DOE/MC/12735-1251
(DE83001046)

STUDY OF NET SOOT FORMATION IN HYDROCARBON
REFORMING FOR HYDROGEN FUEL CELLS

Final Report

By
R. B. Edelman
R. C. Farmer
T. S. Wang

August 1982

Work Performed Under Contract No. AC21-79MC12735

Science Applications, Inc.
Chatsworth, California

TECHNICAL INFORMATION CENTER
UNITED STATES DEPARTMENT OF ENERGY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A03
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts, (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication, NTIS-PR-360 available from (NTIS) at the above address.

STUDY OF NET SOOT FORMATION IN
HYDROCARBON REFORMING FOR
HYDROGEN FUEL CELLS

FINAL REPORT

By
R. B. Edelman
R. C. Farmer
T. S. Wang

Science Applications, Inc.
9760 Owensmouth Avenue
Chatsworth, California 91311

Dr. Larry C. Headley
Project Manager

Prepared for
U. S. Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia 26505

Under Contract No. DE-AC21-79MC 12735

August 1982

TABLE OF CONTENTS

<u>TITLE</u>	<u>PAGE</u>
ABSTRACT	iv
PROGRAM OVERVIEW	1
AUTOTHERMAL REFORMER OPERATION	5
REACTION RATE EVALUATION	11
FLUID MECHANICS AND HEAT TRANSFER	23
SUMMARY OF RESULTS FROM DOE/ATR RESEARCH PROGRAM	26
Experimental Results	27
Model Results	31
CONCLUSIONS	34
RECOMMENDATIONS	36
REFERENCES	38

LIST OF FIGURES

<u>FIGURE NO.</u>	<u>TITLE</u>	<u>PAGE</u>
1	The Autothermal Reformer Process . . .	6
2	Product Distribution vs. Propane Conversion .	14
3	Pressure Dependence of Methane Pyrolysis .	16
4	Flat-Flame Calculation With Quasiglobal Kinetics Model, Propane Fuel, $\phi = 1$. . .	25

LIST OF TABLES

<u>TABLE NO.</u>	<u>TITLE</u>	<u>PAGE</u>
1A	GENERIC QUASIGLOBAL MODEL Part A. Non-Catalyzed Reactions . . .	7
1B	GENERIC QUASIGLOBAL MODEL Part B. Catalyzed Reactions . . .	8
2	REACTION SCHEME FOR ETHANE-PROPANE MIXTURE CRACKING . . .	13
3	QUASIGLOBAL KINETICS MODEL ELEMENTARY STEPS . . .	18
	HYDROCARBON COMBUSTION . . .	19
4	CATALYTIC REACTIONS FOR ATR OPERATION WITH ALIPHATIC FUELS WHICH CONTAIN SULFUR . . .	28
5	CATALYTIC RATES DEVELOPED BY UTC FOR ATR SYSTEMS WITH SULFUR CONTAINING FUELS . . .	29

ABSTRACT

The hydrogen fuel cell is expected to be a valuable addition to the electric utility industry; however, the current fuel supply availability requires that conventional heavier hydrocarbon fuels also be considered as primary fuels. Typical heavier fuels would be No. 2 fuel oil with its accompanying sulfur impurities, compared with the currently used light hydrocarbon gases. The potential future use of alternate fuels which are rich in aromatics would exacerbate the problems associated with hydrogen production. Among the more severe of these problems, is the greater tendency of heavier hydrocarbons to form soot. The development of a quasi-global kinetics model to represent the homogeneous and heterogeneous reactions which control the autothermal hydrogen reforming process and the accompanying soot formation and gasification was the objective of this study.

PROGRAM OVERVIEW

The hydrogen fuel cell would be a valuable addition to the electric utility industry, because it has superior load following capability and can be sited within population centers. A pilot plant scale hydrogen fuel cell will be demonstrated in the early eighties. This plant will obtain its fuel from a dedicated autothermal reformer which uses natural gas as a primary fuel. The uncertainties of fuel supplies mandate the broadening of the range of primary fuels for commercialization; trouble-free operation with the heavier hydrocarbons, petroleum naptha, and even coal derived liquids is desirable.

Among the more severe engineering challenges associated with the extension of existing technology to other primary fuels is their greatly increased tendency to form soot during reforming. Such formation of particulates is unacceptable because their subsequent deposition coats the active sites on the catalyst and increases the pressure drop through the reactor bed, resulting in loss of efficiency and costly downtime. Existing understanding of the process of particulate generation provides an inadequate basis for an engineering solution to the sooting problem.

The work reported here is part of a concerted study by the Department of Energy to provide a better understanding of the autothermal reforming process. Specifically, this study seeks to develop an engineering model of the processes operative during autothermal reforming which result in soot deposits on the catalyst bed. The operational limits for soot-free operation are known to arise from chemical kinetics limitations and not from the thermodynamics of soot formation. The essential kinetics are not known; their determination constitutes a principle focus of this work. The performance of various hydrocarbon fuels in the autothermal reformer also depends, of course, on the accompanying fluid mechanics associated with the feedstock injection and mixing processes. Several aspects of the results of the coupling of aerodynamics and kinetics in reformers were initially addressed to help solve the reported problems of other contract investigators involved in this concerted study. However, these flow problems were at least temporarily

solved by experimental innovations without requiring additional analysis. The fluid mechanics of autothermal reformer operation is still an open issue, but since it was not critical to interpreting the collective results of this current study, these flow problems were not pursued further in this work. Rather, the available effort was redirected to include kinetics modeling of catalyzed reactions in addition to the originally scoped modeling of the homogenous gas phase reactions and soot formation processes.

The kinetics study is built on a proven engineering model of combustion kinetics, the quasiglobal model. The model is extended in three areas: first, the fuel-rich chemistry of appropriate fuels in the autothermal reformer (ATR) is accounted for; second, an empirical model of soot chemistry is postulated; and third, heterogenous catalyzed reactions are considered. Originally, the data to verify the homogenous reactions being modeled were to have been obtained from experiments performed at Pennsylvania State University as a part of the overall DOE program. However, these experimental data were not produced as scheduled and in fact are still not available; therefore the model comparisons and verification have not yet been accomplished.

To demonstrate the modeling approach for the homogenous reactions, including soot formation, which occur in autothermal reformers, SAI relied heavily upon their experience, gained from modeling the experimental data obtained at Exxon Research and Engineering Company [Ref. 1] in an investigation of continuous combustion systems for DOE. The Exxon experiments were conducted in jet-stirred combustors which were operated at temperatures of 1700-2100°K and at a pressure of 1 atm for toluene and iso-octane fuels. Obviously, these conditions do not match ATR operations which are conducted in packed-bed reactors at lower temperatures and over a wider pressure range of very rich combustion of light hydrocarbons with large amounts of steam present. However, the kinetics modeling concepts will remain valid for ATR.

Every effort was made to obtain more representative gas phase data from the literature, particularly from studies on thermal reforming and to insure that the model development was sufficiently sound to allow limited extrapolation. However, the data base needed to verify the homogenous gas phase chemistry in ATR still does not exist.

