HYDROCARBON AUTOTHERMAL REFORMING PROGRAM

ANNUAL REPORT

MASTER

by

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and

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I. INTRODUCTION AND SUMMARY

A goal of the national molten carbonate fuel cell program is to develop the capability to use heavy fuel oil or coal liquids as feed stock for fuel cell power plants. These liquid fuels must be reformed to gaseous fuels which are composed mainly of CO , H_2 , CO_2 , and H_2O (and N_2) for use by the fuel cell. This reforming can be accomplished by steam reforming: the endothermic reaction of the fuel with H_2O in the presence of a suitable catalyst and with external addition of heat. However, steam reforming has two significant drawbacks: heat must be supplied by heat exchangers (at some cost and efficiency penalty) and sulfur in the fuels poisons the catalyst.

An alternative to the steam reformer is the autothermal reformer which is similar to the steam reformer, except that the necessary heat is supplied by the addition of oxygen (air) to the feed to partially oxidize some of the fuel. This then leads to higher operating temperatures and increased sulfur tolerance of the catalyst. The chemical operation of an autothermal reformer is similar to that of coal gasifiers which feed H_2O and O_2 (air) with the coal. "Autothermal" implies that the temperature of the feed and product streams are equal, and that the oxygen feed rate is just enough so that the heat release, due to its reaction with the fuel, just balances the endothermic reaction of the H_2O with the fuel.

The ideal values of oxygen and H_2O feed can be calculated from the thermodynamic properties of the feed and product constituents by equilibrium thermodynamics. However, in practice, H_2O and O_2 (air) above this ideal value must be fed in order to prevent the formation of soot in the reformer. This soot would eventually plug the catalyst bed and lead to shut down of the reformer. Systems studies have been performed which show that in order for autothermal reformers to be cost effective they must operate with O_2 (air) and H_2O feed rates below certain limits. The DOE has embarked upon a program to determine how to meet these goals. This document summarizes the first year's work of the two year program at Physical Sciences Inc. on this DOE program.

The goal of the PSI program is to understand the mechanism for the formation of soot under conditions relevant to autothermal reformers and to translate this understanding to recommendations for modification of autothermal design. This goal is to be accomplished by a combination of experimental and theoretical tasks, including work at Engelhard Industries, a major subcontractor on this program.

The experimental tasks are to study the mechanisms of soot formation under controlled conditions with gaseous fuels, O_2 and H_2O , both premixed, and with well-described mixing, with and without catalysts. The theoretical tasks will develop models to describe the experimental data first by detailed chemical and fluid mechanical processes, second by quasi-equilibrium models, and finally by scaling laws. These scaling laws will then be utilized in recommending reformer design modifications.

In carrying out the experimental tasks, a high temperature flow reactor facility has been constructed at PSI. A description of this reactor is given later in this report. The reactor has been operated at various feed rates of O_2 , N_2 , H_2O and fuel in order to span the range of possible soot formation in autothermal reformers. Premixed runs have been made with ethane as the fuel and with O_2 /fuel carbon, H_2O /fuel carbon, and N_2 /fuel carbon molar ratios of 0 to 0.5, 2.0, and 1.6, respectively. These runs were made at atmospheric pressure with preheat levels from 450 to 700 °C and with reactor wall temperatures from 450 to 800 °C.

At a preheat temperature of 520 °C, no cracking of ethane was observed in the test section. At an O_2 /fuel carbon ratio of 0.35, thermocouples indicate reaction downstream of the test section and at an O_2 /C ratio of 0.47, an unstable "flame" (yellowish) is observed through the viewports. With 620 °C preheat, ethane is cracked to ethylene to varying degrees depending on O_2 /C ratio. Rapid reaction occurs in the test section for O_2 /C ratios as low as 0.1. No O_2 is detected by the GC/MS probe and no sooting is observed. For O_2 /C ratios of 0.35 and higher, reaction occurs upstream of the test section (in the mixer). With the preheat temperature at 400 °C and reactor wall temperatures of 450 °C and higher, it was found

that the reaction was downstream of the test section and moved upstream when the wall temperature was increased or when the flow velocity was decreased.

In addition, during the reactor shakedown period a series of runs were made at reduced pressure (20-100 torr) with various levels of H_2O , N_2 , and O_2 and with ethane as the fuel. These runs were under flame-like conditions. A stable blue flame was usually established in the test section. Intense C_2 and CH spectra were observed with their ratio being a function of the H_2O flow rate.

Engelhard Industries, a subcontractor under the reformer program, has provided information on catalyst reaction rates at reformer temperatures and has performed several runs on a bench scale reactor using a precious metal catalyst with both ethane and number two fuel oil with various H_2O/C and air/C ratios. Engelhard is also providing catalysts for the PSI reactor studies.

PSI has made use of its quasi-equilibrium computer codes to analyze data obtained by Engelhard for catalytic partial oxidation of ethane and finds a reasonable description of the products. This description makes use of correlations of the data which show that C_2 hydrocarbon carryover is linearly related to the O_2/C ratio and that little or no steam participates in reaction (except for some small amount of shift reaction). The Engelhard data on the catalytic partial oxidation of No. 2 fuel oil indicate that perhaps 70% of the oxygen ends up as "equivalent water," H_2O or CO_2 . Further, the amount of the various lighter hydrocarbons is independent of O_2/C ratio. Clearly, further investigation of this area is needed.

A computer model has been developed which describes the gas phase finite rate chemical kinetic reactions which take place in the flow reactor when C_1 and C_2 hydrocarbon fuels are used. This model utilizes rate constant information from recent rate surveys and is limited by the availability of rate information for the scenario of interest (moderate temperature, low O_2 , high H_2O). The model results, however, qualitatively describe the reactor performance. This model assumes premixed plug flow. Other computer

models are available at PSI which allow computation of finite rate chemical reactions with laminar or turbulent mixing, including a one-dimensional turbulent mixing model for rapid computation. However, the need for use of these mixing models for autothermal reformer modeling has not been established.

In the second year of the program, further experiments and modeling will be performed to determine the chemical composition of the reformer products and to understand the formation of soot in autothermal reformers. This work will include experiments with other simple fuels with and without catalysts and a sulfur containing species. Experiments will also be performed with a heavy fuel. The work will include further modeling with a goal of developing simple model descriptions of reformer performance and, in particular, soot formation boundaries.

II. PSI EXPERIMENTAL PROGRAM

A. High Temperature Flow Reactor

The PSI high temperature flow reactor is designed to allow the study of chemical phenomena relevant to vapor fuel conversion processes at inlet and wall temperatures up to 1200 K. The reactor is designed to operate over a pressure range from 0.05 to 4 atmospheres. The higher pressures allow investigation of phenomena in the range of interest for fuel processors and the lower pressures allow for the spreading of the reaction zone so that detailed species and temperature profiles can be recorded.

In order to achieve separation of chemical and fluid mechanical phenomena we have designed the flow in the reactor to be laminar. This requires that

$$Re_D = \frac{\rho u D}{\mu} < 2300$$

where u is the flow velocity, D is the flow diameter, ρ is the gas density, and μ is the gas viscosity. The central half of the flow in a laminar reactor will be unaffected by the reactor walls for a time, τ_F

$$\tau_F \approx 0.008 \frac{\rho D^2}{\mu}$$

For our conditions (~ 1000 K, molecular weight ≈ 23),

$$\rho \approx 3 \times 10^{-4} p \text{ (g/cm}^3\text{)}$$

$$\mu \approx 3 \times 10^{-4} \text{ (g/cm-s)}$$

where p is the pressure in atmospheres. So for our choice of a two-inch diameter flow tube,

$$\tau_F \approx 0.2 \text{ p(s)}$$

$$\text{Re}_D \approx 5 \text{ pu}$$

The properties which are recorded during the experiments are gas temperature, pressure and composition, and the presence of soot. Temperature is measured with thermocouples imbedded in the reactor wall and inserted into the flow at various positions. The species concentrations are measured after quenching by cooling primarily by a HP 5992A gas chromatograph/mass spectrometer. Gas sampling is accomplished by a movable probe connected to the GC/MS. This GC/MS allows automatic identification of species and should prove very valuable in identifying larger hydrocarbons which could be important soot precursors. A conventional gas analyzer is also being purchased by PSI for more rapid analysis of major species composition. The movable probe has been modified so as to have an exposed thermocouple next to the gas sample inlet. For specific short-lived species, such as OH, CH and C₂, spectral measurements can be made with a McPherson 218 scanning monochromator. Sooting is detected visually or by black body radiation on the monochromator spectrum (see below for discussion of soot diagnostic).

A drawing of the flow reactor test section is given in Fig. 1. The reactor is made of 2-1/2" schedule 160 stainless steel 304 pipe and ANSI #300 flanges. There are three inlets in the top flange which feed steam, oxygen and fuel into the mixing assembly placed at the top portion of the reactor. A thermocouple probe measures the mixed inlet temperature. The mixer assembly used in the tests reported here consists of a stainless steel tube, 1.75" I.D., 2.0" O.D. with a 1/8" thick porous (100 μ) Inconel plate welded at the bottom. The static mixer (Koch Engineering Co.) slides inside the assembly. The entire mixing assembly is removable. A second mixing assembly has been constructed without the porous plate. This unit will allow testing to determine the effects of the Inconel on the observed chemical reaction. The porous plate does aid in keeping the flow uniform in the

Fig. 1 - High temperature reactor.

test section. An additional assembly will be constructed by Engelhard which will have a precious metal monolith partial oxidation catalyst downstream of the static mixers for testing of soot formation from partial oxidation products. This unit can also be used without the precious metal (support material only). There are five pairs of windows located below the mixer head in the reactor for studies of spectra. The window ports are cooled by passing cold water through copper pipes brazed to the sidearms. The windows are commercially available 1" sapphire viewports. A slow counterflow of N_2 gas prevents the condensation of moisture on the viewport and allows the cooling of the same. A slit is placed such that it is flush with the inner wall of the main reactor. This arrangement ensures minimal disturbance of the flow of gas stream near the windows.

The top and bottom sections of the reactor are surrounded by heating elements providing approximately 2.7 kW power. The window sections are heated by wires wrapped around the sidearms between the water cooling and the main reactor tube. The entire reactor is insulated by Locon felt blanket. An igniter consisting of a spark gap inserted through one of the thermocouple ports can be used to facilitate ignition of mixtures. The reactor is designed so that it can be reversed end for end and a 12" extension piece added to increase the flexibility of the device.

