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HYDROCARBON AUTOTHERMAL REFORMING PROGRAM

Final Technical Report for September 28, 1979—October 31, 1981

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Physical Sciences Inc.
Woburn, Massachusetts

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FINAL TECHNICAL REPORT

for the period

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David O. Ham, Paul F. Lewis and G. W. Lord
Physical Sciences Inc.

and

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1. INTRODUCTION AND SUMMARY

The goal of the PSI program was to understand the mechanisms of the formation of carbon deposits under conditions relevant to autothermal reformers (ATR). This understanding was pursued by a combination of experimental and analytical efforts, including work at Engelhard Industries, a major subcontractor on this program.

The first year of this two year program was dedicated almost entirely to investigations of gas phase soot formation. It was speculated that soot could form in the gas phase and deposit downstream in the catalyst bed. A high temperature experimental test rig was constructed and computer models developed to aid in understanding this process. Several experimental and many computer runs were performed. These studies are summarized in the body of this report and detailed in Appendix A and the annual report for the first year of the program. The conclusion of these studies is that soot does not form in the gas phase upstream of the catalyst bed, under ATR conditions, at least, not under well mixed conditions.

In the second year, the program was redirected to study carbon formation processes on surfaces and to perform testing and analysis of Engelhard's six inch ATR rig. This work is detailed in this report and the Engelhard final report to PSI. This work has resulted in an operational computer code for use in modeling the Engelhard ATR. This code requires rate constant information for performance prediction. The PSI laboratory experiments have shown that coke formation on surfaces of nickel catalysts is very rapid, particularly from olefins. Filamentary carbon was formed. Various relevant processes and their relative rates were studied on various nickel surfaces. Coke was not observed when precious metal catalysts were used.

Testing on the Engelhard reactor was performed. These preliminary tests show that the Engelhard catalysts can be used to reform number two fuel oil with no problems associated with carbonaceous deposits. Some hydrocarbon breakthrough was observed, increasing at low oxygen to carbon ratio (0.355). These limited data clearly indicate a high potential for a useful ATR. Further testing and analysis are clearly necessary.

2. SUMMARY OF GAS PHASE REACTION STUDIES

Further details of this work are found in Appendix A and the annual report.

2.1 Modeling

A computer model was developed to describe the gas phase reactions of simple fuels (C_2 hydrocarbons) under ATR conditions. Typical ATR conditions are oxygen (in air) to fuel carbon ratio (molar) of 0.36, steam to fuel carbon ratio of 4 and preheat of 1000 K. This model assumes plug flow and contains: conservation equation for mass momentum and energy, and thermochemistry and detailed finite rate chemical reactions of the relevant species. The results of the computations indicate no significant gas phase reaction upstream of the catalyst bed, under conditions relevant to ATR's.

The conservation equations are developed for one dimensional (plug flow) with varying area. A model was also developed for computation with quasi-one-dimensional mixing but was not implemented. The energy equation of the plug flow model utilizes thermochemical data to obtain specific heat of the mixture and chemical heat release due to various reactions. The dominant source of gas heating in this region is radiative heat transfer. For computation of this source term, a band model for the absorption of infrared radiation by the various molecules was used.

The finite rate chemical kinetics model used in the code consists of about one hundred reactions and their reverses. Most of the rates were taken from the literature. Because some of the chemical pathways were not complete with only literature cited reactions, other reactions were posed and rates estimated by standard methods to investigate the effects of these reactions.

Computations were performed using this model to predict the performance of the PSI high temperature flow tube and the Englehard reactor. For ATR conditions, no significant reaction was predicted to occur during flow times of interest. This is in keeping with the experimental results.

Models were also developed to compute carbon formation boundaries as a function of operating conditions assuming various perturbations of chemical equilibrium. These models are useful in data analysis. At the beginning of the program we had hoped to develop such a model (quasi-equilibrium) from constraints imposed by chemical kinetics to the point where it could be used for scaling, design and systems analysis. However, we have not learned enough about the controlling mechanisms for the UTC system to do so for that system. The Engelhard system is only in its infancy of operation and although it appears to be superior to the UTC system in operation, more study is needed before it can be adequately modeled.

2.2 Experiment

The experimental tasks were 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. In carrying out the experimental tasks, a high temperature flow reactor facility was constructed and 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 were 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 0.05, 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/O 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 was made at reduced pressure (20-100 torr) with various levels of H₂O, N₂, and O₂ 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 C₂ and CH spectra were observed with their ratio being a function of the H₂O flow rate.

3. CATALYTIC PARTIAL OXIDATION DATA ANALYSIS

A number of runs were made at PSI and Engelhard to evaluate the performance of the monolithic CPO catalyst used in the Engelhard reactor. The resultant data are discussed in this section.

The results are discussed in terms of outlet composition as a function of operating parameters. All compositions are in moles per mole of fuel carbon. Supplemental composition variables are defined as:

Equivalent hydrogen,

$$EH = CO + H_2;$$

Change in water,

$$\Delta W = 2 O_2/\text{inlet} - CO - 2 CO_2;$$

Change in equivalent water,

$$\Delta EW = \Delta W + CO_2;$$

Carbon balance, the sum of all carbon in molecules less than or equal to C_4

Engelhard performed catalytic partial oxidation of ethane and number 2 fuel oil in its catalyst screening reactor. The details of these tests are given in previous reports. The pressure was atmospheric, the preheat temperature 710 K, the furnace temperature 1070 K, and the residence time in the catalyst section about 3 milliseconds. In these tests the steam and oxygen flow rates were held approximately constant and at a ratio 6.5 and the fuel flow rate varied. The results of these tests are shown in Tables 3.1 and 3.2.

Although at first glance it would appear that the O_2 reactions might dominate the operation of the CPO section, other features may be more important. Indeed, as we will show below, although not conclusively, the effects

TABLE 3.1

Ethane Catalytic Partial Oxidation Results

Run	1	2	3	4
O ₂ in	.252	.322	.386	.262
H ₂ O in	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

Inlet = 710 K

TABLE 3.2

Catalytic Partial Oxidation of No. 2 Fuel Oil (Screening Unit)

CPO Catalyst	O ₂ in	H ₂ O in	H ₂	CO	CO ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₆	Carbon Balance	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	.298	.381	.212
2	.380	2.52	.117	.230	.165	.054	.006	.113	.035	.886	.347	.365	.200
2	.386	2.51	.183	.293	.155	.054	.006	.107	.032	.907	.476	.324	.169
2	.387	2.53	.099	.192	.195	.049	.006	.111	.036	.880	.291	.387	.192
2*	.4	2.56	.162	.258	.201	.104	.007	.119	.021	.90	.420	.341	.140

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

Inlet = 710 K

of importance in these runs were the increased operating temperature due to the increased oxygen and probably the increased stream concentration which accompanied the oxygen.

PSI performed testing of the CPO section in its laboratory reactor. These tests are described in detail elsewhere in this report. The results are summarized in Table 3.3. In these tests the pressure was atmospheric, the preheat temperature 923 K and the furnace temperature 923 K. These tests were conducted with oxygen instead of air. These data indicate that the catalyst is performing very close to ideally by a reaction which could be written as

This reaction would then be followed by some degree of methanation,

From these results we learn that higher preheat temperature and probably higher H_2O cause an extremely large improvement in CPO performance. Note that with no oxygen, the CPO catalyst acts as a steam reformer.

Engelhard performed several tests using propane on its six inch reactor. This reactor facility is described in detail elsewhere. These tests were run at atmospheric pressure and a preheat temperature of 963 K. The reactor was not heated externally and had heat losses. The results of these runs are given in Table 3.4. We note that the performance for the higher oxygen level was very nearly the same as the PSI runs for ethane and ethylene. We do not understand the reduction in performance at the lower oxygen level. This reduction is consistent with the early data at Engelhard on the smaller reactor and indicates limitations at reduced H_2O levels.

More recently, Engelhard has performed testing which includes catalytic partial oxidation of number 2 fuel oil in their six inch reactor.

TABLE 3.3

Catalytic Partial Oxidation of C_2H_4 and C_2H_6

Fuel	O ₂ in	H ₂ O in	H ₂	CO	CO ₂	CH ₄	Other CH	EH	ΔW	ΔEW
C ₂ H ₆	.17	4.2	2.20	.349	.619	.033	0	2.55	-1.25	-0.63
"	.26	4.2	2.17	.234	.666	.028	0	2.41	-1.05	-0.38
"	.41	4.1	2.05	.317	.661	.022	0	2.37	-0.82	-0.16
C ₂ H ₄	0	4.3	2.16	.441	.508	.050	0	2.60	-1.46	-0.95
"	.17	4.2	1.92	.323	.666	.011	0	2.25	-1.32	-0.65
"	.19	4.1	1.87	.344	.680	.023	0	2.21	-1.32	-0.65
"	.28	4.4	1.80	.339	.640	.017	0	2.14	-1.06	-0.42
"	.34	4.7	1.66	.361	.612	.027	0	2.02	-0.91	-0.29
"	.40	4.2	1.63	.369	.615	.016	0	2.00	-0.80	-0.18
"	.40	4.2	1.70	.345	.644	.011	0	2.05	-0.83	-0.19

Inlet = 923 K

TABLE 3.4

Catalytic Partial Oxidation of Propane

O ₂ in	H ₂ O in	H ₂	CO	CO ₂	CH ₄	C ₃ H ₈	Other	EH	ΔW	ΔEW
.35	2.8	1.43	.534	.245	.021	.062	.001	1.96	-0.32	-0.08
.386	2.6	2.11	.481	.495	.019	.005	0	2.59	-0.69	-0.20

Inlet = 963 K

The compositions at the CPO outlet are given in Table 3.5. Pressure was normally atmospheric and preheat 963 K. There is considerable scatter in this data. We have not determined the reason for this scatter.

From this limited data we have been able to make only limited observations: Carbon balance improves with increased oxygen, equivalent hydrogen increases with increased oxygen, the compositions are not given by equilibrium considerations. Further work is clearly needed before the performance of the CPO is understood.

TABLE 3.5

Catalytic Partial Oxidation of No. 2 Fuel Oil

Run	O ₂ in	H ₂ O in	H ₂	CO	CO ₂	CH ₄	$\frac{4}{2}\text{Cn}$	Carbon Balance	EH	ΔW	ΔEW
26	.355	2.84	.25	.34	.11	.049	.26	.75	.58	+0.26	+0.37
28	.37	2.91	.30	.41	.10	.049	.22	.78	.71	-.17	+.13
30	.38	2.57	.62	.61	.09	.036	.11	.85	1.23	-.04	+.05
19	.384	2.73	.63	.57	.12	.043	.11	.80	1.2	-0.04	+0.08
17	.413	2.56	.97	.73	.14	.025	.025	.92	1.7	-0.18	-0.04
25	.39	2.75	.31	.42	.11	.052	.22	.80	.734	+0.14	+0.25
24	.42	3.10	.51	.55	.10	.049	.12	.83	1.06	+0.08	+0.18
31*	.37	2.54	.48	.50	.10	.065	.13	.79	.98	+.04	+.14
32**	.374	2.56	.41	.50	.09	.048	.16	.80	.91	+.07	+.16

Inlet = 963. K

* 3 Atmosphere Pressure

** 1022 K Preheat

4. REFORMER MODELING

In this section we describe the model of the Engelhard reactor. The goal of the model is to describe the performance of the Engelhard reactor as a function of operating parameters. The reactor consists of a mixing section followed by a monolithic partial oxidation catalyst followed by a steam reformer catalyst. The inputs to the model are preheat temperature, mass flow rate, oxygen and steam to fuel carbon ratios, a description of performance of the catalytic partial oxidation section of the reactor, and kinetic rates of reactions in the steam reformer section. The flow is treated as adiabatic plug flow.

4.1 Catalytic Partial Oxidation (CPO) Section

The composition at the exit of the CPO section is determined by a correlation of Engelhard data versus oxygen to fuel carbon ratio (O_2/C). The exit temperature is found from conservation of enthalpy with the enthalpy of the fuel taken as that of n-nonylbenzene ($C_{15}H_{24}$). Species larger than C_3 hydrocarbons are taken to be distributed between CH_4 and C_6H_6 in such a way as to balance hydrogen and carbon.

We have developed correlations for species up through C_3 hydrocarbons. The sum of the carbon and hydrogen obtained from these species is given by

$$\Sigma C = 0.308 + 1.24 (O_2/C)$$

$$\Sigma H = 1.289 + 0.68 (O_2/C)$$

exclusive of the hydrogen in the feed H_2O . In order to conserve atoms we have chosen to place the unconverted hydrogen and carbon in the form of benzene and excess methane. This choice is easily modified in the future. The concentration of these species are then found from

$$\frac{\Delta CH_4}{C} + \frac{6C_6H_6}{C} = 1 - \Sigma C$$

$$\frac{4\Delta CH_4}{C} + \frac{6C_6H_6}{C} = y - \Sigma H$$

where y is the hydrogen to carbon ratio of the fuel. The composition of the products of partial oxidation used are shown in Table 4.1.