The combustion and reforming of hydrocarbon gas mixtures is being actively researched for applications other than to the ATR. For example, SAI is investigating the effects of variations in gaseous fuel composition on burner operation for the Gas Research Institute. Various blends of methane, propane, propylene, butane, and hydrogen have been studied with respect to flashback, flame-lifting, and yellow-tipping. Yellow-tipping is a direct measure of soot formation in the flame. Results to date indicate that propylene is a very significant species in modifying flame behavior; hence, the importance of trace amounts of propylene, as well as other olefins, in ATR operations should be fully evaluated. Furthermore, the modeling tools which have been developed to describe the effects of compositional variations on natural gas type flames are useful to describe the homogenous reactions which occur in an ATR. The kinetics models which have been used involve detailed reaction mechanisms; hence, the chemistry effects caused by steam addition may be predicted. Since the ATR is expected to operate at cooler temperatures, slightly higher pressures and with more steam, the kinetics models must be verified for this wider range of conditions.

Additional homogenous combustion data and also potentially interesting ATR fuel sources may be obtained from coal-derived syngas development. Coal-derived syngases range in heating values from high (900-1000 Btu/hr³), to medium (250-350), to low (100-200) depending on the relative amounts of combustible components contained in the syngases. These gases consist mainly of methane, ethane, hydrogen, carbon monoxide, carbon dioxide and water. Combustion studies of these gases have not been systematically conducted, and a well defined data base of existing information has not been established. SAI is currently conducting a review of data bases of alternative fuels, including syngases, under DOE/NASA sponsorship.

Data to describe heterogenous reactions were obtained from the sub-scale autothermal reformer studies conducted at the California Institute of Technology Jet Propulsion Laboratory [Ref. 2] and the United Technologies Corporation [Ref. 3]. These studies were also part of the DOE fuel cell program. Most of these experimental data were generated simultaneously with the model development program and were not available for detailed analysis prior to the end of this program. As a result, the chemical kinetics model is reported,

and additional analyses are recommended for the full utilization of the currently available autothermal reactor test data. This development and these recommendations are presented in this report.

AUTOTHERMAL REFORMER OPERATION

Autothermal reformers process a fuel-air-steam mixture in a partial oxidation step and a reformer step over catalyst beds to produce a hydrogen-carbon monoxide product. Operating conditions are such that soot can be formed as an undesirable by-product and inefficiencies are evident by the appearance of hydrocarbons as products. The chemical kinetics of the processes involved, especially the description of soot, is the subject of this report.

Typical autothermal reformer operating conditions and process descriptions are given in Figure 1. This figure is representative of reformers which have been experimentally studied by United Technologies Corporation (UTC) and the Jet Propulsion Laboratory (JPL). Extensive process development using various fuel systems have been investigated and reported. The inlet section has been packed with inert catalyst particles to prevent recirculation and provide flow straightening; this procedure was found to eliminate soot deposition at the beginning of the partial oxidation section.

UTC has studied No. 2 Fuel Oil, n-tetradecane, benzene with additives of propylene, naphthalene, and n-tetradecane. No. 2 Fuel Oil normally contains about 0.3 wt % sulfur which must be tolerated by the catalyst system. UTC's small scale experiments used hydrogen sulfide mixed with methane and ethane to simulate No. 2 Fuel Oil. Various air-to-carbon and steam-to-carbon ratios were tested. Mole ratios of $H_2O/C \approx 4.25$ and of $O_2/C \approx 0.35-0.45$ were typical. Intermediate products of C_2H_4 , C_3H_8 and CH_4 were reported for processed methane, ethane and No. 2 Fuel Oil for these tests. The pressure ranged from 1 to 4 atm.

To describe the chemistry of these systems, gas phase pyrolysis and rich combustion, catalytic oxidation, reforming, cracking and shifting must be considered. Since it is not practical to treat all of these processes with elementary kinetic reactions, a quasiglobal kinetics model was designed to represent the chemical aspects of the reforming process. The phenomenology of the autothermal reforming process can be conveniently described in terms of the major reaction steps identified with the generic quasiglobal model given in Table 1.

SIZE	L (in) × D (in)			COMPANY
Pilot Scale	24	×	6	UTC
Bench Scale	24	×	2.0	UTC
	15	×	3.75	JPL
Laboratory Scale	1.8	×	0.375	UTC

FIGURE 1. The Autothermal Reformer Process.

Table 1. GENERIC QUASIGLOBAL MODEL
Part A. Non-Catalyzed Reactions

I. PURE PYROLYSIS	$\begin{bmatrix} \text{ALIPHATICS} \\ \text{AROMATICS} \end{bmatrix} + \begin{bmatrix} \text{C}_2\text{H}_2 \\ \text{CH}_4 \\ \text{C}_2\text{H}_4 \\ \text{H}_2 \end{bmatrix} \equiv \text{INTERMEDIATES}$
II. OXIDATIVE PYROLYSIS	$\begin{bmatrix} \text{ALIPHATICS} \\ \text{AROMATICS} \end{bmatrix} + \begin{bmatrix} \text{OH} \\ \text{O}_2 \end{bmatrix} + \begin{bmatrix} \text{CH}_4 \\ \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_4 \end{bmatrix} + \begin{bmatrix} \text{H}_2 \\ \text{C}_x\text{H}_y\text{O}_z \end{bmatrix}$
III. PARTIAL OXIDATION	$\begin{bmatrix} \text{ALIPHATICS} \\ \text{AROMATICS} \\ \text{CH}_4 \\ \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_4 \end{bmatrix} + \begin{bmatrix} \text{O}_2 \\ \text{OH} \end{bmatrix} + \begin{bmatrix} \text{H}_2 \\ \text{CO} \\ \text{C}_x\text{H}_y\text{O}_z \\ \text{CO}_2 \\ \text{H}_2\text{O} \end{bmatrix}$
IV. ELEMENTARY STEPS TO COMPLETION	$\begin{bmatrix} \text{CO} \\ \text{H}_2 \\ \text{C}_x\text{H}_y\text{O}_z \\ \text{H}_2\text{O}_2 \end{bmatrix} + \begin{bmatrix} \text{O} \\ \text{H} \\ \text{OH} \\ \text{CHO} \\ \text{HO}_2 \end{bmatrix} + \begin{bmatrix} \text{H}_2\text{O} \\ \text{CO}_2 \end{bmatrix}$
V. SOOT FORMATION	$\begin{bmatrix} \text{ALIPHATICS} \\ \text{AROMATICS} \\ \text{INTERMEDIATES} \end{bmatrix} + \text{SOOT}$
VI. SOOT GASIFICATION	$\text{SOOT} + \begin{bmatrix} \text{O}_2 \\ \text{CO} \\ \text{CO}_2 \\ \text{H}_2\text{O} \\ \text{H}_2 \\ \text{OH} \end{bmatrix} + \begin{bmatrix} \text{CO} \\ \text{CO}_2 \\ \text{CH}_4 \end{bmatrix}$
VII. NO _x FORMATION	$\begin{aligned} &\text{FUEL} + \begin{bmatrix} \text{FBN} \\ \text{N}_2 \end{bmatrix} + \begin{bmatrix} \text{HCN} \\ \text{NH}_3 \end{bmatrix} \quad \text{BOUND NITROGEN AND/OR FUEL RICH NITROGEN CONVERSION} \\ &\begin{bmatrix} \text{HCN} \\ \text{NH}_3 \end{bmatrix} + \begin{bmatrix} \text{O}_2 \\ \text{OH} \end{bmatrix} + \begin{bmatrix} \text{NO} \\ \text{NO}_2 \end{bmatrix} \\ &\begin{bmatrix} \text{N}_2 \\ \text{O}_2 \\ \text{N} \end{bmatrix} + \begin{bmatrix} \text{O} \\ \text{N} \\ \text{OH} \end{bmatrix} + \text{NO} + \begin{bmatrix} \text{N} \\ \text{O} \\ \text{H} \end{bmatrix} \quad \text{THERMAL FIXATION} \end{aligned}$
VIII. SULFUR OXIDATION	$\begin{bmatrix} \text{H}_2\text{S} \\ \text{FBS} \end{bmatrix} + \text{O}_2 + \begin{bmatrix} \text{S} \\ \text{SO} \\ \text{SO}_2 \\ \text{SO}_3 \end{bmatrix}$

