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SYNTHETIC FUEL UTILIZATION
Final Report

By
Stanley Singer

June 1983

Work Performed Under Contract No. AC22-77ET10679

The Engineering Societies Commission on Energy, Inc.
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Final Report
Task 330

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Dr. Stanley Singer

June 1983

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Prepared for
The United States Department of Energy
Pittsburgh Energy Technology Center

Under Contract DE-AC22-77ET-10679

ABSTRACT

The presence of large coal resources in this country provided the spur for consideration of liquids derived from hydrogenation of coal in the search for alternate liquid fuels to replace petroleum. Previous developments particularly in German industry beginning in 1910 and reaching a capacity of approximately four million tons of products a year by 1944 and more recently a series of plants in South Africa have shown the practicability of coal liquefaction. A few more advanced processes have been developed variously to bench, pilot or commercial scale from among the thirty or more which were subject to study. Limitation in the amount of hydrogen used in these for reasons of economy and processing facility results in products containing major amounts of aromatics as well as significant portions of the sulfur and nitrogen of the coal feed. Combustion of the largely aromatic liquids can present problems in commercial burners designed for petroleum fuels, and combustion staging used to reduce NO_x emissions with the latter may encounter difficulties from sooting in the coal-derived fuels, which occurs readily with aromatics. This report presents a review of such problems in utilization of synthetic fuels from coal, emphasizing basic engineering and scientific studies which have been made. A research program involving a number of universities, industrial laboratories, and non-profit research institutions was carried out under the direction of the Department of Energy's Pittsburgh Energy Technology Center. This program is also reviewed.

The major subjects covered are those of liquefaction product composition and properties, fuel spray and droplet processes, synfuel pyrolysis, combustion mechanics, soot formation, and pollutant emission.

Recommendations concerning needs for investigation are made from an evaluation of the current status of the field and the results obtained in the program.

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FOREWORD

This report was written during the period when the author, Dr. Stanley Singer, was an ESCOE Engineer in Residence from October 1981 through June 1983 on leave of absence from Athenex Research Associates, Pasadena, California, a basic research and technological consulting firm which he directs. He holds a Ph.D. degree in chemistry from the University of California at Los Angeles, and has held positions of administrative and technical responsibility as a chemist, physicist and engineer in the private and public sectors.

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1.0 PROLOGUE

1.1 INTRODUCTION

The Engineering Societies Commission on Energy, Inc. (ESCOE) is a non-profit corporation established at the request of the U.S. Government by the five Founder Engineering Societies to provide authoritative impartial assessments of existing and emerging energy technologies with respect to changing national needs.

The professional staff in the ESCOE Engineering Program consists of Engineers and Scientists in Residence who are on leaves of absence from their employers in industry and academia. These individuals are selected for 18- to 24-month tours of public duty on the basis of experience and achievement related to the areas current in the ESCOE Engineering Program.

ESCOE technical reports are reviewed prior to publication by peers appointed to this task by the Founder Engineering Societies and cognizant representatives of the client. The published reports are distributed to qualified users and are available through the National Technical Information Service.

1.2 OBJECTIVE

In February, 1982, under the technical direction of the Pittsburgh Energy Technology Center (PETC) — the lead organization in the Department of Energy for coal research — ESCOE undertook a task to review the current state of pulverized coal combustion (PCC) and synthetic fuel (synfuel) utilization (SU) and to review the PETC programs covering the significant areas of these fields.

A previous report, ESCOE Report FE-2468-103, issued in April, 1983, dealt with the PCC Program. The present report covers the second area, Synfuel Utilization.

Following the development of processes for production of synthetic fuels by hydrogenation-liquefaction of coal, the utilization of these fuels in industrial applications as substitutes for petroleum-derived liquids may arise out of necessity. Such a change would bring the requirement for information on several aspects of the new fuels, stability, toxicity, physical properties such as density, viscosity, and surface tension, compatibility with construction materials, and, of course, their combustion characteristics, including pollutant emissions and sooting. While petroleum and coal-derived fuels are similar in several respects, there are significant differences in several characteristics which can affect industrial application. This report is intended as a review and evaluation of the current status of the problems involved in utilization of the new fuels with emphasis on combustion-related factors but little or no consideration of toxicity, storability, etc. The review covers two major sources of information, the literature published from previous but generally recent studies and the results of investigations made under the PETC SU Program in this field by the universities, industrial laboratories, and non-profit research firms taking part.

The PETC SU Program was discontinued at the end of FY 82. The component projects were in varying stages of completion, from a few which had run a course of several years and had assembled an appreciable amount of data to some which had just begun and were still assembling experimental apparatus in preparation for investigation. Thus, this review is in part a record of the stage to which the SU Program had progressed in the acquisition of basic information for utilization of synfuels.

1.3 REPORT CONTENT AND ORGANIZATION

This report deals with the basic work in the development of synfuels for application in industrial combustors. It is based on a review of literature, discussions with authorita-

tive engineers and scientists active in the field, and results obtained in the investigation of the PETC SU Program. The engineering and scientific literature contains hundreds of references concerning the subjects discussed in this report. Recent comprehensive reviews are cited as sources in the respective subjects from which the primary references may be obtained.

A brief review of major coal liquefaction processes is followed by a comparative summary of the properties of coal-derived liquids and common petroleum fuels. The processes involved in combustion of the liquids are discussed in the general order in which they occur. First, spray preparation and droplet interactions are considered, then pyrolysis of the fuel encountered as the droplets warm up. Soot may be formed both in pyrolysis and in reaction initiated by combustion. The chemical reactions of the fuel in combustion ultimately oxidizing the hydrocarbons to carbon dioxide and water are considered. Nitrogen which is part of the chemical structure of the fuel may contribute to pollutant formation. Combustion staging can minimize this contribution, but synfuels require particular care in staging because of their tendency to soot. The presence in the combustor of liquid and solid particles varying in size and the interactions of fluid dynamics with both condensed phase particles and gas phase reagents in the usually turbulent system affect both combustion processes. Modeling of the overall transformation of liquid fuel in combustion in a form suitable to computer solution provides estimates of the relative significance of the processes involved.

The information obtained from the PETC SU Program concerning these areas is discussed following the review of the position of the field based on the literature and material presented in recent meetings.

1.4 CONCLUSIONS

- The information needed to put synthetic fuels to effective use in industry is incomplete.
- There are similarities between traditional petroleum fuels and the liquids obtained from coal liquefaction. The industrial technology of combustors using petroleum fuels is a basis for industrial utilization of coal-derived synthetic fuels.
- There are differences in such factors as composition, viscosity, and density between petroleum fuels and comparable coal liquids. The differences affect combustion strongly under some conditions and require specific consideration to obtain satisfactory performance.
- Synfuels have a greater tendency to soot than petroleum fuels, particularly in fuel-rich combustion staging to reduce NO_x . Basic studies indicate that soot can be controlled by proper selection of conditions for staging.
- Soot formation from synfuels appears a major factor in utilization possibly after toxicity and stability. Significant information has been obtained in the PETC SU Program correlating soot with fuel composition and combustion parameters.

1.5 RECOMMENDATIONS

- Study of synfuel utilization should be continued to provide necessary information for direct industrial use without delay of synthetic fuels when necessary.
- Parameters affecting soot formation should be investigated to assure control of this problem in use of synfuels. Factors to consider include
 - fuel structure
 - combustion conditions including turbulence
 - basic mechanisms
- Heterogeneous combustion of liquids should be improved through further study of
 - spray preparation
 - fluid dynamics of combustors
 - heterogeneous phase rate processes

2.0 COAL LIQUEFACTION PROCESSES

Technological progress in our civilization has been accompanied by rapid change in the major fuel used for home and industry which occurred relatively recently, from wood to coal to petroleum. Although an extremely diverse set of materials is still in use in limited regions of the world from dried cattle droppings to peat (the latter generating approximately 5,000 megawatts in electric power plants in the USSR), the predominant fuel is determined by a combination of economic and technological factors among others. Even with the complexity of the technological processes involved in bringing petroleum fuels to the market compared to that of coal, the role of petroleum as the primary fuel for world energy needs was increasing overwhelmingly in recent years. From 1950, when approximately one-half as much petroleum as coal was consumed worldwide in producing energy, to 1973 the use of petroleum increased by two-thirds while that of coal had fallen to the relative amount formerly obtained from petroleum. In the same period the fraction provided by natural gas doubled from approximately one-tenth to one-fifth of the total. This shift was accompanied by a change from coal to petroleum fuel oil in many electric generating plants designed to use coal. With the institution of market control policies by the Organization of Petroleum Exporting Countries the technologically advanced fuel consuming nations were forced to confront an abrupt change which adversely affected their economy and industry. At this point the trend from coal to petroleum as the major fuel for primary energy production was reversed.

The major sources of energy in the United States in order of decreasing significance according to recent estimates¹⁰ are petroleum (45%), natural gas (27%), coal (20%), and hydro-electric, nuclear, and miscellaneous sources (<8% altogether). Thus, petroleum accounts for more than double the energy production of coal. While the United States is the possessor of

major petroleum resources, possibly ten per cent of the world total, its proven coal deposits represent an energy source over an order of magnitude greater than that of petroleum, sufficient for a period of the order of centuries if used at foreseeable rates. Consideration of alternative liquid fuels to supplant petroleum is thus naturally directed to liquids which can be derived from coal.

The processing of coal to obtain modified materials desired for specific applications has a long history. Retorting in a method similar to that used in distillation of wood produced coke, tar, and gas. Coke was applied in iron smelting in the early eighteenth century. Town gas became a widely used fuel for illumination beginning in London in the first decade of the nineteenth century. Coal tar provided a rich source of organic chemicals, primarily aromatic compounds. A list of those identified contains approximately 350 substances. The first synthetic dye was prepared in the middle of the nineteenth century from coal-tar benzene, giving rise to a major industry. The value of this one compound encouraged study and development of the remaining materials. Coal tar also provided the wood preservative creosote and road tars.

Early investigation of the catalytic hydrogenation of coal producing fuel liquids was carried out by Bergius, who is often cited as the only industrial chemist to become a Nobel laureate. The Bergius process using high pressure (2000 - 10,000 psi), high temperature (900°F), and an iron oxide catalyst was developed from 1910 to 1927 and investigated in several countries. Large scale production was made a national policy in Germany, so that over 3,000,000 tons of oil per year were produced by 1944, approximately two-thirds of which was high-grade aviation fuel.

There is no current production by the Bergius process; all modern liquefaction methods use much lower pressures. Over the same period in which direct coal liquefaction by Bergius' method was being developed, an indirect process of fuel

synthesis by hydrogenation of carbon monoxide, the Fischer-Tropsch synthesis, was also brought into production. The synthesis gas $\text{CO} + \text{H}_2$ is generated by steam-oxygen treatment of coal, for example, in the Lurgi gasifier. Reaction of synthesis gas at $450\text{--}620^\circ\text{F}$ under approximately 350 psi with iron and iron/cobalt catalysts produces a broad range of hydrocarbons from liquid fuels and oils to waxes. In the WWII German synfuel industry this process provided one-quarter as much material as the Bergius. However, it is still in use in the only current industrial scale synfuels production. In operation since 1955, the Union of South Africa SASOL plant produces one-quarter million tons per year of a large slate of petrochemicals by the Fischer-Tropsch method. Expansion with additional plants SASOL II in 1981 and SASOL III provides four- to five-fold in additional production in each. The high ash content of South African coals ($>30\%$ in some cases) was a factor in selection of the indirect liquefaction.

