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GULF SCIENCE & TECHNOLOGY COMPANY
PITTSBURGH, PENNSYLVANIA

EFFECTS OF COMPONENTS OF SYNFUELS ON SOOT FORMATION

QUARTERLY TECHNICAL PROGRESS REPORT NUMBER 3
REPORTING PERIOD APRIL 1 - JUNE 30, 1981

J. E. HAEBIG (PROJECT MANAGER)
P. M. GOLDBERG

PREPARED FOR THE PITTSBURGH ENERGY TECHNOLOGY CENTER
DEPARTMENT OF ENERGY
UNDER CONTRACT NUMBER DE-AC22-80PC 30307
GULF RESEARCH & DEVELOPMENT COMPANY CONTRACT NUMBER - 625CL101

CHEMICALS AND MINERALS DIVISION
REPORT NUMBER G27RM073
PROJECT NUMBER 727-0901-260
FILE NO. TC03-02-20
AUGUST 1981

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TECHNICAL STATUS

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ABSTRACT

The objective of this project is to obtain information about the relationships between the rate and amount of soot formation in the combustion of coal-derived synfuels and the chemical composition and molecular constituents of those fuels. Simple bench-scale premixed and diffusion burners will be used at pressures between one and ten atmospheres to observe soot formation from fuel samples varying in their boiling range and contents of aromatic and heteroaromatic compounds.

During this reporting period, the Gulf-sponsored development of the experimental system was completed for its use in one atmosphere pressure experiments in this DOE contract. Preparatory accomplishments included assembly of the flow control panel for seven gas streams, initial use of the optical components for laser light scattering, and fabrication and installation of the burner and pressure vessel for it. In the DOE contract activities, Task 1 was completed, the combustion literature was surveyed and used to identify needed features of the experiments to be done, and data on the properties and composition of coal liquids were collected for planning of the slate of coal liquids components to be tested.

1. PROGRAM INTRODUCTION

1.1 Objective

It has generally been concluded that most coal-derived liquids (CDL) have a high tendency to form soot in flames. This has been attributed to their high concentration of aromatics (low hydrogen content) compared to petroleum-derived fuels. It is known that the addition of certain components to petroleum-based fuels can produce a disproportionate effect on sooting behavior. At the present time, there is a lack of similar information about the variation of sooting tendency of CDL with the chemical composition and molecular constituents of these fuels. It is within the scope of this program to generate some of this information.

1.2 Approach

In this project, sooting behavior of CDL will be examined by burning synfuel fractions with known compositions or carefully controlled properties such as boiling range and aromatic fractions content. Synfuel behavior will be examined both under premixed and diffusion flame conditions. It is anticipated that a flat-flame burner will be used to produce premixed flame conditions while a rectangular slot burner similar in concept to a Wolfhard-Parker burner will be used to examine CDL sooting behavior in a diffusion flame.

Flames will be probed for temperature, gas composition, soot volume fraction, and mean particle size. Soot sampling will include the measurement of total soot production. Optical sampling in the flame will be done using light attenuation and scattering at various angles to determine volume fraction and mean size. In addition to varying fuel properties and flame type, changes in sooting behavior will be examined as a function of fuel/oxidant ratio (premixed flame) or fuel concentration in carrier gas (diffusion flame), total pressure to 10 atm, and also feed gas velocity and temperature, as necessary.

The objectives of this AR&TD contract will be met by two activities: (1) The development of the required experimental system, a Gulf-funded activity (described in Section 2), and (2) use of this system in the experiments in the AR&TD contract. The contract activities are described in Section 3.

2. DEVELOPMENT OF THE EXPERIMENTAL SYSTEM

The development of the experimental system began in September 1980. Several preliminary scoping experiments were done to provide data for the designing of the system components, pertaining to flame stability, vaporization of liquid fuels, and means for soot collection and weighing.

The preceeding two quarterly reports have described the designs developed and have reported progress in the space renovation efforts also required. Fabrication and installation of system components has been proceeding more recently, and the status of this phase of the system development is emphasized in this report.

2.1 Activities From April Through June

In previous quarters, the designing and drafting of the experimental system was completed and described in the quarterly reports. During this reporting period, the fabrication and installation of most of the major components of the system has been completed, and functional check-outs have been done. This report appends further descriptions of the system to that already provided in the previous reports and reports the functional status of the system problems which have been found, and the solutions are being pursued.