Table 1. GENERIC QUASIGLOBAL MODEL

Part B. Catalyzed Reactions

IX. REFORMING	$\begin{bmatrix} \text{FUEL} \\ \text{C}_2\text{H}_6 \\ \text{C}_2\text{H}_4 \\ \text{CH}_4 \end{bmatrix} + \text{H}_2\text{O} \xrightarrow{\alpha} \text{CO} + \text{H}_2$
X. CRACKING	$\begin{bmatrix} \text{FUEL} \\ \text{C}_2\text{H}_6 \end{bmatrix} \xrightleftharpoons{\alpha} \text{C}_2\text{H}_4 + \text{H}_2$ $\begin{bmatrix} \text{FUEL} \\ \text{C}_2\text{H}_6 \end{bmatrix} + \text{H}_2 \xrightarrow{\alpha} \text{CH}_4$
XI. COMBUSTION	$\begin{bmatrix} \text{FUEL} \\ \text{C}_2\text{H}_6 \\ \text{C}_2\text{H}_4 \end{bmatrix} + \text{O}_2 \xrightarrow{\alpha} \text{CO} + \text{H}_2$
XII. SHIFT	$\text{CO} + \text{H}_2\text{O} \xrightleftharpoons{\alpha} \text{CO}_2 + \text{H}_2$
XIII. SOOT FORMATION	$\begin{bmatrix} \text{FUEL} \\ \text{C}_2\text{H}_6 \\ \text{C}_2\text{H}_4 \\ \text{CH}_4 \end{bmatrix} \xrightarrow{\alpha} \text{soot} + \text{H}_2$
XIV. SOOT GASIFICATION	$\text{soot} + \begin{bmatrix} \text{H}_2\text{O} \\ \text{O}_2 \\ \text{CO}_2 \\ \text{H}_2 \end{bmatrix} \xrightarrow{\alpha} \begin{bmatrix} \text{CO} + \text{H}_2 \\ \text{CO}_2 \\ \text{CO} \\ \text{CH}_4 \end{bmatrix}$

α designates a specific catalyst and its effect on the reaction. Sulfur reactions are not shown explicitly, but the effect of soot is implied by the use of catalytic activities determined in the presence of sulfur contamination.

When a hydrocarbon is heated to elevated temperatures or exposed to active catalysts the molecules tend to pyrolyze into smaller fragments. In the presence of even trace amounts of oxygen, an accelerated pyrolysis, oxidative pyrolysis, occurs. Many stable and radical hydrocarbon species are made by these pyrolysis reactions. It is this large number of species which makes the description of hydrocarbon combustion difficult. However, a small number of stable hydrocarbons including acetylene, ethylene, and methane constitute a large fraction of the pyrolyzed fragments. The parent fuel and these intermediate fragments partially burn to form species such as CO, H₂, and partially oxidized hydrocarbons, such as aldehydes which then react to completion to form CO₂ and H₂O. This model formulation includes the steam reforming and combustion interaction reactions, such that effects on flame temperature and burning velocity may be directly predicted. Homogenous thermal cracking mechanisms such as those conventionally used to represent hydrocarbon pyrolysis, for example, see Sundaram and Froment [Ref. 4], are also included in the treatment of pure pyrolysis. Under rich combustion conditions, soot can form and subsequently gasify as it flows and mixes into leaner regions. Fuel bound sulfur and hydrogen sulfide are directly oxidized. Finally, NO_x either from direct fuel nitrogen conversion or thermal fixation will be produced during the combustion process. The abbreviation of the true reaction mechanism occurs when specific species and reactions are selected to represent these major steps that comprise the overall oxidation process. Thus, the current modeling approach for homogenous combustion includes pure and oxidative pyrolysis, partial oxidation, soot formation and gasification, SO_x formation, and NO_x formation by thermal fixation and fuel bound nitrogen conversion.

Heterogenous reactions consist of reforming, cracking, combustion and shifting. The reactions shown in Table 1B are representative and are not intended to be all inclusive. However, Bett [Ref. 3] has shown that the kinetics of complex fuels like No. 2 Fuel Oil can be represented as a simple combination of the rates for pure methane and ethane. Heterogenous rates also depend on the catalyst type, age and size. As the active catalyst surface is reduced, i.e., mean particle size is increased, mass transfer effects become increasingly important. In practice, experiments are performed using either very small catalyst particles with high specific surface or a range of

particle sizes so that mass transfer effects may be estimated in order to provide purely heterogenous kinetics data. Scale-up experiments are then required to provide data for commercial catalyst sizes. An example of this procedure shall be presented subsequently.

In addition to the basic reformer reactions, soot may also form and gasify both heterogenously and catalytically. Sooting rates are known to be strongly temperature, pressure and composition dependent.

All of the heterogenous reaction rates are determined by catalyst activity. The type of catalyst, activation and aging processes, and poisons which occur in the gas phase, such as sulfur contamination, determine this activity. Such effects must be experimentally determined.

If mass transfer effects are negligible, an ATR may be represented as plug-flow in which both homogenous and heterogenous reactions control the reformer performance. If mass transfer effects are important, the flow and reactions become strongly coupled and, with current technology, may be separated only in an approximate manner by using empirical mass transfer correlations. The implications of this coupling will be discussed further in relationship to interpreting specific sets of experimental data.

The following sections will evaluate the available rate information and the results of the current DOE program to investigate ATR performance.

REACTION RATE EVALUATION

To use the generic quasiglobal mechanism, specific reactions and rates must be chosen to represent the fuels being considered. Small aliphatic fuel molecules (methane, ethane, ethylene, and propane), combinations of these molecules, and No. 2 Fuel Oil are current fuels of interest. Alternate fuels with high aromatic content are of interest but are not expected to be used in the near term. The kinetic behavior of this wide array of fuels has not yet been experimentally defined so that a definitive model may be established. The state of current understanding of these fuels' behavior in autothermal reforming processes will be presented along with a discussion of the quasiglobal model.