The temperature resulting from catalytic partial oxidation is found from conservation of enthalpy. At the inlet temperature the total enthalpy is given as

$$H = \frac{1}{15} h(C_{15}H_{24}) + \alpha h(O_2) + 3.76 \alpha h(N_2) + \beta h(H_2O),$$

where h is evaluated at the inlet temperature. The outlet partial oxidation outlet temperature, T is then found from

$$\sum_i h_i(T_o) \chi_i = H$$

where χ_i is the outlet composition as defined above.

In the experiments for which the correlation was performed, the O_2/C and H_2O/C ratios were varied simultaneously in such a way as to hold O_2/H_2O constant (only fuel flow was varied). Thus, it was not possible to determine the proper correlation parameter. In experiments at PSI using an identical CPO catalyst (see Section 2) the products of the CPO were found to be almost independent of O_2/C at high H_2O/C ratio with C_2H_4 and C_2H_6 as the fuel. The results show that the CPO catalyst is an excellent steam reformer catalyst for C_2H_4 and C_2H_6 . Preliminary results on the Engelhard reactor appear to confirm that the CPO is performing more than partial oxidation. Thus it will be necessary to modify the correlation of Table 4.1 in future work. This would be based upon data from PSI and Engelhard. Table 4.1 was, however, used in the model results described below.

4.2 Flow in Steam Reformer Bed

In this section we describe the equation for gas velocity and temperature in the steam reformer bed. We have not included thermal conduction in

TABLE 4.1

COMPOSITION RESULTING FROM CATALYTIC PARTIAL OXIDATION

$$\alpha = \text{O}_2/\text{C}, \beta = \text{H}_2\text{O}/\text{C}$$

Composition in moles/mole of fuel carbon

$$\text{H}_2\text{O} = \beta + 0.07 + 0.3\alpha$$

$$\text{N}_2 = 3.76\alpha$$

$$\text{CO}_2 = 0.02 + 0.4\alpha$$

$$\text{CO} = -0.11 + 0.9\alpha$$

$$\text{H}_2 = 0.13 + 0.1\alpha$$

$$\text{CH}_4 = -0.013 + 0.2\alpha$$

$$\text{C}_2\text{H}_4 = 0.115$$

$$\text{C}_2\text{H}_6 = 0.0066$$

$$\text{C}_3\text{H}_6 = 0.034 - 0.02\alpha$$

$$\text{C}_6\text{H}_6 = 0.126 - 0.24\alpha$$

the bed and have assumed steady state operation. The effective flow area of the bed is obtained from the reactor internal area which can be a function of position and the void fraction of the catalyst bed

$$A_{\text{flow}} = A\phi$$

where ϕ is the bed void fraction. The mass density of the bed is obtained from the catalyst pellet density,

$$\rho_{\text{bed}} = \rho_{\text{pellet}}(1 - \phi).$$

The initial flow velocity is obtained from the total mass flow

$$\dot{m} = \rho u A_{\text{flow}}$$

where the gas density, ρ , is obtained from the catalytic partial oxidation results

$$\rho = \frac{P}{TZ\bar{R}}$$

where $\bar{R} = 82/\sum \text{mw}_i \chi_i$, $Z = \sum \chi_i$, pressure is in atmospheres, temperature is in kelvins, ρ is in grams per cubic centimeter, and mw is the molecular weight of species i (grams).

The differential equations are written with t , the time experienced by a gas molecule flowing through the bed as the independent variable. The temperature derivative is then

$$\frac{dT}{dt} = - \frac{h_i \dot{\chi}_i}{\sum C_{p_i} \chi_i}$$

where $C_{p_i} = \frac{\partial h_i}{\partial T}$ and $\dot{\chi}_i$ is the rate of change of concentration of species i due to chemical reactions. The differential equation for the gas velocity is found from conservation of mass,

$$\frac{1}{u} \frac{du}{dt} = \frac{1}{T} \frac{dT}{dt} + \frac{\dot{Z}}{Z}$$

where $\dot{Z} = \sum \dot{\chi}_i$. The term $\bar{R}$ is invariant as $\sum m w_i \chi_i$ is the mass of gas per fuel carbon which is constant. The distance through the bed is found from

$$\frac{dS}{dt} = u.$$

4.3 Catalyst Bed Section

Reactions in the catalyst bed are modeled using a combination of mass diffusion to the pellet, diffusion into the pellet pores, and surface reaction. Standard descriptions have been used for these models.

4.3.1. Surface Reactions

The steam reformer bed reactions are assumed to be of the form

where the forward rate is given by

$$-\frac{dA}{dt} = k_j p_A^{\eta_{Aj}} p_B^{\eta_{Bj}}, \quad \frac{\text{moles}}{\text{gram catalyst} \cdot \text{second}}$$

k_j is specified and is the form

$$k_j = f_{1j} T^{f_{2j}} e^{-E_j/T}$$

and η_{Aj} and η_{Bj} are specified for each reaction. The reverse rate is obtained from the forward rate and the equilibrium constant. In our units, moles per mole of fuel carbon per second, the forward flux through the reaction is

$$\text{Rate } j = k_j \chi_A^{\eta_{Aj}} \chi_B^{\eta_{Bj}} \left(\frac{p}{Z} \right)^{\eta_A + \eta_B} \frac{82TZ}{P} \rho_{\text{bed}}.$$

The reactions are then summed over to give the total $\dot{\chi}$.

This rate constant k can be related to a surface reaction rate by

$$k = k_s \sigma_T \frac{p}{82T}$$

where σ_T is the total surface area per gram of pellet (cm^2/g), p is the pressure (atmospheres), and k_s is the reaction velocity (cm/s). The value of a rate constant measured in a catalyst bed under conditions of no diffusion limitations is normally quoted based upon residence time in an empty reactor. So that $k = k_{\text{exp}}/\phi$ for these conditions, where ϕ is the void fraction in the bed. This corrects for the increase in gas velocity due to the presence of the pellets. Our model uses k since the bed void fraction could be somewhat different in the rate measurement apparatus from the actual reformer.

The rate constants used in the initial modeling tests described below are shown in Table II along with their sources.

The rate of reaction utilized in the model for surface limited reaction is then

$$\text{Rate} = k \chi_A^{\eta_A} \chi_B^{\eta_B} \left(\frac{p}{Z} \right)^{\eta_A + \eta_B} \frac{82TZ}{P} \rho_{\text{BED}}$$

where χ_A is moles of A per mole of fuel carbon, Z is total moles per mole of fuel carbon, ρ_B is the density of the bed (g/cm^3), and the rate is moles per mole of fuel carbon per second of average flow time (the empty reactor flow time times ϕ).

4.3.2. Porous Diffusion

Wheeler^{1,2} gives a detailed analysis of how to calculate the limitations of reaction due to diffusion limitations into the catalyst pellet pore. The expressions developed are valid for catalysts with a very narrow pore size distribution and with a nearly round shape. The results are expressed as an

effectiveness factor which is the factor by which the reaction rate should be multiplied to account for gradients of reactants from the catalyst pellet surface inward. We are concerned with reactions of first or second order and the effectiveness factor can be approximated as

$$EF = \frac{\tanh(h)}{h}$$

where

$$h = L_p \sqrt{\frac{\text{Rate}}{(1-\phi) \theta (1-\theta) \chi_A D_A}}$$

and χ_A is the concentration of the first order reactant or the smaller of two second order reactants. θ is the porosity of the catalyst pellet, L_p is the pore length and D_A is the effective diffusivity of molecule A into the average pore size.

The average pore size is given by

$$\bar{r} = \frac{\theta(1-\theta)}{\sigma_T \rho_p}$$

where ρ_p is the catalyst pellet density (g/cm³). The average pore length is $\sqrt{2}$ times the pellet volume over the external surface area which for cylindrical pellets of equal diameter, d_p , and length is

$$L_p = \sqrt{2} d_p / 6.$$

The pore diffusivity is found from a combination of the Knudsen diffusivity, D_{KA} , and bulk diffusivity, D_{BA}

$$D_A = D_{BA} (1 - \exp(-D_{KA}/D_{BA}))$$

$$D_{KA} = 9.7 \times 10^3 \bar{r} \sqrt{T/M_A}$$

$$D_{BA} = 5.2 \times 10^{-5} T^{1.75} / (p \sqrt{M_A})$$

where p is in atmospheres and M_A is the molecular weight of A.

We realize that the above porous diffusion model is approximate and may need to be improved at a future time. However, it should be adequate for most purposes.

4.3.3. External Boundary Layer Diffusion

The rate of mass transfer from the free stream to a packed bed of pellets is found from correlations of data. The mass diffusion velocity can be found by fitting curves of DeAcetis and Thodos (shown in Ref. 3);

$$k_c = \phi u (1.4/\sqrt{R_{ep}} + 2.4/R_{ep})$$

where $R_{ep} = \phi u d_p / D_{BA}$. The work of Rans (cited in Ref. 4) gives an equivalent of

$$k_c = \phi u (1.8/\sqrt{R_{ep}} + 2.0/R_{ep}) .$$

The correlation of Bradshaw and Benent (cited in Ref. 3) agree better with the latter, and the latter also approaches the value for isolated spheres at low velocity and $\phi = 1$.

There is a significant uncertainty in these correlations. The data displayed in Kunii and Levenspiel for fixed beds below $R_{ep} \approx 50$ show a drastic drop in Sherwood number. This would lead to Sherwood number proportional to R_{ep} below $R_{ep} \approx 50$ or

$$k_c = u\phi (0.3).$$

By contrast the isolated sphere gives at $u=0$

$$k_c = \frac{2D_{BA}}{d_p}$$

These results are easily rationalized.

For an isolated sphere the mass transfer rate is determined by diffusion through the external boundary layer on the particle. As the gas velocity slows the boundary layer gets thicker. In a bed of particles, the mass transfer is determined by diffusion through the boundary layer but the boundary layer now overlaps other particles and at low Reynolds number, the flow is all boundary layer. In the isolated sphere case, the mass can be transferred to the particle from a volume much larger than the particle volume. But in the packed bed the volume is limited and thus the rate of mass transfer can not be greater than the external flow

$$k_c < u$$

Kunii and Suzuki⁵ have developed an approximate model for the "apparent" mass transfer rate in packed beds and find

$$k_c = \frac{\phi u}{6(1-\phi)}$$

Since we are modeling the local mass transfer rate in the channels between particles we will use the correlation of Ranz, although it may be off by a factor of order ϕ at low Reynolds number.

4.3.4 Combined Rates

Combining the external mass transfer rate with the effectiveness factor and the surface reaction rate and balancing the flux at the external surface of the particle gives for a first order reaction or a reaction limited by diffusion of one reactant a net rate of

$$\text{Net Rate} = \text{Rate} \cdot \text{EF} \left\{ 1 + \left(\frac{\text{Rate} \cdot \text{EF} \cdot d_p}{6\chi_A (1-\theta)k_c} \right) \right\}^{-1}$$

4.3.5 Experimental Data Analysis

Data can be analyzed from this expression by appropriate manipulation of the above. We assume that the data is from an isothermal reactor where only a small fraction of A disappears. R_0 is the observed reaction rate, moles per gram of catalyst per second and is

$$R_o = \frac{\dot{M}_A}{M_B} f_c$$

where $\dot{M}_A$ is the molar flow rate of A through a bed of mass M_B and f_c is the fraction of A which disappears. Then,

$$R_{exp} = R_o \frac{82TZ}{p\phi} \rho_{BED} = \text{Net Rate}$$

We can find

$$\text{Rate} \cdot EF = \left(\frac{1}{R_{exp}} - \frac{d_p}{6\chi_A (1-\theta)k_c} \right)^{-1}$$

by using the appropriate value of k_c . Here we must be careful if the data is for a packed bed since the "apparent" rate discussed in Section 3.3.3 could be more appropriate. However in the latter case, f_c is likely to be close to unity and the data not appropriate for analysis.

Also since D_A and L_p can be calculated we can find

$$R_D = (1-\phi) (1-\theta) \theta D_A \chi_A / L_p^2$$

and

$$\frac{\text{Rate} \cdot EF}{R_D} = h \tanh(h)$$

Since

$$\frac{\text{Rate} \cdot EF}{\text{Rate}} = \frac{\tanh(h)}{h}$$

we can find Rate/R_D from a plot of $h \tanh(h)$ as a function of $\tanh(h)/h$. This procedure works if the surface reaction is not overwhelmed by diffusion effects. If there are large diffusion limitations, then k_c and R_D must be calculated very carefully to obtain Rate (or k_s).

4.3.6 Example of Diffusion Effects

In this section we give an example of how diffusion effects the reaction rate in a catalyst bed using the above results. As the example we have taken the reaction of the steam reforming of ethylene on G90C nickel catalyst (Reaction 2 in Table 4.2). The rate in moles of ethylene converted per mole of carbon in ethylene per second is computed in the diffusion free limit from

$$\text{Rate} = 4.855 \times 10^{16} \exp(-42627/T) \frac{82}{2} \rho_{\text{Bed}}$$

where the concentration of ethylene is 1/2 mole per mole of fuel carbon. In the units we have chosen, the rate is independent of the mole fraction of ethylene for a first order reaction, even in the diffusion limited regime. The total pressure is atmospheric and the catalyst bed properties are given in the inset of Fig. 4.1.