The Mobil zeolite catalyzed conversion of methanol to gasoline provides an additional route of coal liquefaction when combined with synthesis gas generated from coal. A commercial scale plant using methanol from natural gas in a New Zealand development is under way.

Over twenty direct coal liquefaction processes have been investigated in recent work inspired by the petroleum crisis.^{8,10,12} Perhaps three or four are of greatest current interest, having advanced to pilot plant scale; and two of these are at the stage of consideration for commercial scale operation. The Solvent Refined Coal (SRC-II) process has been the source of possibly the most widely studied synfuel products from these recent developments. SRC utilizes hydrogenation of coal in a recycle solvent at $800\text{--}850^\circ\text{F}$ and 1500 psi. No catalyst is added, but it appears that accumulated recycled minerals from the coal processed, especially the pyrites, confer a catalytic effect. Initially intended for preparation of ash-free solid fuel and accompanying fuel gas (SRC-I), an increase in

the hydrogen to 5% of the coal processed and recycling heavy products for processing forms distillate liquids (SRC-II). The properties of the products are discussed in the following section.

The Exxon Donor Solvent method is based on a hydrogenated recycle solvent which donates hydrogen to the coal in a dissolver section with additional hydrogen also present. Temperatures of 800-900 °F and pressures of 1700-2300 psi are used. The recycle solvent, a distillate of the nature of naphthalene and anthracene, is catalytically hydrogenated in a separate step and then fed into the dissolver where it is mixed with crushed coal under pressurized hydrogen. The solvent is separated from the product distillate, returned to the catalytic hydrogenator, and recycled to the dissolver. The catalytic section is kept separate from the coal processing step to minimize catalyst deactivation. The heavy residues from distillation of the coal hydrogenation product are recycled into the dissolver, forming additional distillate fuels.

The H-Coal liquefaction process utilizes a cobalt-molybdenum catalyst in an ebullated bed through which hydrogen is bubbled into coal suspended in a recycle oil. The hydrogenation is carried out at 825-875 °F and 2000-3000 psi. A synthetic crude oil and hydrocarbon gases are produced. The pressure used is somewhat higher than in other U.S. processes.

Higher pressure liquefaction has been under investigation in German "Kohloel" process studies,⁹ much reduced from those in the Bergius hydrogenation but still approximately double those found in U.S. processes. Pressures of 4500 psi and temperatures of 800 °F are used. A disposable iron catalyst in recycled distillate accomplishes the hydrogenation liquefaction.

3.0 SYNFUEL PROPERTIES

3.1 COAL STRUCTURE AND ITS EFFECTS ON SYNFUEL COMPOSITION

The properties of the synthetic fuels produced by coal liquefaction are determined by the chemical structure of the coal used as the starting material and the chemical changes it undergoes in the hydrogenation and thermal processes to which the coal is subjected. The structure of coal has been under investigation for well over a century by many noted scientists. While much is known, considerable mystery remains. Coal is quite a heterogeneous material, and the composition changes markedly with rank, a classification which distinguishes roughly the extent of transformation of prehistoric plants. Peat and low rank coals such as lignite, brown coal, etc., are presumably deposits from more recent periods or the product of exposure to relatively lower temperature compared to the high rank bituminous and anthracite coals. Remnants of the physical structure of the plants may be detected in some of the low rank substances.

The elemental chemical composition exhibits systematic change with rank. Carbon increases from 70% to 98% in the range from lignite through subbituminous and bituminous coals to anthracite. The hydrogen content remains more or less constant at approximately 5% through increasing rank up to anthracites in which it declines markedly to 2-3%. Oxygen decreases rapidly from as high as 25% in lignite to 5-10% in bituminous coal and perhaps 2% in anthracite. Sulfur and nitrogen are also present. Sulfur content is 1-3%, occasionally as high as 5% or more, while nitrogen is usually from 1-3%, sometimes approximately the same as sulfur or often less.

These changes in composition are indications of a complex chemical structure. Figure 1 depicts a structure proposed for bituminous coal by recent authors.¹⁴ This model is intended as a subunit of the complete molecular structure which is composed of several of similar subunits containing different

polyaromatic nuclei and linked at points P. The structure is based on reactions of functional groups measured quantitatively (e.g., -OH) and physical measurements (NMR spectroscopy, X-ray diffraction) which provide the number and type of hydrogens, aromaticity, and the average dimension of the polyaromatic ring groupings. There are a number of objections to the representation of the structure of coal by such a molecular subunit. With increasing rank and the accompanying increasing carbon content the oxygen-containing functional groups undergo a major change. In coal with 70%C acidic -COOH groups account for the major oxygen content; whereas in 83%C coal, as shown in Figure 1, there are no -COOH functional groups. The oxygen is found in an approximately equal number of hydroxy (-OH) and ether (-O-) groups.^{13,14} Total oxygen decreases from approximately 23% to 9% as carbon increases from 70% to 83%. Other major changes appear possible. In addition coal within a given rank, even within a single mine vein at different locations, can show wide variation in composition.

Figure 1: Coal Molecule; $C_{100}H_{79}O_7NS$; 83.5%C, 5.5%H, 7.8%O, 1.0%N, 2.2%S.
(Reference 14, page 520)

Many studies to determine structure have been made with solvent extracts carefully prepared from samples of the solid obtained in nature to prepare material tractable to the procedures used in investigation. Coal is often resistant to measurement by methods such as nuclear magnetic resonance and electron spin resonance which are commonly effective with chemical compounds and polymers, even natural polymers such as amber. There are thus a number of questions as to whether a structural representation such as Figure 1 is a realistic model of coal. However, consideration of the structure, which is based on substances actually observed in coal studies, should provide some basis for knowledge of the products which will be formed in hydrogenation-liquefaction and the reactions by which they are produced. The postulated structure indicates that multiple ring aromatics or hydroaromatics may readily form, depending on the amount of hydrogen provided in the reduction. The hydrogen content of the feed coal is much lower than that found in crude petroleum, perhaps one-half; and a considerable quantity of hydrogen would be necessary to obtain products comparable in this respect to petroleum fuels. The composition of typical coals which would be logical feed material for coal hydrogenation liquefaction is compared with that of petroleum in Table 1.

Table 1
Coal Vs. Petroleum Composition

Weight % (MAF)	COALS		— PETROLEUM —	
	Colorado Subbituminous	Pittsburgh lv Bituminous	Texas Crude	No. 2 Fuel Oil
C	77.7	83.0	84.9	86.7
H	5.2	5.9	10.9	13.0
O	15.0	6.3	2.1	<0.1
N	1.6	1.8	0.5	0.01
S	<u>0.5</u>	<u>3.0</u>	<u>1.6</u>	<u>0.2</u>
Ash	3.9	7.8	0.1	-

3.2 CHEMICAL PROPERTIES OF SYNFUELS

Consideration of the structure in Figure 1 and comparison of the elemental composition of that model and the coals in Table 1 with those of the petroleum liquids reveal a number of significant differences which will affect the properties of synfuels derived from coal. The great number of aromatic nuclei in the Figure 1 structure and the relatively low hydrogen content associated with it will presumably be reflected in the synfuel product. Low hydrogen composition is accompanied by a reduced heat of combustion. Aromatic substances readily form soot in combustion.

Sufficient hydrogen could be added to coal in the liquefaction process to increase the content up to the amount found in petroleum fuels. The aromatic content would be reduced at the same time with formation of cycloaliphatic (hydroaromatic) ring structures or even aliphatic hydrocarbon side-chains if sufficient hydrogenolysis occurred. However, use of hydrogen increases the cost and reduces overall thermal efficiency in liquefaction.¹¹ Most processes aim at minimum hydrogen use, preferring to discard heavy residue bottoms and to utilize hydrogen available in the feed coal (found in the reduced cyclic structures in Figure 1), concentrating it in a more limited light and middle volatility distillate.

Nitrogen and sulfur in coal generally exceed the quantities found in petroleum crude, and these elements contribute directly to unwanted pollutants emitted in combustion. Nitrogen is normally at least a factor of several fold higher in coal. In the case of sulfur, on the other hand, there are coals with exceptional low sulfur and petroleum with unusually high sulfur. Processing with hydrogen removes both of these potential atmospheric contaminants. Catalytic hydrogenation is especially effective.

The composition of products from the major coal liquefaction methods described briefly in Section 2 are given in Table 2.

Table 2
Coal Liquefaction Product Compositions*

	<u>SRC-II (MD+HD)</u>	<u>EDS</u>	<u>H-COAL</u>	<u>NO. 2 FUEL OIL</u>
Boiling Range, °K	455-755	473-811	455-755	443-611
Specific Gravity @ 289°K	1.0	1.08	1.10	0.83
Weight Per Cent				
C	88.98	89.40	86.50	86.7
H	8.70	7.70	7.69	13.0
O	1.16	1.83	3.19	<0.1
N	0.84	0.66	0.81	0.01
S	0.28	0.41	0.37	0.2

* Compiled from several sources by Science Applications, Inc., during DOE/PETC SU Program.

An almost continuous range from methane to complex, non-volatile aromatic substances is obtained from the three processes represented in Table 2. Distillate fractions corresponding approximately to No. 2 oil have been selected for comparison. The EDS product includes material boiling up to 200°K higher than the upper temperature of the No. 2 oil range. The density of these synfuel liquids is approximately 25% greater than that of No. 2 oil. Presumably those distilling at these higher temperatures contain more polynuclear aromatics, accounting for the greater density. The relative content of aromatics in No. 2 oil (22%, with 70.5% aliphatics and 7.5% olefins) is much less than in a synfuel like SRC-II middle distillate, which contains 65% aromatics and 35% aliphatic compounds. Coal derived fuels of high aromatic content are of premium quality for automotive transport. In the combined SRC-II middle and heavy distillates considered in the table the aromatic content is presumably even greater. Such fuels may first enter industrial use in blends with petroleum.

The products of liquefaction contain approximately 50% more hydrogen than that present in the feed coal but still only 60% of the amount in No. 2 oil. The atom ratio of hydrogen to carbon in the liquids considered is near 1, whereas in No. 2 oil it is slightly below 2, reflecting aromatic and paraffinic content, respectively. An increase to 10.5%H is desirable to obtain storage stability in the synfuels, and production of material with this composition has been investigated.⁶

The substances generating atmospheric pollutants are reduced from the amounts found in the feed coal, nitrogen to perhaps 50% of the initial quantity and sulfur to approximately 10%. Yet, compared to the amounts found in No. 2 oil, the synfuels still contain over an order of magnitude more of the potential nitrogen contaminant. An advanced catalytic hydrogenation method, the Lummus Integrated Two-Stage Liquefaction, produces fuels with greater reductions in nitrogen and sulfur, nitrogen falling to one-fifth or one-sixth of the amounts in the synfuels in Table 2 and sulfur to one-tenth.