Methane pyrolysis products include mainly CH_3 at higher temperatures. The methyl radicals recombine to form C_2H_6 and, hence, other C_2 hydrocarbons appear as products. Since methane is not typical of pyrolyzing hydrocarbon molecules because it contains no carbon-carbon bonds which must be broken, other hydrocarbons will be considered before a more detailed description of pyrolysis is attempted. Ethane and propane fuels pyrolyze in a manner that may be represented by a system of mechanistic steps which include initiation by the formation of two hydrocarbon radicals, propagation by one of the hydrocarbon radicals abstracting a hydrogen atom from a hydrocarbon which produces a large hydrocarbon radical which decomposes into an olefin and another active radical. The large radicals may also isomerize; the olefins may react with available radicals to polymerize. Two of the radicals may react to form stable hydrocarbons and thus terminate the reaction chain. The termination reactions determine the order of the global pyrolysis reaction with respect to the fuel component. The initiation reactions primarily affect the rate of the global pyrolysis reaction; the hydrogen abstraction process primarily affects the extent of the conversion and the distribution of the pyrolysis products. Another phenomena associated with cracking is inhibition or the slowing down of the pyrolysis reaction at high extents of conversion; this phenomena is not readily explainable.

Chemical kinetics models which represent hydrocarbon pyrolysis range from detailed mechanisms which include both stable species and radicals and all elementary reactions which are considered to affect the system, to a smaller detailed mechanism which contains only stable species, to quasiglobal models which include a few, global pyrolysis and oxidation steps and a small detailed mechanism like the wet CO reactions to complete the reactions, to a subglobal system of a few, usually 2 to 4, which represent both pyrolysis and oxidation, to a completely global reaction which represents pyrolysis. This hierarchy of models allows one to choose between a detailed and a simple solution to a given problem. Which model is to be used is determined by the problem being considered and the cost of the solution. For example, using a detailed pyrolysis mechanism Sundaram and Froment [Ref. 5] described a C_1 - C_4 system with 14 stable species, 11 radical species and 133 reactions. This complex mechanism predicts inhibition; however, it is not uniformly accurate with respect to temperature and pressure variations and it is relatively slow and expensive to operate. Neither the many reaction steps, nor the rates which have been postulated for any large reaction system are accurately known. If only stable species are considered, models like that shown in Table 2 for ethane/propane mixtures may be used [Ref. 6]. This model does not predict inhibition, but Figure 2 indicates that it accurately predicts thermal cracking products. Note that 6 of the 10 reactions shown in Table 2 are first-order decomposition reactions; the other 4 are second-order. Thus the system is somewhere between 1st and 2nd order. When single reactions are used to represent pyrolysis, the decomposition rate is frequently taken to be 1st-order [Ref. 7]. Obviously, the pressure dependence of such a 1-step reaction and the mechanism shown in Table 2 would not always be the same. However, for the limited range of conditions for which each of these models has been developed, some agreement might exist. The delineation of the conditions for which a given mechanism is useful is a major step required in establishing the utility of such models.

The successful use of 1st-order rates for hydrocarbon cracking reactions, both in single equation correlations and in many of the steps given in Table 2, is contrary to the behavior suggested by shock-tube data which is measured over a wide range of pressure. Clearly, the utility of the purely empirical correlations is extremely limited. Detailed mechanisms indicate that the fuel is consumed by radical attacks which are initiated

Table 2. REACTION SCHEME FOR ETHANE-PROPANE MIXTURE CRACKING

NO.	REACTION	$A(1/\text{sec or } \frac{1}{\text{mole sec}})$	$E(\text{kcal/mole})$	MODEL
1	$\text{C}_3\text{H}_8 \longrightarrow \text{C}_2\text{H}_4 + \text{CH}_4$	4.692×10^{10}	50.60	P
2	$\text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2$	5.888×10^{10}	51.29	P
3	$\text{C}_3\text{H}_8 + \text{C}_2\text{H}_4 \longrightarrow \text{C}_2\text{H}_6 + \text{C}_3\text{H}_6$	$2.536 \times 10^{13*}$	59.06	P
4	$\text{C}_3\text{H}_6 \longrightarrow \frac{3}{2}\text{C}_2\text{H}_4$	1.514×10^{11}	55.80	P
5	$2\text{C}_3\text{H}_6 \longrightarrow 0.5\text{C}_6 + 3\text{CH}_4$	1.423×10^9	45.50	P
6	$\text{C}_3\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_2 + \text{CH}_4$	3.794×10^{11}	59.39	P
7	$\text{C}_3\text{H}_6 + \text{C}_2\text{H}_6 \longrightarrow \text{C}_4\text{H}_8 + \text{CH}_4$	$1.0 \times 10^{14*}$	60.01	P*
8	$\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$	4.652×10^{13}	65.20	E
9	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 \longrightarrow \text{C}_4\text{H}_6$	$1.026 \times 10^{12*}$	41.26	E
10	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \longrightarrow \text{C}_3\text{H}_6 + \text{CH}_4$	$7.083 \times 10^{13*}$	60.43	E

P, propane; E, ethane; P*, frequency factor modified with respect to pure propane model.

SOURCE: FROMENT [6]

CRACKING OF A 50/50 WT% MIXTURE OF
ETHANE AND PROPANE.

DILUTION FACTOR: 0.4 kg STEAM/kg MIXTURE

LINE, EXPERIMENTAL; POINTS, CALCULATED

FIGURE 2. Product Distribution vs. Propane Conversion.

by pure pyrolysis reactions and are expected to be in the fall-off region not in the high pressure limit for these thermal cracking conditions. Thermal cracking and autothermal reforming units operate in the same temperature and pressure range, but the cracking units use less steam (about 0.3 moles steam/mole C compared to about 4 moles steam/mole C). The pressure dependence of methane pyrolysis has been studied by Hartig, Troe and Wagner [Ref. 8] and of propane pyrolysis by Gardiner, et al [Ref. 9]. Methane data taken from shock tube experiments and shown in Figure 3 indicate that pressures in the 1-2 atm range should exhibit first-order power dependence on the fuel and first-order on the sum of the remaining gases. Such fall-off data are not complete, especially at temperatures typical of autothermal reformer operating conditions, but available data suggest that reported first-order rates for a limited pressure range might be more accurately interpreted as apparent first-order rates with respect to fuel for the conditions under which they were measured.

The pyrolysis of hydrocarbon fuels may be accompanied by the homogeneous formation of soot. Shock-tube and flow reactor studies indicate that aromatics, acetylenes, alkanes (C_1 - C_4) form soot at progressively lower rates and in lesser yields, other factors being the same. There is some evidence that large (C_{14}) alkanes may form soot faster than benzene, but relative-rate data for large alkane and multi-ring aromatic molecules when compared at the same carbon number are not sufficiently adequate to be conclusive. Soot formation data during pyrolysis for CH_4 and C_6H_6 fuels in nitrogen are presented by Prado and Lahaye [Ref. 10], but such data have not been empirically modeled. The temperatures of these experiments are about 600°F hotter than ATR operating temperatures and do not contain any steam or O_2 ; therefore, the data do not constitute a good representation of ATR conditions, but they do represent at least a qualitative description of sooting in an oxidizer free environment.