This figure shows the results of the computation of the rate versus temperature for three conditions. The upper curve is the rate when there are no diffusion limitations (e.g., very small pellets (L_p becomes very small and k_c very large)). The next lower curve shows the results using the properties of G90C (we have not included pore roughness), but ignoring diffusion to the pellet. The lowest curve includes the limitation due to diffusion to the pellet for an average gas velocity of 1 meter per second. (The superficial velocity would be 0.4 meter per second.) Higher velocities would show less external diffusion limitations. It is clear that diffusion into the catalyst pellet is a very severe limitation at temperatures above 1000 K. Diffusion to the pellet is a less serious consideration.

4.4 Sample Computation for the Engelhard Reactor

The above described reformer model has been exercised for a sample condition of Engelhard reactor. We have selected for an example, conditions of interest to fuel cell power plants; $O_2/C = 0.36$, $H_2O/C = 4$, $P = 1$ atm and 800 K preheat. The results are shown in Figs. 4.2 and 4.3. Temperature and

TABLE 4.2

REACTIONS IN REFORMER LED

R 1	$1 \text{ CH}_4 + 1 \text{ H}_2\text{O} = 1 \text{ CO} + 3 \text{ H}_2$	$\text{RC} = 1.800\text{E } 08 \text{ T}^{**}(0.00) \text{ EXP}(-34977./\text{T})$
R 2	$1 \text{ C}_2\text{H}_4 + 2 \text{ H}_2\text{O} = 2 \text{ CO} + 4 \text{ H}_2$	$\text{RC} = 4.855\text{E } 16 \text{ T}^{**}(-1.00) \text{ EXP}(-42627./\text{T})$
R 3	$1 \text{ H}_2\text{O} + 1 \text{ CO} = 1 \text{ CO}_2 + 1 \text{ H}_2$	$\text{RC} = 3.837\text{E } 13 \text{ T}^{**}(-2.00) \text{ EXP}(-27575./\text{T})$
R 4	$1 \text{ C}_3\text{H}_6 + 3 \text{ H}_2\text{O} = 3 \text{ CO} + 6 \text{ H}_2$	$\text{RC} = 2.000\text{E } 10 \text{ T}^{**}(0.00) \text{ EXP}(-35000./\text{T})$
R 5	$1 \text{ C}_6\text{H}_6 + 6 \text{ H}_2\text{O} = 6 \text{ CO} + 9 \text{ H}_2$	$\text{RC} = 2.000\text{E } 10 \text{ T}^{**}(0.00) \text{ EXP}(-35000./\text{T})$
R 6	$1 \text{ C}_2\text{H}_6 + \text{O} = 1 \text{ C}_2\text{H}_4 + 1 \text{ H}_2$	$\text{RC} = 1.000\text{E } 13 \text{ T}^{**}(0.00) \text{ EXP}(-44000./\text{T})$
R 7	$1 \text{ C}_2\text{H}_6 + 2 \text{ H}_2\text{O} = 2 \text{ CO} + 5 \text{ H}_2$	$\text{RC} = 4.760\text{E } 13 \text{ T}^{**}(0.00) \text{ EXP}(-44338./\text{T})$

$$\text{Rate} = k p_A^{\eta_A} p_B^{\eta_B} \text{ moles/g-catalyst-s } \eta_A = 1, \eta_B = 0 \text{ except for shift reaction}$$

$$k_1, k_7 - \text{Ref. 6}$$

$$k_2, k_3 - \text{Ref. 7}$$

$$\left. \begin{array}{l} k_4 = k_5 \approx 100 k_1 \\ k_6 \approx 0.2 k_7 \end{array} \right\} \text{estimated}$$

Fig. 4.1 Rate of steam reforming of C_2H_4 .

Fig. 4.2 Major species and temperature for reformer test case.

Fig. 4.3 Minor species for reformer test case.

the major species are given in Fig. 4.2 and the minor or hydrocarbon species are given in Fig. 4.3. H_2O is plotted minus three for convenience of scale. The initial composition shown is from the correlation of Table 4.1 (CPO output), the initial temperature from conservation of enthalpy. The temperature decay is from the endothermic process of reforming, primarily ethylene. The reforming rate slows because of this drop in temperature.

The above computation is not posed as a prediction of how the Engelhard reactor will perform as an example of how the computer model performs. We have shown that the CPO catalyst bed does not perform as the correlation of Table 4.1. Further, we are not confident that the rates of Table 4.2 are adequate to describe the reformer bed performance. We can use the model to analyze data from the Engelhard reactor and from the PSI reactor. The analysis of the PSI data should lead to better rates for the reformer bed reactions and a better understanding of the CPO performance. Engelhard work should lead to an improved correlation of CPO performance and data for comparison with this model.

5. EXPERIMENTAL DESCRIPTION

5.1 Experimental Approach

PSI experimental studies have continued to emphasize ethane and ethylene as fuels representative of generic paraffin and olefin components of heavy fuels, respectively. As reported previously, we have found that heterogeneous chemistry is dominant. Reactions have been studied on two surfaces; G90C, an alumina supported nickel catalyst identified as promising by Engelhard Industries, and smooth stainless steel balls.

The SS balls have a surface area about 10^{-3} times that of the Ni in G90C and a catalytic activity between 10^{-3} and 10^{-4} that of G90C. This very inactive "catalyst" allows us to identify the fastest reactions, because only the fastest will go at all. The solid balls have the added advantage that they remain at the controlled furnace temperature for all reaction conditions; calculations of thermal conductivities and reaction heat release indicate isothermal conditions within the 2-3 K accuracy of the controller. Using the SS balls we have shown that a variety of higher hydrocarbons, those larger than the C_2 fuels, is formed very rapidly; the dominant higher hydrocarbon (HHC) is benzene.

These HHC species have not been detected under any conditions with G90C as the catalyst, presumably they react further on a more active surface, possibly to produce carbon deposits.

5.2 Description of Apparatus

A small reactor was constructed and operated to accumulate data in regimes relevant to ATR operation. With this reactor, different sets of parameters can be investigated on a two-day experimental cycle. A diagram of this small reactor is shown in Fig. 5.1.

Fig. 5.1 Small high temperature reactor.

The high temperature section of this apparatus is constructed from one-quarter inch stainless steel tubing and Swagelok® fittings. A catalyst holder is made from one-half inch Swagelok® fittings in which the catalyst is held by a stainless steel screen. The main reaction zone is heated by a temperature-controlled tube furnace. Temperature-controlled heating tapes are used to preheat all gases to about 300°C prior to mixing and entering the reaction zone. Flows are measured using rotometer flow tubes calibrated with a wet test meter.

Thermal accommodation calculations showed that, over the range of temperatures and flows used, the gas was heated to within a few degrees Centigrade of the furnace control temperature before reaching the catalyst surface being tested. Thermal conductivity calculations showed that the materials under study remain at a constant temperature equal to the furnace temperature throughout the experiment. The experimental conditions are isothermal within about $\pm 3^\circ\text{C}$ for all catalysts except the CPO monolith which has a very low thermal conductivity.

The effluent gas composition was measured three to five times for each set of conditions and carbon formation was detected by visual examination of the surfaces after disassembly. The major gas species with the exceptions of H_2O (C_2 hydrocarbons, H_2 , CO , CO_2 and CH_4) were measured quantitatively with a Carle Model 111-H, 158-A gas chromatograph (GC). The output of the GC was recorded and integrated by a Shimadzu Model C-R1A Recording Data Processor. Standard calibration mixtures were used to calibrate the GC output for all gases used. Standard deviations were less than two percent for concentrations of five samples measured over a period of three hours while reactor conditions were held constant. Water was removed by a room temperature trap and calcium chloride drying tube prior to entering the GC. Calibration runs were made for every set of conditions with the furnace and preheaters off to obtain accurate measures of the unreacted gas with the same instruments.

Our Hewlett-Packard Model 5990A Gas Chromatograph/Mass Spectrometer (GC/MS) was used in its most sensitive mode for qualitative identification of

hydrocarbon species larger than C_2 . This instrument was used for all of the measurements of higher hydrocarbon formation reported in Sec. 6.3. The experimental configuration including the GC/MS is shown in Fig. 5.2.

5.3 Experimental Conditions

Initial conditions for the experiments performed on G90C are listed in Table 5.1 along with a qualitative evaluation of the coke formed. All experiments were run at compositions for which carbon deposition was expected since we are trying to determine the gas phase species that correlate with coke. The conditions for the first two runs and the 5/15 and 5/26 runs were nearly identical except for interchanging ethane and ethylene. Both pairs of runs show that carbon forms more readily from ethylene than from ethane. No HHC's were detected in the effluent of any of these G90C runs. Ethylene and ethane were interconverted to a negligible extent.

A much more extensive set of runs was made on SS balls since in these experiments it was possible to study the production of the HHC's; conditions for these experiments are displayed in Fig. 5.3. Carbon was deposited on the SS balls only from ethylene and then only for the most extreme (low H_2O/C) conditions. HHC's were detected throughout the range of inlet compositions but with concentrations ranging over a factor of a hundred; details of these variations are discussed in Section 6.3.

An especially interesting set of runs is indicated by the triangles connected by a bar in the lower right of Fig. 5.3. Over this region soot was formed; carbon was carried along with the gas flow indicating gas phase as opposed to surface formation. These runs at high O_2/C and low H_2O/C on SS balls were the only runs in which significant amounts of carbon were carried with the effluent. In experiments run in our 2 1/2" hot flow reactor at such high O_2/C , an unstable flame was visible through the windows; the flow in our small reactor was unsteady during these soot producing conditions. From these separate observations we conclude that gas phase formation of soot occurs in the

Fig. 5.2 Small flow tube system schematic.

TABLE 5.1

Conditions for G90C Experiments

All experiments were run at 1 atmosphere total pressure.

Run	T(°C)	Fuel	Total Flow (cm ³ /s)	H ₂ O/C	O ₂ /C	Carbon Deposit
1/28	680	C ₂ H ₄	---	0.60	0.08	clogged (1/2 hr)
2/3	685	C ₂ H ₆	---	0.64	0.105	clogged (1 3/4 hr)
2/9	695	C ₂ H ₄	---	1.06	0.11	only at top
5/15	665	C ₂ H ₄	10.4	3.0	0.24	lots
5/26	665	C ₂ H ₆	9.5	3.1	0.26	no
5/26	665	C ₂ H ₆	8.9	3.4	0.26	no

Fig. 5.3 Experimental runs for C_2H_4 on SS, $T_p = 660^\circ C$, $f_t = 9-10 \text{ cm}^3/\text{s}$.

flame composition region and that our previous conclusion is correct, that carbon forms on and adheres to catalyst surfaces in composition regions appropriate for ATR operation.

A less extensive set of experiments was run on the Engelhard partial oxidation catalyst (CPO) for $H_2O/C \cong 4$ over a range of O_2/C from 0 to 0.4. The inlet temperature for these runs was $660^\circ C$, as in the experiments on the other catalysts, but the temperatures inside the CPO monolith undoubtedly increase by about $200^\circ C$ due to the negligible thermal conductivity of the monolith support material. It is impossible to measure the temperature profile in the small channels of this monolith without blocking the flow and thereby changing the temperature. The best information on the temperature profile must come from a difficult calculation which requires a knowledge of the enthalpy changes due to the chemical reactions.

6. REACTIONS ON NICKEL CATALYSTS

6.1 Analysis of Coke Composition

The coke deposits from three of our runs and a deposit from a run on the Engelhard large reactor were analyzed for C/H/N atom compositions and for non-combustible residue. These analyses were performed on a Perkin-Elmer Elemental Analyzer by GTE Laboratories Inc. Results of these determinations are summarized in Table 6.1.

The most surprising result of these analyses is the large (greater than 50% by weight) non-combustible residue. Preparation of each sample involved removing any visually distinguishable bits of catalyst and care to avoid breaking the catalyst cylinders to insure that the analysis determined only coke; in fact, the catalyst cylinders appeared to be unbroken in the PSI runs. The larger amount of residue in the EI sample resulted because this catalyst was used until completely clogged and was therefore presumably more broken by the carbon growth than were the PSI catalysts. The residue content was determined by GTE using emission spectrography and found to have Ni as the major species and Al (from the support) as a minor component. All of the coke was magnetic, emphasizing our previous conclusion that carbon deposits form on the metal catalyst in heterogeneous reactions.

As carbon deposition occurs, pieces of the metal catalyst are lifted from the surface. This is a well known characteristic of filamentary coke formation. Electron microscope pictures showing the filamentary structure of the PSI coke samples were presented by Dr. Jon McCarty as part of the SRI presentation at the 6th ATR Working Group.

The coke formed under ATR operating conditions is characterized by a mole ratio of about 8. Estimates of the effect of this amount of hydrogen on the free energy of formation of the deposit, used in the calculation of equilibrium carbon formation boundaries, indicated that a pure carbon value is a good approximation.

