

Combustion of Synthetic Fuels

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Based on a symposium sponsored
by the ACS Division
of Petroleum Chemistry
at the 183rd Meeting
of the American Chemical Society,
Las Vegas, Nevada,
March 28–April 2, 1982

A C S S Y M P O S I U M S E R I E S **217**

AMERICAN CHEMICAL SOCIETY
WASHINGTON, D.C. 1983



Library of Congress Cataloging in Publication Data

Combustion of synthetic fuels.

(ACS symposium series, ISSN 0097-6156; 217)

Includes index.

Contents: "An overview of synthetic fuel combustion: issues and research activities / A.A. Boni . . . [et al.]—characteristics of typical synthetic fuel components" / R. B. Edelman, R. C. Farmer, and T.-S. Wang—"An experimental study of synthetic fuel atomization characteristics" / R. G. Oeding and W. D. Bachalo—[etc.]

1. Combustion—Congresses. 2. Synthetic fuels—Congresses.

I. Bartok, William, 1930— . II. American Chemical Society. Division of Petroleum Chemistry. III. Series.

QD516.C6155 1983 621.402'3 83-2822
ISBN 0-8412-0773-9

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**American Chemical
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FOREWORD

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PREFACE

WITH THE INEXORABLE DEPLETION of premium fossil fuels, oil and gas, it appears that synthetic fuels derived from coal, shale, and tar sands will become part of the overall energy supply in the United States. Synthetic fuels comprise an array of different products including coal derived liquids and gases, shale oil, and methanol. In comparison to conventional fuels, the principal changes that will be introduced by the advent of synthetic fuels affect their production, refining, and end utilization. These are interrelated issues because the end utilization imposes product-quality requirements to which synthetic fuel properties should conform; conversely, it may be possible in certain instances to modify the design of combustion hardware to accommodate properties peculiar to synthetic fuels. This alternative would be particularly attractive from the standpoint of energy efficiency, thus decreasing the need for costly hydrogenative refining steps.

In the utilization of synthetic fuels, the key issues are impact on performance, equipment integrity, and emission characteristics of combustion hardware. Emissions of oxides of nitrogen and soot are the most actively researched emission problems for continuous combustion systems, which range from burners to gas turbine combustors.

This volume provides an overview of current fundamental and applied combustion research studies that address the use of synthetic fuels. The main emphasis in these studies is on the combustion of liquid fuels, ranging from research on spray atomization to pilot-scale testing of the combustion of synthetic fuels.

I wish to thank the contributing authors for their efforts and to acknowledge the help received from Jack Fisher in the early stages of organizing the ACS symposium.

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December 1982

Research Issues and Technology—An Overview

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The need to conserve energy and to control pollutant emissions while at the same time introducing a new generation of fuels derived from coal, oil shale and tar sands is introducing severe requirements on the design and retrofit of combustion equipment. The different chemical and physical properties of these synthetic fuels leads to substantial differences in their combustion characteristics and emissions. In particular there is the potential for increased soot formation, higher NO_x emissions, increased and modified radiation and heat-load distribution, and increased contamination and fouling of combustion and heat transfer surfaces when compared to more conventional fuels. Staged combustion techniques to simultaneously control NO_x and soot production are being developed. However, various burner, boiler and furnace configurations are involved in practical applications and they each have different aerodynamic flow patterns and turbulence characteristics. These flow field characteristics couple with the fuel physical and chemical properties in controlling the efficiency, emissions and fuel flexibility characteristics of practical systems. The U. S. Department of Energy, Advanced Research & Technology Development Program in Direct Utilization, AR&TD (DU), is providing the scientific and technical information for improved, expanded, and accelerated utilization of synthetic fuels in the generic utility and industrial market sectors. In the present paper, we review the current understanding of synfuel combustion, and present an overview of the AR&TD (DU) program.

0097-6156/83/0217-0001\$08.25/0

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With the reduction in the availability of conventional hydrocarbons for fuels in the transportation, utility, and industrial sectors, there is a need to include fuels produced from low hydrogen-to-carbon ratio sources, such as coal, oil shale, and tar sands. Various processes are being developed to produce coal-derived liquids, solids and gases, oil from shale, and heavy oils from tar sands. It has been established that the cost and energy intensive requirements to refine these syncrudes to a hydrogen-carbon ratio and boiling range more typical of conventional fuels is very large (1). Therefore, there is a large economic driving force for the design, development, and implementation of combustion equipment capable of burning synthetic fuels of widely varying properties in a thermally efficient and environmentally acceptable manner.