Detailed oxidation models for small hydrocarbons have been reported by several investigators for combustion at atmospheric pressure, but the lower temperatures and high steam levels found in autothermal reformers require careful consideration of these data. The number and type of hydrocarbon radicals and the H, O, OH radical system are very important, but at these low temperatures and high steam levels direct O_2 and HO_2 reactions with hydrocarbon

FIGURE 3. Pressure Dependence of Methane Pyrolysis.

radicals have been shown [Ref. 11] to be important. Important hydrocarbon radical reactions for C_2H_6 oxidation were [Ref. 9] found to be:

If hydrocarbon radicals are omitted from the reaction mechanism, their effects must be represented by other reactions.

Partially oxygenated hydrocarbons are essentially absent from most hydrocarbon oxidization mechanisms, except for HCHO and CH₃O. Larger partially oxygenated hydrocarbons have not been found in flames. Molecular beam experiments [Ref. 12] have been conducted to measure the products of hydrocarbon - oxygen atom reactions; several ketenes, ketones and aldehydes have been identified by these experiments. However, molecular beam experiments are conducted at such low pressures (about 10^{-3} atm) that extrapolation to flame conditions is questionable.

A quasiglobal model of the CH_4/C_2H_6 fuel system which treats C_2H_4 as the only hydrocarbon intermediate and includes a HCHO, H_2O_2 and wet CO detailed mechanism would represent hydrocarbon oxidation with the global pyrolysis and oxidation steps being used to empirically represent the complex hydrocarbon radical reactions. Such a model is given in Table 3.

Petroleum distillate fuels like No. 2 Fuel Oil contain many components, most of which are larger than C_2 hydrocarbons. Such fuels may be represented as one aliphatic and one aromatic component of suitable H/C content and mean molecular weights as to approximate the proper boiling point and heat of combustion. No. 2 Fuel oil is about 73 mole % normal- and cyclo-paraffin and 77% aromatic. Letting C_nH_m = n-tetradecane and C_aH_b = tetralin and using reaction rates which have been established for iso-octane and toluene [Ref. 1], would create a No. 2 Fuel Oil model from

Table 3. QUASIGLOBAL KINETICS MODEL
ELEMENTARY STEPS

Wet CO Mechanism*

H₂O₂ Mechanism*

HCHO Mechanism*

* Rates were taken from (1).

Table 3. QUASIGLOBAL KINETICS MODEL (FOR HYDROCARBON COMBUSTION) (Contd.)

GLOBAL REACTIONS

C_aH_b = Aromatic or a second aliphatic

C_nH_m = Aliphatic

ME = Used only if methane is an intermediate

GLOBAL REACTIONS.

SOOT MODEL

Table 3. Of course verification would be required, but this model identifies all of the reaction elements necessary to represent the combustion of No. 2 Fuel Oil.

Soot is formed directly by reactions involving intermediate hydrocarbons like acetylene and from fuel molecules like toluene. The formation rate given in Table 3 was determined for toluene combustion in jet-stirred combustor experiments. Operating conditions for incipient soot formation have been reported for octane and ethylene in jet-stirred combustor experiments, but formation rates have not been quantitatively determined. For octane, the incipient soot limit occurs at an equivalence ratio which is very close to the rich blow-out limit. In general, aliphatics and acetylene type intermediates readily produce soot in other types of experiments, such as flat-flames. The implication is that soot formation from aromatic precursors is much faster than from small aliphatic fragments. Soot is gasified by oxidation with O_2 , O , OH and by reactions with H , H_2 , CO , CO_2 and H_2O . Lewis, et al [Ref. 13] report reactivities of oxygen, steam and carbon dioxide at low reactant pressures to be in the ratios of 1.0:0.2:0.001. At high pressures and at 2000°K these ratios are 1.0:0.01:0.01 and at 1000°K 1.0:0.0002:0.0001. Catalysts increase all of these rates by about a constant factor of 10^3 . Alkali minerals appear to be the catalytic agent responsible for these increases. Studies attempting to evaluate specific radical reaction rates, especially OH , have been reported [Ref. 13, 14] but generally valid rate expressions are not yet available. The reactions in Table 3 are recommended for current use.

Non-catalyzed heterogenous gasification rates for soot have been suggested by Haynes [Ref. 15] for the reactions in Table 1, part B, item XIV. The soot formation rates from propane, propane/propylene and propane/ethylene mixtures on a metal wall have been represented by the expression:

$$\dot{\omega}_c = 4.38 \times 10^{12} \exp \left\{ -32567/T \right\} [C_2H_4] A_c$$

$$\dot{\omega}_c = \text{sooting rate, g coke/sec}$$

$$A_c = \text{surface area of the wall/volume of reactor, m}^2/\text{m}^3$$

$$T = \text{temperature, K}$$

$$[C_2H_4] = \text{concentration of } C_2H_4, \text{ gm moles/l}$$

This rate expression was developed by Sundaram and Froment [Ref. 16] to model results from a well-stirred reactor experiment in which soot was formed on a metal sleeve in the reactor. In this microbalance experiment the weight of the sleeve and soot was measured continuously. Such experiments produce interesting results, but an analysis of the potentially important flow phenomena that occur in the vicinity of the sleeve was not performed. Similar experiments using methane by Chen and Back [Ref. 17] have also been reported. More general reviews of catalytic combustion [Ref. 18] and formation and removal of coke from nickel catalyst [Ref. 19] are useful qualitative descriptions of sooting processes. Coking studies within catalyst pores for steam reforming and a model of the results were reported by Ovenston and Walls [Ref. 20]. Flow phenomena probably had a significant effect on all of these heterogeneous sooting studies, but the coupled effects of kinetics and flow were not treated. Such experimental data [Ref. 16-20] are the best currently available for determining heterogeneous sooting rates.

This section postulates a quasiglobal kinetics model to represent the homogeneous and heterogeneous reactions which occur in an ATR, for the conditions under which mass transfer effects are negligible. Since the heterogeneous reactions in Table 1B are 1st-order with respect to fuel, any one of these reactions may be written for fuel disappearance as

$$-\dot{\omega}_f = k C_f \eta \quad (1)$$

where k is specific reaction rate
 C_f is fuel concentration
 η is efficiency

If $\dot{\omega}_f$ is controlled by mass transfer

$$-\dot{\omega}_f = K (C_{f0} - C_f) (3/R) \quad (2)$$

K is the mass transfer coefficient
 C_{f0} is the local gas phase fuel concentration
 R is the particle radius

Equation (2) represents mass transfer across a gas-phase boundary-layer (i.e., film) surrounding the particle. Combining equations (1) and (2)

$$-\dot{\omega}_f = \frac{C_{fo}}{(R/3K + 1/k\eta)} \quad (3)$$

If the rate is experimentally observed by studying beds of various size catalyst particles and K is empirically determined by a j -factor correlation for fixed catalyst-beds, for example

$$j_D = \left(\frac{K P}{G} \right) N_{sc}^{2/3} = 0.357 / \epsilon N_{Re}^{0.359} \quad (4)$$

G is mass flow rate per unit of cross-sectional area of the empty reactor, ϵ void fraction of reactor volume, N_{sc} is the Schmidt No., and N_{Re} is the Reynolds number. Now η can be determined, and it approaches 1 for small particles. The use of this analysis allows the development of a model to represent packed-bed reactors which undergo homogenous and heterogenous reactions to be analyzed in terms of homogenous reactions only, if the mass transfer effects are accounted for as indicated by (3). This technology is described in [Ref. 21]. A more rigorous analysis to obtain K is desirable but is not essential to providing design information. Heterogenous reaction rates correlated for mass transfer effects with equation (3) and homogenous rates which are shown in Table 1 may be incorporated directly into a plug-flow model to represent an ATR. Such a model may be compared to the bench-scale and laboratory-scale test results which were part of the DOE's ATR research program.