TABLE 6.1

5116-8

CHEMICAL ANALYSIS OF COKE DEPOSITS

Sample	Source Conditions				Analyses			
	Fuel	Cat.	H ₂ O/C	O ₂ /C	%C	%H	%Res.	C/H
1/28/81	C ₂ H ₄	G90C	0.60	0.08	44.8	0.20	55.9	18.7
2/3/81	C ₂ H ₆	G90C	0.64	0.10	31.8	0.10	51.8	26.5
5/15/81	C ₂ H ₄	G90C	3.0	0.24	46.8	0.48	52.9	8.1
EI: 5/16/81	C ₃ H ₈	G90C	1.8	0.36	21.7	0.22	80.4	8.4

6.2 Equilibrium Carbon Boundary Calculations

It is useful to compare ATR gas compositions with equilibrium compositions to evaluate the extent of reactions among the major species. It is necessary to use thermodynamic data for the appropriate form of solid carbon for equilibrium calculations to be correct. Having determined the carbon morphology, as presented in the previous section, and having found values for the equilibrium constant appropriate to this form, we have calculated equilibrium carbon deposition boundaries.

The equilibrium carbon deposition boundary at 925 K was calculated for filamentary carbon deposited on nickel surfaces. The correct equilibrium constant for this reaction was obtained from Ref. 7. The calculated curves for filamentary carbon and graphite are shown in Fig. 6.1 along with an insert which is Fig. 6-3 from Rostrup-Nielsen's text. These equilibrium data were obtained on a supported nickel catalyst. As Fig. 6.1 shows, different morphologies of solid carbon have significantly different free energies of formation. Values for amorphous carbon are frequently, incorrectly used for equilibrium carbon calculations. Compositions for experiments run on G90C are shown on an equilibrium plot in Fig. 6.2 Filled symbols on this figure indicate carbon was deposited. Ethylene clearly caused carbon fouling well into the equilibrium carbon free region, whereas ethane and CO did not.

The important species to consider are H_2 , H_2O , CO , CO_2 , CH_4 and solid carbon. All larger species are present at concentrations several orders of magnitude smaller than these major species at equilibrium. A complete set of three independent reactions can be used to discuss the chemistry:

All three reactions are reversible, heterogeneous reactions.

Fig. 6.1
Equilibrium Carbon
Deposition: Graphite
and Filamentary Carbon
on Supported Nickel
Catalyst

T = 923 K

P = 1 atm

○ : CO
4 : C₂H₄
6 : C₂H₆

FILLED SYMBOL MEANS
CARBON FORMED

T = 923 K
P = 1 ATM

Fig. 6.2 G90C runs plotted
on equilibrium
diagram.

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Calculations of carbon deposition boundaries (CDB) were made using Rostrup-Nielsen's data⁷ by using the relationships between mole fractions of the gas phase species involved. The equations can be derived using a simplified nomenclature for the major species: C, CO(1), CO₂(2), H₂(h), H₂O(w) and CH₄(m). For the gaseous species the mole fractions are related by

$$X_1 + X_2 + X_h + X_w + X_m = 1. \quad (6.4)$$

At equilibrium all three reactions among these species, (1)-(3), must each be at equilibrium with equilibrium constants defined in terms of mole fractions and total pressure as

$$K_s = \frac{X_2 X_m}{X_1 X_w} \quad (\text{for reaction (1)}) \quad (6.5)$$

$$K_m = \frac{X_m X_w}{X_1 X_n^3} \frac{1}{P^3} \quad (\text{for reaction (2)}) \quad (6.6)$$

and

$$K_B = \frac{X_2}{X_1^2} \frac{1}{P} \quad (\text{for reaction (3)}) \quad (6.7)$$

Substitution of Eqs. (5)-(7) into Eq. (4) gives

$$1 = X_1 + PK_B X_1^2 + (1 + PK_B X_1 / K_s) X_h + P(K_m K_s / K_B) X_h^2. \quad (6.8)$$

Equation (8) can be solved for X_h in terms of X_1 as

$$\begin{aligned} X_h = & \left\{ \left[1 + 4P(K_m K_s / K_B) + 2PK_B(K_s^{-1} - 2K_m K_s / K_B^2) X_1 \right. \right. \\ & \left. \left. + P^2 K_B^{-2} (K_s^{-2} - 4(K_m K_s / K_B^2)) X_1^2 \right]^{1/2} \right. \\ & \left. - (1 + P(K_B / K_s) X_1) \right\} K_B / 2K_m K_s P \end{aligned} \quad (6.9)$$

The physically acceptable values of X_1 , X_h pairs can be used to calculate the remaining X 's using Eqs. (5) through (7).

This procedure can be used to calculate any gas composition lying on the CBD for the particular pressure and temperature of interest. The CBD can be plotted on a standard C-H-O triangular diagram by using the additional relations between the molecule mole fractions (X) and atom mole fractions (Y):

$$Y = 2X_1 + 2X_n + 3X_2 + 3X_w + 5X_m \quad (6.10)$$

$$YY_c = X_1 + X_2 + X_m \quad (6.11)$$

$$YY_H = 2X_h + 2X_w + 4X_m \quad (6.12)$$

$$YY_O = X_1 + 2X_2 + X_w \quad (6.13)$$

If methane is excluded from the system, as indicated by the experimental results, the same analysis can be used but with $X_m = 0$ and neglecting the methanation reaction (2). The resulting equation is

$$X_h = \frac{1 - X_1 - PK_B X_1^2}{1 + PK_B K_S^{-1} X_1} \quad (6.14)$$

Equations (10) through (13) are still correct with $X_m = 0$.

The values used for equilibrium constants were all taken from Ref. 7 for 925 K and 1 atm: $K_S = 1.984$, $K_m = 0.357 \text{ atm}^{-2}$ and $K_B = 1.85 \text{ atm}^{-1}$. CBD curves for full equilibrium with graphite and filamentary carbon were shown in Fig. 6.1. The difference between these two curves is due to the lower free energy of formation of graphite compared to filamentary carbon and this difference will be maintained in partial equilibrium calculations. The difference between these two curves increases with decreasing temperature as shown in the inset of Fig. 6.1.

6.3 Major Gas Phase Species - GC Analysis

The major product species resulting from reforming of either ethylene or ethane are H_2 , H_2O , CO , CO_2 and CH_4 . We obtain quantitative concentration measurements for these species from the areas under the output peaks of our Carle gas chromatograph (GC). This GC also provides concentration measurements for C_2H_2 , C_2H_4 , C_2H_6 , O_2 and N_2 . Standard calibration mixtures have been used to calibrate the GC output for all of these gases. The standard deviations were less than 2% for concentrations measured for five samples taken over a period of three hours while reactor conditions were held constant.

Concentrations of the major species remained constant during a run, even when large amounts of carbon were being deposited on the catalyst. The data in Fig. 6.3 show this for the 5/15 experiment in which about 80% of the ethylene fuel was reacted on G90C catalyst and a large carbon deposit formed.

The relative reactivities of ethylene (C_2H_4 , our model olefin) and ethane (C_2H_6 , our model paraffin) under ATR conditions are demonstrated by comparison of Figs. 6.4 and 6.5. Forty percent of ethylene is reacted with an O_2/C of 0.5; clearly addition of oxygen decreases the ethylene and converts it to CO_2 , CO and H_2 . For ethane, no reaction with O_2 or H_2O is observed, only a negligible amount (~3%) of cracking to ethylene was detected. For both fuels the initial concentrations measured per fuel carbon is 0.5 since both are C_2 molecules.

No carbon deposits were formed during the runs of Fig. 6.4. The initial gas mixture in these cases consisted only of C_2H_4 , O_2 and H_2O . The product species can be explained in terms of four independent reactions:

C₂H₄ on G90C, T_p = 660°C, H₂O/C = 3.0, O₂/C = .24

5/15/81

Fig. 6.3 Effluent composition during coke deposition.

$H_2O/C = 4.0$, total flow $\approx 9.5 \text{ cm}^3 \text{ s}^{-1}$

5/20/81

Fig. 6.4 Reaction products for C_2H_4 on SS.

5116-17

$H_2O/C = 4.0$, total flow $\approx 9.5 \text{ cm}^3 \text{ s}^{-2}$

5/22/81

Fig. 6.5 Reaction products for C_2H_6 on SS.

The values for extent listed with each reaction are the fractional approach to completion for the reaction as written evaluated for $O_2/C = 0.5$. Since reaction (6.15) is limited by the amount of O_2 , an extent of 0.56 corresponds to 85% utilization of the O_2 . The attainable extents of reactions (6.17) and (6.18) are limited by equilibrium compositions. Still these extents give an indication, over the range of ATR conditions, of the importance of the reactions of ethylene.

6.4 Higher Hydrocarbon Products - GC/MS Analysis

Our gas chromatograph/mass spectrometer (GC/MS) was adapted for detection of the higher hydrocarbons (HHC), those species larger than the C_2 hydrocarbons measured by the GC. A column was used with an increasing temperature profile to reduce the retention times of benzene and toluene.

Sample spectra recorded in this operating mode are displayed in Figs. 6.6 and 6.7 in order to show the number of peaks, peak separations and good signal to noise obtained. Figure 6.6 shows the two traces printed out in real time, as the column elutes. Six ion masses can be stored simultaneously and one of these plus the sum of all are printed in Fig. 6.6. The smallest mass chosen was 39 because it is common to all HHC; thus, all peaks in Fig. 6.6 are HHC peaks. Only the two at latest times have been identified specifically, as benzene and toluene, respectively. The other peaks correspond to C_4 and C_5 species which we have been unable to correlate with any available calibration samples.

The printout in Fig. 6.7 shows how each of the six selected ion masses is displayed as a function of retention time. In this mode of operation areas under each peak are automatically calculated and printed out by the computer which controls the GC/MS. Operating in another mode the GC/MS will record a complete mass spectrum for each peak; for qualitative identifications these spectra were obtained for each run also. With this degree of sophistication our ability to identify species sampled is limited by lack of availability of standard samples and standard spectra for calibration.

MASS 39

49

SIX IONS
MONITORED

5/6 - SIM 1 GC/MS Intensities vs. Retention Time

Fig. 6.6 GC/MS real time data plot.

5/6 - SIM 1

Fig. 6.7 GC/MS data plot for six ions.

Of course, we cannot sample any species that are very soluble in water as these will be trapped with the water which cannot be introduced to our GC columns; no such species are expected. We are also unable to sample species larger than toluene (C_7H_8) because they have insufficient vapor pressure at room temperature to pass through our inlet system.

Results of measurements made of HHC's produced on SS balls from C_2H_4 with $H_2O/C = 4$ are shown in Fig. 6.8. In this figure mass 78 corresponds to benzene, 91 to toluene, 84 to an unidentified C_6H_{12} compound and 51 to a fragment of an unidentified C_5 compound.

The most obvious characteristic of the production of HHC's is that their concentrations vary over a factor of ten for variations of O_2/C from 0.1 to 0.5; these variations are much larger than those for the major species shown in Fig. 6.4. HHC peaks are detected for all gas compositions reacting on SS surfaces and are never detected after G90C catalyst. Since the activity on G90C is more than one thousand times faster than on the smooth SS balls, this behavior demonstrates that formation of HHC's is extremely fast, faster in fact, than reactions of the major species whose concentrations change little at low O_2/C .

Large HHC concentrations are always detected when carbon is deposited on SS balls; HHC's are also detected when no carbon is formed. Combined with the observations that carbon formation occurs more readily on G90C than on SS and no HHC's are detected with G90C, this information implies that the HHC's react rapidly to form coke deposits on G90C. If this speculation is true, the HHC's are transient intermediates that are at such low concentrations in the presence of active catalysts that they cannot be measured.

At the lower water level $H_2O/C=2$ the concentrations of HHC's also vary drastically with oxygen concentration as shown in Fig. 6.9. Benzene concentration was high in the sooty flame region when carbon particles were formed in the gas as opposed to on the surface. Figure 6.10 shows an even more dramatic change of benzene concentration with variations of H_2O/C than with O_2/C .

Abundances of Various Masses versus O_2/C for $H_2O/C = 4$

Fuel = C_2H_4

$T_p = 660^\circ C$

Fig. 6.8 Higher hydrocarbon abundances as a function of O_2/C for $H_2O/C = 4$.

O_2/C
Benzene Abundance versus O_2/C

Fuel = C_2H_4

$T_p = 660^\circ C$

Fig. 6.9 Benzene abundance as a function of O_2/C for $H_2O/C = 4, 2$ and 0.5

Fuel = C₂H₄
 T_p = 660°C

Fig. 6.10 Benzene abundance as a function of H₂O/C for different values of O₂/C and total flow.

Benzene formation is kinetically limited under these conditions as shown by its decrease with increasing total flow rate at constant H_2O/C and O_2/C .