The components and their overall layout in the laboratory are shown in Figure 1. Comments on some of the more important components follow. The renovation of this laboratory included the addition of one wall, installation of safety interlocks between the doors and the laser power supply, and installation of cooling water and electrical power for the laser. The three main components of the system are apparent in Figure 1: (1) the flow control panel, (2) the burner vessel, and (3) the optical table and components.

2.1.1 Flow Control Panel

The flow control panel contains control sets for seven gas streams fed to the burner vessel. Each set contains (in downstream order) a dome-loaded downstream pressure regulator, a rotameter flow meter, a pressure guage, and a needle valve to set the flow rate. Cylinders for reactive gases are located outside the building for safety, with a manifold of piping leading to the laboratory. The panel also contains safety shutoff valve actuated by a flameout-indicating thermocouple. Certain components will be needed as safety features for high-pressure operation and are not yet installed. These components include pressure and temperature limit sensors, which actuate safety shutoff and relief valves.

2.1.2 Burner Vessel

Previous reports have provided a description of the design of the burner and pressure vessel. This is summarized here in Figure 2. The burner is mounted on the end of a vertical 2 in. OD pedestal which emerges through a pair of seals in the bottom flange of the vessel, which permit translation of the burner vertically or horizontally. The fuel and oxidant gas feed tubes to the burner are contained within the pedestal, and the fuel feed tube is heated to prevent condensation of vaporized liquid fuel. The pressure vessel consists of three sections connected by flanges. The center section contains the five windows for optical soot measurements and several probe access ports. The vessel is mounted on a stand so as to permit removal of individual sections as needed. The fuel spray-vaporizer unit is also mounted on this stand close to the pedestal inlet. A probe is used to withdraw gas from the flame; it is delivered through a heated sample line, through a condenser to analyzers for carbon dioxide, carbon monoxide, and oxygen.

During this reporting period, the fabrication of the vessel was completed, and hydrostatic pressure testing of the vessel was started to permit its use at 10 atmospheres in compliance with safety regulations of these laboratories. This testing was done at 900 psi, the overpressure

expected in the event of the accumulation of a fuel and air mixture and its ignition. This test demonstrated the mechanical integrity of the vessel. However, leakage occurred at the windows and at the bottom flange seal around the pedestal, and it exceeded one cc/hr, the limit of the regulations. Solutions have been found for the window seal leakage but not the bottom flange seal. The present plan for use of the vessel in one atmosphere experiments will be followed, and the remaining problems for pressurized operation will be solved within a few months.

2.1.3 Optical System

During October through December 1980, the basic approach to the optical measurement of soot was designed, following the methods used by D'Alessio¹ and others. The volume fraction and average size of the soot will be determined from measurements of the intensity of the laser light scattered at 90 degrees and the extinction of the laser beam. The main components were ordered and received. During the next quarter, the details of the design were developed as shown in Figure 3 and parts were procured. Included were means for local flame temperature measurement.

During April through June, the development of the functioning of the optical system emphasized the light scattering measurement. The argon-ion laser operation was checked and found to be flawless. The components to detect laser light scattered at 90° to the incident beam were assembled and aligned. The detection train's line-of-sight was aligned to intersect the laser beam, and a temporary sooty flame over a Meker-type burner was placed at this point. This established that the laser intensity and detecting train sensitivity were sufficient to give an adequate signal. The unenclosed temporary burner fluctuated in the room air; steady flames will be established in the burner vessel, and then laser scattering measurement will be quantitatively checked out.

2.2 Projections for the System

- Completion of safety interlocks for laser and for flow shutdown upon burner malfunction for operation at one atmosphere pressure.
- Gas analyzers (CO_2 , CO, and O_2) installed and used to verify calibrations of flow meters and fuel/air ratios.
- Production of flat flames in burner vessel at ambient pressure, damping of buoyant fluctuations by screens over flame, and cylindrical extension of open vessel top.
- Alignment and operation of optical system for flame in vessel.

3. CONTRACT ACTIVITIES

3.1 Survey and Planning (Task 1)

Most of the efforts to date have been devoted to the Gulf-supported development of the experimental system, which will then be used in measurements in the contract Tasks 2-5. However, during this past quarter, the final portion of Task 1 of the contract (Survey and Planning) was completed.

3.1.1 Survey of Combustion Literature

Task 1 has been divided into two main areas: (1) a survey of the combustion literature, and (2) collection of data about the composition and properties of coal liquids.