A schematic of the facility is shown in Fig. 2. Water is metered by a rotameter and fed to a steam generator before it is fed to a pebble bed preheater. Oxygen and nitrogen are also metered by rotameters and then fed to a pebble bed preheater. The pebble bed preheaters were selected because they provide excellent control of the preheat temperature. The fuel can be preheated in a small steady state heater, as a long dwell time at high temperature is not desirable when cracking of the fuel is to be avoided. The gases are then fed into the mixing section of the reactor. The preheaters, each two feet long made of 2" schedule 80 stainless steel 304 pipe, are packed with 1/4" diameter stainless steel balls. The furnaces for the preheaters are each 3.6 kW Mellen split tube-type and are capable of reaching a maximum temperature of 1500 K. The exhaust from the reactor is cooled by a heat exchanger before venting to the atmosphere.

Fig. 2 - Schematic of reactor facility.

The system is designed so that the reactor can be operated under conditions of vacuum as well as high pressure. This is accomplished by use of a liquid ring pump. Simply stated, the liquid ring pump is a vacuum pump that removes gases by means of rotating impeller blades entering and leaving a ring of liquid, usually water. The Kinney Vacuum Company KLRC-75 pump has a pumping capacity of 60 CFM at 760 torr and 22 CFM at 25 torr. Using the liquid ring pump as the second stage for an airjet ejector allows us to attain lower pressures of about 10 torr. The advantage of liquid ring pumps over oil-sealed rotary pumps is that combustible mixtures can be pumped without danger of explosion. Further, sulfur compounds are removed from the effluent by the running water. The exhaust gases are vented and mixed rapidly with air by 2500 CFM blower on the roof to bring the CO concentration to a safe level.

An interlock system consisting of series of relays guarantees the shut down of the system in case of a malfunction during a run such as abnormal increase of temperature and pressure. A pressure sensor on the cooling water line and a microswitch on the blower are also part of the interlock system. Further, the solenoid valves on the feed lines are wired so that the oxidant and fuel supplies are shut and replaced by N_2 in case of system malfunction. A barrier is erected in front of the apparatus to ensure the safety of the operator.

B. Soot Formation Detection

For the soot formation detection one can use absorption, emission or scattering techniques. In order to assess the sensitivity of these techniques, we performed simple calculations which are detailed below.

Scattering and Absorption Coefficients

Consider a sphere of radius, r , embedded in a nonconducting medium and a beam of monochromatic radiation of wavelength λ_m , striking its surface. According to Mie's theory, it can be shown that the scattering and total (absorption plus scattering) cross-sections are given by^{1,2}

$$K_s = \frac{2\pi}{k_m^2} \left\{ \sum_{n=1}^{\infty} (2n+1) \left(|a_n^r|^2 + |b_n^r|^2 \right) \right\}$$

and

$$K_t = \frac{2}{k_m^2} \operatorname{Re} \left\{ \sum_{n=1}^{\infty} (2n+1) (a_n^r + b_n^r) \right\},$$

respectively. The absorption cross-section is then given by

$$K_a = K_t - K_s.$$

In the above $k_m = 2\pi/\lambda m'$; the coefficients a_n^r and b_n^r are functions of the complex index of refraction $m = m_1 + i m_2$ and a size parameter $k_m r$. The calculations of the cross-sections are non-trivial since the coefficients in the summation involve Bessel functions and functions derived from them.

For cases where $2\pi r/\lambda_m \ll 1$ the higher order terms in the above infinite series can be neglected and it can be shown that the expressions for the scattering and total cross-sections reduce to

$$K_s = \pi r^2 \frac{128}{3} \left(\frac{\pi r}{\lambda} \right)^4 \left| \frac{m^2 - 1}{m^2 + 1} \right|^2$$

and

$$K_t = -\pi r^2 \frac{128}{3} \frac{\pi r}{\lambda} \operatorname{Im} \left(\frac{m^2 - 1}{m^2 + 2} \right),$$

respectively.

Absorption

Measurement of soot particles by absorption has the advantage that when the particles are small, as is the case for carbon soot, the measurement is independent of the size of the particles depending only on the volume loading, and is also only slightly dependent on particle temperature. Using the values of m (1.56 - 0.48 i) obtained by Dalzell and Sarofim³ for propane and acetylene soot one finds

$$K_a = 3.5 \times 10^{-14} \text{ cm}^2 \quad \text{at } \lambda = 6328 \text{ \AA}$$
$$\text{and } r_p = 50 \text{ \AA}$$

The absorption coefficient is then

$$k = NK_a \text{ cm}^{-1}$$

where N is the number of particles per unit volume given by

$$N = \frac{\rho}{\frac{4\pi}{3} \rho_o r_p^3}$$

and ρ is the mass loading of soot in g/cm^3 and ρ_o is the density of carbon, 2.25 g/cm^3 . At a mass loading of 10^{-8} g/cm^3 , which is the lowest soot level of interest, N is 8.49×10^9 particles/ cm^3 , and the absorption in a path-length l of 5 cm is:

$$\frac{\Delta I}{I} = -kl \approx 1.5 \times 10^{-3}$$

This corresponds to a small, but measurable absorption.

Emission

The emissivity, ϵ , being similar to the absorption also shares the advantage of being independent of particle size, and only slightly dependent on temperature. However, as the emitted radiation is the product of the black body function and the emissivity, and the former can be a strong function of temperature, this measurement requires an accurate knowledge of the temperature. However, as this can be obtained by measuring the emitted light at two wavelengths this is not a serious disadvantage.

The choice of wavelength is not an obvious one. In the infrared (2-5 μm) the emission is not a big function of temperature and there are lots of photons. However, alignment becomes harder and the background radiation from the gas molecules (CO_2 , CO and H_2O) is large. In the visible, everything is easier except that there are fewer photons. We have chosen to evaluate the emission in the visible at 7500 Å. In this regime the emissivity is calculated to be $\epsilon = 1.25 \times 10^{-3}$ at a mass loading of 10^{-8} gm/cm^3 .

The black body function can be written as

$$R_{\omega} = \frac{2c \omega^3}{1.438 \frac{\omega}{T}} \left(\frac{\Delta\omega}{\omega} \right)^{-1} \frac{\text{photons}}{\text{cm}^2 \cdot \text{sr} \cdot \text{s}}$$

and

$$R_{\omega} = 1 \times 10^{15} \left(\frac{\Delta\omega}{\omega} \right)^{-1} \frac{\text{photons}}{\text{cm}^2 \cdot \text{sr} \cdot \text{s}} @ 1000 \text{ K}$$

c is the speed of light

ω is wave number in $\text{cm}^{-1} \approx 1.3 \times 10^{-4} \text{ cm}^{-1}$

T is 1000 K

The number of photoelectrons at the detector is given by

$$I = \epsilon R_{\omega} \frac{\Delta\omega}{\omega} A_s \Omega \epsilon_f \epsilon_Q$$

where $\frac{\Delta\omega}{\omega}$ is given by the spectrometer dispersion to be 2.7×10^{-3}

$$\begin{aligned} A_s & \text{ slit area} = 6.4 \times 10^{-2} \text{ cm}^2 \\ \Omega & \text{ solid angle} = 2.2 \times 10^{-2} \quad (F = 6) \\ \epsilon_f & \text{ spectrometer efficiency} = .3 \\ \epsilon_Q & \text{ quantum efficiency} = 3 \times 10^{-2} \\ I & = 4.3 \times 10^4 \text{ photo-electrons/s} \end{aligned}$$

This value is well above the detector noise level of 50 photo-electrons/s. Even at 800 K we are a factor of ten above the detector noise level. These calculations assume that proper aperturing has removed the background radiation from the hot walls.

Scattering

The advantages of scattering for the detection of soot are that by using a laser it is straightforward to reject the background emissions and the scattering is independent of temperature. More importantly, if the laser beam is placed along the axis of the reactor, a point measurement on the centerline is obtained. Again using $m = 1.56 - 0.48i$, the molecular scattering cross-section for 50 Å particles is found to be

$$K_s = 2.5 \times 10^{-18} \text{ cm}^2$$

for the scattering of He-Ne laser light at a wavelength of 6328 Å. The fraction of the laser beam scattered at right angles into a unit solid angle is

$$f = K_s N \ell \frac{3}{16} (1 + \cos \theta)$$

where

N is the number of 50 Å particles = $8.5 \times 10^{-9} \text{ cm}^{-3}$
 at a mass loading of $10^{-8} \frac{\text{gm}}{\text{cm}^3}$

l is the path length = 2 cm

θ is the angle = 90°

Thus $f = 2.5 \times 10^{-9}$.

If a 2 mW He-Ne laser is used and the entrance slit of the monochromator is adjusted to accept the image of the laser beam then

$$I_{\text{photo-electrons}} = I_{\text{LASER}} \times f \Omega_{\epsilon} \epsilon_f \epsilon_Q$$

where

$$I_{\text{LASER}} = 6.38 \times 10^{15} \frac{\text{photons}}{\text{s}}$$

$$\epsilon_f = .3$$

$$\epsilon_Q = .08$$

and Ω is the solid angle of the spectrometer reduced by the magnification ($m = 2.5$) required to project the laser beam image into the entrance slit

$$\Omega_{\epsilon} = \text{cm}^2 \Omega = 3.52 \times 10^{-3} \text{ sr} ,$$

$$I_{\text{photo-electrons}} = 1.3 \times 10^3 \text{ s}^{-1} .$$

This is again well above the noise level of the detector.

The emission seems to be the most sensitive technique of the three for our apparatus. Hence, we have chosen to look for emission from hot soot particles for the on-set of soot formation. By comparing the soot particle emission intensity with the intensity received by the monochromator by replacing the burner with a calibrated tungsten lamp, one can determine the particle temperature and concentration. This method has been described by Feugier⁴ and later used also by Delfau and co-workers.⁵

The experimental set-up consists of a simple focusing arrangement with a lens on a 0.3 meter McPherson Model 218 scanning monochromator equipped with a grating 1200 grooves/mm blazed at 5000 Å. Light is detected with an EMI 9659QA photomultiplier thermoelectrically-cooled to -20°C. The output of the PM is fed through a picoammeter to a recorder.

C. Test Results

Low Pressure Flame Studies

Our first experiments were done without steam using fuel rich conditions (C_2H_6 , N_2 and O_2). At $O_2/C = 0.68$ and $N_2/C = 1.90$ and $T_p = 456$ K, at 50-100 torr we observed intense emission in the 4000-6000 Å region. The structured emission spectrum as scanned by the monochromator was identified as due to C_2 and CH species. A portion of the emission due to C_2 species is shown in Fig. 3. A series of experiments were performed at 30 to 40 torr and $T_p = 495-550$ K. O_2/C ratio was varied from 1.10 to 0.65, while the C_2 emission was monitored. Under these conditions the observed color of the flame was bluish-green, indicating no significant amount of soot was formed. It was found that the C_2 emission increased by a factor of four as the O_2/C was varied from 1.10 to 0.65. Addition of water increases the relative intensity of emission of CH relative to C_2 . Attempts to lower the O_2/C ratio below 0.65 resulted in the "blow-out" of the flame. This lower limit was relatively insensitive to the H_2O/C and N_2/C ratios except at high H_2O/C ratio (i.e., $H_2O/C > 1$) where a higher O_2/C ratio limit is found. This may be more of a diluent effect than a chemical effect. This phenomena was not investigated further when it was found that the region of interest could not be readily approached by reduction of O_2 from a flame-like condition.