Concurrently, the need to conserve energy and to control pollutant emissions is also forcing improvements in combustion efficiency and reductions in pollutant emissions of existing energy-conversion devices using present-day fuels including heavy and residual oils. The requirements on the design of combustion equipment to meet these objectives will be severe and will demand substantial improvements in our ability to understand the combustion process and its controlling parameters. Many recent studies have considered the combustion of synthetic fuels, c.f. Black, et al. (2), Bowman and Birkeland (3), England, et al. (4), and Muzio, et al. (5). The problem is that current combustor technology has evolved slowly, is based upon empirical methods, and contains little consideration for fuel flexibility. The situation is particularly acute now because of the present uncertainties in fuel supplies and the corresponding uncertainties in design for fuel flexibility. Because of these uncertainties, equipment manufacturers and industrial users are currently reluctant to make the necessary investments required for either retrofitting or manufacturing new equipment designed specifically for synthetic liquid fuels.

There is a near term need for existing equipment to utilize synthetic fuels and low grade residual fuels that have many of the same combustion problems. Also, there is a longer term need to develop new and advanced equipment to meet the role these fuels may play in the future. Because of the preponderance of existing combustion equipment in place it is necessary to modify current burner devices and systems for synthetic fuels use. Until recently, petroleum-based fuels have been both plentiful and cheap, and design practice has not had to consider the impact of fuel type. Improvements that have evolved have been of mechanical design rather than aerothermochemical. This is no longer sufficient and a better understanding of the effect of synthetic versus conventional fuel properties on combustion process control is required. Through the understanding of the performance of existing hardware and of the effect of fuel types (conventional and synthetic), design criteria for modifying cur-

rent systems can be established. Moreover, this understanding of the effect of fuel type on the combustion process forms the basis for new concept development and will contribute to the upgrading of design procedures through a reduction in the level of empiricism underlying current design methodologies.

Technical Issues Related to Combustion of Synfuels

The physical and chemical properties of synthetic crudes are different from those of petroleum. Increased NO_x and soot production are the principal problems of the combustion of synthetic fuels, and control concepts for these two problems are in conflict. Fuel-rich combustion decreases NO_x but augments soot production, while fuel-lean combustion decreases (and can eliminate) soot production but augments NO_x emissions. Moreover, control procedures can affect combustion efficiency and heat-transfer distribution to the chamber surfaces. Table I, taken from Grumer (6), illustrates some specific relevant properties of synthetic liquid fuels and petroleum-based fuels. The principal differences between these fuels as related to their combustion behavior are summarized in Table II.

In the following discussion, we consider these property differences and illustrate their effect on the combustion process and combustor performance by use of data available in the literature.

The higher aromatic content and the lower hydrogen-to-carbon ratio are chemical properties which combine to promote the increased formation of soot and other related combustion problems. Figure 1, taken from Naegeli (7), illustrates the correlation of increased smoke emission with reduction in H/C ratio for measurements on a T63 gas turbine combustor operating on aromatic-doped petroleum fuels. Similar results have been reported by Pillsbury, et al. (8, 9). The increased soot formation is responsible for the increased luminosity and corresponding enhanced thermal radiation from synfuel flames, c.f. Figure 2, again taken from Naegeli (7). These results and those reported by Pillsbury, et al. (8, 9) indicate the success in using the H/C ratio of the fuel to correlate the sooting tendency and the enhanced thermal radiation which occur for low H/C ratio fuels. The sharp increase of exhaust smoke when the H/C is reduced below 2 is significant, because synfuels made from coal may approach a H/C ratio of 1.2 whereas petroleum fuels have a H/C ratio of about 2.