3.3 PHYSICAL PROPERTIES OF SYNFUELS

Physical properties of the synfuels are significant in combustion processes involving drop formation through spraying and subsequent drop processes during combustion. The density of the synfuel fractions equivalent in boiling range to No. 2 fuel oil and heavier oils is approximately 10-25% greater than the petroleum fuels. Viscosity is generally approximately the same for equivalent fractions. The surface tension of SRC-II middle distillate is perhaps 10% higher than that of No. 2 oil. The heat capacity of the synfuel is approximately 10% less. The heating value of No. 2 oil is, on the other hand 15% higher on a weight basis. Values of the properties of synfuels are being determined but are still not complete, particularly in comparison with those available on petroleum fuels which have been the subject of study over several decades by industry organizations devoted to this field.

4.0 SYNFUEL COMBUSTION

The combustion of the coal-derived liquids produced in synthetic fuel processes is considered here in two arbitrary but traditionally separate areas, the fluid dynamic or physical processes of liquids reacting in a spray and the chemical steps of pyrolysis and combustion. Consideration of spray dynamics is extended to interactions resulting from the heat release in combustion.

4.1 FLUID DYNAMIC ASPECTS OF LIQUID COMBUSTION

Extensive analytical and experimental work has been done on basic aspects of spray formation, droplet-gas interactions, and the effects on the two-phase system of enthalpic flow from combustion. Consideration of this area may be based on review of analytic descriptions progressing from the most simplified model to the most complete and complex, covering the physical parameters and their interactions which investigators have been able to include in models. The recent review by Faeth⁷ is quite an extended and comprehensive discussion of this type. The present review, on the other hand, is much more limited in extent and is restricted to a brief description of the processes the liquid fuel undergoes as it is successively sprayed, ignited, and burned in a combustion system.

The liquid fuel is pumped through rigid pipe to the atomizer or spray head, often a nozzle containing a restriction and thus imposing a pressure drop. The drop provides resistance to the transmission of oscillations from the combustor back into the liquid feed system, but they can occur nevertheless at a natural resonant frequency of the liquid system. The liquid ejected through the sprayer disintegrates into droplets through shear or is broken up by a combination of forces as in sprayers using air impingement. Several different drop spray generators utilizing what appear to be different methods of breaking up the liquid are found in commercial devices. The

details of drop formation from bulk liquid in or close to the sprayer have been investigated very little. Rapid laser pulse photography has shown the process in two commercial sprayers in studies made during the SU Program reviewed here. The physical properties of the fuel affect the drop size as shown in the correlation for mean drop size S

$$S = \frac{K \dot{m}^a \nu^b \sigma^c}{\Delta p^d}$$

where K is a constant of the sprayer, $\dot{m}$ is the fuel flow rate, ν the kinematic viscosity, σ the surface tension, and Δp the pressure drop in the sprayer; a, b, c , and d are constants, the first three being specific for each liquid and, according to experimental measurement, differing from sprayer to sprayer. The mean drop size increases with viscosity as shown. However, the effect of viscosity is weak. In one atomizer the exponent is approximately $1/5$, in another $1/3$. Near the atomizer the exponent is resulting in agglomeration to larger size are conceivable in dense sprays, or fragmentation to smaller size may occur under the continuing effect of spray forces. Drop size measurements such as those considered in the correlation are made after equilibrium is attained at a moderate distance from the sprayer.

On emission from the sprayer the fuel drops enter the gas flow and are heated in the increasing temperature of the flow as it approaches the combustion zone. Droplets up to $10\mu\text{m}$ in diameter are effectively homogeneous with the gas phase flow.⁷ Droplets of this dimension were considered to burn effectively as gas components in early rocket studies. Aerosols of suspended droplets of this size are long lasting when generated in laboratory vessels and appear almost subject to Brownian motion. Larger drops disperse according to the momenta imparted on initial injection and interaction with the coflowing gas which is presumably at higher velocity. Aerodynamic forces now affect drop transport: drag, the inertia of the gas the drop

is traversing, Bassett force from unsteady flow around the drop, Saffman lift force, and Magnus rotation force. In uniform flow at moderate Reynolds numbers the drag outweighs the latter four factors which are generally an order of magnitude lower. However, high drop velocity, and high pressure increase the relative importance of the virtual mass (gas inertia) and Bassett forces, particularly in low Reynolds number flows.

At realistic higher velocities found in combustors turbulence occurs in the reacting flow with the appearance, first, of fluctuations and separations in otherwise laminar flow, and then of complete structures in the form of eddies, vortical cells, as velocity increases further above a critical transition value.⁴ Turbulence causes a marked change in drop processes and transport.⁵ The drag coefficient of the drops falls below the normal value in uniform laminar flow in transition regions and then increases so that drag coefficients are higher in marked turbulence than in laminar flow.⁷ Decreases in the coefficient occur again at higher flow velocities in a further transition to supercritical flow. The presence of the heterogeneous phase in the flow reduces turbulence through damping by the drops via drag and other mechanisms. On the other hand, the drops may themselves contribute to turbulence by production of turbulent wakes. The damping has been observed experimentally in reduction of turbulence and the narrowing of a gas jet issuing from a pipe on addition of fine solid particles to the gas.¹³

As the drops of liquid fuel leave the sprayer and enter the heterogeneous flow into the combustor, they are subjected to rapidly increasing temperature. This results in vaporization of the fuel, then, as temperature continues to increase, ignition of the vapor. At rapid heating rate large drops may reach temperatures sufficient to pyrolyze the fuel liquid before vaporization is complete. Observation indicating that this occurs is reported from experiments with injection of

drops into a burner, in which droplets suddenly eject soot trails after decreasing to small size. The ejection of material resulting in soot can affect the droplet trajectory. The vaporization of drop liquid prior to this affects the drag coefficient; and turbulence changes both the rate of vaporization and the drag, thus further influencing drop transport. Synfuels contain mixtures of relatively volatile and nonvolatile liquids, as is common in petroleum fuels for various specific uses. Rapid heating rates encountered in a combustor cause evaporation of volatile components near the surface of a fuel drop, but low diffusion rate in the liquid within the drop prevents replenishment of that component to the surface before the drop is consumed in other processes. Experimental observations mentioned below support the intervention of this surface depletion of volatiles in drop evaporation and combustion.

As the processes discussed above are occurring, the major change in the drops following their injection into the combustor is, of course, a continuous decrease in size as material vaporizes and enters the combustion region. The distribution of drop size provided by the injector spray initially, however, may be markedly affected by subsequent processes which are size-specific. For example, larger drops on entering combustors with highly turbulent regions may be fragmented, or very small droplets may be eradicated by microexplosions which have been observed at termination of synfuel and No. 2 fuel oil droplet combustion. Such perturbations of the normal drop size distribution present difficulties for modeling.

With vaporization of the fuel drops and transport in the combustor, the fuel material approaches the combustion zone, increasing in temperature until ignition occurs. Ignition appears as a discontinuity frequently attributed to the onset of chain branching rather than a gradual increase in progressive reaction of fuel and air from lower temperatures, for

example. The location of the flame is determined by the equilibrium between the fuel materials transported from the liquid drop and the rate at which they are consumed in the combustion reaction although a number of factors affect the equilibrium. Around a stationary single drop in the absence of gravity a spherical flame zone may be formed. Gravity, acceleration of the drop, or gas flow around the drop modify the equilibrium processes and change the position and shape of the flame. For example, the effects of gravity and of the warm vapor flow at the top of a stationary drop may contribute to a flame shape approaching that of a candle or Bunsen burner.

The combustion of drops in a spray has been considered by some investigators in terms of an array of the liquid drops, each surrounded by its individual or envelope flame. Experimental observations indicate, however, that sprays burn with a unified or collective flame zone. It appears that vaporized fuel from individual drops is transported to a collective reaction region supported by contributions of fuel gas from the spray as an assembly. The concentration of drops in the spray may control a transition from envelope to unified flames, but in sprays with drop concentrations approaching realistic values it is difficult to find reports of appearance of envelope flames.⁷ The occurrence of such flames would markedly affect combustion. The flame in relatively close proximity to the drop surface would increase fuel vapor transport to the flame zone and thus increase combustion rates, at least at moderate laminar or low intensity turbulent flow rates in the system below blow-off. Combustion in the collective flame mode occurs at a greater distance from the fuel drops and requires consideration in terms of multi-component diffusion and energy transfer (heat and radiation) over somewhat greater mean distances.

With increasing turbulence in more intense spray combustion the scale of recirculation regions, eddies, or vortexes, decreases. The flame divides into small cells presumably approximating

the scale of turbulence and filling the combustion volume more completely with the actual combustion reactions. In this condition the flame is presumably again closer to the vaporizing drops increasing energy transfer to the liquid, and convection transport of the gas phase fuel is high. Realistic levels of turbulence in liquid fuel combustors increase the complexity of almost every process considered. For example, drop motion may be affected strongly, and evaporation appreciably.⁷ Much further investigation of turbulence effects is needed.

4.2 COMBUSTION PROCESSES

The combustion of liquid SRC-II fuels in the form of a drop spray involves consideration of a somewhat complex mixture of coal-derived compounds including, for example, xylene, naphthalene, tetralin, methylnaphthalene, phenol, and various alkyl substituted derivatives of these and similar basic structures, using SRC-II middle distillate as an example. Detailed study of the oxidation and combustion reactions of such compounds is thus far quite limited compared to the aliphatic substances which make up the major portion of petroleum fuels. The use of global reaction models to approximate the combustion process is an effective approach. In place of the actual step-wise reactions by which a fuel molecule is converted finally to CO_2 and H_2O , an overall reaction representing the change of the starting material to the products is written; and the effective rate of the gross conversion is estimated or measured.

Several processes occur in liquid spray combustion, as indicated in the description of the physical changes drops undergo which were discussed in the preceding section. Specific chemical transformations may be associated with each physical change depending on the conditions of combustion. The spray entering the combustion chamber is heated. The liquid and the vapors emitted may reach temperatures causing pyrolysis

in the absence of oxygen. Typical cracking reactions can occur under this condition, producing H_2 , CH_4 , C_2H_4 , and C_2H_2 as gaseous products and soot as a solid. Synfuels exhibit a greater tendency to form soot than petroleum-derived fuels.^{2,11} This is evidently associated with the greater polynuclear aromatic content of the synfuels.