Fig. 3 Emission band of C_2 ; $O_2/C = 0.93$ $H_2O/C = 1.31$, $N_2/C = 0.27$
 $P = 44$ torr $T_p = 480$ °K.

Atmospheric Pressure Studies

A series of experiments were performed with ethane as fuel at atmospheric pressure (18 psi) and various reactor and preheat temperatures. The steam and nitrogen feed rates corresponded to $H_2O/C = 2.0$ and $N_2/C = 1.7$ with a gas velocity in the test section of 60 cm/s. The O_2/C ratio was varied from 0 to 0.6 with inlet temperature varied from 400°C to 630°C and wall temperature from 450°C to 750°C.

Typical temperature measurements for 520°C preheat are shown in Fig. 4. The temperatures are given at various locations along the reactor as shown by the schematic of the reactor in the lower portion of the figure. Temperatures measured by thermocouples imbedded in the reactor wall are shown by crosses and those measured by thermocouples in the flow are shown as circles. The thermocouple in the flow at the location of the second window pair (595°C) read high throughout the experiments and should only be taken as a relative measurement. With the O_2 feed off (dashed curve), the measured wall temperatures are as set by the heating elements. The gas temperature is as determined by mixing of the preheated steam and nitrogen with the room temperature fuel. Measurement of the gas composition via the sampling probe located as shown in the figure, indicated no change in composition.

With the O_2 feed at an O_2/C ratio of 0.36, the temperature profile is given by the points along the solid line. Reaction did take place as indicated by the temperature rise of the walls, however, this rise is downstream of the intended test section and appears to start just upstream of the gas sampling probe. The chromatogram of the gas sample taken at this point indicates no measurable (within noise limits) reaction products as indicated by total ion current on the mass spectrometer. However, a chromatogram taken simultaneously at mass number 28 indicates counts at retention times corresponding to C_2H_4 and CO_2 as well as C_2H_6 and N_2 . This observation is consistent with the temperature measurement and indicates some reaction in the test section.

Fig. 4 - Temperature profile for low preheat condition.

With the O_2/C ratio increased further to 0.47, an unstable reaction is seen. The flow thermocouple indicates an average temperature above $900^\circ C$ with fluctuations of the order of $50^\circ C$ and visually the flow is unstable with flickering "orange" radiation. The flow was too unstable to make meaningful monochromometer measurements.

At higher preheat, the reaction is much more rapid. Results for $620^\circ C$ preheat and hotter walls is shown in Fig. 5. Some gas temperature rise at the first thermocouple location is seen even for the condition of no O_2 feed. Such a temperature rise is commensurate with that predicted by the model (see later section) due to absorption of wall radiation. With O_2 added, the temperature rise appears to be immediate. No O_2 is seen in the gas sample of O_2/C ratios as low as 0.1, the lower limit of the testing. For the runs depicted by Fig. 5, the chromatograms are shown in Fig. 6. The first peak corresponds to O_2 and CO. The mass spectrum for this peak is given in the figure and shows the presence of CO by the appearance of mass number 12 (the main peak of CO is at mass 28 along with N_2). The unresolved peak just after this peak corresponds to CH_4 . The last three peaks represent CO_2 , C_2H_4 and C_2H_6 , respectively. The chromatograms show the dramatic drop in C_2H_6 and the appearance of CO_2 and C_2H_4 with O_2 addition. At an O_2/C ratio of 0.35 the reaction moved upstream into the mixer.

A series of runs was performed with an inlet of $400^\circ C$ and with wall temperature between $450^\circ C$ and $650^\circ C$ and with various velocities. Under these conditions the reaction took place downstream of the test section, however, thermocouple readings indicated that increased wall temperature or reduced velocity caused the reaction to occur further upstream. This is as expected.

The above described experiments indicate that there exists a range of O_2/C ratio which probably narrows with increased preheat temperature such that in this range reaction is unstable. At higher O_2/C ratio, a flame-like mechanism stabilizes the reaction whereas at lower O_2/C ratios a flow-tube-like reaction takes place.

$$\frac{H_2O}{C} = 1.91$$

$$\frac{N_2}{C} = 1.66$$

$$\frac{O_2}{C} = .25$$

Fig. 5 - Temperature profile for high preheat.

$$O_2/C = 0$$

$$H_2O/C = 1.91$$

$$N_2/C = 1.66$$

MASS	ABUNDANCE (%)
14.00	62.1
28.05	100.0
29.05	1.2

$$O_2/C = 0.25$$

$$H_2O/C = 1.91$$

$$N_2/C = 1.66$$

MASS	ABUNDANCE (%)
12.00	2.2
14.00	53.7
17.05	1.1
18.05	1.4
28.05	100.0
105.00	1.3

Fig. 6 - Chromatograms of typical gas samples at high preheat.

Future Plans

In the above experiments, there is concern that the Inconel porous plate acts as a catalyst. In the next series, runs will be performed without the Inconel plate. Runs will also be performed with other fuels (e.g. C_2H_4 , C_2H_2 , CH_4) and with sulfur bearing compounds. If time permits, runs will also be performed with a liquid fuel.

III. MODEL DESCRIPTIONS

A. Reactor Flow Model

Plug Flow Model

The main purpose of the reactor flow model is to describe the flow in the PSI high temperature flow reactor and to assist in understanding results. The initial model is a premixed stream tube (plug flow) model upon which the chemical model is superimposed. The conservation equations used in this model are developed in terms of a set of chemical variables which are not standard, and are defined as

X_i = moles of species i /fuel carbon

$Z = \sum X_i$ = moles of gas/fuel carbon

$WT = \sum X_i W_i$ = grams of gas/fuel carbon

W_i = molecular weight of species i

$\tilde{n} = p/kTz$ = modified number density

$\tilde{R} = Ro/WT$ = modified gas constant

$\dot{X}_i$ = chemical production rate of species i

$Ro = k a$

$k = 1.38 \times 10^{-16}$ = Boltzmann's constant

$a = 6.02 \times 10^{23}$ = Avagadro's number

$h = \tilde{R} \sum h_i X_i$ = enthalpy (ergs/gram)

$C_p = \tilde{R} \sum C_{p_i} X_i$ = specific heat (ergs/gram K)

$\rho = p/\tilde{R}TZ$ = density in grams/cm³

where h_i and C_{p_i} are obtained for example, from curve fits of the JANAF tables (see Chemical Model section).

Conservation of elemental mass requires that $\tilde{R}$ be constant, so the conservation of mass becomes (for a constant area duct)

$$\frac{d}{dx} \tilde{n}u = 0.$$

Conservation of momentum gives

$$\rho u \frac{du}{dx} = \frac{dp}{dx}.$$

Conservation of energy gives

$$\rho u C_p \frac{dT}{dx} + \rho \tilde{R} \sum_i h_i \dot{X}_i = - \rho u^2 \frac{du}{dx} + \dot{E},$$

where $\dot{E}$ is the heat transferred into the volume at location x (ergs/cm³ s). For our initial modeling we have assumed that once the gas has passed through the porous plate, it "sees" the radiation from the walls of the reactor which are assumed to be black at a temperature T_w . If the gas is assumed to be thin (that is, it doesn't absorb a significant fraction of the radiation), we can use a simple model for the energy absorbed which gives

$$\dot{E} \equiv \rho \tilde{R} \dot{e} = \rho \tilde{R} \sum_{ij} X_i \left\{ f_{ij}(T) - f_{ij}(T_w) \right\}$$

where j is assumed over the radiating vibrational bands of the molecule

$$f_{ij} = \frac{C_2 \omega_{ij}}{\tau_{ij}} \left(e^{C_2 \omega_{ij}/T} - 1 \right)^{-1}$$

and ω_{ij} is the frequency of the band center and τ_{ij} is the band lifetime $C_2 = 1.4288$ is the second radiation constant. Band center frequencies

and lifetimes are given in Table 1, and were taken from various sources with the hydrocarbon values being from Sverdlov et al.⁶ In order to assess the validity of the assumption that the gas is thin, we have made a comparison of the emissivity of the strongest bands with the thin limit value.

The emissivity of a band can be calculated from¹

$$\epsilon = \frac{R_{\omega}^0}{\sigma T^4} \int \left(1 - e^{-kx} \right) d\omega ,$$

where R_{ω}^0 is the black body function evaluated at the band center, σ is the Stefan-Boltzmann constant, k is the absorption coefficient, x is the path length, and ω is the wave number. This equation can be approximated in the high pressure limit as⁷

$$\epsilon = \frac{R_{\omega}^0}{\sigma T^4} \Delta_0 I(K)$$

where $\Delta_0 = \frac{kTB}{hc}$, $K = \frac{\alpha n}{\Delta_0 L_0} x$ and where B is the average rotational constant, α is the band strength and n/L_0 is the density of the radiator in amagats (1 amagat = $L_0 \approx 2.5 \times 10^{19}$ particles/cc). For symmetric top molecules, the appropriate value of B is the square root of the product of the two rotational constants. The integral $I(K)$ is shown as a function of K in Fig. 7. When $I(K) \approx K$, the gas is thin. We have evaluated K for the strongest band (3000 cm^{-1} for C_2H_6) and for a representative average band (3000 cm^{-1} for C_2H_2). Using rotational constants from Hertzberg⁸ and integrated band intensities from Sverdlov et al.⁶ we find the values shown in Table 2 for $T = 1000 \text{ K}$, $x = 5 \text{ cm}$ (the reactor diameter) and a radiator density of 0.1 amagats. We can see that even for this relatively high density, the C_2H_4 band is thin; however, the C_2H_6 band is quite thick and only about 20% of the radiation from a hot wall would reach the center. It is possible to correct this deficiency of the thin limit model by applying

TABLE 1

Infrared band lifetimes

Molecule	Band Center (cm^{-1})	Lifetime (sec)
H_2O	1595	5×10^{-2}
	3700	1.1×10^{-2}
CO_2	2349	2.3×10^{-3}
	667	3.3×10^{-1}
	3700	2×10^{-2}
CO	2143	3×10^{-2}
CH_4	3020	1.2×10^{-2}
	1306	1×10^{-1}
C_2H_2	729	1×10^{-1}
	3287	1.2×10^{-2}
C_2H_2	949	1.2×10^{-1}
	3000	2.2×10^{-2}
	1443	4×10^{-1}
C_2H_6	821	2.1×10^{-1}
	1430	2.3×10^{-2}
	2970	5.6×10^{-4}

Fig. 7 - Emissivity integral.