From a heat-transfer point of view, the high soot concentrations resulting from the combustion of synthetic fuels will tend to cause both higher radiation heating and more severe fouling of heat-transfer surfaces. Depending on the soot concentration and temperature of the combustion gases, as much as 95 percent of the total heat transfer in a furnace or a gas turbine combustor may take place due to radiation; Sarofim (10). The

TABLE I PHYSICAL AND CHEMICAL PROPERTIES OF COAL LIQUIDS*

	SRC LT. ORG. LIQ.	SRC WASH SOLV.	SRC REC. SOLV.	H-COAL LIGHT	H-COAL MEDIUM	EXXON EDS FUEL	No. 2 FUEL. PETROLEUM
SPECIFIC GRAVITY	0.811	0.943	1.031	0.875	0.9426	0.960	0.855
GROSS HEAT OF COMB., BTU/LB	19,000	17,050	17,229	18,800	18,331	18,343	19,500
KINEMATIC VISCOSITY, CS							
@ 104°F	1.03 @ 50°F	1.75	6.04	1.14	2.56	2.67	2.61
@ 212°F	-	0.77	1.45	0.61	0.99	1.11	1.09
CONRADSON CARBON RESIDUE, WT %	< 0.01	0.07	4.95	0.03	0.08	0.03	< 0.01
BOILING POINT RANGE, °F	125-394	302-458	411-730	208-467	367-586	311-686	358-672
AROMATICITY	28.0	61.0	76.0	32.0	43.0	53.0	15.0
CARBON, WT %	83.63	84.48	89.10	87.09	88.37	89.59	86.68
HYDROGEN, WT %	12.2	9.2	7.7	11.3	10.0	10.0	13.0
NITROGEN, WT %	0.29	0.35	0.69	0.16	0.33	0.08	0.006
SULFUR, WT %	0.57	0.26	0.30	0.14	0.09	0.03	0.2
OXYGEN, WT %	3.3	5.7	2.2	1.3	1.2	0.3	< 0.1
ASH, WT %	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.0	< 0.01

*Grumer, Reference 6.

Table II

SUMMARY OF SYNFUEL CHARACTERISTICS RELATIVE TO CONVENTIONAL FUELS

- o High Aromatic Content
- o Lower Hydrogen Content
- o High Fuel Nitrogen Content
- o Lower Volatility
- o Higher Ash Content
- o Higher Trace Element Content
- o Lower Thermal Stability
- o More Corrosive in Nature
- o Lower Heat of Combustion