The formation of soot has been the subject of much study, but the process by which it is generated has not been established. Among currently favored theories is the proposal that polyaromatic, multiple condensed-ring materials are formed which condense as a solid similar in structure to graphite or coal of high rank.¹³ Another explanation is based on the fragmentation of the carbon structures of the fuel into two-carbon or acetylenic species, or even further to single carbon fragments, which subsequently recondense or polymerize to produce soot. Experimental observations on soot formation from aromatic hydrocarbons showed that the rate of soot production decreased above $2780^{\circ}F$ ($1800^{\circ}K$), after increasing rapidly with temperature up to that point. Fragmentation of aromatic rings is commonly associated with such temperatures. The change in rate was attributed to rapid soot formation from ring compounds at the lower temperatures being replaced by a slower process of fragment condensation at the higher temperatures. Another theory attributes a major role in generation of soot to ion chemistry. Ionization in hydrocarbon flames is a much investigated subject. Ionization occurs as a result of thermal ionization and chemi-ionization from specific reactions. Mass spectrometric study of flames in the PETC SU Program reviewed here showed larger ions of 3000 AMU and greater becoming relatively more important with respect to the total ion current with distance from an experimental burner. Presumably the larger ions result from a polymerization which eventually produces soot.

Pyrolysis can also occur with formation of CH_4 and olefinic gases from the synthetic fuel in the presence of limited amounts of oxygen, as in combustion staging to limit production of NO_x .

With progression of the fuel spray and vaporized components into the combustion zone where mixing with oxygen has taken place, the combustion oxidation of the fuel occurs. In a modified global reaction model of the process which permits numerical evaluation of the reactions with appropriate rate constants, the "quasiglobal" model, complex fuel molecules are first viewed as reacting to form acetylene (if aromatic) or ethylene (if aliphatic), CO , and H_2 . The succeeding reactions in which CO and H_2 are transformed to the final oxidation products, CO_2 and H_2O , are then considered in detail with a more comprehensive kinetic mechanism and rate constants from basic studies. A mixed fuel of toluene and iso-octane has been studied as a model of the complex aromatic-aliphatic SRC-II fuel in the DOE/PETC Synfuel Utilization Program. The system of reactions by which combustion of the model fuel proceeds to the intermediate oxidation products is given in Table 3. The sequence of reactions (1) - (12) illustrates how a complex initial fuel is oxidized step-wise to more simple substances in stages permitting estimates or experimental measurements of the rates of parameters. Completion of oxidation in the better known elementary steps is presented in Table 4.

Continuing evaluation of the reactions in the complete system may reveal that a limited number are significant. For example, investigators at Princeton in the PETC SU Program have concluded that reaction 13 of Table 4, the attack of CO by OH , accounts for 90% of the oxidation of CO in combustion.

Table 3. Quasiglobal Reactions of
Toluene and Iso-Octane Fuel Model*

GLOBAL REACTION STEPS

1. $C_7H_8 + \frac{7}{2} C_2H_2 + \frac{1}{2} H_2$
2. $C_7H_8 + OH + \frac{7}{2} C_2H_2 + H_2 + \frac{1}{2} O_2$
3. $C_7H_8 + \frac{7}{2} O_2 + 7 CO + 4 H_2$
4. $C_2H_2 + 6 OH + 2 CO + 4 H_2O$
5. $C_2H_2 + 2 OH + 2 CO + 2 H_2$
6. $C_8H_{18} + 4 C_2H_4 + H_2$
7. $C_8H_{18} + OH + 4 C_2H_4 + \frac{3}{2} H_2 + \frac{1}{2} O_2$
8. $C_8H_{18} + 4 O_2 + 8 CO + 9 H_2$
9. $C_2H_4 + 8 OH + 6 H_2O + 2 CO$
10. $C_2H_4 + 2 OH + 3 H_2 + 2 CO$
11. $\frac{7}{2} C_7H_8 + C_2H_2 \equiv HC + SOOT$
12. $SOOT + O_2 + CO_2$

* Model from Science Applications, Inc., prepared for DOE/PETC
Synfuel Utilization Program

Table 4. Elementary Reactions*

Wet CO Mechanism H₂O₂ Mechanism HCHO Mechanism

* Model from Science Applications, Inc., prepared for DOE/PETC Synfuel Utilization Program

The removal of soot occurs by further reaction with a number of components of the combustion gases which have been discussed elsewhere.¹³ In the reaction system shown only the interaction with molecular oxygen is considered (reaction 12, Table 3). This is the fastest reaction by several orders of magnitude with the common molecular species which may be present (e.g., CO_2 , H_2O , H_2) according to studies with carbon. Oxidation of soot can be appreciable in combustors with extended residence time.

In fuel drops of mixed composition containing a volatile and a non-volatile material, the volatile component contributes to a short ignition time, while the non-volatile component determines the time required for drop burn-out.

The processes of coal liquefaction by hydrogenation give a marked reduction from the initial nitrogen content of coal to the synthetic fuel products, although the remaining amount is still much higher than that of common petroleum fuels (Tables 1 and 2). Nitrogen contained in the fuel contributes to the pollutant NO_x produced in combustion. In addition to oxidation of fuel nitrogen, high temperature flames such as those encountered in hydrocarbon combustion cause reaction of atmospheric nitrogen with oxygen in air forming "thermal" NO_x . A method has been developed for reduction of NO_x by fuel-rich combustion in a initial stage limiting the access of oxygen to the fuel nitrogen and reducing either flame temperature or the time in which the substances are exposed to the full flame temperature.⁴ Combustion staging in this way promotes reaction of fuel nitrogen under conditions favoring formation of molecular nitrogen in place of NO_x and reduces the extent of thermal NO_x formation. The ease of soot formation from synfuels, which is favored under the fuel-rich conditions of combustion staging, requires especially careful selection of the fuel:air ratio and combustion conditions in general to obtain effective minimization of NO_x without excessive formation of soot. Studies of pyrolysis

of pure aromatic molecules containing nitrogen as models of synfuel components has shown that nitriles (Ar-CN) are formed. Such reactions are analogous to production of HCN from aliphatic hydrocarbons, which can also appear by the intervention of hydrogen-containing species from synfuels if there are sufficient present. The aromatic nitriles can form NO_x by reactions similar to those of HCN if they react with oxygen or form N_2 instead if provided with suitable reducing conditions.

5.0 REVIEW OF THE SYNFOEL UTILIZATION PROGRAM

The investigations making up the PETC Synfuel Utilization Program are reviewed in this Section. Discussion of the individual projects covers results obtained through September 30, 1982.

5.1 ORGANIZATION OF THE SU PROGRAM

Management responsibility for the SU Program was held by the Pittsburgh Energy Technology Center, and direction was provided by its staff with experience spanning several decades in synfuel investigations and combustion studies. Mr. Daniel Bienstock of PETC supervised the overall course of the SU Program. Leading investigators and institutions including universities, non-profit research institutes, and industrial research laboratories contributed to the studies.

Three tables summarize the projects making up the SU Program; Table 5 is a listing by subject in the order found in the preceding review of the field and in the following discussion of the individual projects. The order is generally that of the processes encountered by the synfuels as they progress through a combustor. Table 6 is a listing of organizations taking part in the work, and Table 7 is a numerical index by contract number.

5.2 NATURE AND SCOPE OF THE SU PROGRAM

The major subject of the SU Program is combustion of synfuels, including aspects of spray preparation and drop interactions in flame processes. Laser optical studies of liquid sprays in commercial atomizers have provided detailed pictures of drop formation and the effects of temperature and pressure on the spray. An analytical model of a spray warming under the influence of combustion was initiated containing parameters of heating, vaporization, and aerodynamic drag on drops dependent on drop spacing. An experimental study of vaporization was made using known compounds to provide identification of substances from vaporization of a middle distillate SRC-II

Table 5
LISTING OF CONTRACTS BY SUBJECT

SUBJECT	INVESTIGATORS	ORGANIZATION	TITLE	CONTRACT NO.
Spray Properties	R.G. Oeding	Spectron	Synfuel Spray Characteristics & Combustion Dynamics	DE-AC22-80PC30299
Fuel Vaporization	A.M. Agnone V. Zakkay	New York University	Effect of Fuel Vaporization on Combustion Efficiency	DE-FG22-81PC40288
	W.A. Sirignano S.C. Yao	Carnegie-Mellon Uni- versity	Vaporization of Synthetic Fuels	DE-FG22-81PC40277
	A. Vranos	United Technologies Research Center	Chemical Effects in Vaporizing Synthetic Fuels	DE-AC22-81PC40278
Soot Formation	J.E. Haebig	Gulf Research & De- velopment Co.	Effect of Synfuel Components on Soot Formation	DE-AC22-80PC30307
	R.M. Kowalik	Exxon Research and Engineering	Alternate Fuel Effects in Combustion Systems	DE-AC22-77ET11313
	D.B. Olson	Aerochem Research Labs	Soot Formation in Synfuels	DE-AC22-80PC30304
	R. Payne	Energy & Environmental Research	Soot Formation in Synfuel Droplets	DE-AC22-80PC30298
	W.T. Rawlins	Physical Sciences, Inc.	Soot Initiation in Burning Aromatics	DE-AC22-80PC30292
	J.J. Sangiovanni	United Technologies Research Center	Combustion and Soot Formation in Synfuel Spray Flames	DE-AC22-80PC30195

Table 5 (Cont'd)

<u>SUBJECT</u>	<u>INVESTIGATORS</u>	<u>ORGANIZATION</u>	<u>TITLE</u>	<u>CONTRACT NO.</u>
Synfuel Combustion	J.M. Beér W.K. Cheng	Massachusetts Institute of Technology	Combustion Characteristics of Synthetic Liquid Fuels	DE-AC22-81PC40275
	R.B. Edelman P.T. Harsha S.N. Schmotolocha	Science Applications	Spray Combustion of Synthetic Fuels: Modeling & Experiment	DE-AC22-81PC40276
Combustion Staging	A. Levy J.R. Longanbach	Battelle Columbus Labs	Synfuel Aromaticity and Staged Combustion	DE-AC22-80PC30302
Combustion Mechanisms	F.L. Dryer I. Glassman	Princeton University	Mechanisms of Hydrocarbon Combustion	DE-FG22-81PC40283

Table 6

LISTING OF CONTRACTS BY ORGANIZATION

ORGANIZATION	PRINCIPAL INVESTIGATOR	TITLE	CONTRACT NO.
Aerochem Research Labs	D.B. Olson	Soot Formation in Synfuels	DE-AC22-80PC30304
Battelle Columbus Labs	A. Levy	Synfuel Aromaticity and Staged Combustion	DE-AC22-80PC30302
Carnegie-Mellon University	W.A. Sirignano	Vaporization of Synfuels	DE-FG22-81PC40277
Energy & Environmental Research	R. Payne	Soot Formation in Synfuels	DE-AC22-80PC30298
Exxon Research & Engineering	R.M. Kowalik	Alternate Fuel Effects in Combustion Systems	DE-AC22-77ET11313
Gulf Research & Development	J.E. Haebig	Effect of Synfuel Components on Soot Formation	DE-AC22-80PC30307
Massachusetts Institute of Technology	J.M. Beér	Combustion of Synfuels	DE-AC22-81PC40275
New York University	V. Zakkay	Fuel Vaporization vs. Combustion Efficiency	DE-FG22-81PC40288
Physical Sciences, Inc.	W.T. Rawlins	Soot from Aromatics	DE-AC22-80PC30292
Princeton	F.L. Dryer	Mechanisms of Hydrocarbon Combustion	DE-FG22-81PC40283
Science Applications, Inc.	R.B. Edelman	Spray Combustion of Synfuels	DE-AC22-81PC40276
Spectron	R.G. Oeding	Synfuels Spray and Combustion	DE-AC22-80PC30299
United Technologies	J.J. Sangiovanni	Soot in Synfuel Spray Flames	DE-AC22-80PC30195
United Technologies	A. Vranos	Chemical Effects in Vaporizing Synfuels	DE-AC22-81PC40278