TABLE 2

Optical Thickness Properties

<u>Molecule</u>	<u>$\omega(\text{cm}^{-1})$</u>	<u>$B(\text{cm}^{-1})$</u>	<u>$\alpha(\text{ama}^{-1} \text{cm}^{-2})$</u>	<u>K</u>
C_2H_6	3000	1.28	6700	78.
C_2H_4	3000	2.1	150	1.4

this correction. This has not yet been done. A radiation source of more importance is that of the expected "flame" that could occur from the oxidation. Unfortunately, the radiation from this flame, although intense, is not that of a black body but is banded with radiation in the bands characteristic of the species present in the flame. Our calculations show these species to be predominantly CO, CO₂, H₂ and H₂O. A model to describe the radiative transport in such a scenario is complex and is well beyond the scope of this study. As an alternative to such a model, we can use the temperature profile measured in the reactor in the modeling reactor for chemical data comparison.

The energy equation can be rewritten to give the temperature derivative with respect to flow time

$$\left\{ S_p + D \right\} \frac{dT}{dt} = \dot{e} - \dot{e}_h - \frac{TD}{Z} \sum \dot{X}_i$$

where

$$D = Z \tilde{M}^2 / (1 - \tilde{M}^2)$$

$$\tilde{M}^2 = u^2 / \tilde{R}TZ$$

$$S_p = \sum C_{p_i} X_i$$

$$\dot{e}_h = \sum h_i \dot{X}_i$$

The velocity derivative is then found from

$$\frac{du}{dt} = \frac{\tilde{R}}{u} \left\{ \dot{e} - S_p \frac{dT}{dt} - \dot{e}_h \right\}$$

The pressure derivative is negligible for the low velocities of interest but can be found from

$$\frac{dp}{dt} = - \rho u \frac{du}{dt}$$

Mixing Model

We also have developed a one-dimensional mixing model to describe a turbulent mixing configuration of the flow reactor. A schematic of the regions addressed in this model are shown in Fig. 8.

Referring to Fig. 8 for stream identification we can infer that the input streams are not directly effected by the mixed stream. With the rate of growth of the mixed region specified by data from Abramovich⁹ we can derive the conservation equations for the three streams.

$$\dot{m}_j = \rho_j u_j A_j$$

$$\dot{m}_j \frac{du_j}{dx} = -A_j \frac{dp}{dx}, \quad j=1,2$$

$$\dot{m}_j C_{pj} \frac{dT_j}{dx} = -\dot{e}_{hj} + \dot{e}_j, \quad j=1,2$$

$$\dot{m}_0 \frac{du_0}{dx} = -A_0 \frac{dp}{dx} + (u_0 - u_1) \frac{d\dot{m}_1}{dx} + (u_0 - u_1) \frac{d\dot{m}_2}{dx}$$

$$\begin{aligned} \dot{m}_0 C_{p0} \frac{dT_0}{dx} = & -\dot{e}_{h0} + \dot{e}_0 + \dot{m}_0 \frac{T_0 Z_0}{p} \frac{dp}{dx} + C_{p1} (T_0 - T_1) \frac{d\dot{m}_1}{dx} + C_{p2} (T_0 - T_1) \frac{d\dot{m}_2}{dx} \\ & - \frac{(u_0 - u_1)^2}{2} \frac{d\dot{m}_1}{dx} - \frac{(u_0 - u_1)^2}{2} \frac{d\dot{m}_2}{dx} \end{aligned}$$

$$\frac{d}{dx} x_j^i = \frac{\dot{x}_j^i}{u_j}, \quad j=1,2$$

$$\dot{m}_0 \frac{d}{dx} x_0^i = \left(x_0^i - x_1^i \right) \frac{d\dot{m}_1}{dx} + \left(x_0^i - x_2^i \right) \frac{d\dot{m}_2}{dx} + \frac{\dot{x}_0^i \dot{m}_0}{u_0}$$

Fig. 8 - Mixing model geometry.

where definitions are as for the plug flow model with the subscript for the stream number and with the species concentrations, X , defined so that the modified gas constant, $\tilde{R}$, is the same for all three streams.

Plug Flow with Quasi-equilibrium Chemistry

We have also constructed a model which couples the fluid mechanics and the quasi-equilibrium chemistry model. Again we utilize the plug flow equations with the same definitions. The subtle difference between quasi-equilibrium, equilibrium and full finite rate fluid mechanical models is in the enthalpy equation

$$\dot{m} \frac{dh}{dx} = \text{losses} + uA \frac{dp}{dx}$$

where

$$\frac{dh}{dx} = \frac{d}{dx} \tilde{R} \sum h_i X_i$$

and since $\tilde{R}$ is a constant by the chosen definition

$$\frac{1}{\tilde{R}} \frac{dh}{dx} = \left(\sum \frac{\partial h_i}{\partial T} X_i \right) \frac{dT}{dx} + \sum h_i \frac{\dot{X}_i}{u} + \sum \left(h_i \frac{\partial X_i}{\partial T} \right) \frac{dT}{dx}$$

The first term is the frozen specific heat times the temperature gradient, the second term is the chemical heat release due to finite rate chemistry, $\dot{e}_h$. The third term is zero for true finite rate chemistry since the species concentrations are then functions of time and not of temperature. In strict equilibrium, the second term is zero because species concentrations are functions of temperature and not time so that the first and third terms sum to form the equilibrium specific heat. For our purposes it is necessary to carry all three terms. It is impractical to compute analytically the value of the third term, however, if the conservation equations are written in finite difference form this difficulty is reduced to the simpler problem of finding the solution of simultaneous equations.

The finite difference equations for the change from location x_1 to location x_2 are

$$\rho_2 u_2 A_2 = \rho_1 u_1 A_1$$

$$P_2 - P_1 = - \frac{\rho_2 u_2 + \rho_1 u_1}{2} (u_2 - u_1) + \Delta p$$

$$h_2 - h_1 = - \frac{u_2 + u_1}{2} (u_2 - u_1) + \Delta H ,$$

where Δp and ΔH are the pressure and heat losses between positions (zero for conservation flow) and

$$\rho = P / \tilde{R} T Z$$

We then only need a thermal equation of state to complete the set. The thermal equation is represented by a relation (computer subroutine) which, given P , and certain composition relations of the form

$$C_j = \sum \lambda_{ij} X_j ,$$

and a guess for T and the X_j 's will obtain T and the X_j 's. For equilibrium flow these composition relations (constraints) are the conservation of atomic nuclei equations. However, in quasi-equilibrium, we extend these to include additional constraints for, say, the concentration of combustion products ($CO_2 + H_2O$). In this model, we include, for these additional constraints, the ability to remove these constraints as a function of time, i.e.,

$$\dot{C}_j = f (X_i, T, P)$$

and thus obtain

$$C_{j2} - C_{j1} = \frac{(C_{j2} + C_{j1})}{2} \Delta t ,$$

where

$$\Delta t = 2 \frac{x_2 - x_1}{u_2 + u_1} .$$

So that we now call the thermal equation of state subroutine with C_{j1} , C_{j2} (estimated), C_{j1} , Δt and the partial derivatives of C_{j2} with respect to the X_i 's. The subroutine then finds the temperature and X_i 's. An iteration is performed until the system converges.

B. Chemical Model

Finite Rate Gas Phase Chemistry

The "baseline" chemical kinetic reactions and rate constants used in the modeling effort were taken primarily from two surveys. The hydrocarbon reactions and rates were taken from the work of Westbrook,¹⁰ and the hydrogen/oxygen reactions from the review of Baulch et al.¹¹ The CO/CO₂ reaction rates and mechanisms were taken from the more recent review of Baulch et al.,¹² except for the reaction

for which we have fit the data which appear in Baulch et al. for both the forward and reverse rates to obtain an expression for the forward rate, which gives a good fit to all the data. The complete set of "baseline" reactions and rates used are given in Table 3. This reaction set has not been tested against data for conditions of such low oxidizer fuel levels or with large H₂O concentrations, mainly due to the lack of data. Most of the hydrocarbon rates have been determined so as to give a good description of methane combustion at fairly high temperature. Our conditions are