Benzene and the other HHC concentrations increase with increasing oxygen and decrease with increasing water. The dependence of carbon formation on H_2O/C is the same. The dependence of carbon formation on O_2/C is complicated; at low H_2O/C adding oxygen produces a sooty flame and at high H_2O/C we have not formed carbon on the inactive SS surface. These results provide some support for the implication of a connection between HHC's and carbon deposits, however, this connection cannot be firmly established by the available data.

We have concluded that the complexity and the difficulty of making detailed measurements of the HHC chemistry preclude a detailed mechanistic understanding of the combined heterogeneous-homogeneous chemistry involved in carbon deposition under ATR conditions at this time. Speculations about coke precursors cannot be addressed experimentally to a significant extent under the present program. Therefore, we will concentrate on understanding the reactions of the major species at a more global level for the remainder of this project. This approach has the advantage of increasing the interaction between our experimental and modeling tasks.

7. REACTIONS ON NOBLE METAL CPO

The same small flow reactor was used to study a partial oxidation catalyst (CPO) provided by Engelhard Industries. The catalyst used was in the form of a three inch long by one-half inch diameter cylinder with parallel, one millimeter square channels longitudinally. This is the same catalyst used in the Engelhard ATR.

The CPO is a much more active catalyst than G90C, both for oxidation and reforming. Complete reaction of C_2H_4 was achieved on the CPO for conditions which would result in 80% reaction on G90C as shown in Fig. 7.1. Over the range of $O_2/C = 0 - 0.4$, most of the C_2H_4 reacted with H_2O in a reforming reaction. The water-gas shift reaction is also very fast. These reactions combine to give the rather constant composition as O_2/C is varied.

A measure of the approach of the concentrations of the major species to equilibrium is the ratio of the activity quotient to the equilibrium constant at the furnace temperature. The activity quotient is the ratio of species concentrations for the equilibrium constant expression for a particular reaction. If equilibrium is attained, this ratio will be unity. This measure is useful in the case of the CPO since it can indicate equilibrium over a range of temperature. As discussed earlier, the temperature varies substantially over the length of the CPO due to its low thermal conductivity. The partial oxidation heats the gas and the endothermic reforming reaction removes heat to cause the temperature profile.

Figure 7.2 shows a plot of this measure of equilibrium as a function of O_2/C for both ethane and ethylene; the results are the same as both fuels were completely reacted to form the major product species. The lower curve for the water-gas shift reaction corresponds to an equilibrium composition at $860^\circ C$, $200^\circ C$ higher than the furnace temperature. If this result indicates equilibrium was attained, it is strange that the effective temperature does not change with O_2/C , especially since all of the fuel was burned. The methanation reaction, upper curve in Fig. 7.2, appears to have produced less methane than an equilibrium concentration.

$H_2O/C = 4.3$, total flow $\approx 9.5 \text{ cm}^3 \text{ s}^{-1}$

5/8/81

Fig. 7.1 Gas composition after reaction of ethylene on CPO as a function of O_2/C .

○ - C_2H_4 , △ - C_2H_6

Blue - Water Shift Reaction; $CO + H_2O = CO_2 + H_2$

Red - Methanation Reaction; $CO + 3H_2 = CH_4 + H_2O$

Flow = $9 \text{ cm}^3 \text{ s}^{-1}$

$H_2O/C = 4$

Fig. 7.2 Activity quotients for water-gas shift reaction (lower points) and methanation reaction (upper points) for ethane and ethylene on CPO as a function of O_2/C .

The ratio of activity quotient to equilibrium constant is used to compare experimental results for CPO to those on stainless steel in Fig. 7.3. Essentially no reaction occurs among the major species on stainless steel, while the composition approaches equilibrium, a value of 1, for the CPO. The stainless steel and CPO case was a case in which half of the catalyst holder was filled with stainless steel balls followed by CPO in the second half. Clearly very little reaction occurred. This is probably because of a strong temperature effect on the chemistry and the CPO temperature did not increase as much in half the distance. No HHC's were produced in the CPO only case, whereas HHC's were produced on stainless steel only and in the stainless steel and CPO combination. The very fast production of HHC may have prevented the approach to equilibrium to some extent if these large species reform relatively slowly.

W: Water Shift; $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$

M: Methanation; $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$

Fuel: Ethylene

$\text{H}_2\text{O}/\text{C} = 4$, $\text{O}_2/\text{C} = .4$

Fig. 7.3 Extent of equilibrium on CPO on stainless steel.

8. CONCLUSIONS FROM EXPERIMENTAL RESULTS

The complexity of the chemistry in an ATR has prevented an understanding in terms of a detailed mechanism even for the case of simple model fuel compounds. However, several conclusions can be derived from these studies which provide important qualitative guidelines for design and operation.

Carbon deposits form on and adhere to the catalyst surface. Filamentary coke is formed which has a high metallic content and a C/H ratio about equal to 8. Equilibrium carbon deposition boundaries are significantly affected by the coke morphology. The activity of the catalyst is unaffected by relatively large amounts of coke deposit.

Ethylene is much more reactive than ethane in every way: with oxygen, with water, to produce higher hydrocarbons, and to produce coke. Ethylene and ethane are not rapidly interconverted under ATR conditions. If we generalize these results to olefins and paraffins, it is the olefins which cause catalyst fouling problems in complex fuels. Essentially all of the important chemistry is heterogeneous on the catalyst surfaces.

Higher hydrocarbons, larger than C_2 species, are produced from simple fuel molecules extremely rapidly. The rate of coke formation is also very fast. Though generalization is difficult in these catalyzed reactions because these rates are specific to each catalyst, it seems that kinetic solutions to carbon fouling problems are extremely unlikely. This discouraging result is caused by the fact that carbon formation is much faster than reactions among the major species that can inhibit it. This means ATR's must be operated in equilibrium carbon free regions.

A promising and somewhat surprising result is that the CPO tested is a very effective reforming catalyst.

The qualitative chemistry for the worst trouble causer, ethylene, can be summarized in a reaction diagram which compares relative rates:

C/H = 1/2

C/H = 1

C/H = 8

Coke

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APPENDIX A
GAS PHASE EXPERIMENTS

APPENDIX A

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

$$\text{Re}_D = \frac{\rho u D}{\mu} < 2300$$

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,

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

$$Re_D \approx 5 \text{ pu}$$

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}

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

and

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

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

$$K_t = -\pi r^2 8 \frac{\pi r}{\lambda} \operatorname{Im} \left(\frac{m^2 - 1}{m^2 + 2} \right),$$

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

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

The absorption coefficient is then

$$k = N K_a \text{ cm}^{-1}$$

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:

$$\frac{\Delta I}{I} = - k l \sim 1.5 \times 10^{-3}$$

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

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

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}

$$A_s \quad \text{slit area} = 6.4 \times 10^{-2} \text{ cm}^2$$

$$\Omega \quad \text{solid angle} = 2.2 \times 10^{-2} \quad (F = 6)$$

$$\epsilon_f \quad \text{spectrometer efficiency} = .3$$

$$\epsilon_Q \quad \text{quantum efficiency} = 3 \times 10^{-2}$$

$$I = 4.3 \times 10^4 \text{ photo-electrons/s}$$

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

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

where

N is the number of $50 \text{ \AA}$ 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.

Fig. 5 - Temperature profile for high preheat.

$$\text{O}_2/\text{C} = 0$$

$$\text{H}_2\text{O}/\text{C} = 1.91$$

$$\text{N}_2/\text{C} = 1.66$$

$$\text{O}_2/\text{C} = 0.25$$

$$\text{H}_2\text{O}/\text{C} = 1.91$$

$$\text{N}_2/\text{C} = 1.66$$

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

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ENGELHARD INDUSTRIES CONTRIBUTION

HYDROCARBON AUTOTHERMAL REFORMING PROGRAM

FINAL REPORT

by

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HYDROCARBON AUTOTHERMAL REFORMING PROGRAM

ABSTRACT

The objective of this subcontract was to assist Physical Sciences, Incorporated in their efforts to develop a comprehensive model of the autothermal reforming process. This support effort consisted of supplying catalysts to PSI for their coking studies and in providing experimental data from Engelhard's test equipment.

The test equipment, which included both a small catalyst screening unit and a 3 kW autothermal reformer (ATR), was built under contract DE-AC-03-79-ET15383 on Catalyst and Process Development for Hydrogen Preparation from Future Fuel Cell Feedstocks.

Data from these ATR units are presented for both propane and No. 2 oil. With No. 2 oil, the 3 kW ATR could be operated coke-free at O_2/C levels down to 0.37. Gas composition and temperature profiles are presented from a point $7/8$ " below the CPO section and down the steam reforming bed.

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Hydrocarbon Autothermal Reforming Program

Final Report

I. Catalyst Selection, Formulation and Preparation

During the period of this contract two types of catalyst were provided to Physical Sciences, Incorporated:

- 1) Monolithic Partial Oxidation Catalyst
- 2) Pelleted Steam Reforming Catalyst

The monolithic partial oxidation catalyst (CPO) was prepared by Engelhard and delivered to PSI along with a specially designed holder for their 2" diameter reactor tube as shown in Figure 1. This monolithic catalyst has 62 square channels per cm^2 (400 cells/in 2). Accounting for the web and the coating used as the catalyst support, each channel is about 0.106 cm x 0.106 cm with an area of 0.0113 cm^2 . The web thickness is about 0.021 cm and the open area of the monolith is about 70%. The active metals for the partial oxidation catalysts are Pt and Pd in equal portions by weight.

As a baseline steam reforming catalyst, a commercial nickel catalyst was selected and sent to PSI for their studies. This catalyst, G90c (also called T2043), was obtained (without charge) from United Catalysts, Incorporated.

II. Catalyst Characterization

The chemical and physical properties of the G90c nickel type steam reforming catalyst have been determined by Engelhard and are reported in Table I. Sample A was provided by John Bett of United Technologies and is labeled UTC-G90c to distinguish it from Sample B, labeled T2043, obtained directly from United Catalysts. Figure 2 is a graph showing the pore size distribution as determined by Hg penetration.

Table I

Chemical and Physical Properties of a
Commercial Steam Reforming Catalyst, G90C

	<u>Sample A</u>	<u>Sample B</u>
	<u>UTC- G90C</u>	<u>T2043</u>
CHEMICAL COMPOSITION:		
Ni % (wt)	15.4	-
Ca %	0.21	-
Al ₂ O ₃ %	Balance	-
PHYSICAL PROPERTIES:		
Surface Area m ² /g	16.2	7.9
Compacted Bulk Density, g/ml	1.2	-
Total Porosity, (Hg), ml/g	0.215	0.239
Shape	Tablets	Tablets
Size	1/8" x 1/8"	1/8" x 1/8"

MATERIAL:
304SS

TO FIT
MIXERS

1.738" + .020"
- .000"

1" I.D. TO HOLD
3/4" MONOLITH
PLUS FIBERFRAX

REMOVABLE CONE;
FLARES OUT FROM
2" O.D. TO 2.110"
TO MAKE SNUG FIT
TO TUBE

FIGURE 1

INSERT TO HOLD MONOLITHIC CATALYST

FIGURE 2

III. Fundamental Reaction Tests and Kinetic Data

When this proposal was prepared it was intended to obtain steam reforming kinetic data from a micro-reactor being assembled by Engelhard. Experimental difficulties with that micro-reactor negated that approach. In their model development, PSI has used kinetic data reported by United Technologies in their contract work. In addition, PSI has set up a small reactor to study the coking phenomenon which also provides kinetic data.

A key observation made by both Jet Propulsion Laboratory and United Technologies is the strong effect of sulfur on the catalytic rates. Any future work directed at obtaining catalytic rates should take this into consideration.

Engelhard did perform a series of tests on their small catalyst screening unit to provide information about the catalytic partial oxidation section. Tests with ethane and with No. 2 oil were run and the data have been used by PSI in their modelling efforts. The results have been reduced to a consistent basis by PSI (in terms of moles of product per unit of carbon in the feedstock) and are listed in Tables II and III for ethane and No. 2 oil, respectively. These results were obtained in a small reactor with a CPO monolith of about 1/4" diameter with inlet temperatures of about 710K. The larger ATR unit operated at higher inlet temperature (1022K) and therefore converted more feedstock at a given O₂/C ratio. These results will be discussed under the next task.

Table II
Ethane Partial Oxidation Results

Run	1	2	3	4
O_2/C	.252	.322	.386	.262
H_2O/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_2H_6	.213	.136	.077	.211
C_2H_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

Inlet Temperature = 710K

Products are in moles per atom feed carbon.

EH = CO + H_2 = Equivalent Hydrogen

ΔW = Increase in H_2O from inlet to outlet

$$= 2(O_2/C)_{\text{Inlet}} - CO - 2CO_2$$

ΔEW = Change in equivalent water ($CO_2 + H_2O$)

$$= \Delta W + CO_2$$

Table III
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.

Inlet Temperature = 710K

Products are in mole per atom feed carbon.

C/C = Conversion to species lighter than C₄.