From the combustion literature, available experimental results on soot formation in simple flames were obtained for the purpose of planning the details of the system development and the conditions to be used in the

contract experiments. Most of this information is summarized in previous quarterly reports. However, recently obtained information has included the following. It was shown by Flossdorf² and Wagner, and confirmed recently by others, that the amount of soot formed in a premixed flame is strongly affected by the flame temperature. Flossdorf varied the flame temperature by altering the burner gas feed velocity and, thus, the heat flux from the flame to the burner. Thus it will be important in our experiments to measure the flame temperatures and to control them by controlling the gas velocity, heat flux, and preheat of the burner feed for purposes of vaporizing the liquid fuels.

3.1.2 Properties and Composition of Coal Liquids

The purpose of this project is to study soot formation from coal liquids as it is affected by their composition. It is known that for many compounds the sooting tendency varies greatly for varying molecular structures. For example, we have found in a test in a preliminary type of burner that some aromatic hydrocarbons formed many-fold more soot than their nitrogen-heterocyclic analogues (e.g., benzene vs pyridine). Such compounds are typical constituents of coal liquids. Similar large effects on sooting are caused by other fairly minor features of molecular structure, such as placement of the double bonds in a diolefin, or cyclic vs n-alkanes. Similar effects are likely to occur with many coal liquids components, and it is the purpose of this project to explore this effect of molecular structure.

Tasks 4a-4d are organized along this line. Some pure compounds representative of these classes of compounds will be used. Regarding actual coal liquids, there are far too many compounds present in coal liquids to easily identify, isolate, and test for sooting, which is also the case for petroleum-derived natural products. There are several responses to this fact, as follows:

1. A comparatively small number of compound types are dominant in concentration in coal liquids, and only these will be tested.
2. Coal liquids will be partially separated into chemical group types for a partial compositional characterization or for preparation of such samples for sooting tests.
3. Relationships will be sought between the processing conditions and the sooting tendencies of processed samples, without benefit of detailed data on their molecular composition. However, less basic inspection test data on such samples will be obtained and correlated. These processing parameters are distillation, hydrotreating, and possibly some liquid extraction methods.

The following lists Tasks 4a-4d of this project together with the samples to be studied and the corresponding chemical class or processing method.

Task 4a Narrow Distillation-Range Fractions:

- Coal-derived liquid (CDL) (not hydrotreated)
- Mildly hydrotreated CDL
- Moderately hydrotreated CDL
- Severely hydrotreated CDL
- Shale oil
- Petroleum-derived high-aromatic oils

Task 4b Effects of Aromatic Hydrocarbon Structure:

- Aromatic hydrocarbons
- Saturated hydrocarbons
- Partially hydrogenated aromatics

Task 4c Heteroaromatic Hydrocarbons:

- Nitrogen-heterocyclics
- Extracted nitrogen compounds
- Products of hydrotreating nitrogen compounds

Task 4d Effects of Concentrations of Sooting Compounds in Fuels:

- Blends of CDL with low-aromatic oils
- Composites of known compounds resembling CDL's

3.2 Projections

The preparation of the experimental system, described in Section 2, is expected to be completed for operation at one atmosphere pressure in early July, at which time Task 2, Selection of Flame Conditions, will begin. In this Task, the burner will be operated over ranges of flame conditions, i.e., fuel equivalence ratio, burner gas feed velocity, and flame temperature, to observe the operating ranges with acceptable flame stability, shape, and soot yields. Completion of this Task with the premixed burner at one atmosphere operation is expected by September 30. From these data, a set of mid-range conditions for a "standard" flame will be selected for use in Tasks 4a-4d, in which a wide variety of fuels will be given preliminary tests of their relative soot-forming tendencies.

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REFERENCES

1. A. D'Alessio, et al., Sixteenth Symposium (International) on Combustion, p. 695 (1976).
2. J. Flossdorf and H. G. Wager, Z. Phys. Ch.N.F. 54 113 (1967).

FIGURE 1. Layout of Combustion System

Electronic Components not shown:

HV supply

Chopper Controller

Preamplifier

Phase-Locked Amplifier

Recorder or CRO

Laser Power Supply

PD Photo Detector (photomultiplier tube or diode)

R Optical Rail

PH Pinhole

L Lens

FR Frame

SH Safety Shutter

PY Optical Pyrometer

BV Vurner in Vessel

P Polarizer

FI Filter

CH Synchronous Chopper

M Mirror

LA1 4W Laser under Table (AR Ion)

LA2 10MW HE-NE Laser (Alignment)

* To be installed

W Windows (5) in Vessel

FIGURE 3. Optical System Components