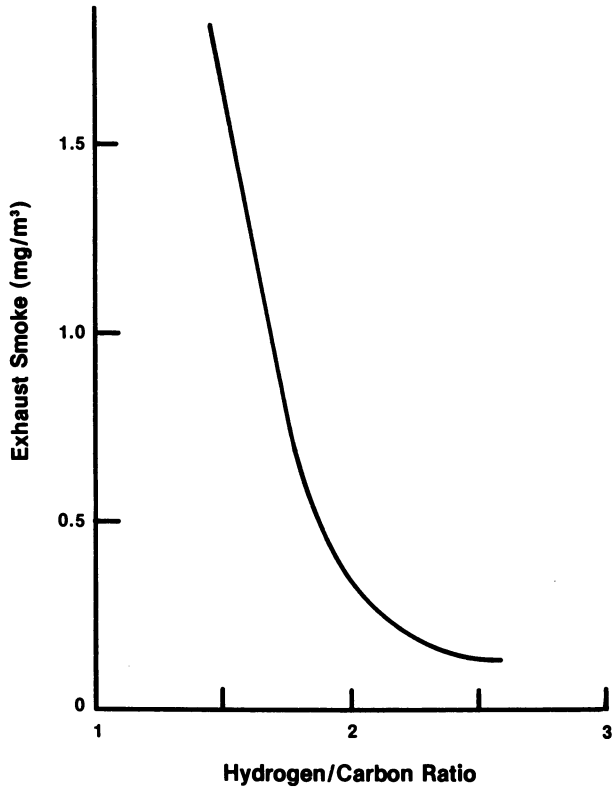


Figure 1. Effect of hydrogen to carbon ratio on exhaust smoke.
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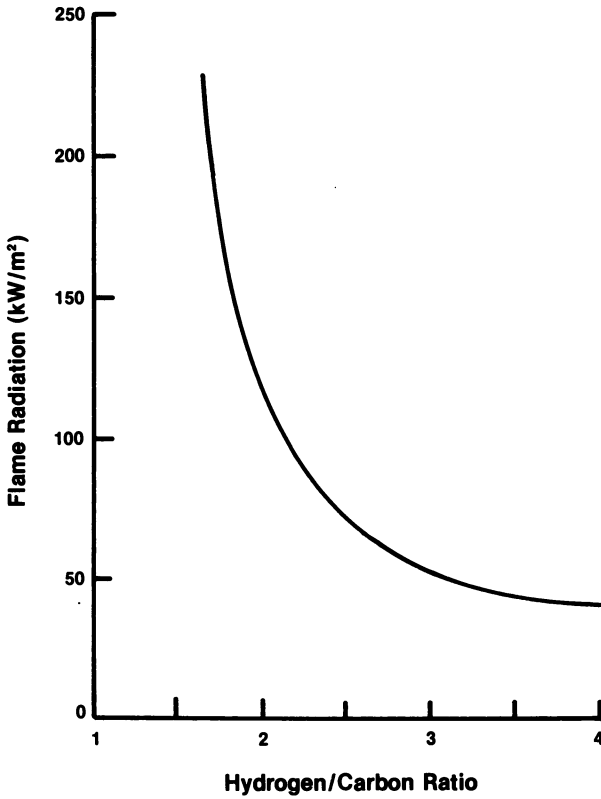


Figure 2. Effect of hydrogen to carbon ratio on flame radiation. (Reproduced with permission from Ref. 7. Copyright 1978, ASME.)

importance of increased soot concentrations in the hot gases to wall heat flux is very well illustrated in Figure 3, taken from Toor (11), and developed from the data given by Gosman, et al. (12).

- o Radiative heat flux is the major mode of heat transfer for the typical combustor conditions described in the caption over a wide range of carbon concentrations.
- o Both radiative heat flux and the total heat flux are at their maximum value corresponding to a particular optical thickness. Higher soot concentrations, resulting in increased optical thickness, may lead to lower wall heat fluxes.

The first point is obvious, because soot is an efficient emitter and radiation emissions are dependent on the fourth power of temperature, whereas, convective heat transfer is dependent on the first power of temperature. For non-uniform temperatures, such as encountered in practical combustion systems, the lower-temperature, soot-laden gases near the walls of the furnaces may actually decrease the amount of radiation arriving at the walls thus decreasing the wall heat flux.

The major contributors to radiation are soot, carbon dioxide, water vapor, inorganic particulates and other intermediate products whose concentrations depend upon the particular fuel. The presence of solid particles such as ash and carbonaceous material affects the radiation heat transport as they are continuous emitters, absorbers, and scatterers of radiation. Carbonaceous particles tend to be large relative to the wavelength of radiation and have surfaces with high absorptivity.

Toor and Boni (13) gave results of an investigation in which they assessed the effect of flow conditions and surface reflectivity on the wall heat flux for a model combustion chamber. They employed two approximate radiation heat-transfer procedures. These were the Mayer-Goody molecular band model used in conjunction with a modified Curtis-Godson scaling approximation to account for inhomogeneous gases along a line of sight, and a second technique involving a simpler band model, the just-overlapping line model, and an exact integration of the radiation transport equation. Three absorbing emitting species, H_2O , CO_2 , and soot were considered. Figure 4 presents a typical result of the calculations made by Toor and Boni (13) who also reported on the effect of temperature profiles, concentration profiles, and soot on radiation quantities in a model combustor. Of particular note is the strong contribution shown for the presence of soot.

The formation of soot in a combustion system has been shown to correlate well, at least to first order, as a function of the H/C ratio of the particular fuel. However, for a specific fuel the actual amount of soot formed is a function of the combustion