EH = H₂ + CO = Equivalent Hydrogen

$$\Delta W = 2(O_2/C) - CO - 2CO_2$$

$$\Delta EW = \Delta W + CO_2$$

IV. Correlate ATR Test Data with Chemical and Fluid Dynamic Model

The bulk of the work done under this sub-contract involved this task. The work reported here was carried out in the summer of 1981 and involved several runs on a bench scale ATR unit which was approximately an order of magnitude larger than the catalyst screening unit mentioned above. The results described herein were used by PSI in their model development effort.

A. Reactor System

Based on the results obtained from the combined process and catalyst development using the catalyst screening unit, a larger autothermal reforming reactor system (called ATR II) was designed and constructed for the production of hydrogen from No. 2 oil. As compared to the screening unit, a scale-up factor of approximately 10 was used in the design of this ATR II reactor system. The detail schematic flow diagram is shown in Figures 3 and 4.

For this reactor system, three feed lines were used, namely, No. 2 oil, air and water. An additional propane feed line was also included in this unit for the initial reactor start-up. To produce hydrogen from No. 2 oil, feed rates of No. 2 oil, air and water are separately controlled and these reactants are then mixed in the injector. For example, ambient air is compressed by a two-stage compressor to about 150 psig. After passing through a dryer to remove moisture, the total air feed rate to the reactor was controlled by a mass flowmeter; for the water feed, the distilled water was delivered into the system by a metering pump. This feed water was first vaporized by the product gas and subsequently further vaporized and preheated to the desired preheat temperature by electric heaters. The super heated steam was mixed with the preheated air and then admitted into the injector. For the 3rd reactant, the feed rate of No. 2 oil was controlled by a metering pump. This oil was first vaporized in a preheater and mixed with air and steam at the injector. The combined reactant mixture was passed through a static mixer for additional mixing and subsequently admitted into the autothermal reformer. The purpose of the autothermal reformer was to convert catalytically the No. 2 oil into the desired hydrogen and carbon monoxide by means of catalytic partial oxidation (CPO) and steam reforming (SR) reactions.

FIGURE 4

SCHEMATIC DRAWING OF THE NEW ATR REACTOR

After coming out of the reactor, the heat in the product gas was used to evaporate the feed water and, then, the gas was cooled to room temperature in heat exchangers. The total amount of product gas was measured by a dry test meter.

Shown in Figure 5 is the design and construction of this autothermal reactor. Note that a ceramic insert, which was made of 99+% Al_2O_3 , was used in this reactor to avoid any direct contact between the metal wall and the reactants. Furthermore, Fiberfrax insulation was used between the ceramic insert and the reactor wall. By avoiding the direct contact between reactants and reactor wall, coke formation on the reactor wall could be avoided; by lowering the reactor wall temperature, cheaper materials could be used to construct this reactor even though the reactions are taking place at temperatures above 1600°F.

The temperatures at various locations within the steam reforming bed were measured by 8 thermocouples, and these temperatures were automatically recorded by a digital data logger. The dry gas compositions at 5 different locations within the steam reforming bed were monitored on-line by a gas chromatograph. The exact location of each thermocouple and each sample probe is shown in Figure 6.

B. Experimental Details

1. Start-Up Procedure

Since No. 2 oil has a tendency to form coke easily and quickly in the preheater as well as in the catalyst bed, the less complex reactions involved in the autothermal reforming of propane were used to start up this ATR II reactor system. For a typical run, the reactor was initially heated up in N_2 , water was then admitted into the system at a preheat temperature of 690°C, propane was subsequently admitted into the reactor via the propane feed line. The feed rate of propane (c.p. grade) was measured and controlled by a mass flowmeter; it was then preheated in a heater and was admitted into the injector to mix with steam. Following the introduction of propane, air was finally admitted into the reactor. By properly controlling the preheat temperature, the O_2/C , and the H_2O/C ratios, a steady state autothermal reforming of propane could easily be accomplished in a short period of time. Typically, this autothermal reforming of propane would be run for about 3 hours before switching from propane to No. 2 oil.

FIGURE 5 AUTOTHERMAL REFORMER

FIGURE 6
LOCATIONS OF SAMPLE PROBES AND THERMOCOUPLES
IN ATR II REFORMER

2. Catalyst Evaluation

The catalysts used in each experiment run during the course of this work are summarized in Table IV. For example, for runs II-8 through II-13, a total of eight inches of fresh CPO-4 catalyst (3 sections of monolithic catalyst, 3/4" O.D. x ~3" long) was loaded into the CPO section, followed by a total of 1130 cc sample of a fresh, commercial G-90C steam reforming catalyst (Ni/Al₂O₃ 1/8" x 1/8" pellet). To start this series of experiments, the samples were reduced in situ for at least 4 hours by running the autothermal reforming of propane (c.p. grade). The standard reduction condition used throughout this project was similar to the one reported for run II-11 in Table V. At the end of the reduction, the above reduced catalysts were immediately purged overnight in N₂. After starting Run II-9 early in the morning, the experimental conditions, namely the feed rates of each reactant, O₂/C ratio, H₂O/C ratio and the preheat temperature, were adjusted to the desired values, and these conditions were kept the same throughout the whole run (normally 6 hours). During the experiment, the dry gas composition of the intermediate as well as the final product gases were analyzed by a on-line gas chromatograph; the reactor temperature profiles within the steam reforming bed and the pressure drop across the steam reforming bed were measured and recorded every 10 minutes by a digital recorder. The total amount of dry product gas produced from these reactions was measured by a dry test meter. At the end of this run, the reactor was purged in N₂ overnight and was then re-reduced by using the standard reduction procedure before Run II-10. The purpose of this re-reduction before Run II-10 was to regenerate the catalysts so that the initial activities could be restored.

For Run II-10, the new feed rates were adjusted to the desired values, the experimental results were taken and the catalyst samples were re-reduced before the next run. For the subsequent experiments in the same series, similar experimental procedures were repeated for each run, until all the desired experiments in the same series were completed.

To start a new series of experiments, for example Run II-14 through Run II-21, fresh samples of CPO-4 and FP-34 catalysts (1075 cc, 1/16" pellet) were loaded into the reactor. After in situ-reduction of these samples, similar experimental procedures described above were used to obtain data for each run, and for all the desired runs in this new series.

Table IV

Summary of Catalyst Used in Each Experiment

<u>Series No.</u>	<u>Run No.</u>	<u>Catalyst</u>		<u>Comments</u>
		<u>CP0</u>	<u>S.R.</u>	
I	II-8 to II-13	CP0-4	G-90C	Fresh 8" CP0-4; 1130 cc G90C
II	II-14 to II-21	CP0-4	FP-34	Fresh 8" CP0-4; 1075 cc FP-34
III	II-22 to II-29	CP0-4	FP-34	Fresh 9" CP0-4; ~150 cc Fresh FP-34 and 925 cc used FP-34
IV	II-30 to II-32	CP0-2B	FP-34	Fresh CP0-4 (9"); ~150 cc Fresh FP-34 and 925 cc used FP-34

Table V

Experimental Results for Autothermal Reforming of Propane

RUN NO.	II-9	II-11	II-14
CATALYST			
CPO	CPO-4 (Pt/Pd)	CPO-4 (Pt/Pd)	CPO-4 (Pt/Pd)
SR	G90C (Ni)	G90C (Ni)	FP-34 (Pt/Rh)
CONDITIONS			
HC	C_3H_8	C_3H_8	C_3H_8
H_2O/C	2.35	2.85	2.60
O_2/C	0.40	0.47	0.386
TEMPERATURE, °C			
PREHEAT	690	690	690
S.R. TOP (TSRB1)	692	832	658
S.R. MID (TSRB4)	660	776	651
S.R. END (TSRB5)	631	708	638
DRY GAS COMPOSITIONS* (MOLE %)			
H_2	47.19	44.37	48.49
CO	8.67	8.99	7.87
CO_2	12.02	10.98	12.88
N_2	31.69	35.44	30.26
CH_4	0.25	0.03	0.33
C_2H_6	-	-	-
C_3H_8	-	-	-
C_2H_4	-	-	-
C_3H_6	-	-	-
OTHER	-	-	-
EQUIVALENT H_2	2.67	2.54	2.67
HC CONV. %	98.8	99.9	98.4

* Composition at probe #3 (i.e., 5" in S.R. bed)

C. Results

Previous work indicated that the autothermal reforming of No. 2 oil, the equivalent hydrogen (EH), hydrocarbon conversion (% HC conv) and carbon balance (% C bal) are important responses in screening a given steam reforming catalyst as well as in evaluating the thermal efficiency of the reformer. These three parameters are defined as follows:

$$\begin{aligned}\text{Equivalent Hydrogen (EH)} &= (\text{H}_2 + \text{CO}) / \text{C}_f \\ &= \frac{\text{Total moles of CO and H}_2 \text{ in the product gas}}{\text{Total moles of C in the feed}}\end{aligned}$$

$$\begin{aligned}\text{Hydrocarbon Conversion (\% HC Conv)} &= \left[(\text{CO} + \text{CO}_2) / \sum \text{C}_p \right] (100\%) \\ &= \left[\frac{\text{Total moles of CO and CO}_2 \text{ in the product gas}}{\text{Total moles of C in the product gas}} \right] (100\%)\end{aligned}$$

$$\begin{aligned}\text{Carbon Balance (\% C Bal)} &= (\text{C}_p / \text{C}_f) (100\%) \\ &= \left[\frac{\text{Total moles of C in the product gas}}{\text{Total moles of C in the feed}} \right] (100\%)\end{aligned}$$

For each run, the values of the above three responses are calculated and reported in the summary tables. If leaks developed during an experiment, the calculated values of EH and carbon balance would be low. Furthermore, if unconverted oil were observed in the condenser, the total amount of carbon calculated from the product gas (C_p) will be less than the carbon (C_f) calculated from the oil feed. Since the amount of carbon present in the unconverted oil was not included in the calculation of C_p , the calculated results of the carbon balance will be less than 100%. The larger the amount of unconverted oil present in the product stream, the smaller the value of the carbon balance.

1. Autothermal Reforming of Propane

Because of the strong tendency of coke formation in the preheaters as well as in the reformer when No. 2 oil was used as a feed, a less complex and more reliable autothermal reforming of propane was used for the initial shakedown runs. During this period, equipment modifications as well as experimental techniques were developed for this ATR II reactor system to ensure a trouble-free operation. The results of some successful runs are summarized in Table V and the dry gas composition vs. hours on steam are shown in the Appendix.

The purpose of Runs II-9 and II-14 was to use the autothermal reforming of propane to test the steam reforming activity of Engelhard's Pt-Rh/ Al_2O_3 catalyst and compare its activity to a commercial Ni/ Al_2O_3 catalyst (G-90C). As shown in Table V, the equivalent H_2 and % HC conversion for both runs were about the same, indicating that, at $\text{O}_2/\text{C} > 0.40$, there was no advantages of using noble metal catalyst over the commercial nickel catalyst in the steam reforming bed. However, more experimental data should be collected to determine whether there are any advantages of using noble metal steam reforming catalyst when O_2/C ratio of less than 0.40 is used in the experiments.

2. Autothermal Reforming of No. 2 Oil

The autothermal reforming of No. 2 oil has been run in this ATR II reactor system, and the results are summarized in Tables VI, VII, VIII, and IX and the dry gas composition at various locations in the steam reforming bed are listed in the Appendix.

a. Reproducibility of Experimental Results

Runs II-10 and II-13 were duplicate runs to test the reproducibility of the experimental data obtained under the same conditions, i.e., at $\text{O}_2/\text{C} = \sim 0.42$, $\text{H}_2\text{O}/\text{C} = \sim 2.6$). As listed in Table VI, the product gas composition, the reactor temperature profiles, the equivalent H_2 made, % carbon balance and % HC conversion for these two runs were approximately the same (within the experimental errors). Therefore, it may be concluded from these results that, under the same experimental conditions, reproducible data could be obtained with this test unit.

b. Comparison of Steam Reforming Activity Between Nickel and Noble Metal Catalysts

Runs II-15 and II-17 were designed to test the steam reforming activity of Pt-Rh/ Al_2O_3 catalyst under the conditions similar to those of Run II-13. In other words, all the feed rates and preheat temperature for these two runs were kept at the same conditions. The results were summarized in Table VI, and the intermediate dry gas composition at various locations inside the steam reforming bed were listed in the Appendix.