FLUID MECHANICS AND HEAT TRANSFER

In addition to chemical kinetics effects, this program was originally structured to model liquid droplet and spray effects as well as turbulent jet mixing and backmixing. However, the initial phases of the DOE/ATR research program were most successful in generating a data base of laboratory- and bench-scale performance information under conditions which were controlled primarily by heterogeneous and homogeneous chemical kinetics. Therefore, the fluid mechanics and heat transfer problems associated with ATR operations were not addressed in detail, and SAI's study was redirected to emphasize kinetics modeling to aid in interpreting the performance data which were being generated.

Fluid mechanics and heat transfer problems associated with ATR operation are expected to be of concern when scale-up and full-scale design are further considered. In particular, when mass transfer limitations associated with using catalysts of the large sizes employed in commercial reactors are evaluated, the coupled effects of local flow and heating phenomena will need to be investigated in detail.

The one flow configuration which was investigated in this study was a laminar flat-flame. A flat-flame model which employs the quasiglobal kinetics model was developed to interpret experimental flame data; this model is described by the following discussion.

To determine a kinetics model for the homogeneous gas-phase reactions in an autothermal reformer, a laminar flat-flame model was developed to represent the type of experimental data which was to be obtained from the Pennsylvania State University experiments. Stable and radical species, including soot, and temperature profiles through the flat-flame were to be predicted, and kinetic rates were to be inferred by comparing these predictions to measurements. A sufficient experimental data base was not generated to develop new kinetics models. However, the analysis was completed and is presented in this section.

A laminar flat-flame may be realized by flowing premixed, combustible gases through flow distributors which cause the mixture velocity profile

leaving the burner to be essentially flat. The flame is operated at constant pressure. For a range of flow-rates, the flame, once ignited, assumes a steady burning configuration. Thus, to a very good approximation, steady, one dimensional species and energy conservation equations can be used to represent the flame. These equations have been formulated and a computer program has been written to solve these equations [Ref. 22]. Predictions using the original one-step quasiglobal kinetics model for propane [Ref. 23] indicate a flame speed of 42 cm/sec and the species distributions shown in Figure 4 for a freely propagating flame. This flame speed is in good agreement with measured values for stoichiometric flames.

Experiments such as those performed at PSU frequently use cooled burners to stabilize the flame. Such cooling is a critical operating condition which must be reported if the flame is to be interpreted. The burner cooling rate enters directly into the mathematical model of quenched flames as a boundary condition. Extensive comparisons of model predictions to flat-flame data have not yet been made. Some comparisons have been presented by Warnatz [Ref. 24] for hydrocarbon flames, but rich combustion of sooty flames has not been rigorously investigated. Application of the flat-flame model to experimental results typical of ATR operation still requires the development of a suitable experimental data base.

FIGURE 4. Flat-Flame Calculation With Quasiglobal Kinetics Model, Propane Fuel, $\phi = 1$.

SUMMARY OF RESULTS FROM DOE/ATR RESEARCH PROGRAM

The DOE research program to investigate distillate-fuel reforming in autothermal reformers so as to improve the fuel flexibility of fuel processors for hydrogen fuel cells was generally directed toward the goals of minimizing the O_2/C ratio required and of eliminating methane leakage. Systems studies indicate the minimum ratio of 0.35 moles of O_2 per C atom and the minimum methane leakage of 0.3 mole % (dry) were necessary in order that a power plant could achieve a heating rate of 9500 Btu/kwh or better [Ref. 25]. In attempting to meet the low O_2/C requirement the oxidation part of the process becomes very susceptible to carbon formation. The desired products of the reformer are H_2 and CO, thus, the presence of methane and other hydrocarbon gases represents an inefficiency. The DOE program consisted of two types of investigations of ATR. United Technologies Corporation (UTC), Engelhard Industries (EI), and Jet Propulsion Laboratory (JPL), undertook process development to improve the yield and performance of ATR as represented by bench-scale experiments. Another group of contractors addressed specific problems relevant to improving ATR performance. Stanford Research Institute (SRI) experimentally investigated the nature of carbon which was deposited on nickel steam-reforming catalyst. Argonne National Laboratory (ANL) experimentally studied the effect of sulfur on steam-reforming activity. Pennsylvania State University measured soot formation in rich, gaseous flames. Physical Sciences, Inc. (PSI) modeled the process steams during ATR operation. Science Applications, Inc. (SAI) modeled ATR process streams with particular emphasis on describing the carbon formation process.

Experimental Results

The results of the UTC experimental studies are represented by the catalytic reactions given in Table 4. Rates for these reactions for a range of fuels and catalysts have been reported by Bett [Ref. 3]. These rates are given in Table 5. UTC also developed models of the homogenous reaction rates, but the gas-phase results are global curve fits, which are not appropriate for generalization. The catalytic rates given in Table 5 are for commercial nickel, supported noble metal, and metal oxide catalysts in the presence of sulfur containing reactants.

A direct comparison of the effect of sulfur content was a goal of the JPL program. JPL's work will be accomplished by studying pure fuels with and without sulfur contamination. The pure fuels work has been reported, and the sulfur contamination studies are in progress. A second objective of the JPL program was to study the specific effect of fuel composition by evaluating mixtures of benzene and naphthalene, benzene and tetradecane, and benzene and propylene. JPL found that, when soot formed in the entrance to the partial oxidation section, precursor radiation heated the inlet flow and exacerbated the soot formation problem. In general, soot formation was found to be more critical in the steam reforming section than in the partial oxidation section. Although these experiments are qualitatively interesting, the catalyst particles and/or monolith support used presented a surface area such that mass transfer effects through the gas-phase to the catalytic surface were significant. Hence, the kinetics of the catalytic reactions cannot be quantitatively evaluated without utilizing a theoretical analysis of the mass transfer involved. Such an analysis was not a part of the DOE ATR research program.