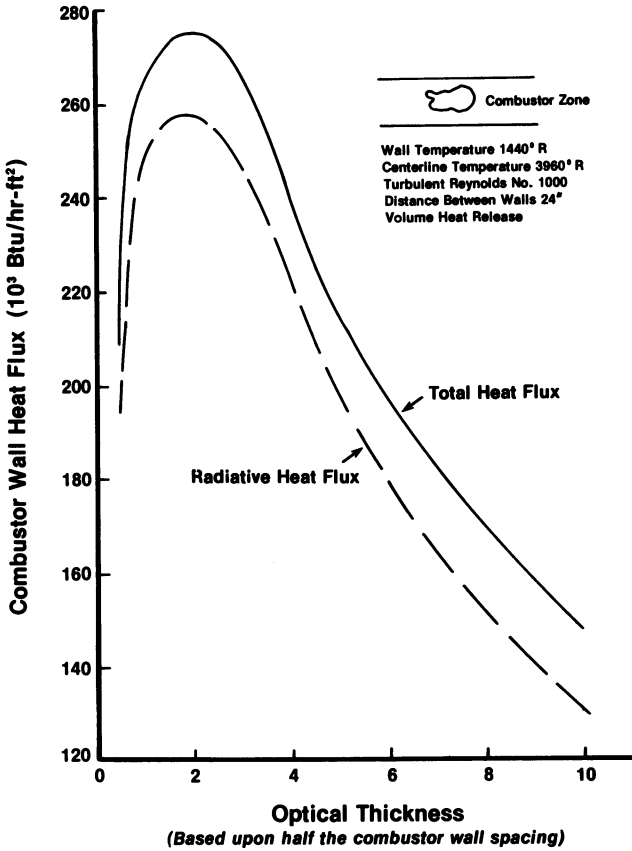


Figure 3. Radiative, convective, and total heat flux to the combustor wall. (Reproduced with permission from Ref. 11. Copyright 1979, Science Applications, Inc.)

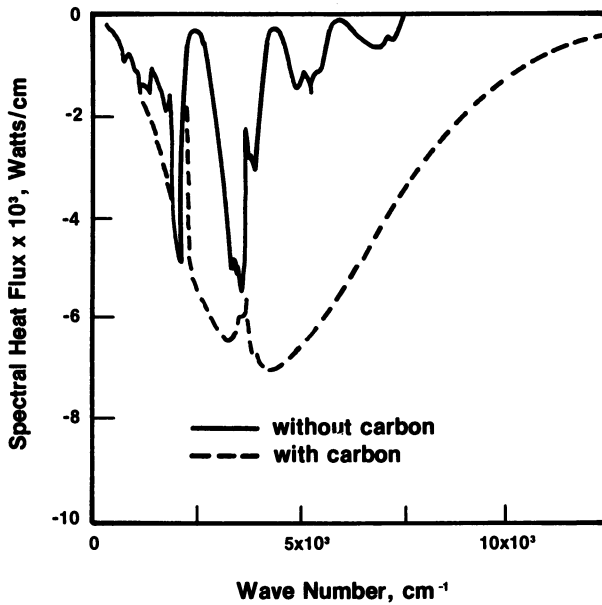


Figure 4. Effect of carbon on the wall heat flux with diffuse walls. Results of coupled radiation-aerodynamic model calculations by Toor and Boni (1974).

system with particular emphasis on the droplet distribution, evaporation, fuel/air mixing, etc. For vaporized fuel and air mixed to stoichiometric proportions, a non-luminous flame results upon burning. However, reduction of the amount of air to below the stoichiometric ratio (fuel-rich combustion), results in the formation of carbon particles at some oxygen/carbon ratio. Subsequent decrease of the oxygen/carbon ratio results in the presence of unoxidized carbon in the combustion products. This result was illustrated very nicely by the early work of Wright (14), c.f. Figure 5. In Figure 5, results are shown for two different combustion systems operating with toluene/air. The upper curve illustrates the results obtained in a flat-flame system while the lower curve demonstrates the behavior of a backmixed, well-stirred reactor. Thus, we also observe that fuel/air mixing is an important determinant of sooting behavior. The intense back-mixing system permits a wider range of soot-free combustion than does a flat flame, where diffusion controls the mixing of products and reactants.

Since carbon is not expected to be formed under equilibrium conditions at the temperatures characteristic of combustion and at an oxygen/carbon ratio in the range of 1.3-2.0, it is apparent that the formation of carbon is a kinetic process. Its presence will therefore depend on the time available for formation and oxidation relative to the flow time available. Wright, (15) for example, interpreted the backmixing observations as an indication that the polymerization process to form soot is a higher order process than the fuel oxidation process. In any event, the essential point to be made here is that the combustion of low H/C ratio fuels, without flame luminosity or soot is made possible by proper preparation of the mixture, including intense mixing in the combustion zone. This point has been made by Longwell (1) who also presented data on the equivalence ratio for incipient carbon formation for fuels with H/C ratio which varied from 2.33 (hexane), 1.14 (toluene), and 0.91 (methyl naphthalene). Table III, taken from Longwell (1) illustrates these points.