TABLE VI

EXPERIMENTAL RESULTS FOR AUTOTHERMAL REFORMING OF NO. 2 OIL

RUN NO.	II-10	II-13	II-15	II-17
CATALYST				
CPO	CPO-4 (Pt/Pd)	CPO-4 (Pt/Pd)	CPO-4 (Pt/Pd)	CPO-4 (Pt/Pd)
SR	G90C (Ni)	G90C (Ni)	FP-34 (Pt/Rh)	FP-34 (Pt/Rh)
CONDITIONS				
HC	#2 Oil	#2 Oil	#2 Oil	#2 Oil
H ₂ O/C	2.60	2.59	2.67	2.56
O ₂ /C	0.42	0.41	0.43	0.413
TEMPERATURE, (°C)				
PREHEAT	690	690	690	690
S.R. TOP (TSRB1)	997	997	875	861
S.R. MID (TSRB4)	908	897	866	806
S.R. END (TSRB5)	812	793	818	733
DRY GAS COMPOSITIONS** (MOLE %)				
H ₂	34.96	34.48	38.82	39.55
CO	11.11	11.45	9.70	8.71
CO ₂	11.91	11.93	12.93	14.15
N ₂	41.22	41.08	38.36	37.31
CH ₄	0.51	0.75	-	0.06
C ₂ H ₆	-	0.01	-	-
C ₃ H ₈	-	-	-	-
C ₂ H ₄	0.01	0.01	-	-
C ₃ H ₆	-	-	-	-
OTHER	-	-	-	-
EQUIVALENT H ₂	1.79	1.72	2.06	***
HC CONV. %	97.7	96.7	100	99.7
CARBON BAL.	91.3*	90.6*	96	***

* Unconverted oil was observed in the condensate.

** Composition at probe #5 (i.e., end of S.R. bed)

*** No unconverted oil observed, but leak from dryer was detected.

For the combination of CP0-4 and G90C catalyst system (Run II-13), unconverted oil was observed in the condensate. Also, coke formation in the steam reforming bed was observed, because the pressure drop (ΔP) across the steam reforming bed increased from 0.8 psig initially to about 8 psig at the end of the run. After this run, it was observed that most of the coke was formed in the entrance section of the steam reforming bed. Thus, the coke boundary for this catalyst system (i.e., CP0/G-90C) was at an O_2/C ratio of about 0.42 and H_2O/C of about 2.60.²

For Runs II-15 and II-17, the noble metal steam reforming catalyst was used in the whole steam reforming bed. Under the same conditions described above (Table VI), no unconverted oil was observed in the condensate and there was no significant increase in pressure drop across the steam reforming bed, indicating that the catalyst system was capable of converting No. 2 oil to the desired product at an O_2/C ratio of 0.41 and H_2O/C ratio of ~ 2.60 . Although a small amount of coke was observed in both CP0 and the top first inch of the steam reforming bed, upon inspection, the autothermal reforming of No. 2 oil over this catalyst system was steady throughout the whole run.

If the experimental data for Run II-13 were compared to those of Run II-13, it was found that, for FP-34 catalyst, both the hydrocarbon conversion and equivalent hydrogen make were higher. Furthermore, the coke accumulation in the steam reforming bed was insignificant. Therefore, it may be concluded that with the same amount of sulfur in the feed oil, Engelhard's noble metal catalyst (FP-34) has higher initial steam reforming activity than the commercial Ni catalyst, and that this FP-34 catalyst is compatible with this autothermal reformer.

c. Effect of Pressure

After loading samples of CP0-2B catalyst and replacing the entrance section of FP-34 with the fresh material (~ 150 ml), the autothermal reforming of No. 2 oil was tested at an O_2/C ratio of 0.38, H_2O/C ratio of 2.57 and preheat temperature of $690^\circ C$ (Run II-30). As shown

in Table VII, the reactions were steady under these testing conditions and only a trace amount of wax was found in the condensate. The equivalent hydrogen conversion was 98.9% and the pressure drop across the steam reforming bed was maintained throughout the run at 1.5 psig. Therefore, it may be concluded that this combination of catalysts and conditions permits successful operations.

To find out the effect of reactor pressure on the autothermal reforming of No. 2 oil, the reactor pressure was increased to 29.3 psig in Run II-31. Again, steady state was obtained, only a trace of wax was observed in the condensate and the Δp across the steam reforming bed was constant throughout the run at 0.5 psig. By comparing the results obtained for Run II-31 to those for Run II-30, in Table VII, the methane breakthrough was slightly increased from 0.25 to 0.41 as expected thermodynamically and, thus, the hydrocarbon conversion was slightly decreased from 98.9% in Run II-30 to 98.3% in Run II-31. However, the difference in experimental data between these two runs was small. Thus, it may be concluded that no significant pressure effect was observed within the pressure range studied.

d. Stability of the Autothermal Reforming System and No. 2 Oil

Run II-32 was designed to test the stability of these catalysts as well as to find out the coke boundary for this combination of CP0-2B and FP-34 catalysts. Thus the purpose of the first 24 hours was to find out the stability of its steam reforming catalytic activity, while the subsequent 48 hours was to find out the coke boundary. Since an increase in the preheat temperature will raise the reactor temperature in the steam reforming bed, which in turn will increase the reaction rate and thus the degree of hydrocarbon conversion, a higher preheat temperature (at 749°C) was used in this run.

For the stability test, the autothermal reforming of No. 2 oil was tested at O_2/C ratio of 0.374, H_2O/C ratio of 2.56, and preheat temperature of 749°C. The dry gas compositions at various locations in the steam reforming bed were measured and are listed in Tables VIII and IX. The dry gas compositions at Probes #1 and #5 were plotted in Figure 7 as a function of time. As shown in Figure 7, the dry gas compositions determined at Probe #5 were constant, indicating that steady state was indeed obtained over this 24 hour period. However, the H_2 concentration determined at Probe #1 was slightly decreased. Thus, it shows a slight deactivation of this CPU sample.

TABLE VII

AUTOTHERMAL REFORMING OF NO. 2 OIL -
SUMMARY OF RUNS II-30 AND II-31

RUN NO.	II-30	II-31	
CATALYST			
CPO	CPO-2B (Pt/Pd)	CPO-2B	
SR	FP-34	FP-34	
CONDITIONS			
H ₂ O/C	2.57	2.54	
O ₂ /C	0.38	0.37	
P (psig)	4.4	29.3	
TEMPERATURE, °C			
PREHEAT	690	690	
S.R. TOP (TSRB1)	877	907	
S.R. MID (TSRB4)	789	791	
S.R. END (TSRB5)	761	758	
DRY GAS COMPOSITIONS (MOLE %)			
H ₂	41.35	41.60	
CO	10.38	9.47	
CO ₂	13.08	13.89	
N ₂	34.73	34.43	
CH ₄	0.25	0.41	
C ₂ H ₆			
C ₃ H ₈			
C ₂ H ₄			
C ₃ H ₆			
OTHERS			
EQUIVALENT H ₂	2.12	2.07	
HC CONV. (%)	98.9	98.3	

TABLE VIII

AUTOTHERMAL REFORMING OF NO. 2 OIL, RUN II-32

RUN NO.	II-32*	II-32*	
CATALYST			
CPO	CPO-2B (Pt/Pd)	CPO-2B	
SR	FP-34 (Pt/Rh)	FP-34	
CONDITIONS			
H ₂ O/C	2.57	2.56	
O ₂ /C	0.378	0.374	
P (psig)	4.7	4.8	
TEMPERATURE, °C			
PREHEAT	749	749	
S.R. TOP (TSRB1)	942	948	
S.R. MID (TSRB4)	809	808	
S.R. END (TSRB5)	778	779	
DRY GAS COMPOSITIONS (MOLE %)			
H ₂	41.11	40.25	
CO	11.52	11.58	
CO ₂	12.51	12.70	
N ₂	34.37	34.92	
CH ₄	0.26	0.31	
C ₂ H ₆	0.01	0.03	
C ₃ H ₈			
C ₂ H ₄			
C ₃ H ₆			
OTHERS			
EQUIVALENT H ₂	2.17	2.09	
HC CONV. (%)	98.8	98.5	

* Column 1 based on 7th hour data; column 2 based on 18th hour data. Only trace of wax was found in the condensate.

TABLE IX

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF NO. 2 OIL, RUN II-32

(Run II-32; $H_2O/C = 2.56$; $O_2/C = 0.374$)

Hours on Stream	Sample Probe	Temp.* °C	% DRY GAS COMPOSITION									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	5	796	40.80	11.41	12.71	34.55	0.30	0.01				
2	4	796	39.84	12.04	12.06	35.46	0.35	0.02				
3	3	802	39.99	14.16	10.64	34.76	0.23	0.01				
4	2	804	26.24	18.24	5.86	46.87	1.14	0.07	0.01	0.93	0.23	0.06
5	1	807	16.67	19.31	3.69	55.29	1.78	0.12	0.01	2.01	0.53	0.13
7	5	809	41.11	11.52	12.51	34.37	0.26	0.01				
8	4	809	40.24	12.23	11.91	35.08	0.31	0.01				
9	3	808	39.89	14.44	10.43	34.77	0.24	0.02				
10	2	808	21.69	19.28	4.52	50.54	1.57	0.10	0.01	1.51	0.32	0.08
11	1	808	16.62	19.54	3.48	55.15	1.89	0.12	0.01	2.10	0.52	0.13
13	5	808	39.49	11.17	15.58	33.30	0.27					
14	4	809	39.00	12.46	12.64	34.84	0.34	0.48				
15	3	809	38.73	14.78	10.77	35.05	0.29	0.16				
16	2	810	21.04	20.31	4.56	49.08	1.85	0.25	0.01	2.02	0.36	0.09
17	1	809	15.87	19.53	3.55	55.43	1.99	0.20	0.01	2.32	0.51	0.12
19	5	808	40.25	11.58	12.70	34.92	0.31	0.03				
20	4	807	39.30	12.63	11.83	35.61	0.38	0.03				
21	3	807	39.09	15.08	10.19	35.07	0.32	0.03				
22	2	809	19.02	19.44	4.11	52.69	1.85	0.12	0.01	1.88	0.38	0.09

* Mid bed temperature.

** Trace of wax was observed in condensate.

FIGURE 7. GAS COMPOSITION DURING THE STABILITY TEST

FIGURE 8

TEMPERATURE PROFILE IN STEAM REFORMING BED.

RUN II-32

 $(O_2/C = 0.374; H_2O/C = 2.56)$

The reactor temperature profiles in the steam reforming bed for this run are plotted in Figure 8. Note that the temperature profile at the first 9" of the steam reforming bed was slightly shifted to a higher temperature as the time on stream increased from 5 hours to 24 hours. This shift of temperature profile also indicates a slight deactivation of FP-34 sample, probably due to the decrease of the initial steam reforming activity. However, the overall reactor performance was steady over these 24 hours as indicated by the dry gas compositions determined at Probe #5.

Figure 9 is a plot of dry gas composition vs. depth of steam reforming bed. It was found that all of the higher hydrocarbons (i.e., C_2^+) were steam reformed within the first 5" of the steam reforming bed, and that only small changes in the product composition were measured in the remaining bed. It is also interesting to observe that coke formation in the steam reforming bed was mostly found in the entrance section of this steam reforming bed. Therefore, it may be concluded that most active catalyst should probably be loaded in the entrance section, so that the unstable intermediate compounds and/or coke precursor could be quickly removed from the reactor, and that the remaining section of this steam reforming bed serves to convert the residual methane.

e. Oil Breakthrough Boundary

Because of the good activity of the Pt/Rh catalyst, it was possible with the Engelhard ATR-II unit to explore the boundary where oil breakthrough occurs before the onset of the coke boundary. This was not possible with G90C as the pressure drop was increasing simultaneously with oil breakthrough, indicating that carbon was accumulating.

Several runs were designed to test the oil breakthrough boundary for the combination of CP0-4 and FP-34 catalysts. As shown in Table X, at a preheat temperature of 690°C, H_2O/C ratio of 3.10 and O_2/C ratio of 0.43, all of the feed oil converted into the desired product in Run II-24. By keeping the preheat temperature at 690°C and H_2O/C ratio at 2.75, the O_2/C ratio was decreased to 0.39 in Run II-25 to test the catalyst's activity under a more severe steam reforming condition. Again, all of the oil was converted to CO and H_2 in this run. However, when the O_2/C ratio was decreased further to 0.355 in Run II-26, a small amount of oil was observed in the condenser. But the pressure drop across the steam reforming bed was the same throughout the

FIGURE 9

DRY GAS COMPOSITIONS IN STEAM REFORMING BED

RUN II-32

run, indicating that there was no significant coke accumulation in the steam reforming bed. The experimental results for the above three runs are summarized in Table X, and the dry gas compositions at various locations for each run are shown in the Appendix.

The search of the coke and/or the oil breakthrough boundary was continued in Run II-32. After finishing the stability test as described in the last section, the oil feed rate was increased to decrease the O_2/C ratio and, thus, to test these catalysts under a more severe steam reforming condition. Because of the difficulties in controlling the feed rate (the oil pump was operating at its upper limit), the O_2/C ratio was fluctuating between 0.33 to 0.36 during this period (i.e. 24 to 72 hours). As the O_2/C ratio decreased, an oil film was constantly observed in the condensate, but the measured pressure drop across the steam reforming bed was constant until the end of this run. As shown in Figure 10 and Table XI, the increase in pressure drop was small (about 0.2 psig). Since pressure drop is an effective way of measuring the coke accumulation in the steam reforming bed as reported earlier, it may be concluded from this constant ΔP that the coke accumulation in the steam reforming bed was not significant during the course of this experiment. Furthermore, although the unconverted oil was constantly observed in our reactor system during this coke boundary study, coke was not significantly accumulated in our steam reforming bed. This phenomenon indicates that FP-34 is apparently a more coke-resistant catalyst than the commercial G-90C catalyst. However, more experiments are needed to find out the coke boundary of these CP0-2B and FP-34 catalysts.