Table 7
CONTRACT INDEX

<u>CONTRACT NO.</u>	<u>PRINCIPAL INVESTIGATOR</u>	<u>ORGANIZATION</u>	<u>SUBJECT</u>
DE-AC22-80PC30195	J.J. Sangiovanni	United Technologies Research Center	Combustion and Soot Formation in Synfuel Sprays
DE-AC22-81PC40275	J.M. Beér	Massachusetts Institute of Technology	Combustion of Liquid Synfuels
DE-AC22-81PC40276	R.B. Edelman	Science Applications	Spray Combustion of Synfuels
DE-FG22-81PC40277	W.A. Sirignano	Carnegie-Mellon U.	Vaporization of Synfuels
DE-AC22-81PC40278	A. Vranos	United Technologies Research Center	Chemical Effects in Vaporizing Synfuels
DE-FG22-81PC40283	I. Glassman	Princeton University	Hydrocarbon Combustion Mechanisms
DE-FG22-81PC40288	V. Zakkay	New York University	Fuel Vaporization vs. Combustion Efficiency
DE-AC22-80PC30292	W.T. Rawlins	Physical Sciences	Soot in Burning Aromatics
DE-AC22-80PC30298	R. Payne	Energy & Environmental Research	Soot Formation in Synfuel Droplets
DE-AC22-80PC30299	R.G. Oeding	Spectron	Synfuel Sprays and Combustion
DE-AC22-80PC30302	A. Levy	Battelle Columbus Labs	Staged Combustion of Synfuels
DE-AC22-80PC30304	D.B. Olson	Aerochem Research Labs	Soot Formation in Synfuels
DE-AC22-80PC30307	J.E. Haebig	Gulf Research & Dev.	Synfuel Components and Soot
DE-AC22-77ET11313	R.M. Kowalik	Exxon Research & Engi- neering	Synfuels in Combustion Systems

synfuel. A burner utilizing vaporized No. 2 oil was investigated to determine combustion characteristics. Several investigations dealt with soot formation, considering specific effects of the aromatics content of synfuels as well as drop combustion. The combustion of synfuel sprays in experimental combustors was studied with some work on burn-out time, mixing chemical processes, and mechanisms. A portion of this included development of an analytic model covering drop processes and kinetics of the chemical transformations. Combustion staging to reduce NO_x pollution was also under investigation. Advanced experimental methods were used, including nanosecond laser photography and capillary gas chromatography, in various studies.

5.3 REVIEW OF PROJECTS

At the time of this review some of the projects had been completed after several years work, while others were in an early stage. This accounts for the wide range in amount of information obtained which may be noted among different studies.

PROJECT: SYNFUEL SPRAY CHARACTERISTICS AND COMBUSTION DYNAMICS

Observations of synfuel sprays in the process of formation from commercial sprayers and in combustion flames have been made with laser holography at Spectron Development Laboratories under the direction of R.G. Oeding. Successive short-exposure holograms reveal the stages of formation of liquid drops from the injected liquid. Size of the drops produced and their velocity were measured by interferometry and determined as a function of temperature, injection pressure, viscosity, etc. The SRC-II middle distillate was compared with No. 2 and No. 6 oils.

Initial studies were made in cold flow in the absence of combustion. Photographs obtained by laser illumination of a conical spray generator show a conical liquid sheet near the orifice with instability appearing as the cone expands. The sheet separates into filaments which in turn break up into

droplets. Measured droplet size from two commercial sprayer types were obtained, one a pressure swirl orifice, the other an air atomization nozzle. Mean droplet size typically ranged from 55 μm to 150 μm . The results were in general agreement with empirical correlations with respect to viscosity, surface tension, and density of the liquid. The behavior of SRC-II middle distillate was similar to that of No. 2 fuel oil, which it closely resembles in boiling range, viscosity, and surface tension. The density of the middle distillate is higher, however, exceeding even No. 6 fuel oil. Large drops become distorted in spray burning. Large soot trails were observed in both SRC-II and No. 2 fuel oil. These have been observed in combustion or pyrolysis of pulverized coal.

PROJECT: EFFECT OF FUEL VAPORIZATION ON COMBUSTION EFFICIENCY

An oil burner utilizing 1 gph of fuel in which the fuel oil is vaporized rather than sprayed for combustion was studied at New York University under the direction of V. Zakkay. The burner was developed using No. 2 oil. Preliminary tests with satisfactory results were made with SRC-II middle distillate.

The burner is started by a preheat phase of approximately 40 sec in which a fuel spray with lean stoichiometry ignited by a spark heats the vaporization cylinder surrounding the fuel injector and a nickel steel screen flame holder. The vaporizing surface is kept hot by air recirculation thereafter above the 650 F vaporization temperature needed. The vaporized fuel is mixed with regeneratively heated air, and the close-to-stoichiometric mixture ignites on the hot screen. The preheat spray has a yellow flame. Transition to the vapor combustion mode with a blue flame occurs when the spray ignition spark is discontinued, fuel is very briefly withheld, and ignition is subsequently obtained on the screen with renewal of the fuel flow. Control was obtained with a commercial blue flame sensor.

Calorimetric measurements with water showed a thermal efficiency of 86%. At optimum operation near stoichiometric the smoke

number was zero, CO₂ 15.1%, O₂ 0.6%, CO<200 ppm, NO ~400 ppm. The high NO level was ascribed to high flame temperature, and staging was suggested to reduce the level.

PROJECT: VAPORIZATION OF SYNTHETIC FUELS

The vaporization of droplets containing mixtures of volatile and nonvolatile liquids was investigated at Carnegie-Mellon University under the direction of W. Sirignano. Both theoretical and experimental work was done. The goal is to find the loss from mixed droplets and the associated composition resulting from heating and gas flow in high temperature, high velocity streams such as synfuel droplets encountered in combustion.

For individual drops the processes considered are vaporization, internal circulation, and liquid phase mass diffusion. The external fluid dynamic influences are obtained from a relationship derived between the Nusselt and Reynolds numbers. The analysis was then extended to the interaction between drops, as in a spray, where Nusselt number and drag coefficient are affected by the spacing between drops in a simple array.

PROJECT: CHEMICAL EFFECTS IN VAPORIZING SYNTHETIC FUELS

Drops of SRC-II middle distillate were heated on a vaporizing surface at temperatures from 200-510°C and in the gas phase of a furnace at 1000-1300°C to study vaporization and decomposition at United Technologies Research Center under the direction of A. Vranos.

The greatest change in concentration from heating on a surface occurred in the temperature range of 200-250°C. The compounds determined by analysis (capillary gas chromatography) were 2-methylnaphthalene (6%) dimethylnaphthalene (2.8%), o-cresol (2.3%), fluorene (0.6%), and phenanthrene (0.2%) in order of decreasing concentration in the fuel. The change in concentration from that in the fuel to the distillate was closely a linear function of the boiling point of the respective substances, the phenol, cresol, and naphthalene concentrations increasing in the distillate, methyl- and dimethylnaphthalenes remaining approximately

the same, and the less volatile fluorene and phenanthrene decreasing, as expected from the relative boiling points which fall in the region of the heating temperatures studied. Droplets of the SRC-II fuel exposed to furnace temperatures of 1000°C and 1150°C for ~100-300 ms produced light gases (CH_4 , C_2H_4 , C_2H_6) from which the extent of pyrolysis was estimated as 1.4-4.5%.

PROJECT: EFFECT OF SYNFUEL COMPONENTS ON SOOT FORMATION

The soot produced by different chemical fuels of structure related to those found in SRC-II liquids was the subject of study by J.E. Haebig at Gulf Research and Development Co.

Soot was measured with a laser optical system by the scattering caused by the small particles. Combustion of pyridine gave no soot, whereas toluene produced an appreciable amount. A 3:1 (by volume) blend of toluene-pyridine gave considerably less soot than expected from the high toluene/pyridine ratio. An SRC-II middle distillate fraction gave less soot than toluene, in accord with a higher hydrogen content (9.2-9.6% vs. 8.7% in toluene). More soot was observed from fuel with higher aromatic content, but there were exceptions.

Combustion in a premixed flat-flame burner was chosen for investigation to provide a stable system better suited to quantitative optical measurements than more realistic droplet burning and possibly physically more simple. However, the flat-flame burner introduced problems of its own. Higher molecular weight fuels give cellular flames in which there is non-uniform production of soot. Individual cells each produce a concentration of soot, and the cells exhibit lateral motion on the burner, causing fluctuations in the laser signal. Dissipation of the cellular structure in this type of burner to give a homogeneous flame requires low molecular weight fuel with two carbon atoms or less providing improved diffusion. Ethylene was used for this purpose. However, ethylene was required to be 60% of the fuel equivalence ratio in ethylene-toluene mixtures to obtain a uniform flame. Ethylene-pyridine mixtures produced considerably less soot

than would be estimated from a linear function of composition compared to pure ethylene, the same effect noted in ethylene-toluene mixtures. Additional problems of flame instability, blow-off, and inadequate premixing were encountered with the flat-flame burner. The laser measurement of soot requires that particle diameters be less than 1/10 of the wavelength used (488 nm), attenuation only by Rayleigh scattering (not absorption), and particles so dilute that multiple scattering not occur.

PROJECT: ALTERNATE FUEL EFFECTS IN COMBUSTION
SYSTEMS

The effect of fuel structure and of mixing and other combustion variables on sooting and NO_x formation was investigated in experimental work at Exxon Research and Engineering Company by W.S. Blazowski, R.M. Kowalik, and L.A. Ruth, associated with analytic modeling at Science Applications, Inc., by R.B. Edelman, R.C. Farmer, and E. Wang. More realistic evaluation of soot and pollution problems in practical combustors such as stationary turbines was sought than the traditional laminar flame studies provide. The well-stirred spherical reactor was selected as an experimental device, and fuels of aliphatic and aromatic molecular structure were tested in both gas phase and liquid spray combustion.

Three groups of fuels were distinguished according to soot formation in homogeneous gas phase burning. The first group, aliphatic hydrocarbons including ethylene and hexane, gave no detectable soot over a wide range of conditions, even at very fuel-rich ratios with air and when hydrocarbon fragments were present in the product gas at high levels. The second group contains aromatic compounds, such as toluene and tetralin, which formed quantities of soot beginning sharply at the equivalence-ratio threshold indicated by "hydrocarbon breakthrough," the first appearance of unburned hydrocarbons in the product gases. With most second-group compounds this occurred at an equivalence ratio (fuel:air/stoichiometric

fuel:air) of approximately 1.4. The concentration of oxygen in the product gases increased with increasing hydrocarbon after breakthrough. The only substance tested in the third group was 1-methylnaphthalene, which was so strongly sooting at even low equivalence ratios that it demands a separate class. Presumably other condensed-ring (multiple ring) compounds fall in this class.