Table III

STOICHIOMETRY FOR CARBON FORMATION

Fuel	H/C	Equivalence Ratio for Incipient Carbon Formation		
		O/C=1	Flat Flame	Well-Stirred Reactor
Hexane, C ₆ H ₁₄	2.33	3.17	1.45	-
Toluene, C ₇ H ₈	1.14	2.57	1.34	1.50
Methyl Naphthalene, C ₁₁ H ₁₀	0.91	2.45	1.03	1.51

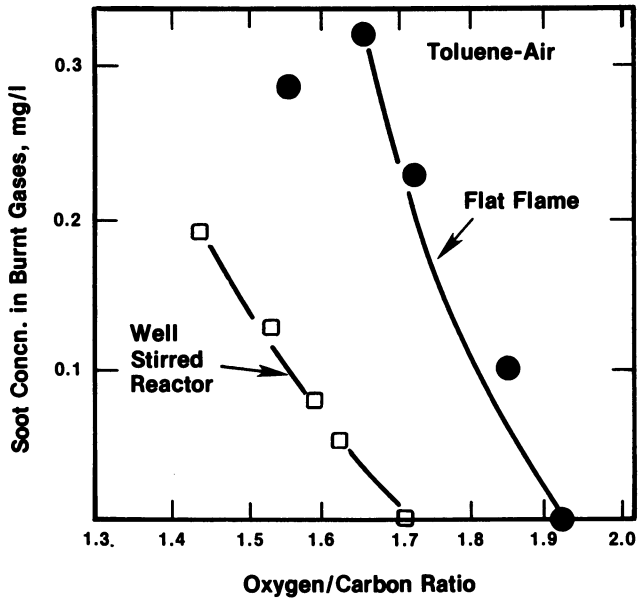


Figure 5. Soot production in laminar and backmixed system for a toluene-air flame. From Wright (1968).

The organically bound nitrogen found in syncrudes, Table I, accounts for the increased NO_x emissions in synthetic fuel flames. This source of NO_x is in addition to the thermal NO_x formed at the elevated temperatures which promote $\text{N}_2\text{-O}_2$ reactions. However, the organically bound nitrogen can be the dominant source of NO_x , as shown in Figure 6, which has been taken from the furnace data of Grumer (6). An additional source of relevant data on residual oil flames (0.05-0.79 wt. percent nitrogen) has been reported by Pershing, et al. (16), and reproduced in Figure 7. They reported that fuel- NO_x formation increased approximately linearly with increased nitrogen content over the range that they studied. It can be seen from Figure 6 that this trend is expected to continue for the nitrogen content of typical synfuels. Figure 7 also illustrates that the percentage conversion of bound nitrogen to NO_x decreases with increasing nitrogen content. Of lesser concern for synthetic fuels is the SO_x problem because of the lower sulfur content compared with that of petroleum crudes. However, doping studies have shown that fuel-bound sulfur can enhance fuel-bound NO_x formation (6).

The fuel physical properties of importance to the combustion process are the viscosity, surface tension, and volatility. The viscosity and surface tension are known to affect the droplet size distribution produced by a given fuel injection system, Figure 8. For example, with the increased values of these properties, we would expect larger fuel droplets from synfuels atomized from the same atomizer used for conventional fuels. Coupled with lower volatility, synfuel droplets are expected to take longer to evaporate than petroleum liquids, Figure 9. For a longer droplet lifetime, there will be a longer time for the fuel to coke. In combination, the droplet size distribution and droplet lifetime affect the large-scale fuel/air distribution and consequently affect the heat-release distribution, emissions and efficiency. In addition, the presence of droplets creates small-scale fuel/air inhomogeneities that can persist depending upon the liquid volatility. These inhomogeneities also affect heat-release distribution, emissions, and efficiency. However, Pershing, et al. (16) found that with a rapid-mix burner operating under fuel-lean conditions, hydrocarbon and nitrogen volatility was not a first-order parameter for NO_x production, fuel NO_x was insensitive to droplet size, but thermal NO_x increased with decreased mean droplet size.

Table IV summarizes the expected impact of the synfuel physical and chemical properties on the combustion process. In general, the properties of alternative and synthetic liquid fuels vary considerably as the fuel types range from unrefined to hydrogenated liquid fuels from coal, shale, and tar sands. Synthetic fuels of various levels of refinement will be used by the industrial, commercial, and utility sectors to produce thermal energy for direct process heat, mechanical energy, steam, hot water, and the production of electricity. Consequently,