The experiments conducted by Engelhard Industries were primarily catalysts screening studies which resulted in input/output measurements for a particular catalyst system and set of operating conditions. Kinetics models cannot be developed from such data, although if a kinetics model were available, it could be used to predict reformer output and thereby compared to the Engelhard results. However, since the catalysts used were not studied by UTC or JPL the required axial composition data do not exist and an appropriate kinetics

Table 4. CATALYTIC REACTIONS FOR ATR OPERATION WITH ALIPHATIC FUELS WHICH CONTAIN SULFUR

1	$\text{FUEL} + \text{H}_2\text{O} \longrightarrow a\text{CO} + b\text{H}_2$	(composite of CH_4 and C_2H_4)	Reforming
2	$\text{C}_2\text{H}_6 + 2\text{H}_2\text{O} \longrightarrow 2\text{CO} + 5\text{H}_2$		
3	$\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \longrightarrow 2\text{CO} + 4\text{H}_2$		
4	$\text{CH}_4 + \text{H}_2\text{O} \longrightarrow \text{CO} + 3\text{H}_2$		
5	$\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$		Cracking
6	$\text{C}_2\text{H}_6 + \text{H}_2 \longrightarrow 2\text{CH}_4$		
7	$\text{C}_2\text{H}_6 + \text{O}_2 \longrightarrow 2\text{CO} + 3\text{H}_2$		Combustion
8	$\text{CH}_4 + \frac{1}{2} \text{O}_2 \longrightarrow 2\text{CO} + 2\text{H}_2$		
9	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$		Shift

Table 5. CATALYTIC RATES DEVELOPED BY UTC FOR ATR SYSTEMS WITH SULFUR CONTAINING FUELS

REACTION	A	E	CATALYST
1	$(1-\alpha)^2 \dot{\omega}_3 + \alpha^2 \dot{\omega}_4$, where	$\alpha =$ fraction of fuel converted at any time	nickel
2	2.52E18 3.71E12 4.79E8	86.9 51.5 -41.8	nickel noble metal metal oxide
3	3.98E18 ~0 3.21E10	84.7 44.553	nickel noble metal metal oxide
4	1.10E10 1.71E9 5.53E2	51.856 40.723 11.243	nickel noble metal metal oxide*
5	~0 3.36E7 ~0	31.644	nickel noble metal metal oxide
6	~0 ~0 ~0		nickel noble metal metal oxide
7	~0 4.5E12 9.6E9	40.0 48.0	nickel noble metal metal oxide
8	~0 4.5E13 9.6E10	40.0 48.0	nickel noble metal metal oxide
9	1.17E11 1.08E10 6.78E11	19.862 12.056 21.066	nickel noble metal metal oxide

REACTION EXPRESSIONS

Reactions 1-8

$$\frac{d\alpha_i}{dt} = A \exp \{-E/RT\} [\text{FUEL}] G$$

Reaction 9

$$\frac{d\alpha_i}{dt} = A \exp \{-E/RT\} [\text{CO}] [\text{H}_2\text{O}] G$$

where G is catalyst loading (gm cat/cc); $G \approx 1$ (gm/cc)

* Reported as questionable by UTC.

model of their reactor system does not currently exist. The microscopic examinations of soot and the microbalance experiments of Stanford Research Institute provided some interesting qualitative results on carbon formation. However, quantitative interpretation of microbalance results is questionable because of the flow effects which have been previously discussed.

Homogenous gas-phase reactions representative of the partial oxidation and reforming of distillate fuels under typical autothermal reformer operating conditions are not well known and were not a part of the DOE ATR research program. Available data from the literature do not include sufficiently high steam levels to be adequate, nor have sufficient soot determinations been made. Conceptually, the gas-phase soot formation studies in rich, pure-hydrocarbon flames by Pennsylvania State University were to provide some of the needed partial oxidation data. Unfortunately, a sufficient data base to describe this important process was never established. In addition to the quantity of data produced, sufficient measurements to fully define any one flame were not reported.

Model Results

UTC is preparing models to represent their bench scale-reactor data. The heterogenous reactions from Table 5 are taken along with a set of global homogenous reaction to represent the operation of both the partial oxidation and reformer sections of ATR. A soot formation and gasification model is being added to the basic model. The model is reasonable except that the inefficiency problem associated with rich combustion has not been dealt with and that the soot model has not been developed to the point of giving useful results. The extent of rich combustion is over-predicted and simple modifications to their global type models are not expected to solve this problem.

The PSI model studies have been limited to modeling the reformer section of the Engelhard ATR system. Experimental conditions at the exit of the partial oxidation section are used as initial conditions for modeling the reformer. This model has not yet been proven successful, and even if it were successful major effort would be required to develop a partial oxidation model. Global rates for reactions used by this model have not yet been quantitatively evaluated.

The SAI model described in previous sections of this report does not have the conceptual problems cited for the UTC and PSI models. However, none of the models have been demonstrated to represent ATR test data which includes sooting. Further work is required to compare the SAI model with the limited UTC data which are available.

The bench-scale ATR data from the UTC experiments may be used as a data base for heterogenous kinetics data, provided that catalysts particles of sizes sufficiently small to eliminate mass transfer effects were used. Two size particles were used in the UTC experiments, one of which was definitely large enough to cause mass transfer resistance. The small size particle (about 1 mm) were assumed to have not been effected by mass transfer effects, this assumption requires verification by using several small size particle beds and proving that the mass transfer had negligible effect on the reported apparent heterogenous kinetics.

The UTC experiments were conducted on gases which contained sulfur at levels typical of distillate fuels. Data on sulfur free systems would also be valuable but would not be essential to developing a complete interpretation of the performance of ATR using distillate fuels.

All of the JPL data were taken with catalyst particles which were large enough to exhibit mass transfer effects on the overall composition data. The EI composition data were taken only at the reactor inlet and exit. Neither of these data sources is sufficiently complete to be analyzed in more detail for heterogenous reaction rate data. This appraisal is not a criticism of the work because the experiments were designed to describe the overall performance of the system, not provide a kinetics data base. These bench-scale experiments have identified radiation problems at the entrance to the reactor when sooting occurs, a satisfactory method of inlet design, and general ranges of operating conditions under which sooting is not a problem.

Homogenous reaction rate data for rich combustion in the presence of steam under ATR operating conditions are needed. Data from PSU were expected to provide this information, but such data have not been reported. The adequacy of sample data which were reported at contractor review meetings cannot be judged, because basic data were not reported. Relative soot concentrations not absolute concentrations were reported. The OH radicals were measured, but much of the data were reported as the sum of OH, O and H concentrations. The O and H levels were calculated by assuming equilibrium. The UTC experiments were in the 1-4 atm pressure range; the PSU flames were conducted at 0.25-0.75 atm.

Homogenous reaction rate data are still needed for fuels which were studied by UTC: $\text{CH}_4/\text{C}_2\text{H}_6$ mixtures and distillate fuels, temperatures of 1000 K to 1400 K, and pressures of 1-4 atm. Mole ratios of O_2/C of 0.35-0.4 and $\text{H}_2\text{O}/\text{C}$ ratios of about 4 are also required. Furthermore, sufficient data to describe the burner operation must be provided. These data include concentration and temperature profiles in flat-flame experiments. Reactant flowrates and burner heat losses, if cooled flames were used, must also be specified. The effects of any other experimental modifications, such as using stabilizing disks in the flame must also be completely described.

Specific recommendations as to the best use of this ATR data base are offered in the conclusions and recommendations section which follows.

CONCLUSIONS

This report describes the progress made on the development of an engineering model to represent the deposition and gasification of soot in an autothermal reformer.