TABLE 3 Gas phase chemical reactions and rates*

10	O	+ O	+ O	= O2	+ O	+	RC = 6.20E-20T ^{1/2} exp(-1.50)EXP(0./T)
10	O	+ O	+ O2	= O2	+ O2	+	RC = 2.20E-20T ^{1/2} exp(-1.50)EXP(0./T)
10	O	+ O	+ N2	= O2	+ N2	+	RC = 1.70E-32T ^{1/2} exp(-0.50)EXP(0./T)
104	H2	+ OH	+	= H2O	+ H	+	RC = 3.60E-11T ^{1/2} exp(0.00)EXP(-2590./T)
105	H	+ O2	+	= OH	+ O	+	RC = 3.70E-10T ^{1/2} exp(0.00)EXP(-0450./T)
106	O	+ H2	+	= OH	+ H	+	RC = 3.00E-14T ^{1/2} exp(1.00)EXP(-4490./T)
107	H	+ O2	+ H2	= H2O2	+ H2	+	RC = 1.40E-32T ^{1/2} exp(0.00)EXP(500./T)
109	H	+ O2	+ H2O	= H2O2	+ H2O	+	RC = 0.70E-32T ^{1/2} exp(0.00)EXP(500./T)
110	H	+ O2	+ N	= H2O2	+ N	+	RC = 4.10E-33T ^{1/2} exp(0.00)EXP(500./T)
111	H	+ H	+ H2	= H2	+ H2	+	RC = 5.40E-30T ^{1/2} exp(-1.00)EXP(0./T)
112	H	+ H	+ H	= H2	+ H	+	RC = 3.00E-29T ^{1/2} exp(-1.00)EXP(0./T)
113	H	+ H	+ H2O	= H2	+ H2O	+	RC = 2.00E-29T ^{1/2} exp(-1.00)EXP(0./T)
114	H	+ H	+ N	= H2	+ N	+	RC = 1.00E-30T ^{1/2} exp(-1.00)EXP(0./T)
115	H	+ OH	+ H2O	= H2O	+ H2O	+	RC = 3.90E-25T ^{1/2} exp(-2.00)EXP(0./T)
115P	H	+ OH	+ H2	= H2O	+ N2	+	RC = 1.30E-31T ^{1/2} exp(0.00)EXP(925./T)
116	H	+ OH	+ N	= H2O	+ N	+	RC = 6.00E-26T ^{1/2} exp(-2.00)EXP(0./T)
118	H	+ O	+ N	= OH	+ N	+	RC = 1.70E-31T ^{1/2} exp(0.00)EXP(0./T)
119	OH	+ O	+ N	= H2O2	+ N	+	RC = 1.00E-33T ^{1/2} exp(0.00)EXP(0./T)
121	H2O	+ O	+	= OH	+ OH	+	RC = 1.10E-10T ^{1/2} exp(0.00)EXP(-9240./T)
122	H	+ H2O2	+	= OH	+ OH	+	RC = 4.20E-10T ^{1/2} exp(0.00)EXP(-950./T)
123	H	+ H2O2	+	= H2	+ O2	+	RC = 4.20E-11T ^{1/2} exp(0.00)EXP(-350./T)
124	O	+ H2O2	+	= OH	+ O2	+	RC = 0.00E-11T ^{1/2} exp(0.00)EXP(-500./T)
125	H2	+ H2O2	+	= H2O2	+ H	+	RC = 2.60E-10T ^{1/2} exp(0.00)EXP(0./T)
126	H2O2	+ H2O2	+	= OH	+ OH	+ H2O2	RC = 2.00E-07T ^{1/2} exp(0.00)EXP(-23150./T)
127	H2O2	+ H2O	+	= OH	+ OH	+ H2O	RC = 2.30E-07T ^{1/2} exp(0.00)EXP(-23150./T)
128	H2O2	+ O2	+	= OH	+ OH	+ O2	RC = 3.40E-08T ^{1/2} exp(0.00)EXP(-23150./T)
130	H2O2	+ H2O2	+	= H2O2	+ O2	+	RC = 3.00E-12T ^{1/2} exp(0.00)EXP(0./T)
131	H2O2	+ OH	+	= H2O2	+ H2O	+	RC = 1.00E-10T ^{1/2} exp(0.00)EXP(-2950./T)
132	H2O2	+ H	+	= OH	+ H2O	+	RC = 2.50E-11T ^{1/2} exp(0.00)EXP(0./T)
133	O	+ H2O2	+	= OH	+ H2O2	+	RC = 4.50E-15T ^{1/2} exp(0.00)EXP(0./T)
201	H	+ CO2	+	= CO	+ OH	+	RC = 2.16E-10T ^{1/2} exp(0.00)EXP(-12030./T)
202	CO	+ O	+	= CO2	+	+	RC = 2.50E-14T ^{1/2} exp(0.00)EXP(-2110./T)
203	CO	+ H2O2	+	= CO2	+ OH	+	RC = 2.50E-10T ^{1/2} exp(0.00)EXP(-11900./T)
204	CO2	+ N	+	= CO	+ O	+ N	RC = 0.50E-10T ^{1/2} exp(0.00)EXP(-55560./T)
205	O	+ CO2	+	= CO	+ O2	+	RC = 2.00E-11T ^{1/2} exp(0.00)EXP(-26500./T)
(1)	CH4	+ N	+	= CH3	+ H	+ N	RC = 2.10E-07T ^{1/2} exp(0.00)EXP(-44500./T)
(2)	CH4	+ H	+	= CH3	+ H2	+	RC = 2.10E-10T ^{1/2} exp(0.00)EXP(-5990./T)
(3)	CH4	+ OH	+	= CH3	+ H2O	+	RC = 5.27E-21T ^{1/2} exp(3.00)EXP(-1010./T)
(4)	CH4	+ O	+	= CH3	+ OH	+	RC = 2.64E-11T ^{1/2} exp(0.00)EXP(-4630./T)
(5)	CH4	+ H2O2	+	= CH3	+ H2O2	+	RC = 3.33E-11T ^{1/2} exp(0.00)EXP(-9060./T)
(6)	CH3	+ H2O2	+	= CH3O	+ OH	+	RC = 2.64E-11T ^{1/2} exp(0.00)EXP(0./T)
(7)	CH3	+ OH	+	= CH2O	+ H2	+	RC = 6.64E-12T ^{1/2} exp(0.00)EXP(0./T)
(8)	CH3	+ O	+	= CH2O	+ H	+	RC = 2.10E-10T ^{1/2} exp(0.00)EXP(-1010./T)
(9)	CH3	+ O2	+	= CH3O	+ O	+	RC = 4.19E-11T ^{1/2} exp(0.00)EXP(-14600./T)
(10)	CH2O	+ CH3	+	= CH4	+ HCO	+	RC = 1.67E-14T ^{1/2} exp(0.50)EXP(-3020./T)

*Rates (RC) in cm³/molecule-second

TABLE 3 (Cont.) Gas phase chemical reactions and rates

(11)	CH ₃	+ HCO	+	= CH ₄	+ CO	+	RC = 5.27E-13T***(0.50)EXP(0./T)
(12)	CH ₃	+ H ₂ O	+	= CH ₄	+ O ₂	+	RC = 1.67E-12T***(0.00)EXP(-201./T)
(13)	CH ₃ O	+ M	+	= CH ₂ O	+ H	+ M	RC = 0.35E-11T***(0.00)EXP(-10600./T)
(14)	CH ₃ O	+ O ₂	+	= CH ₂ O	+ H ₂ O	+	RC = 1.67E-12T***(0.00)EXP(-3020./T)
(15)	CH ₂ O	+ M	+	= HCO	+ H	+ M	RC = 0.35E-08T***(0.00)EXP(-36200./T)
(16)	CH ₂ O	+ OH	+	= HCO	+ H ₂ O	+	RC = 0.35E-10T***(0.00)EXP(-3170./T)
(17)	CH ₂ O	+ H	+	= HCO	+ H ₂	+	RC = 6.64E-12T***(0.00)EXP(-1910./T)
(18)	CH ₂ O	+ O	+	= HCO	+ OH	+	RC = 0.35E-11T***(0.00)EXP(-2320./T)
(19)	CH ₂ O	+ H ₂ O	+	= HCO	+ H ₂ O ₂	+	RC = 1.67E-12T***(0.00)EXP(-4030./T)
(20)	HCO	+ OH	+	= CO	+ H ₂ O	+	RC = 1.67E-10T***(0.00)EXP(0./T)
(21)	HCO	+ M	+	= H	+ CO	+ M	RC = 3.64E-10T***(0.00)EXP(-9560./T)
(22)	HCO	+ H	+	= CO	+ H ₂	+	RC = 3.33E-10T***(0.00)EXP(0./T)
(23)	HCO	+ O	+	= CO	+ OH	+	RC = 1.67E-10T***(0.00)EXP(0./T)
(24)	HCO	+ H ₂ O	+	= CH ₂ O	+ O ₂	+	RC = 1.67E-10T***(0.00)EXP(-1510./T)
(25)	HCO	+ O ₂	+	= CO	+ H ₂ O ₂	+	RC = 5.27E-10T***(0.00)EXP(-3520./T)
(26)	C ₂ H ₆	+	+	= CH ₃	+ CH ₃	+	RC = 2.51E-19T***(-1.00)EXP(-44400./T)
(27)	C ₂ H ₆	+ CH ₃	+	= C ₂ H ₅	+ CH ₄	+	RC = 0.35E-25T***(4.00)EXP(-4180./T)
(28)	C ₂ H ₆	+ H	+	= C ₂ H ₅	+ H ₂	+	RC = 0.35E-22T***(3.50)EXP(-2620./T)
(29)	C ₂ H ₆	+ OH	+	= C ₂ H ₅	+ H ₂ O	+	RC = 1.05E-10T***(0.00)EXP(-1210./T)
(30)	C ₂ H ₆	+ O	+	= C ₂ H ₅	+ OH	+	RC = 4.19E-11T***(0.00)EXP(-3220./T)
(31)	C ₂ H ₅	+	+	= C ₂ H ₄	+ H	+	RC = 3.90E-13T***(0.00)EXP(-19100./T)
(32)	C ₂ H ₅	+ O ₂	+	= C ₂ H ₄	+ H ₂ O ₂	+	RC = 1.67E-12T***(0.00)EXP(-2520./T)
(33)	C ₂ H ₅	+ C ₂ H ₃	+	= C ₂ H ₄	+ C ₂ H ₄	+	RC = 5.27E-07T***(0.00)EXP(-17900./T)
(34)	C ₂ H ₄	+ O	+	= CH ₃	+ HCO	+	RC = 1.67E-11T***(0.00)EXP(-554./T)
(35)	C ₂ H ₄	+ M	+	= C ₂ H ₃	+ H	+ M	RC = 1.67E-10T***(0.00)EXP(-49400./T)
(36)	C ₂ H ₄	+ H	+	= C ₂ H ₃	+ H ₂	+	RC = 1.05E-10T***(0.00)EXP(-3020./T)
(37)	C ₂ H ₄	+ OH	+	= C ₂ H ₃	+ H ₂ O	+	RC = 1.67E-10T***(0.00)EXP(-1760./T)
(38)	C ₂ H ₄	+ O	+	= CH ₂ O	+ CH ₂	+	RC = 4.19E-11T***(0.00)EXP(-2520./T)
(39)	C ₂ H ₃	+ M	+	= C ₂ H ₂	+ H	+ M	RC = 5.27E-08T***(0.00)EXP(-20400./T)
(40)	C ₂ H ₂	+ M	+	= C ₂ H	+ H	+ M	RC = 1.67E-10T***(0.00)EXP(-57500./T)
(41)	C ₂ H ₂	+ O ₂	+	= HCO	+ HCO	+	RC = 6.64E-12T***(0.00)EXP(-14100./T)
(42)	C ₂ H ₂	+ H	+	= C ₂ H	+ H ₂	+	RC = 3.33E-10T***(0.00)EXP(-9560./T)
(43)	C ₂ H ₂	+ OH	+	= C ₂ H	+ H ₂ O	+	RC = 1.05E-11T***(0.00)EXP(-3520./T)
(44)	C ₂ H ₂	+ O	+	= C ₂ H	+ OH	+	RC = 5.27E-09T***(-0.60)EXP(-8560./T)
(45)	C ₂ H ₂	+ O	+	= CH ₂	+ CO	+	RC = 1.05E-10T***(0.00)EXP(-2010./T)
(46)	C ₂ H	+ O ₂	+	= HCO	+ CO	+	RC = 1.67E-11T***(0.00)EXP(-3520./T)
(47)	C ₂ H	+ O	+	= CO	+ CH	+	RC = 0.35E-11T***(0.00)EXP(0./T)
(48)	CH ₂	+ O ₂	+	= HCO	+ OH	+	RC = 1.67E-10T***(0.00)EXP(-1060./T)
(49)	CH ₂	+ O	+	= CH	+ OH	+	RC = 3.33E-13T***(0.60)EXP(-12600./T)
(50)	CH ₂	+ H	+	= CH	+ H ₂	+	RC = 4.19E-13T***(0.67)EXP(-12900./T)
(51)	CH ₂	+ OH	+	= CH	+ H ₂ O	+	RC = 4.19E-13T***(0.67)EXP(-12900./T)
(52)	CH	+ O ₂	+	= CO	+ OH	+	RC = 2.10E-13T***(0.67)EXP(-12900./T)
(53)	CH	+ O ₂	+	= HCO	+ O	+	RC = 1.67E-11T***(0.00)EXP(0./T)
(54)	CH ₃ OH	+ M	+	= CH ₃	+ OH	+ M	RC = 3.33E-06T***(0.00)EXP(-40300./T)

greatly different from those of flames and much more work is necessary before confidence can be increased to the point where we can expect to predict the performance of the flow reactor (flow reactor data should give important information on these reaction rates). We can, however, observe trends in calculated performance, identify important mechanisms and evaluate other reaction mechanisms.