Blends of isooctane and toluene were investigated to examine the characteristics of fuels which are typically mixtures of aliphatic and aromatic compounds. Synfuels generally contain larger amounts of aromatics compared to petroleum-derived liquids. Blends containing greater than 50% toluene produced soot at fuel-rich equivalence ratios (generally ≥ 1.4 required for soot). Little soot was formed at ratios less than 1.6 with the 50% blend. Soot was not observed from combustion of blends with less than 25% toluene. Study of parameters in the stirred spherical reactor showed that increasing temperature decreased sooting at a fixed fuel-air ratio, and a higher ratio was possible without sooting at higher temperature. The amount of soot increased when the pressure increased. Improved mixing decreased soot. Soot yield from aromatic fuel increased with increased concentration of unburned hydrocarbons observed in the product gases. On the other hand, there was no soot from isooctane even in the presence of quantities of unburned hydrocarbons in homogeneous gas combustion in the stirred spherical combustor.

Acetylene was observed as a major component of the product gases in both toluene and isooctane combustion. The investigators concluded that formation of soot from toluene but not isooctane indicates that the path to soot does not go through acetylene as proposed in some theories but through some other intermediate readily formed from toluene. At 1900°K and 2000°K combustion of 1-methylnaphthalene gave only slightly more soot than toluene, unlike combustion at lower temperatures. This change

was ascribed to fragmentation of the aromatic rings at the higher temperatures (associated with a threshold temperature of 1800°K). Possibly, the condensation of aromatic rings to soot occurring at lower temperatures is replaced by a process of fragmentation followed by polymerization.

Experiments in the well-stirred combustor with injection of liquid sprays gave more soot than with the gases from both toluene and isooctane. With toluene sooting was no longer correlated with hydrocarbon breakthrough. Isooctane formed soot only when injected as a liquid spray. These observations were taken to indicate that mixing was incomplete in the spherical combustor during experiments with liquid sprays. A reduction in drop size led to reduction in soot.

Combustion processes involving fuel nitrogen were investigated by blending pyridine with the fuels studied to give a concentration of 1%N by weight. The conversion of fuel nitrogen to "fixed nitrogen," $\text{NO} + \text{NH}_3 + \text{HCN}$, was measured under different conditions. The type of fuel (toluene vs. isooctane) had the greatest effect on conversion at very rich fuel equivalence ratio (1.8) and short residence time (≤ 10 msec). Toluene gave lower fixed nitrogen while giving more soot. Conversion in fuel-rich mixtures was associated with the concentration of unburned hydrocarbons; there was a lower conversion when the hydrocarbons were present in lower amounts. In experiments with lower fuel nitrogen (about 0.2%) at very fuel-rich ratios the amount of fixed nitrogen species produced was greater than that which could be provided by the fuel nitrogen. Evidently fuel fragments reacted with combustion air nitrogen to produce the added amount. The added reaction appeared greater when there was fuel nitrogen than where there was none. The reduction in HCN when toluene burned at very rich ratio producing much soot was noted as indicating a possible soot-fixed nitrogen interaction. Previous investigations of homogeneous gases in a flame burner and of pulverized coal particle combustion showed similar inverse relationships between soot

and HCN production. The effect of pressure on soot yield was studied. Experimental difficulties from severe deposits prevented the work with pure toluene at increased pressure. Instead, 40:60 toluene-to-isooctane volume percent blends were used. Soot increased from a maximum observed yield of 0.1 weight percent of fuel carbon at 1.2 atmospheres to 0.7 percent at 2.0 atmospheres.

Considerable experimental difficulty was encountered with the well-stirred spherical combustors in this work, as in previous studies of the last few decades with such devices. Thermocouple temperature measurements were increased by 100K for estimated radiation loss. Temperature estimates based on species concentration, however, indicated the possibility of even greater error up to 400^oK in the worst case. This parameter, of course, has a marked, exponential effect on the rates of the reactions concerned in soot formation and conversion of fuel nitrogen. For example, a rule of thumb associates an increase of 10K in reaction temperature with a two-fold increase in rate. Soot measurement also proved difficult. Two methods were used. In one, the product gases were sampled directly by passage through fine Teflon filters, weighed, and analyzed. In the second, the extinction of a laser light beam of 632.8 nm wavelength by absorption and scattering from the soot particles was used to measure soot concentration. The amounts of soot measured with the filter probes varied from one-sixth to one-third of those found by the optical method. In addition, in comparing different experiments some filter measurements showing greater soot concentration in the product gas were associated with laser measurements showing appreciably less. The laser measurements were beset with problems from soot depositing on the combustor observation windows in the path of the light beam and in other regions of the combustor both in and out of the measurement region. Circulation of combustion products in small passages of the experimental device, as in the insulation, contributed to these problems. Observations from probe

sample analysis, the effect of temperature, and the variation in soot yield indicated that mixing was incomplete in the reactors under study.

Modeling of the rate of soot formation from toluene giving good agreement with experimental measurements was provided by the following expression

$$\text{Net soot formation} = R_{SF} - R_{OX} \cdot A_{OX}$$

in which Arrhenius formulations of the respective rates were used;

$$R_{SF} = AT^a C_{HC}^b C_{O_2}^c \exp(-E/RT) \quad \text{gm/cm}^3 \text{sec}$$

where the rate of soot formation R_{SF} is given by coefficient A , 4.66×10^{14} ; exponent a of the temperature T , -1.94 ; exponent b of the fuel concentration C_{HC} , 1.81 ; exponent c of the oxygen concentration C_{O_2} , -0.5 ; and the activation energy E/R , $16,110^\circ\text{K}$. The rate of soot oxidation was found from

$$R_{OX} = 12 \left[\left(\frac{K_Z P_{O_2}}{1 + K_Z P_{O_2}} \right) X + K_B P_{O_2} (1-X) \right],$$

where $X = (1 + K_T/K_B P_{O_2})^{-1}$, and $K_A = 20 \exp(-30,000/RT)$, $K_B = 4.46 \times 10^{-3} \exp(-15,200/RT)$, $K_Z = 1.51 \times 10^5 \exp(-97,000/RT)$, and $K_T = 2.13 \exp(4100/RT)$. A diameter of $250 \text{ \AA}$ was assumed for the soot particles to provide the area undergoing oxidation A_{OX} . Soot oxidation according to this relation is less than 25% of the rate of formation, and the particle size had only a small effect on the net rate of soot formation.

Soot modeling of the experimental results was obtained with these parameters, which were derived from the measurements, despite the experimental difficulties discussed above.

The effect of pressure on soot formation according to this model is a variation of $P^{-0.6}$, which is contrary to the marked increase of soot yield observed with a slight pressure increase. The investigators suggested that the role of pressure in greatly improving nucleation could account for the observed result. On the other hand, the parameters in the soot model were derived from the combustor measurements of this project and may be inaccurate on that account.

The combustion of toluene and isooctane and the conversion of nitrogen in the fuel and air were modeled beginning with quasiglobal reactions for the specific fuels, followed by detailed specific reaction steps for carbon, hydrogen, and nitrogen intermediates. In the quasiglobal summarizing reactions toluene is first converted according to the following processes (balanced equations given in Table 3):

The analogous processes for isooctane were

These initial reactions are followed by further oxidation of the acetylene and ethylene, respectively, and combined with remaining oxidations in the categories of "wet" oxidation of CO, intervention of peroxide species, of formaldehyde, the thermal

nitrogen and oxygen reactions, hydrocarbon fragment-nitrogen oxidations, and hydrocarbon fragmentation (largely oxidative). A total of 124 reaction steps and rates are considered in the complete model. Good agreement was obtained with the experimental measurements from model calculations for combustion of toluene and isooctane.

PROJECT: SOOT FORMATION IN SYNFUELS

A study of soot formation from synfuels by testing many chemical compounds to find if there are systematic effects of molecular structure and investigating basic processes particularly of ionic species and the influence of pressure was made at Aerochem Research Laboratories by D.B. Olson, H.F. Calcote, and colleagues.

The molecular structure studies were based on the Threshold Sooting Index, for premixed flames

$$TSI = a - b\phi,$$

where a and b are experimental constants, and ϕ is the minimum equivalence ratio at which soot appears; and for diffusion flames

$$TSI = \frac{a' (M)}{(S)} + b',$$

where a' and b' are experimental constants, M is the molecular weight of the fuel, and S is the fuel smoke point (in ASTM Method DI 322-75).

Available values on premixed flames indicated a structure correlation, with aromatic compounds exhibiting large values of TSI and aliphatic substances low values. Measurement of some 40 fuels representative of aromatic, alicyclic, aliphatic, and olefinic structures did not show a well-defined relationship of Threshold Sooting Index with number of carbon atoms in the fuel within the classes of molecular structure, although

aromatic compounds were clustered around a markedly higher value (~80) than alkanes and alkenes (~40) and alkynes (~20). The distinction among the latter three structures with lower TSI values was very unclear. There was no correlation of the TSI with flame temperature at the minimum equivalence ratio giving soot.

Another parameter, the soot volume fraction (the ratio of soot volume to flame volume in premixed flames), was studied at different equivalence ratios. The soot volume fraction increased exponentially with increasing equivalence ratio in the case of aromatic compounds with substituent methyl groups. For example, the soot volume fraction of o-xylene and toluene increased smoothly from 0 at the equivalence ratio threshold, between 1.4 and 1.5, to close to 1×10^{-6} at a ratio of 1.94. The soot volume fraction was much lower and increased more slowly in aliphatic-hydrocarbons and olefins. For example, with isooctane, 1-octene, and 1-decene the soot volume fraction increased only from 0 at the threshold equivalence ratios of 1.7-1.8 to approximately 0.1×10^{-6} at a ratio of approximately 2.1. Thus, the soot volume fraction of these non-aromatic fuels increased approximately one-tenth as rapidly with equivalence ratio as the aromatic fuels. Ethyl benzene and decalin fell between these two groups, the former more closely resembling the aromatics with which it would reasonably be associated on the basis of its molecular structure. The markedly higher soot volume fractions of the others may indicate a special effect of the methyl aromatic substituent. This is supported by the greater sooting of 2-heptyne compared to 1-heptyne. However, 1-octyne was found to produce even more than 2-heptyne at the same equivalence ratios. Linear relationships of soot volume fraction with number of carbons were obtained for alkanes, alkenes, and alkynes. The good fit observed with the first two types of compounds may be associated with the fact that all gave low soot, from 0- 0.1×10^{-6} as the volume fraction. There was wide scatter of experimental points from the mean squares

line for aromatic compounds, which produced five times as much. Alkynes, with soot volume fraction somewhat lower than this and overlapping that of alkenes and alkanes exhibited intermediate scatter and relatively satisfactory agreement in the linear function obtained. Correlation of the soot volume fraction with flame temperature was weak, but it correlated much better in all four types of compounds with the soot threshold equivalence ratio.

