation in three critical areas of the rapid pyrolysis and hydropyrolysis of coal: (1) effects of coal type and of tradeoffs in key operating conditions such as reaction temperature, hydrogen partial pressure, coal particle diameter, (2) the effects of secondary reactions of volatiles within and external to the coal particles; and (3) catalytic effects of the inherent mineral matter of the coal and of low cost additives. Measurements are performed using relatively small scale reactors that permit the effects of controlled, independent variations in reaction conditions of commercial interest to be determined. All reaction products including gases, oils, liquids, tar and char are collected to allow closure of material balances. Specific operating conditions of interest in Areas (1) and (3) include:

total pressure, (0.001 to 100 atm), final temperature (400 to 1100°C), particle size (25 to 1000 μm with a few runs down to 5 μm), heating rate (100 to 30,000°C/s), solids residence time (0.02 to 20 s with a resolution of 0.02 s), gas residence time (for entrained flow conditions only, 0.2 - 3s, with a resolution of 0.1 s), and coal type in Area (3) mainly Pittsburgh No. 8 with some runs on a lower rank coal; in Area (1) Pittsburgh No. 8, Montana lignite and two to three additional coals possibly including Illinois No. 6 and Hiawatha bituminous coals and a lignite from the Texas Arkansas region. Captive sample and entrained flow reactors are used primarily in these measurements. A packed bed tubular flow reactor will also be developed in this program for studies pertinent to Area (2). Operating conditions of interest in this Area include:

temperature 250 - 1000 °C, total pressure mainly (1 to 20 atm with a few runs to 40 atm), heating rate (0.1 to 5°C/s), gas residence time (0.1 to 10 s), with a resolution of 0.02 to 0.1 s), solids residence time (1 s to 30 min, with a resolution of 0.1 s), particle diameter (0.5 to 35 mm) and coal type (probably a coking bituminous coal such as Pittsburgh No. 8 and a modestly or non-coking coal or lignite with relatively high liquid yields such as Texas Lignite). Parametric studies of different gaseous atmospheres and of coal surface area are also of interest. Information pertinent to this area will also be provided by some of the studies in Areas (1) and (3). Correlations and predictive models of pyrolysis and hydropyrolysis behavior are developed from the experimental data.

2. Summary of Progress in this Reporting Period

2.1. Reporting Category No. 1: Effects of Tradeoffs in Operating Conditions

A relatively small level of activity was maintained in this part of the project during the past reporting period. Work focussed primarily on improving the methods of feeding coal and collecting products from the laminar flow reactor. The original feeder was a conveyor-belt type where the coal is dropped off a belt into a vibrating funnel and then sent through the feed tube. However, this feeder gave a pulsating rather than a steady feed rate, which led to occasional plugging of the feed tube and particle agglomeration. The first problem hindered the normal operation of the reactor while the latter obscured to some extent the effect of particle size that was being studied. A new feeder was developed which feeds coal into a thin tube that rests on a spinning disk. This is being tested now and seems to show significant improvements over the older version.

There has also been some activity on improving the product collection system by redesigning the collector probe and the gas trap. When these improvements are optimized to give satisfactory performance, the data collection phase of the program will begin.

2.2. Reporting Category No. 2: Secondary Reactions

Under sponsorship from the Electric Power Research Institute a comprehensive review of the literature on secondary reactions was performed during this reporting period. Emphasis was given to reaction conditions pertinent to three gasifiers of interest to E.P.R.I. for use in combined cycle electric power generation: the British Gas/Lurgi moving bed slagger, the Combustion Engineering atmospheric pressure entrained flow gasifier, and the pressurized Texaco entrained flow gasifier. Our present D.O.E. supported project will benefit greatly from this project which also included a detailed survey of university and industrial experimental facilities capable of providing data on coal devolatilization including secondary reactions under the above mentioned conditions.

2.3. Reporting Category No. 3: Catalysis of Coal Pyrolysis and Hydropyrolysis by Mineral Matter and Low Cost Additives

At the end of the last reporting period some experiments were performed which had indicated that the two asbestos sheets used to insulate the thermocouple wire in the screen might be acting as a local heat sink in some cases, and thus lowering the screen temperature in their vicinity. In an effort to eliminate the need for the asbestos a month was spent investigating other possible thermocouple designs. Attempts were made to coat the base .001" wires with various refractory oxides, either by dipping in pastes or by flame spraying. The wire size, however, defeated all these attempts as it was found impossible to wet the wires, no matter how clean they were. A sheathed, commercially-purchased thermocouple, with exposed junction and .01" diameter sheath was tried, but the bead proved to be too close to the sheath and thus lagged the time screen temperature significantly.

After several similar attempts at new designs a slight modification of the original design was shown to be both the best available choice, and an acceptable solution in terms of absolute accuracy. The asbestos sheets are

retained but the thermocouple is placed on the screen so that the asbestos does not overlay any of the coal sample, and the bead is extended sufficiently far from the asbestos so that it measures the temperature of the coal, rather than the region of the screen covered by the asbestos. Tests showed that this design gave comparable results to that of a bare wire uninsulated thermocouple.

Preparation of coal samples pretreated with minerals was completed in this period. Samples of demineralized coal were impregnated with CaO from solution, or co-slurried with suspensions of quartz, pyrite, kaolinite, shale, montmorillonite, or acid-treated montmorillonite. These, along with the calcite and $FeSO_4$ pretreated coals prepared earlier form the complete suite of treated samples of the Pittsburgh Seam bituminous coal to be investigated in this program.

The remainder of the reporting period was spent obtaining pyrolysis data. Runs were performed on demineralized bituminous coals under 1000 psi H_2 which, on completion, will give base case curves similar to those previously obtained under 1 atm He. Pyrolysis of the calcite and CaO pretreated samples was carried out at 1 atm He, under the test conditions of 700°C zero holding time, and 1000°C, 5 second holding time. While complete calculations have not yet been completed, a definite mineral matter effect was noted in both cases. Tar production was suppressed, light gas yield and ethylene/ethane ratio increased slightly, and there was a multi-fold increase in production of carbon oxides, CO_2 at lower temperatures, shifting to CO at higher temperatures. This effect was more pronounced with the $CaCO_3$ sample than with the CaO sample, the excess carbon oxides in the former case probably originating from calcite decomposition. These results have interesting implications for the modelling of coal pyrolysis, and further study of these minerals will probably be undertaken after test case analysis of the remaining mineral treated samples is completed.

3. Future Plans

3.1. Effects of Tradeoffs in Operating Conditions

Work on routine data collection using the laminar flow reactor will be performed during the next reporting period.

3.2. Secondary Reactions

Most of the work for the next reporting period will involve the design and construction of the packed bed tubular reactor and the associated control and analytical systems. This would be followed by a debugging phase which probably would last until the end of the reporting period.

3.3. Catalysis of Coal Pyrolysis and Hydropyrolysis by Mineral Matter and Low Coat Additives

The next reporting period will be devoted to gathering data on all mineral samples under the test conditions at 1 atm He, completing the data set on demineralized coal curves for 1000 psi H_2, and if time permits, gathering test case data for mineral treated samples under 1000 psi H_2.

4. Acknowledgements

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