D. Discussion and Conclusions

The results obtained in these experiments provide the basis for the model to be developed by Physical Sciences. They illustrate several points about ATR development.

- a) The scale-up from the small catalyst screening unit was satisfactory. This provides confidence for further increases in size as would be needed for commercial fuel cells.

TABLE X

AUTOTHERMAL REFORMING OF NO. 2 OIL

SUMMARY OF RUNS II-24, 25, 26

RUN NO.	II-24	II-25	II-26
CATALYST			
CPO	CPO-4 (Pt/Pd)	CPO-4 (Pt/Pd)	CPO-4 (Pt/Pd)
SR	FP-34 (Pt/Rh)	FP-34 (Pt/Rh)	FP-34 (Pt/Rh)
CONDITIONS			
H ₂ O/C	3.10	2.75	2.84
O ₂ /C	0.42	0.39	0.355
TEMPERATURE, °C			
PREHEAT	690	690	690
S.R. TOP (TSRB1)	928	937	917
S.R. MID (TSRB4)	831	809	772
S.R. END (TSRB5)	794	773	742
DRY GAS COMPOSITIONS (MOLE %)			
H ₂	39.79	40.41	41.67
CO	7.89	9.64	9.54
CO ₂	14.68	13.53	13.54
N ₂	37.29	36.02	34.57
CH ₄	0.13	0.19	0.45
C ₂ H ₆	-	-	0.02
C ₃ H ₈	-	-	-
C ₂ H ₄	-	-	-
C ₃ H ₆	-	-	-
OTHERS	-	-	-
EQUIVALENT H ₂	2.10	2.00	1.98
HC CONV. (%)	99.4	99.2	97.9*

* Oil breakthrough was observed.

FIGURE 10

PRESSURE DROP (ΔP) ACROSS STEAM REFORMING BED AND HYDROCARBON (HC) CONVERSION
VS. TIME ON STREAM

TABLE XI

PRESSURE DROP ACROSS THE STEAM REFORMING BED
DURING THE AUTOTHERMAL REFORMING OF NO. 2 OIL

RUN II-32

<u>HOURS ON STREAM</u>	<u>PRESSURE DROP (PSIG)</u>
3	1.3
9	1.3
15	1.3
21	1.3
27	1.3
33	1.3
39	1.3
45	1.3
51	1.3
57	1.4
63	1.4
68	1.5

- b) Both the small and large units gave the same relative ranking between the nickel catalyst and the Pt/Rh catalyst. This lends confidence to the use of a small unit for catalyst screening.
- c) The large unit was not adiabatic and heat was lost from the flanges and the reactor shell. This must be taken into account in the model development when using these results. It also implies that a truly adiabatic unit would perform even better as the steam reforming bed temperatures would be higher. Further experiments are needed to prove this point.
- d) Only a limited amount of parametric studies were carried out due to time limitations. The H_2O/C ratio was essentially constant in these runs and needs further study. Only one batch of No. 2 oil was used. These and other parameters need further study.
- e) It is concluded that this ATR system can operate over a wide range of O_2/C levels primarily due to the good activity of the Pt/Rh catalyst. It permits the investigation of hydrocarbon conversion, oil breakthrough, without the simultaneous problem of carbon accumulation. Therefore, it is a good tool for further research on the autothermal reforming process.

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V. APPENDIX

The following tables (A1 to A11) list the dry gas composition for various runs as a function of time on-stream and bed position.

TABLE A1

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF PROPANE, RUN II-9

(Run II-9; $O_2/C = 0.40$; $H_2O/C = 2.35$)

Hours on Stream	Sample Probe	Temp. °C	% DRY GAS COMPOSITION									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	1	669	41.69	9.29	10.98	37.20	0.06		0.49	-	0.05	-
2	3	655	47.15	8.47	12.16	31.69	0.34		-	-	-	-
3	5	660	46.19	7.32	13.00	32.35	0.96		-	-	-	-
4	3	662	47.19	8.67	12.02	31.69	0.25		-	-		-
5												
6												
7												
8												

TABLE A2

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF NO. 2 OIL, RUN II-10

(Run II-10; $O_2/C = 0.42$; $H_2O/C = 2.60$)

Hours on Stream	Sample Probe	Temp.* °C	% DRY GAS COMPOSITION**									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	5	898	34.31	11.72	11.41	41.61	0.59	0.01	-	0.01	0.05	-
2	3	907	34.73	13.97	9.62	40.92	0.47	-	-	-	-	-
3	5	907	34.96	11.11	11.91	41.22	0.51	-	-	0.01	-	-
4	3	908	35.09	13.61	9.37	40.74	0.42	-	-	-	-	-
5	5	907	35.23	10.57	12.24	41.15	0.53	-	-	0.01	-	-
6												
7												
8												

* Mid bed temperature (TSRB4)

** Unconverted oil observed in the condensate.

TABLE A3

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF PROPANE, RUN II-11

(Run II-11; $O_2/C = 0.47$; $H_2O/C = 2.85$)

Hours on Stream	Sample Probe	Temp. °C	% DRY GAS COMPOSITION									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	1	753	36.69	14.43	7.06	41.01	0.14	-	0.35	0.01	0.04	-
2	3	771	42.78	9.20	11.24	36.46	0.06	-	0.06	-	-	-
3	5	776	42.59	8.16	12.20	36.72	0.07	-	0.05	-	-	-
4	3	778	44.37	8.99	10.98	35.44	0.03	-	-	-	-	-
5	5	778	42.64	8.03	12.36	36.64	0.06	-	0.07	-	-	-
6	3	767	43.12	9.05	11.34	36.18	0.03	-	0.08	-	-	-
7												
8												

TABLE A4

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF NO. 2 OIL , RUN II-13

(Run #13; $H_2O/C = 2.59$; $O_2/C = 0.41$)

Hours on Stream	Sample Probe	Temp* °C	% DRY GAS COMPOSITION **									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	5	859	33.02	12.00	11.47	42.32	0.83	-		0.02	0.02	
2	5	893	33.70	11.77	11.68	41.73	0.79	0.01		0.01	-	
3	5	897	34.48	11.45	11.93	41.08	0.75	0.01		0.01	-	
4	5	896	34.80	10.69	12.36	41.19	0.67	-		0.01	-	
5	3	893	34.07	14.08	9.8	41.18	0.59	-		-	-	
6	3	891	34.56	14.00	9.90	40.64	0.62	-		-	-	
7	5	891	35.57	10.50	12.72	40.34	0.59	-		0.01	-	
8	5	892	35.35	10.46	12.80	40.59	0.52	-		0.01	-	

* Mid bed temperature (TSRB4)

** Unconverted oil observed in the condensate

TABLE A5

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF PROPANE, RUN II-14

(Run II-14; $O_2/C = 0.386$; $H_2O/C = 2.60$)

Hours on Stream	Sample Probe	Temp.* °C	% DRY GAS COMPOSITION									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	1	640	45.97	8.26	12.47	31.72	1.32	-	0.07	-	-	-
2	1	645	46.30	8.67	12.14	31.58	1.04	-	0.06	-	-	-
3	3	651	48.49	7.87	12.88	30.26	0.33	-	-	-	-	-
4	3	661	48.54	8.15	12.58	30.32	0.23	-	-	-	-	-
5	5	665	48.11	7.82	12.92	30.61	0.37	-	-	-	-	-
6	5	668	48.20	7.92	12.80	30.59	0.32	-	-	-	-	-
7	1	670	46.01	10.49	10.80	31.98	0.42	-	0.12	-	-	-
8	1	678	46.08	10.40	10.87	31.95	0.41	-	0.11	-	-	-

* Mid bed temperature (TSRB4)

TABLE A6

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF NO. 2 OIL, RUN II-15

(Run II-15; $O_2/C = 0.43$; $H_2O/C = 2.67$)

Hours on Stream	Sample Probe	Temp.* °C	% DRY GAS COMPOSITION **									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	5	856	38.65	9.50	13.10	38.51	-	-	-	-	-	-
2	5	863	38.82	9.70	12.93	38.36	-	-	-	-	-	-
3	3	866	37.44	11.69	11.48	39.15	-	-	-	-	-	-
4	3	872	37.19	11.77	11.52	39.28	-	-	-	-	-	-
5	1	873	27.24	21.01	4.26	46.38	0.68	0.02	-	0.07	0.03	-
6	1	877	27.32	20.76	4.41	46.37	0.70	0.02	-	0.07	0.03	-
7												
8												

* Mid bed temperature

** No oil observed in the condenser

TABLE A7

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF NO. 2 OIL, RUN II-17

(Run II-17; $O_2/C = 0.413$; $H_2O/C_f = 2.56$)

Hours on Stream	Sample Probe	Temp. * °C	% DRY GAS COMPOSITION **									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	1	813	26.82	21.08	3.95	46.43	0.95	0.04	-	0.31	0.08	0.01
2	5	800	39.64	8.78	14.06	37.22	0.07	-	-	-	-	-
3	5	806	39.55	8.71	14.15	37.31	0.06	-	-	-	-	-
4	5	806	39.94	8.85	14.16	36.78	0.06	-	-	-	-	-
5	1	808	28.45	21.24	4.05	44.91	0.77	0.04	-	0.18	0.06	0.01
6	1	810	28.13	21.14	4.09	45.31	0.73	0.04	-	0.18	0.08	0.01
7												
8												

* Mid bed temperature

** No oil observed in condensate

TABLE A8

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF NO. 2 OIL, RUN II-24

(Run II-24; $O_2/C = 0.42$; $H_2O/C = 3.10$)

Hours on Stream	Sample Probe	Temp. °C	% DRY GAS COMPOSITION									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	6	823	39.76	7.81	14.62	37.44	0.14					
2	1	827	17.23	19.22	3.63	55.80	1.65	0.07	0.02	1.58	0.33	0.08
3	4	829	40.04	9.48	13.60	36.61	0.04	-	-	-	-	-
4	6	831	39.79	7.89	14.68	37.29	0.13	-	-	-	-	-
5	1	831	18.55	19.41	3.62	54.41	1.78	0.06	0.02	1.46	0.24	0.05
6												
7												
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TABLE A9

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF NO. 2 OIL, RUN II-25

(Run II-25; $O_2/C = 0.39$; $H_2O/C = 2.75$)

Hours on Stream	Sample Probe	Temp. °C	% DRY GAS COMPOSITION									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	6	798	39.44	9.28	13.64	36.99	0.34	0.01	-	0.01	0.06	-
2	4	802	40.61	10.75	12.76	35.50	0.15	-	-	-	-	-
3	1	804	12.72	16.98	4.43	59.34	2.09	0.14	0.02	2.83	0.76	0.18
4	3	807	38.17	14.28	10.21	36.83	0.26	0.01	-	-	-	-
5	5	809	40.41	9.64	13.53	36.02	0.19	-	-	-	-	-
6												
7												

TABLE A10

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF NO. 2 OIL, RUN II-26

. (Run II-26; $O_2/C = 0.355$; $H_2O/C = 2.84$) **

Hours on Stream	Sample Probe	Temp. °C	% DRY GAS COMPOSITION									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	6	775	39.86	9.65	13.51	36.14	0.52	0.03	-	0.02	0.05	-
2	5	778	41.27	9.64	13.67	34.83	0.37	0.02	-	-	-	-
3*	1	769	11.20	15.29	5.11	60.66	2.25	0.18	0.033	3.38	1.08	0.29
4	5	771	41.67	9.54	13.54	34.57	0.45	0.02	-	-	-	-
5	6	772	39.65	9.52	13.27	36.47	0.63	0.03	-	0.05	0.05	-
6	3	774	38.51	15.34	9.54	35.82	0.50	0.04	-	0.02	0.04	-
7	4	776	41.27	10.98	12.75	34.42	0.36	0.02				
8												

* Feed rates changed

** Oil breakthrough was observed

TABLE A11

DRY GAS COMPOSITION FOR AUTOTHERMAL REACTIONS OF NO. 2 OIL, RUN II-30

(Run II-30; $O_2/C = .38$; $H_2O/C = 2.57$)

Hours on Stream	Sample Probe	Temp. °C	% DRY GAS COMPOSITION									
			H ₂	CO	CO ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	Σ C ₄
1	6	778	40.22	9.58	13.69	35.85	0.39	0.01	-	-	0.03	-
2	5	781	41.22	9.86	13.39	35.02	0.28	-	-	-	-	-
3	3	780	40.16	13.26	10.99	35.09	0.26	0.01	-	-	-	-
4	1	784	21.83	20.71	3.34	50.72	1.28	0.08	0.01	1.18	0.36	0.10
5	4	786	41.05	11.15	12.48	34.83	0.28	0.01	-	-	-	-
6	5	789	41.35	10.38	13.08	34.73	0.25	-	-	-	-	-
7												
8												

* After 3rd hour, trace of oil was observed in the condenser.