Mass spectroscopic study of ions in acetylene-oxygen flames as a function of position above the burner was made to determine the role of charged species in soot formation. The major portion of the total current of approximately 10^{-8} A was in the form of ions of 0-100 AMU and 100-300 AMU. Up to 10% of the total current close to the burner was 300-1000 AMU, the amount decreasing rapidly at greater distance. Ions greater than 3000 AMU made up approximately half as much current as the latter at the location of the maximum 1-2 cm from the burner. These larger ions decreased less rapidly so that they became relatively more important, although only approximately 1% of the total at farther distances. Ions in the range of 1000-3000 AMU were present in lowest concentration, 10^{-10} A at their peak, approximately half of the peak current of those with masses greater than 3000 AMU. Their concentration decreased precipitously in the region from the peak at 1 cm distance to 2 cm. These preliminary results provide some support for the view that increasing ion size through polymerization occurs in sooting.

PROJECT: SOOT FORMATION IN SYNFUEL DROPLETS

Droplet combustion parameters affecting soot formation particularly associated with staging to control NO_x were investigated at Energy and Environmental Research under the direction of R. Payne. The fuel rich stoichiometry used in staging can readily give increased soot. Comparison of No. 6 fuel oil with the SRC-II middle distillate and heavy distillate, a blend of the two, and EDS and H-Coal synfuels was made under a number of conditions. Droplets of the respective fuels were

passed through a cylindrical combustion furnace to observe droplet processes, and similar studies were carried out by injection of droplets across a down-firing flat flame burner.

The overall sequence of physical processes which the droplets undergo is depicted in a series of alternate pathways. The droplets are warmed to the boiling temperature as they enter the combustion region. Vaporization may cause fragmentation into smaller droplets which terminate their existence in microexplosions. Particularly with synfuels smaller droplets remaining after vaporization or combustion processes commonly disappear in microexplosions of approximately 100 msec duration. The nonfragmented drops burning while vaporizing, in rich stoichiometry form soot trails and on progressive reaction either become smaller in size and terminate in microexplosions or complete their combustion, leaving a residue in the form of a cenosphere. Burning drops in lean stoichiometry exhibit an attached flame when gas velocities are low. Drops burning in this mode also either attain a small size which terminates in a microexplosion or leave a cenosphere from which the combustible material has been used up during the process. If gas velocities are higher, drops burning in lean stoichiometry exhibit non-attached flames (blow-off) or extinction and on reduction in size through materials loss end in microexplosions or burn at approximately constant size and leave a cenosphere residue.

Measurement of NO_x produced at different stoichiometric (equivalence) ratios in the combustion furnace showed that all the fuels exhibited a minimum at an oxidizer/fuel ratio of 0.75 which changed little for most fuels from 0.7-0.8. The average concentration at this ratio was approximately 160 ppm, only SRC-II heavy distillate and Synthoil producing appreciably more at this ratio (about 200 ppm and 300 ppm, respectively). Soot formation is increasing significantly with decreasing oxidizer/fuel stoichiometry at the NO_x minimum and, depending on the fuel, can be 15-100% higher than at the lean equivalence ratio of 1.15.

Comparison of SRC-II heavy distillate, No. 6 fuel oil, and SRC-II middle distillate in the tube furnace indicated similarities in the behavior of all three with respect to sooting. Both heavy distillate and No. 6 oil gave a Bacharach smoke number of 9 in larger drop size (70 μm peak of 20-100 μm broad distribution), soot, and large cenospheres. The heavy distillate formed more particles less than 1 μm in diameter in the coarse sprays than both other fuels. Soot increased by an order of magnitude with a two-fold increase in the C/H ratio accompanying increased aromatic content found in the range of fuels studied (diesel marine fuel, SRC-II middle distillate, SRC-II middle and heavy distillate blend, and SRC-II heavy distillate). With drop size decreasing to 40 μm , 20 μm , and below, particulates from both SRC-II heavy distillate and No. 6 oil decreased. The SRC-II heavy distillate then produced only very fine ash, no soot or cenospheres. No. 6 oil gave decreasingly small cenospheres and fine ash. SRC-II middle distillate gave much less particulate solids, approximately one-fifth at the largest drop size, in the form of soot. The amount of residual solids decreased only slightly with smaller drop size, and the product was very fine ash. These comparisons were made at the conditions of minimum NO_x emission at low secondary air flow. With higher spray velocity from a three-fold increase in secondary air flow the changes with drop size in amount of residual solids from SRC-II heavy distillate almost disappeared, although some cenospheres were obtained at lower drop size than before. No soot was observed in the largest drop size of SRC-II middle distillate, unlike the result in low flow.

The microexplosions of small synfuel droplets produced a jet of soot, occasionally two in opposite directions. The jet sometimes formed a mushroom-shaped cloud.

Additional details were obtained from the droplets observed traversing a flat flame. Diffuse trails of finely divided soot became visible in the wake of the droplets. These bands

collapse rapidly into fine filaments somewhat longer than 1 mm. The filaments are aggregations of spherical particles 500 Å in diameter such as those noted previously in droplet wakes and pulverized coal flames. The least soot was produced by SRC-II middle distillate, which has relatively little aromatic content, these compounds occurring largely in the heavy distillate fraction. In fuel-rich stoichiometry maximum sooting was observed at 1700°K, similar to observations in pyrolysis of aromatic compounds. The maximum was attributed to the net result of the competitive processes of polymerization and thermal dissociation of the fragments of aromatic compounds.

The concentration of fuel fragments produced when the droplets pass through the flat flame was measured. In fuel-lean combustion, the species observed from droplets of SRC-II middle distillate at the closest position, approximately 4 mm from the methane-air flat flame, were C₂H₂ (210 ppm), CH₄ (110 ppm), C₂H₄ (50 ppm), and C₃ species (ca. 10 ppm). These concentrations were greatest at the first position measured and decreased rapidly at positions further from the flame. At 2 cm distance C₂H₄ and C₃ species had disappeared, CH₄ was reduced to approximately 15 ppm, and only acetylene (C₂H₂) was still present in moderate quantity, 40 ppm.

Thus, major chemical activity has been completed within the 2 cm distance in a time scale of 200 msec. The soot concentration reaches its maximum of approximately 6000 mg/m³ within a few millimeters after this zone, peaking at the location where the hydrocarbons (in particular, methane) have disappeared. After this point the soot concentration drops, presumably by dispersion of the particles in the stream and by oxidation of the material. The gas temperature is fairly uniform through the reaction zone, decreasing steadily from 1250°K to approximately 1185°K. The soot temperature exceeded the gas temperature appreciably, about 1900°K vs. 1250°K, close to the flame.

PROJECT: SOOT INITIATION IN BURNING AROMATICS

Mechanisms of soot formation from pure aromatic compounds were sought in shock tube kinetics at Physical Sciences, Inc. in work directed by W.T. Rawlins. Conditions found in combustion were used in study of pyrolysis of toluene and pyridine in the absence of oxygen over the temperature range 1400-2500°K. Ultraviolet, visible, and infrared spectroscopy were used as diagnostics. Attenuation of 632.8 nm light appeared to be primarily due to soot.

Toluene was found to give soot readily, over half of the compound being converted at approximately 1960°K after 2 ms. The initial soot formation rate was reported as $6.0 \times 10^{12} \exp(-34.9 \text{ kcal/RT})$. Soot yield decreased at both lower and higher temperatures. The yield was lower at shorter reaction time. At 0.5 ms, the maximum soot yield occurred at 2150°K. A discontinuity in soot formation was indicated by the optical diagnostics in beam attenuation at approximately 1800°K, in agreement with previous reports that a change in mechanism evidently takes place at this temperature. While earlier investigators associated the change with a transition from aromatic ring condensation to soot at lower temperature to fragmentation followed by polymerization/condensation at higher temperature, recent mass spectroscopic study indicates that C_2 fragments are the primary intermediates in both temperature regions. An additional light attenuating process appeared above 2000°K at an earlier time (at approximately 100 μ s or less) than the maximum at around 500 μ s seen at lower temperature. This was ascribed to an additional fast soot process.

Comparison of the optical attenuation at different wavelengths (305, 389, and 633 nm) indicated that the soot particles are larger than permissible for use of the Rayleigh limit theory in accounting for the extinction. The complete treatment of the Mie scattering theory is required. A particle radius of

approximately 400Å was estimated, which is larger than previously reported.

Pyridine formed no detectible soot over the 1400-2500°K temperature range.

PROJECT: COMBUSTION AND SOOT FORMATION IN
SYNFUEL SPRAY FLAMES

A study of droplet interactions in combustion and formation of soot was made at United Technologies Research Center by J.J. Sangiovanni.

The ignition delay of droplet streams increased markedly when the space between droplets was reduced below five droplet diameters. This was ascribed to the reduction in heating rate from the effect of larger droplet concentrations. The time required for complete burning of droplets also increased as their concentration increased and the space between droplets became smaller. The parameters considered are the increase in droplet burning time and the ratio of droplet spacing to diameter. The burning time increase was measured as the ratio of time observed at the spacing of interest to a reference time found at spacings of 35-40 diameters where little or no change in burning time occurs with increase in spacing. The burning time of 100-300 μm droplets increased rapidly as the inter-droplet spacing decreased below 15 diameters. The experimental points for a number of fuels including n-hexadecane, i-octane, and their mixtures, No. 2 fuel oil, furfuryl alcohol, and butyl alcohol were in good agreement with the near-hyperbolic curve which approached asymptotes at a spacing of five drop diameters (i.e., giving almost infinite increase in burning time at this spacing) and at 40 drop diameters (zero slope at this spacing). The burning time evidently depended on drop spacing only and was not affected by flame temperature or fuel. The investigator ascribed the effect to limitation of oxygen diffusion to the drops.

The ignition of nonvolatile fuel drops was improved by a small amount of volatile fuel, i.e., ignition time was reduced; but the burning time of such fuel blends was determined by the nonvolatile fuel. This combination of effects was attributed to early volatilization of the light fuel near the drop surface. Following depletion of the volatile fuel from the surface of the drop, its diffusion from the drop interior is relatively slow; and burnout is controlled by the nonvolatile component.

The temperature of the droplet flame was measured as a function of distance from the droplet with a reversal method using a temperature calibrated source. A smooth curve was obtained with temperature varying from 1500°K to 2000°K as the distance varied from 2 to 10 droplet radii.

The soot produced from n-hexadecane varied with the time elapsed in droplet burning. With spacing between drops of 10 diameters the distribution of particle size formed at the time of first appearance of soot exhibited a peak at $35\text{\AA}$, where the peak represented 20% of the total soot formed. At intermediate time the maximum of a broader distribution was $220\text{\AA}$ representing 10% of the total. At burnout the peak in the size distribution was $385\text{\AA}$ in a much broader range of which this size region was approximately 6% of the total. Infrared spectroscopy of the successive products showed changes in chemical structure. The early soot exhibited absorption bands of aliphatic C-H and carbonyl structures. These structures had disappeared in the intermediate time material. In the soot obtained at burnout aromatic hydrogen and aromatic C=C frequencies were observed. There was also an absorption at slightly greater than 800 cm^{-1} taken as a possible indication of acetylenic hydrogen, but bands at other characteristic acetylenic frequencies were evidently absent.