The important mechanisms to study are those that initiate the reaction of the gases and those that determine the state of the gas downstream of the reaction zone. An understanding of these mechanisms will lead to the development of scaling laws.

An investigation of this reaction set shows that there are no reactions for the direct reforming of C_2H_2 by H_2O , OH or H . Reactions of C_2H_2 with OH and H form C_2H and there are no listed reactions of C_2H with H , OH , or H_2O . Thus, C_2H_2 becomes a major product. No data have been found on such reactions, but it is likely that such reactions occur. Possible reactions are:

However, these reactions are all endothermic as indicated and would be unlikely to occur to an appreciable extent. A more reasonable pathway for the destruction of C_2H_2 would be through the reaction of C_2H_y with H and OH where $y > 2$ and C_2H_y is formed by hydrogen addition reactions, e.g., the reverse of our reaction (60) in Table 3:

followed by reactions such as

In addition, we find that the reactions of CH radicals with fuel-rich species are not included in the baseline reaction set. These reactions and rates have been estimated by Englemann¹³ and are given in Table 4 along with estimates for other reactions we have included in calculations.

In further review of the reaction set we find that there are several four center reactions which may be questionable as they could be combinations of other reactions included in the reaction set. These are shown in Fig. 4 with a rate constant of zero. Although these reactions may, in fact, go at an appreciable rate, one should be skeptical and take a close look at such reactions. In general, the references for the four center reactions are by no means definitive works. Often the reaction in question was not the subject of the study, but perhaps its rate was estimated for the purposes of determining its importance, or perhaps the products were not known or in some cases, the reference is erroneous.

It is clear from our cursory review that a careful review of C₂ hydrocarbon chemical kinetics is needed. Several groups¹⁴⁻¹⁷ are in the process of developing models for this chemistry, and we will utilize their work as it becomes available.

TABLE 4

Additional reactions and rate constants

$C_2H_3 + OH$	$\rightarrow CH_2 + CH_2O$	$10^{-12} e^{-4000/T}$
$C_2H_5 + H$	$\rightarrow CH_3 + CH_3$	$10^{-10} e^{-3000/T}$
$CH_3 + CH_3O$	$\rightarrow C_2H_5 + OH$	$10^{-12} e^{-3000/T}$
$CH_2 + CH_3OH$	$\rightarrow C_2H_5 + OH$	$10^{-12} e^{-3000/T}$
$C_2H_6 + H$	$\rightarrow CH_3 + CH_4$	$10^{-12} e^{-3000/T}$
$C_2H_6 + OH$	$\rightarrow CH_3 + CH_3OH$	$10^{-12} e^{-3000/T}$
$CH + CH_4$	$\rightarrow CH_2 + CH_3$	$4.2 \times 10^{-13} T^{0.7} e^{-3000/T}$
$CH + CO_2$	$\rightarrow HCO + CO$	$1.7 \times 10^{-14} T^{0.5} e^{-3000/T}$
$CH + OH$	$\rightarrow HCO + OH$	$8.4 \times 10^{-13} T^{0.5} e^{-3000/T}$
$CH_3 + OH$	$\rightarrow CH_2 + H_2O$	$2 \times 10^{-13} T^{0.7} e^{-1000/T}$
$CH_2 + H_2$	$\rightarrow CH_3 + H$	$5.3 \times 10^{-12} e^{-3500/T}$
$C_2H_4 + O$	$\rightarrow CH_3 + HCO$	0
$C_2H_4 + O$	$\rightarrow C_2H_3 + OH$	$10^{-10} e^{-3000/T}$
$C_2H_2 + O_2$	$\rightarrow HCO + HCO$	0
$C_2H_2 + O$	$\rightarrow CH_2 + CO$	0
$C_2H + O_2$	$\rightarrow HCO + CO$	0
$CH_2 + O_2$	$\rightarrow HCO + OH$	0
$CH + O_2$	$\rightarrow CO + OH$	0

Thermochemistry

We have updated the thermochemical tables used by these codes and the kinetics codes to include data of species not included in the JANAF tables. These species are the hydrocarbon radicals: CH_3O^{13} , $\text{C}_2\text{H}_3^{18}$, and $\text{C}_2\text{H}_5^{18}$; and other primary C_2 hydrocarbons¹⁹ seen or expected in reformers: C_2H_6 , C_3H_4 , C_3H_6 , and C_4H_6 . We have also included several fuel molecules¹⁹ used in experiments at JPL: C_6H_6 , $\text{C}_{14}\text{H}_{30}$, C_{10}H_8 , C_6H_{14} . The data¹⁹ for $\text{C}_{15}\text{H}_{24}$ has also been included. This compound (n-nonylbenzene or 1-phenyl-nonane) has properties similar to number two fuel oil and is useful as a thermodynamic model compound (heat of combustion = 19,900 Btu/lb.). Unfortunately, the bulk of the hydrocarbon data is tabulated¹⁹ only to 1000 K and care must be taken in extrapolating curve fits of the thermodynamic properties.

In our procedure we curve-fit the Gibbs free energy for species. We then check the resultant fit of the enthalpy derived from differentiating the curve fit against data. If the comparison is good, we use the fit. If the comparison is not good, and the species is not a trace species (its enthalpy will be important), we curve-fit the enthalpy and match the Gibbs free energy at 1000 K to determine the additional curve fit parameter. The curve-fits have seven parameters and have the form

$$-G/RT = L_1 + L_2 \ln T - L_3/T + L_4/T^2 + L_5T + L_6T^2 + L_7T^3$$

This form works very well for simple molecules but can lead to difficulties for the higher hydrocarbons.

Catalytic Rates

A review of the literature in combination with Engelhard's ATR test results indicates the following:

1) Methane steam reforming is slow in comparison to the rates for steam reforming and composition of the C_2 compounds. A first order rate constant of $12,700 \text{ hours}^{-1}$ has been estimated at 850°C , 1 atm from Engelhard's ATR unit using the G90C catalyst obtained from UTC. This rate constant is based on the dry exit gas flow rate at standard conditions per unit volume of steam reforming catalysts. The data used and the calculation procedures are attached. An activation energy of 26.2 kcal/mole is suggested by Rostrup-Nielsen²⁰. More precise measurements may be obtained in the literature, but the effect of H_2S on these rates is uncertain. The Engelhard results, though crude, are obtained using No. 2 oil containing sulfur (see Appendix).

The effect of particle size on conversion is illustrated by Schnell:²¹

<u>Particle Size</u>	<u>Conversion of Propane %</u>
1/8" Pellets	8.7
5-16 British Standard Screen	24.3
14-22 British Standard Screen	42.0
22-36 British Standard Screen	41.5

This strong effect of particle size (pore diffusional effect) makes it very difficult to compare literature data on various catalysts. Experimental details are questionable in many references.

2) Above 850°C , ethane decomposes to ethylene and H_2 faster than it is steam reformed. Various rates are available in the literature are already included in PSI's homogeneous reaction model.

3) In the presence of hydrogen, acetylene is hydrogenated rapidly to ethylene (and 1-3 butadiene). These rates are also available from the literature. Acetylene is probably involved in the formation of coke via competitive reactions.

4) Ethylene is the main C_2 compound of interest in high temperature steam reforming (above 850 C). A first order rate constant of $50,300 \text{ hrs}^{-1}$ is estimated for G90C at 850 C, 1 atm from Engelhard ATR data. An activation energy of 20 kcal/mole should be assumed in lieu of experimental data. Ethylene is also probably involved in the coking reactions.

A computer-based search of the recent literature (last 12 years) yielded four references of interest. The Chemical Abstracts review of the references is given in the appendix. McMahon and Milliken steam reformed ethane/ethylene at 750 C at steam to carbons as low as 1.6. Morita, et al. showed the rate of ethylene disappearance at 370-450 C to be approximately twice that for 1-butene. If so, this is the reverse of the relative rates for the paraffins which react faster with steam as molecular weight increases.

The brief literature review on olefin/steam reforming shows a need for experimental rate data for the olefins under conditions to be expected in the ATR.

IV. MODELING RESULTS AND DATA ANALYSIS

A. Kinetic Modeling Results

A representative calculation utilizing the chemical kinetics model and the plug flow fluid mechanics model is shown in Figs. 9-10. This particular computation was performed for the PSI high temperature flow reactor for C_2H_6 as the fuel with $O_2/C = 0.4$ and $H_2O/C = 2.8$ and no nitrogen in the flow. The initial flow velocity is 100 cm/s; the initial gas temperature, 500 K; and the wall temperature, 1200 K. The axial coordinate is measured from the porous plate (that point where the gas first "sees" the reactor walls). For reference, the gas sampling probe was located at approximately 15 cm from the porous plate in the experiments reported in Section II.

Figure 9 shows the temperature history and Fig. 10 the history of the major gas phase species. The gas temperature rises initially due to radiant heating from the walls. Significant chemical reaction does not occur until almost 20 cm downstream where $T \approx 1070$ K. At this station the endothermic pyrolysis of the C_2H_6 to C_2H_4 and H_2 begins to take place at an appreciable rate, holding the temperature approximately constant until the H_2 begins to burn. At this point (≈ 32 cm) a series of very rapid reactions take place to varying extent which can be described by the global reactions

These reactions account for the rapid rise in temperature at this location. The velocity is determined by conservation of mass and the perfect gas law where the pressure is constant. Therefore, the velocity is directly proportional to the temperature. The distance to the "ignition" point is shortened by increasing preheat wall temperature and lengthened by addition of nitrogen or increased flow velocity. Changing the composition of the fuel to various

$P = 1 \text{ atm}$

$O_2/C = 0.4$

$H_2O/C = 2.8$

Fig. 9 - Temperature Profile for C_2H_6

CONCENTRATION, MOLES/MOLE FUEL CARBON

$P = 1 \text{ atm}$

$O_2/C = 0.4$

$H_2O/C = 2.8$

Fig.10 - Species Profiles for C_2H_6

combinations of C_2H_2 , C_2H_4 and C_2H_6 does not change the behavior in a simple way since although the lower H/C ratio fuels tend to be more reactive, they are also not as good absorbers of the wall radiation. However, the predicted products of the reaction remain qualitatively the same.