1. An approach to modeling the chemical kinetics effects which describe the operation, including soot formation and gasification, in both the partial oxidation and reforming sections of an autothermal reformer has been identified.
2. Mass transfer effects significantly influence apparent chemical kinetics in sub-scale studies and must be modeled to interpret these data. Model development of fluid mechanic and heat transfer processes associated with turbulent jet mixing and backmixing and with liquid droplet and spray effects were not found to be essential to the initial interpretation of ATR performance studies of distillate fuels. One critical heat transfer problem that has been identified is the precursor radiation caused by the formation of soot in the entrance region to the partial oxidation section under some operating conditions.
3. It remains to be demonstrated that current models of the chemical effects which occur in ATR are adequate to predict soot formation behavior and product gas composition over the range of operating conditions necessary to provide adequate design information. Certain key experimental data are missing and must be determined before the current ATR model development studies can be successfully completed. The following specific data are required:
 - i. Additional catalyst-particle sizes should be studied in a laboratory-scale type reactor to span the range of conditions necessary to identify both the diffusion and kinetic limits of operation and to determine the required rate parameter data.

Mass transfer limitations must be evaluated by parametric studies to determine the effect of particle size and Reynolds numbers on scale-up of ATR experimental data. Part of these studies must include a determination of the capacity of the commercial processing units which are of potential current and future interest.

Nickel, metal oxide, and noble metal catalysts in the size range of 0.01 to 0.125 in. should be evaluated.

- ii. Homogenous gas-phase reactions with representative fuel species of interest must be determined to evaluate the relative contribution to soot formation from both homogenous and heterogenous reactions. These reactions must be determined in the O_2/C range of about 0.35, in steam/C range of about 2.5 to 5, over the pressure range of 1 to 4 atm, and for residence times in the approximate range of 10 to 200 msec. Flat-flame experiments may provide most of these data, but improved spatial resolution of measurements for the high pressure data will be required, i.e., pressures in the range of 1 to 4 atm. Alternate experiments might be considered because of these anticipated measurement problems. The ranges of required data just cited constitute a minimum data base; data for a wider range of conditions would provide confidence in scale-up using the models developed from the data and would provide basic information for future ATR design concepts.

RECOMMENDATIONS

The following program is recommended for completing an adequate and useful engineering model to interpret ATR studies. The next phase of research devoted to developing ATR must utilize the information just developed by DOE, supplemented when necessary, to establish the current design capability. Subsequent phases of research activity should be directed toward identifying and solving scale-up problems which arise from future ATR development.

1. Utilize the existing ATR data base and the recent literature on catalytic reactors to determine potential critical chemistry, fluid mechanics or heat transfer problems which might arise in ATR operations. The coupled soot formation/precursor radiation problem has been identified as critical and, hence, is a high priority area for research. Priorities for future investigations to evaluate other potential problems should be established as a result of this task.
2. An expanded data base for the development of homogenous reaction rate mechanisms should be established. The quantitative determination of sooting is an essential element of these studies.
3. Evaluate existing ATR models with respect to currently available laboratory- and bench-scale data using homogenous reaction rates developed under recommendation number 2 and use available ATR data for small catalyst sizes to evaluate heterogenous effects.
4. Develop the information itemized in conclusion 3 for evaluating mass transfer effects and evaluate the ATR model over this full range of operating conditions. Existing information from the DOE/ATR studies may be used to augment this data base, but such data cannot be evaluated without at least a rudimentary homogenous gas phase reaction model for each of the potentially important fuel mixtures. Fluid mechanics problems are anticipated to become increasingly important as the scale of the ATR being considered increases. Thus, the following task is suggested to complete both the chemical and physical information base required for ATR scale-up and design.

5. Develop the framework and data base for fuel flexibility requirements including theoretical and experimental determinations of droplet and spray effects in turbulent flow ATR environments.

REFERENCES

1. Kowalik, R. M. and L. A. Ruth, "Fundamental Characterization of Alternate Fuel Effects in Continuous Combustion Systems," Final Report on DOE Contract DE-AC22-77-ET-11212, Exxon R&D Co., Linden, NJ (January 1982).
2. Stephanopoulos, M. F. and G. E. Voecks, "Conversion of Hydrocarbons for Fuel Cell Applications," Reports on DOE Contract DE-AI03-79ET-11326, Jet Propulsion Laboratory, Pasadena, CA (December 1980).
3. Bett, J. A. S. et al, "Investigation of Carbon Formation Mechanisms and Fuel Conversion Rates in the Adiabatic Reformer," Reports on DOE Contract DE-AC21-80-MC-14395, United Technologies Corporation, South Windsor, CT, (March 1981).
4. Sundaram, K. M. and G. F. Froment, Chem. Eng. Sci., 32, pp. 601-608 (1977).
5. Sundaram, K. M. and G. F. Froment, IEC, 17, p. 174 (1978).
6. Froment, G. F., Chem. Eng. Sci., 36, 1271-1282 (1981).
7. Hautman, D., et al, "Overall and Detailed Kinetic Studies of Propane Pyrolysis," submitted for publication.
8. Hartig, R., J. Troe and G. Gg. Wagner, Thirteenth Symposium (International) on Combustion, pp. 147-154 (1970).
9. Simmie, J. M., W. C. Gardiner, Jr. and C. S. Eubank, J. Phys. Chem., 86, pp. 799-802 (1982).
10. Prado, G. and J. Lahaye, in Particulate Carbon Formation During Combustion, eds. D. C. Siegla and G. W. Smith, pp. 143-175 (1981).
11. Notzold, D. and J. Algermissen, Comb and Flame, 40, pp. 293-329 (1981).
12. Hoyerman, K. and R. Sievert, Seventeenth Symposium (International) on Combustion, pp. 517-524 (1978).
13. Lewis, P. F., et al, "Pulverized Fuel Combustion: Modeling and Scale Up Methodologies," Third Quarterly Report, DOE/PC/30294-3, Physical Sciences, Inc., Woburn, MA (1981).
14. Neoh, K. G., "The Study of Soot Burnout in Flames," PhD Thesis, MIT (1981).
15. Haynes, H. W., Jr., AIChEJ, 28, pp. 517-521 (1982).
16. Sundaram, K. M. and G. F. Froment, Chem. Eng. Sci., 34, pp. 635-644 (1979).
17. Chen, C. J. and M. H. Back, Carbon, 17, pp. 175-180, (1979).

18. Margolis, L. Ya., Catalysis Reviews, 8, pp. 241-267 (1973).
19. Trimm, D. L., Catal. Rev. - Sci. Eng., 37, pp. 1-7 (1982).
20. Ovenston, A. and J. R. Walls, Chem. Eng. Sci., 37, pp. 1-7 (1982).
21. Satterfield, C. N., Mass Transfer in Heterogenous Catalysis, MIT Press, Cambridge, MA (1970).
22. "Spray Combustion of Synthetic Fuels Phase II - Spray Combustion Phenomena," 82-032 CHATS, Science Applications, Inc., (1982).
23. Edelman, R. B. and O. F. Fortune, AIAA Paper 69-86, AIAA, NY, NY (1969).
24. Warnatz, J. Eighteenth Symposium (International) on Combustion, pp. 369-384 (1981).
25. Ushiba, K. K., "Assessment of R&D Programs for Fuel Processors for Fuel Cells," Catalytica Associates, Inc., Santa Clara, CA (January 1981).