SRC-II middle distillate gave approximately eight times as much soot as n-hexadecane. The soot produced by different

fuels increased as droplet spacing was reduced. The rate of increase with change in spacing was linear and approximately the same for fuels studied, even for cases in which widely different amounts of soot were formed.

PROJECT: COMBUSTION CHARACTERISTICS OF SYNFUELS

Combustion studies in turbulent and flat flame burners with chemical modeling of reactions to examine fuel nitrogen processes were made at Massachusetts Institute of Technology under the direction of J. M. Beér.

In the flat flame experiments product species HCN, NH_3 , NO, C_2H_2 , and CH_4 were measured as a function of distance from the burner for C_2H_4 /air with added NH_3 to simulate fuel bound nitrogen. Formation of HCN is complete prior to the first measurement in fuel-rich experiments, all showing the highest HCN concentration initially followed by rapid decay. HCN was present in larger quantities than NO_x and with NH_3 represented a major species of fuel nitrogen conversion under fuel-rich conditions. The hydrocarbon fuel reactions were provided by four sets of kinetic stages, the H_2/O_2 reactions, the oxidation of CO, reactions involving HCHO, and C_1/C_2 species coupled reactions. With the best current kinetic values CH_4 and C_2H_2 burnout rates in the flames were computed in good agreement with those observed. C_2H_2 disappearance was always somewhat greater than could be accounted for, however. Addition of the reaction of OH with acetylene producing ketene CH_2CO instead of CH_3 free radical increased acetylene burnout but was still insufficient to account for the rate observed. CH_3 recombination in competition with oxidation by OH was significant. On the other hand, CH reactions gave no effect in the computed values, and this species was omitted.

A condensed kinetic scheme was used as the basis for combustion system calculations in plug flow and for a well-stirred reactor.

The plug flow model gave unrealistically low NO produced (e.g., 10 ppm), while the stirred reactor model gave calculated formation of greater amounts (45-55 ppm), although still lower than observed. Thus, the latter model is more representative of realistic back-mixed combustors.

Study of a stretched flame surface theory was initiated for modeling turbulent diffusion flames. The flame is depicted as a thin sheet with reacting species transported by convection made up of turbulent diffusion and flame stretching and merging processes. The model separates fluid mechanic and chemical aspects of combustion; decoupling presumably assists in handling complexities in both aspects.

PROJECT: SPRAY COMBUSTION OF SYNFUELS:
MODELING AND EXPERIMENT

An investigation to develop a more comprehensive spray combustion model and obtain experimental data needed for its support as well as pertinent physical, chemical, thermodynamic, and kinetic data concerning synfuels was made under the direction of R.B. Edelman at Science Applications, Inc.

First, the properties of known components of SRC-II fractions were tabulated and compared to those of No. 2 fuel oil. Expansion of the quasiglobal kinetics model utilized for other fuels was considered with respect to the substances found in synfuels and the intermediates which might be produced in their combustion. Description of laminar flat flames was extended to cover diffusion of the numerous components. Spray transport dynamics with turbulence, droplet vaporization, droplet trajectory with a coupled Eulerian-Lagrangian method, and spray size distribution, vaporization, and drag were combined for modeling of spray processes.

An elliptic fluid flow model was developed for experiments planned in a sudden expansion configuration in a burner.

Additional components covering (axisymmetric) swirl flow and turbulence (K- ϵ two-equation model) were included in this model.

PROJECT: SYNFUEL AROMATICITY AND STAGED COMBUSTION

The aromatic and nitrogen-containing components of synfuel fractions, effects of pyrolysis, and pyrolysis in the presence of limited quantities of oxygen were investigated to provide data applicable to NO_x and soot formation from SRC-II synfuel combustion at Battelle Laboratories in work directed by A. Levy.

Pyrolysis of SRC-II middle and heavy distillates in droplet form at the temperatures indicated (residence times 0.3, 1, and 5 sec) gave at 500°C, 95% of the initial liquid recovered (but sulfur content decreased from 0.21 to 0.06 weight %); at 700°C, 74%, and at 900°C, 54%. This progression occurred in the absence or presence of oxygen. The major change found in the liquid recovered was an increase in aromatic content, specifically in unsubstituted aromatics present. There was a decrease in total hydrogen content but an increase of aromatic hydrogen with increasing pyrolysis temperature. At the same time the content of basic nitrogen compounds (determined by strong acid titration) decreased, while non-basic nitrogen compounds increased. In the presence of 8-25% of the stoichiometric amount of oxygen there was a decrease in the unsubstituted aromatics at the highest temperature and a slight decrease in total nitrogen content. The oxygen content was not changed up to the 900°C exposure.

The results were taken to indicate that in staged combustion of SRC-II fuel unsubstituted aromatics and non-basic nitrogen compounds will be the sources of soot and of NO_x in the second stage of combustion. The oxygen-containing compounds, presumably phenolics, are also found in this part of the fuel remaining after the primary combustion stage. The investigators concluded that the presence of oxygen in the fuel-rich

first combustion stage reduces the volatilization of basic nitrogen materials in that stage.

From NMR analysis of the liquid subjected to pyrolysis the increase in aromaticity with temperature was determined. The aromaticity of the starting SRC-II liquid was 0.53. Pyrolysis at 500°C gave only a slight increase to 0.56. At 700°C the aromaticity increased to 0.83 and at 900°C to 0.95. While aromaticity increased with temperature, the number of ring substituents decreased from three groups per ring in the initial liquid to 2.8 in fuel heated to 500°C, 2.3 groups at 700°C, and one remaining at 900°C. Approximately 90% of the aromatic substances from the highest pyrolysis temperature were unsubstituted. The unsubstituted aromatic compounds in the fuel from pyrolysis at 900°C were primarily benzene, naphthalene, phenanthrene, and pyrene.

PROJECT: MECHANISMS OF HYDROCARBON COMBUSTION

Chemical mechanisms and kinetics of oxidation of model compounds similar to those found in liquid fuels or those possibly produced from them by pyrolysis and combustion were under study at Princeton University in work directed by I. Glassman.

Gas chromatographic analysis of products from fuel-rich oxidation of aromatic compounds (ethylbenzene) showed that a range of substances was formed with all possible numbers of carbon atoms from one up to the total in the compound being considered (eight). A sequence of one-carbon degradation reactions was suggested proceeding by way of a free radical, its reaction with oxygen, and loss of CO from the resulting intermediate with concurrent formation of the next lower C_{n-1} compound as in the following:

Study of the "wet" oxidation of CO led to the conclusion that 90% of the reaction proceeds by way of

of the 26 reactions considered.

5.4 SUMMARY OF SYN FUEL UTILIZATION PROGRAM

Studies in the PETC SU Program were focused in three areas of major interest, preparation and properties of sprays including vaporization, formation of soot, detailed chemical reactions related to combustion of synfuel components, such as oxidation, pyrolysis, and kinetic modeling.

The drop studies dealt with details of spray preparation observed by laser holography showing drop formation, distortion, and the formation of soot jets from droplets at high temperature. Vaporization of drops and the interaction among drops in assemblies with different spacing were examined for representative liquids and SRC II distillates. Ignition and burning time are affected by interaction of drops in sprays. The performance of a burner using vaporizing fuels was studied.

Soot formation from representative fuel liquids and synfuels was investigated by laser observation of droplets injected into stable flames. Fuels containing aromatic chemical structure produced more soot than aliphatic hydrocarbons. Stoichiometry of the air-fuel mixture affected the quantity of

soot. Synfuel drops of small size were observed to explode in a flame, forming soot trails. No soot was formed by pyridine under conditions in which much soot was obtained from toluene in shock tube studies.

Research on the chemical reactions occurring under combustion conditions identified intermediate products from coal-derived synfuels. Additional studies concerned synfuel pyrolysis in the absence of oxygen and in its presence and fuel-rich oxidation of model compounds, which produced a full range of degradation products containing from one carbon atom to the full number of carbon atoms in the fuel under study.

Several aspects of the SU Program thus involved advanced research on traditional problems of liquid combustion, such as spray preparation, drop interactions, ignition, and burnout, with consideration of factors specific to synfuels. In addition, formation of soot and combustion processes of fuel nitrogen compounds, which are subjects of major significance in synfuel utilization, were investigated. While important observations were made concerning effect of chemical structure on soot formation and transformation of nitrogen-compound models of synfuel structures, the investigations necessary for adequate understanding and control of these aspects of synfuel utilization are far from complete.

REFERENCES

1. W.S. Blazowski, "Future Jet Fuel Combustion Problems and Requirements," Prog. Energy Combust. Sci. 5, 177-199(1980).
2. W.S. Blazowski, "Dependence of Soot Production on Fuel Structure in Backmixed Combustion," Combust. Sci. Tech. 21, 87(1980).
3. A.A. Boni, R.B. Edelman, D. Bienstock, and J. Fischer, "An Overview of Synthetic Fuel Combustion Issues and Research Activities," American Chemical Society Symposium on the Combustion of Synthetic Fuels, 1982.
4. N.A. Chigier, "Energy, Combustion, and Environment," McGraw-Hill, New York, 1981.
5. P. Chiu, "Spray Combustion of Synthetic Fuels," Proc. Seventeenth Symp. (Inter.) on Combustion, The Combustion Institute, Pittsburgh, PA, 1979.
6. W.R. Epperly, "EDS Product Quality," Interim Report FE 2893-68, Exxon Research and Engineering Co., Florham Park, N.J., March, 1981.
7. G.M. Faeth, "Evaporation and Combustion of Sprays," Prog. Energy Combust. Sci. 9, 1-7(1983).
8. I. Howard-Smith and G.J. Werner, "Coal Conversion Technology," Noyes Data Corporation, Park Ridge, New Jersey, 1976.
9. R. Kollrack and Y. Ksander, "High-Pressure Coal Liquefaction Technology," Report FE-2468-101, August 1982, The Engineering Societies Commission on Energy, Washington, D.C.
10. B.S. Lee, "Synfuels from Coal," AIChE Monograph Series, Vol. 78, No. 14, 1982.
11. J.P. Longwell, "Synthetic Fuels and Combustion," Prog. Energy Combust. Sci. 3, 127-138(1977).
12. R.F. Probststein and R.E. Hicks, "Synthetic Fuels," McGraw-Hill, New York, 1982.
13. S. Singer, "Pulverized Coal Combustion," Report FE-2468-103, April 1983, The Engineering Societies Commission on Energy, Washington, D.C.
14. I. Wender, L.A. Heredy, M.B. Neuworth, and I.G.C. Dryden, "Chemical Reactions and the Constitution of Coal," In: "Chemistry of Coal Utilization, Second Supplementary Volume," M.A. Elliott, ed., John Wiley & Sons, N.Y., 1981, pp.425-521.
15. D.D. Whitehurst, T.O. Mitchell, and M. Farcasiu, "Coal Liquefaction," Academic Press, New York, 1980.