We have performed several computations using this model for comparison with the data presented in Section II with limited success in predicting the results. A typical result is shown in Fig. 11-12. The result should be compared with the high preheat case discussed in Section II (Fig. 5). The computer result gives a reasonable account of the temperature which was measured in the case for no O_2 feed as seen by comparison of Fig. 11 and Fig. 5. However, the computation was for the condition with $O_2/C = 0.25$. A comparison of Fig. 12 and Fig. 6 further shows the discrepancy between the computations and the data. This discrepancy was unaltered by variations in the kinetic model as discussed in Section III or by increasing initial radical concentrations to reasonable levels. This discrepancy is not surprising in view of the status of the rate information and as stated in Section II, may be strongly influenced by the nickel in the porous plate. However, testing at Engelhard using an empty reactor with C_2H_6 and steam indicates that C_2H_6 begins to measurably thermally decompose at 650 C. Thus it would appear that the model may have shortcomings even in the absence of O_2 . Recent work by White and Gardiner¹⁵ and by Westbrook and Dryer¹⁶ indicate that even for laboratory experiments with temperature and compositions comparable with conventional flames, the models for C_1 hydrocarbon chemistry do poorly. Recent reviews²²⁻²⁴ of data on the pyrolysis of C_2H_6 would not predict significant C_2H_6 pyrolysis, however these reviews do not include the effects of H_2O . This reactor modeling will continue as additional data become available.

B. Sooting Data Analysis

PSI has performed some simple computations for assistance in understanding the data of UTC and JPL on sooting observations. JPL has determined sooting boundaries for various fuels in a laboratory scale autothermal reformer. For a given fuel type and preheat, the O_2/C and H_2O/C ratios were varied so as to map the carbon boundary. This was done with various catalysts. This carbon boundary can be computed based upon equilibrium thermodynamics, assuming no heat losses (adiabatic). Such a computation is shown by the

Fig. 11 Computed temperature profile for Reactor Conditions

Fig. 12 Computed major species profiles for reactor conditions.

dashed lines in Figs. 13-15 for n-tetradecane ($C_{14}H_{30}$), n-hexane ($C_{10}H_{14}$) and n-nonylbenzene ($C_{15}H_{24}$). $C_{15}H_{24}$ is also called 1-phenylnonane and is used as a model compound for fuel oil. The dashed lines were computed for 900 and 840 K preheat and show little effect due to this variation (see Fig. 15). This computation assumes full chemical equilibrium, however, the desired product of the reformer has minimal hydrocarbons. Thus we have also performed computations assuming that no hydrocarbons are present in the product. These computations are shown as the solid lines in Figs. 13-15. The JPL data for $C_{14}H_{30}$ and $C_{6}H_{14}$ are shown as the cross-hatched area and include values for preheats from 810 to 900 K and various catalyst conditions. Most of the data lie between the dashed and solid curves. This bounding is a very reasonable result and indicates good reformer performance. At the higher O_2/C ratio where the data extend outside of these "bounds", the adiabatic temperature reaches 1200 K or more and heat losses could play a significant role (give results corresponding to a lower preheat temperature). It is likely that other processes are also involved. It is, however, important to recognize that in utilizing a catalyst that is designed to form H_2 and CO from hydrocarbons and steam that the thermodynamic sooting boundary appropriate for the "goal" condition should be computed without these hydrocarbons as products. The computation for $C_{15}H_{24}$ shown in Fig. 15 represents this difference for "fuel oil". The difference is somewhat less than for the simpler hydrocarbons but is clearly important at O_2/C ratios of interest.

A further computation has been performed for comparison of data taken at UTC. In these experiments, the H_2O/C ratio is held constant at 4 and the fuel is number 2 fuel oil. The O_2/C ratio and preheat temperature are varied to map the adiabatic carbon boundary. If equilibrium chemical compositions are allowed, the computations yield very low preheats required to prevent soot. When hydrocarbon products are not allowed, the resultant preheats are shown in Fig. 16. The adiabatic temperature is also shown and is seen to vary only slightly about 800 K (1000 F). The UTC goal line is shown as the dashed line, i.e., the maximum preheat for a given O_2/C . This line is seen to be several hundred degrees higher in

$C_{14}H_{30}$ (n-tetradecane) $P = 3$ atm

Fig. 13 Sooting boundaries for $C_{14}H_{30}$

Fig. 14 Sooting boundaries for C_6H_{14}

Fig. 15 Sooting boundaries for $C_{15}H_{24}$

Fig. 16 Sooting boundaries for $C_{15}H_{24}$ at constant H_2O/C

preheat for a given O_2 and would correspond to a similarly higher final (adiabatic) temperature. Current best performance obtained by UTC tends to be around the dashed line. It should be expected that this would occur because it is necessary to raise the operating temperature of the catalyst to 1000 K or so to provide sulfur tolerance. This indicates that a substantial reduction of the feed steam (bypassing of steam) to raise the operating temperature would be beneficial.

The difference between the simple fuel and the fuel oil data is likely due to the presence of sulfur in the fuel. Data taken at UTC²⁵ have indicated that the presence of sulfur greatly effects the sooting boundary. This is certainly true in gas phase flames, although the form of the sulfur appears to be important there.²⁶ In addition, sulfur has a profound effect upon flame chemistry.²⁷ Thus the inclusion of sulfur in any test program would appear to be advisable.

C. Partial Oxidation Data Analysis

Engelhard Industries has performed testing on catalytic partial oxidation of ethane and number 2 fuel oil under the subcontract from PSI for this contract and under their catalyst screening contract for DOE. The partial oxidation catalysts is a monolith about 0.25 inches in diameter and 6 inches long. The channels are square and there are 400 channels per square inch. Accounting for the Pt/Pd coating and the web, each channel is about 0.035 inches square with an area per channel of about 0.0079 cm².

A simplified flow diagram is shown in Fig. 17. A sampling probe is inserted to a point just below the catalyst section. The gases remain hot for a time of about 19 ms (this time has been varied for two tests) in the probe before they are quenched to room temperature. The gases are then analyzed, after drying, using a Carle refinery gas analyzer. This analyzer cannot detect acetylene which could be a reaction product.

The inlet conditions are nominally 710 K and the exit of the catalyst is controlled at 1073 K using a heater surrounding that section of the reactor. Typical total gas flow rates are 0.180 standard liters per second. Typical residence time in the catalyst channel is 3 milliseconds and pressure is atmospheric. The air and steam feed rates are held approximately constant and the fuel feed rate is varied. Thus, the H_2O/C ratio is 6.5 ± 0.2 times the O_2/C ratio for all runs discussed below.

Ethane Partial Oxidation Data

The data collected for the four runs with ethane as the fuel are given in Table 5. All values in the table are given in moles per mole of carbon in the fuel feed. Equivalent hydrogen (EH) is $\text{CO} + \text{H}_2$ in these same units. ΔW is the increase in H_2O from the inlet to the outlet and is obtained by oxygen balance

$$\Delta W = 2 \text{ O}_2/\text{inlet} - \text{CO} - 2 \text{ CO}_2$$

ΔEW is the change in "equivalent water" ($\text{CO}_2 + \text{H}_2\text{O}$) and is found from

$$\Delta \text{EW} = \Delta W + \text{CO}_2$$

Strong correlations are found for the last three quantities with feed ratios. The equivalent hydrogen (EH) is plotted vs O_2/C ratio in Fig. 18. The experimental values fall very close to the dashed line which is what could be expected for partial oxidation of an ideal fuel, i.e.,

Of course, this ideal breaks down as O_2/C approaches 0.5 since CO_2 and H_2O will become products in the absence of O_2 carryover, an unlikely possibility. This correlation shows that the catalytic partial oxidation of C_2H_6 is essentially ideal and shows no kinetic limitations.

The hydrocarbon distribution is shown in Fig. 19. The CH_4 data points are labeled by the order in which the data was taken. The apparatus was operated for five hours at each O_2/C ratio and between the second and third hour of run 3 ($\text{O}_2/\text{C} = 0.386$) there was a large increase in CH_4 as indicated by the vertical line. Run 4 ($\text{O}_2/\text{C} = 0.262$) gave a similarly high value of CH_4 compared to run 1 ($\text{O}_2/\text{C} = 0.252$). The C_2H_4 result for run 4 is substantially higher than run 1. There is no obvious explanation

Fig. 17 Engelhard experimental test unit.

TABLE 5
Ethane Partial Oxidation Results

Run	1	2	3	4
O ₂ /C	.252	.322	.386	.262
H ₂ /C	1.63	2.03	2.44	1.66
H ₂	.916	1.175	1.343	.818
CO	.392	.497	.562	.373
CO ₂	.143	.188	.231	.126
N ₂	.948	1.208	1.451	.985
CH ₄	.0034	.0058	.0205	.0085
C ₂ H ₆	.213	.136	.077	.211
C ₂ H ₄	.0185	.0172	.0175	.0360
EH	1.308	1.672	1.905	1.191
ΔW	-0.174	-0.229	-0.251	-0.101
ΔEW	-0.031	-0.041	-0.021	-0.025

Fig. 18 EH for ethane partial oxidation.

Fig. 19 Hydrocarbon distribution from C_2H_6 partial oxidation.

for this result. For the first three runs, the C_2H_4 is markedly independent of O_2/C ratio. The CH_4 increases with O_2/C ratio, however, this may be more a function of the H_2O concentration which is directly proportional to the O_2 concentration.

The change in H_2O concentration and equivalent H_2O concentration are plotted in Fig. 20. The change in equivalent H_2O is seen to be small, negative and apparently independent of O_2/C ratio. This indicates some steam reforming is taking place, but the identity of the species being steam reformed is unclear. This small change in equivalent water may indicate some bias in the data reduction procedure.

The change in water concentration is substantial and is due to shift reaction. The dashed line through the data indicates a shift reaction proportional to the O_2/C ratio. The H_2O/C ratio is directly proportional to the O_2/C ratio for the experiments performed so that the shift reaction

should be proportional to H_2O . The CO concentration, by hypothesis, should be proportional to the O_2/C ratio also; however, saturated adsorption on the surface by CO would account for the apparent first order reaction. Computation of the shift reaction ratio, $CO \cdot H_2O / CO_2 \cdot H_2$, yields a value of 5 ± 1 with the lower numbers corresponding to the higher O_2/C ratio. This corresponds to a shift temperature of around 2000 K and is clearly far from equilibrium and indicates kinetic limitation. The ratio H_2/CO is approximately 2.3 for all runs as opposed to 1.5 for only partial oxidation. Shift reaction increases the H_2/CO ratio as does cracking of C_2H_6 to C_2H_4 . Further variation of experimental parameters (H_2O/O_2 , space velocity) are necessary before mechanistic understanding can be established.

Fig. 20 Change in water concentration from partial oxidation of C_2H_6 .

We have performed a number of quasi-equilibrium calculations using constraints based upon the above correlations and have obtained success in comparing with the data. However, at this time, this process is equivalent to data correlation because too little has been learned about the mechanisms.

Fuel Oil Partial Oxidation Results

The compositions of gases from partial oxidation of number 2 fuel oil are markedly different from those obtained with ethane. Two catalytic partial oxidation (CPO) catalysts were used where the Pd/Pt ratio was varied (CPO-2 and CPO-3). The test results are given in Table 6. Again, all units are moles per mole of fuel carbon. The column labeled "C/C" is hydrocarbon conversion to species lighter than C_4 's.

The results for the major values of interest are displayed in Fig. 21. In this figure we have plotted the equivalent hydrogen, EH; carbon conversion, C/C; change in water, ΔW ; and change in equivalent water, ΔEW , versus O_2/C ratio. The circles are data for catalyst CPO-2, the squares for catalyst CPO-3 and the triangles for catalyst CPO-2 at 340 ms sampling probe residence time (other data with 19 ms residence time). This data shows a clear increase in equivalent hydrogen with increased O_2/C ratio; however, the level and the slope are both quite different than would be predicted from pure partial oxidation,

This would give a line of slope 3.8. The data show that $EH \approx 3.2 \left(\frac{O_2}{C} - 0.23 \right)$ for O_2/C greater than 0.23. The change in H_2O appears to be constant at $\Delta W \approx 0.16$ and the change in equivalent water, $\Delta EW \approx 0.7 O_2/C + 0.1$. These correlations indicate that fairly substantial complete oxidation of the hydrocarbon takes place. This could be a particular component of the fuel which preferentially oxidizes to CO_2 and H_2O and which does so at a fairly rapid rate compared to the partial oxidation. A possible explanation would be that 0.08 oxygen molecules form H_2O and of the additional oxygen, 70% of them form CO_2 and 30% of them form CO. However, the scatter in the data and

TABLE 6

Partial Oxidation of No. 2 Fuel Oil

CPO Catalyst	O ₂ /C	H ₂ O/C	H ₂	CO	CO ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₆	C/C	EH	ΔEW	ΔW
3	.287	1.86	.064	.131	.137	.048	.006	.108	.038	.776	.195	.306	.176
2	.292	1.92	.088	.150	.139	.055	.007	.119	.040	.834	.238	.295	.156
2	.297	1.92	.071	.121	.161	.056	.006	.118	.041	.872	.192	.312	.151
2	.324	2.18	.138	.228	.137	.073	.007	.116	.031	.845	.366	.283	.146
3	.326	2.16	.075	.167	.150	.049	.006	.111	.037	.818	.242	.287	.137
2	.330	2.18	.090	.156	.172	.049	.006	.110	.038	.830	.246	.332	.160
2	.332	2.18	.091	.172	.149	.055	.007	.118	.038	.870	.263	.342	.193
2*	.340	2.18	.100	.259	.121	.119	.008	.113	.016	.810	.359	.300	.179
3	.374	2.50	.120	.251	.156	.063	.006	.112	.031	.871	.371	.341	.185
3	.379	2.50	.090	.208	.169	.048	.006	.108	.035	.855	.469	.381	.212
2	.380	2.52	.117	.230	.165	.054	.006	.113	.035	.886	.497	.365	.200
2	.386	2.51	.183	.293	.155	.054	.006	.107	.032	.907	.569	.324	.169
2	.387	2.53	.099	.192	.195	.049	.006	.111	.036	.880	.486	.387	.192
2*	.4	2.56	.162	.258	.201	.104	.007	.119	.021	.90	.562	.341	.140

* Sample time = 340 ms, all others 19 ms.

Fig. 21 Major products of partial oxidation of number two fuel oil.

the proportionality of the O_2 and H_2O flows makes even global mechanistic interpretation very speculative.

The light hydrocarbon composition is displayed in Fig. 22 for these same runs. The notation for the symbols is the same. For the runs with probe residence time of 19 ms, the light hydrocarbon composition is essentially independent of O_2/C ratio (within 20%). The clear indication is that the probe residence time had a strong effect on the CH_4 and C_3H_6 measurements. The invariance of these hydrocarbons with O_2/C is quite in contrast to the C_2H_6 oxidation data except for the C_2H_4 . Interestingly, the C_2H_4 is higher with the fuel oil than with the C_2H_6 indicating that either the C_2H_4 is formed after the O_2 has been consumed or that C_2H_4 is much less reactive than the O_2 consumers. The constancy of all the values indicates that they are formed by a pyrolysis process and that other components of the fuel react with the O_2 without forming any significant amounts of these species. However, this is only an indication. Further investigation is clearly warranted.

Fig. 22 Hydrocarbons from partial oxidation of number two fuel oil.

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APPENDIX

ABSTRACTS OF REFERENCES ON STEAM REFORMING OF OLEFINS

123674s Catalysts for propene steam reforming. Nicklin, Thomas; Odgen, David; Whittaker, Robert J. (Gas Council) Ger. Offen. 1,945,042 (Cl. B 01j), 09 Apr 1970, Brit. Appl. 06 Sep 1963; 8 pp. Catalysts for propene steam reforming contg. oxides of Ni, U, Th, and K were prepd. (a) by calcination of a melt contg. NiNO_3 , $\text{Th}(\text{NO}_3)_3$, and $\text{UO}_2(\text{NO}_3)_2$ and subsequent addn. of KNO_3 , or (b) by calcination of a melt contg. the 4 nitrates. Thus, a melt of NiNO_3 240, $\text{UO}_2(\text{NO}_3)_2$ 100, and $\text{Th}(\text{NO}_3)_3$ 120 parts was prepd. After immersion of $\alpha\text{-Al}_2\text{O}_3$ spheres (diam. 3.2-4.3 mm) at 300° for 20 min, the melt was heated at 500° for 4 h. The immersion and calcination was repeated, the product was soaked in 5% KOH for 10 min, and dried at 120° . The reaction of CH_3CHMe with steam (6.7 moles H_2O /carbon atom) on the catalyst at $750^\circ/15$ psia gave a gas mixt. which, after H_2O removal, contained CH_4 0.7, CO 5.7, CO_2 25.3, and H_2 68.3%.

45559s Hydrogen from hydrocarbons and steam. McMahon, Joseph F.; Milliken, Thomas H. (Pullman Inc.) U.S. 3,476,536 (Cl. 48-214; B 01j, C 10j), 04 Nov 1969, Appl. 02 Feb 1965; 6 pp. A catalyst contg. 0.01-0.7 wt. % Ni on a zirconia carrier has a longer life than conventional catalysts at lower steam-to-C ratios in the steam reforming of highly olefinic hydrocarbons; thus, zirconia, contg. small amts. of CaO, SiO_2 , TiO_2 , and Fe oxide and having a surface area $<1 \text{ m}^2/\text{g}$ was impregnated with a 2% aq. soln. of Ni nitrate hexahydrate, dried at 240°F , and calcined for 2 hr at 1000°F to give a catalyst contg. 0.1% Ni expressed as elemental Ni. Feedstock contg. ethane 30 and ethylene 70 mole % was passed over this catalyst (12/20 mesh) at 1 atm and 1400°F with gradually decreasing amts. of steam. The steam was decreased until C started forming in the catalyst bed as noted by an increased ΔP across the bed. No carbon deposit formed at a steam-to-C ratios as low as 1.6 whereas a com. catalyst contg. 32.0% Ni oxide on a cement-type support had C deposition at a steam-to-C ratio of 7.0 with the same feed stock and reactor conditions. Similar runs showed 0.1 wt. % Ni on zirconia to be superior to 1.3 and 3.6% Ni on zirconia.

113980f Catalyst compositions for reforming hydrocarbons. Pullman, Inc. Brit. 1,361,882 (Cl. B 01j, C 10g), - 31 Jul 1974, US Appl. 120,971, 04 Mar 1971; 32 pp. Zirconia [1314-23-4]--supported cobalt oxide [11104-61-3]-nickel oxide [1313-99-1] steam reforming catalysts for ethane [74-84-0] and ethylene [74-85-1] were manufd. by impregnating ZrO_2 with aq. solns. of Co and Ni nitrates, drying 160-1440 min at 240°F , and calcining 2-16 hr at $1000\text{-}2000^\circ\text{F}$ or by dry mixing the oxides and calcining 5 hr at 3000°F . A mixt. of 31.7 wt. % C_2H_6 and 68.3 wt. % ethylene at 40, H_2O at 0.70, and H_2 at $50 \text{ cm}^3/\text{min}$ was passed over 100 cm^3 H-pretreated ZrO_2 catalyst initially contg. 3.52 wt. % NiO and 2.49 wt. % CoO to give, with 100% conversion, a mixt. of H_2 74.5, CO 6.3, and CO_2 19.2 mole %. Thirteen other catalyst samples were detailed.

153520t Reactions of n-butane, ethylene, and 1-butene with steam over a silica-supported nickel catalyst in the temperature range $370\text{-}450^\circ$. Morita, Yoshiro; Saito, Masahiro; Tokuno, Michiaki (Dep. Appl. Chem., Waseda Univ., Tokyo, Japan). Mem. Sch. Sci. Eng., Waseda Univ. 1970, No. 34, 125-36 (Eng). Steam reforming of 8.4:1 $\text{H}_2\text{O}\text{-C}_4\text{H}_{10}$ mixt. at 370° over a Ni/silica gel catalyst gave CH_4 , H_2 , and CO_2 in essentially theoretical distribution. The rate was independent of C_4H_{10} and proportional to H_2O partial pressure. Reaction of C_2H_4 or 1-butene at $370\text{-}450^\circ$ gave H_2 and CO_2 , but negligible yields of CO and CH_4 . Redn. and polymn. were not obsd., but some isomerization of C_4H_8 took place. Owing to deposition of C on the catalyst, product distribution deviated markedly from theoretical. The rate was independent of olefin partial pressure above 0.01 atm. The rate of C_2H_4 disappearance was approx. twice that of C_4H_{10} .

APPENDIX

DATA BASE AND CALCULATIONS FOR ESTIMATED FIRST ORDER RATE CONSTANTS FOR METHANE AND ETHYLENE

- TEST RUN NO. 7302 WITH G90C (30 cc)

H₂O 2.63

O₂/C 0.42

DRY EXIT GAS:

FLOW 679 SLPH

		<u>CONCENTRATION, MOLE %</u>			
OIL PREHEAT, °C	479	H ₂	30.72	CH ₄	1.60
AFTER CPO, °C	878	CO	13.58	C ₂ H ₆	.07
MIDBED, °C	850	CO ₂	10.34	C ₂ H ₄	.54
BOTTOM BED, °C	846	N ₂	43.11	C ₃ H ₆	.05

- ESTIMATED GAS COMPOSITION ENTERING STEAM REFORMING SECTION:

CONCENTRATION, MOLE %

CH₄ 2.80

C₂H₆ 0.30

C₂H₄ 5.00

- FIRST ORDER RATE CONSTANTS:

$$k_{CH_4} = -SV \ln (1-X), X = (2.80-1.60)/2.80 = .43$$

$$SV = 679,000/30 = 22,600 \text{ hrs}^{-1}$$

$$k_{CH_4} = 12,700 \text{ hrs}^{-1}$$

$$k_{C_2H_4} = 50,300 \text{ hrs}^{-1}$$

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