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MASTER

CATALYST AND PROCESS DEVELOPMENT FOR HYDROGEN PREPARATION FROM FUTURE FUEL CELL FEEDSTOCKS

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ABSTRACT

Work continued in the effort to develop catalysts and a process for the production of hydrogen from heavier fuels. Progress was made in developing the calculations required to compare the experimental results from the autothermal reforming of No. 2 oil with those predicted by thermodynamic equilibrium. A computer program called ATR-6 facilitates these calculations.

A prescreening test is being developed to study steam reforming catalysts under controlled conditions with mixtures of pure compounds. A gas chromatograph was installed and some preliminary runs with ethane were made.

A screening test was developed to evaluate steam reforming catalysts under autothermal reforming conditions. During this development work, it was demonstrated that a monolithic CPO catalyst could be started under rich conditions. The catalytic partial oxidation of No. 2 oil produced considerable quantities of olefins (including butadiene) and unreacted oil was also observed.

In preliminary runs it was shown that this small test unit was not adiabatic. These early tests also demonstrated that a rhodium containing catalyst is better for steam reforming olefins than a nickel containing catalyst.

By adding heat to the reformer section in the amount to compensate for heat losses from this small unit, catalysts could be tested under conditions to be expected from an adiabatic rig. By operating at higher space velocities (about 21,000 V/Hr/Vc) it is possible to distinguish among catalysts during a test lasting 5-10 hours.

TECHNICAL SUMMARY

Task 2. Technical Analysis

Following the decision to pursue the development of the autothermal process for producing hydrogen from No. 2 and heavier oils, it was desirable to calculate the composition of the product gas expected at equilibrium for this type of process. These calculations have been summarized in a computer program called ATR-6, which is described in this report. In addition to generating the equilibrium composition for various operating parameters, the program calculates the temperature after the partial oxidation zone and the temperature at the exit of the steam reforming section. It also predicts whether the conditions selected are in the coke producing or coke-free region.

Task 5.1.A Catalyst Screening Using a Microreactor

To better differentiate catalyst performance, the space velocity was increased five-fold in the pressure microreactor which uses ethane steam reforming as the model reaction. As expected, conversion falls [from 99 to 75% at 393°C (740°F)] as the VHSV is increased from 1900 to 10000 hr^{-1}. The hydrogen make remains essentially constant for this increase in space velocity, but both the amounts of CH_4 and CO produced fall. Another operational change was to use pure hydrogen to reduce the samples hopefully assuming that all samples are fully reduced prior to steam deactivating, then measuring conversion.

Two catalysts were evaluated using this new operating procedure. For our baseline sample SF-3B, which contains 15 wt% nickel, rate constants were calculated using the ethane converted at 282°C (540°F), 338°C (640°F) and 393°C (740°F) and assuming a first-order reaction in terms of ethane:

$$k_{obs} = \frac{1}{\tau} \ln \frac{1}{(1-X)}$$

where τ = space time = reciprocal space velocity, and
X = amount of ethane converted.

From the slope of the Arrhenius' plot of ln k_{obs} vs 1/T, an apparent activation energy of 24 kcal/mole was found.

For the second catalyst FP-13, also containing 15 wt% nickel, the apparent activation energy found was 11 kcal/mole using conversions over the temperature range of 393°C (740°F) to 485°C (905°F). Since the temperature ranges differ, direct comparison of catalytic activity between these two samples cannot be made without further experiments.

Task 5.1.B Catalyst Screening Using an ATR Test Unit

A catalyst screening procedure was established during the quarter which can distinguish among steam reforming catalyst samples. The test uses a small sample of catalyst (30 ml) and can demonstrate differences in a short test period (5-10 hours).

During test development several preliminary runs were made which produced some significant observations and results.

1. It was demonstrated that a monolithic, partial oxidation catalyst could be started in the fuel-rich mode. This is significant since small amounts of oxygen can quickly deactivate a nickel type catalyst.

2. Propane and No. 2 oil were partially oxidized over the monolithic CPO section alone. Both fuels showed considerable concentration of olefins in the product gas which will be fed to the steam reforming section. With No. 2 oil some butadiene was detected and unconverted oil was observed in this small rig.

3. Preliminary runs showed rhodium to be more selective to steam reforming olefins than is nickel. The nickel catalysts produced more equivalent hydrogen $[(CO + H_2)/C_{Feed})]$. These runs demonstrated that the small unit is not adiabatic with temperatures about 200°F below those predicted.

4. After modifications to the unit to supply about 200°F more temperature to the steam reforming section, catalysts could be screened under conditions similar to those that may be expected in a full scale adiabatic rig. The effect of steam reforming catalyst space velocity was demonstrated:

Space Velocity, *V/Hr/Vc	10,800	21,600
Hydrocarbon Conversion	97.2	95.6
Dry Gas Composition:		
H_2	37.2	35.4
CO	15.5	16.5
CO_2	11.7	10.9
CH_4	0.78	1.22
C_2H_4	0	0.02

* Based on dry exit gas

Under the higher space velocity conditions, coke was noted throughout the bed within four hours and an increase in pressure drop was noted.

5. Screening test conditions for the steam reforming catalyst were selected for future testing:

O_2/C	0.38
H_2O/C	2.54
Feed	No. 2 Oil
Feed Rate, ml/hr	105
CPO Catalyst Type	Monolith (Pd/Pd)
Volume SR Catalyst, ml	30
Injector Temperature, °F	860°F

REVIEW BY TASKS

PHASE I. PRELIMINARY CATALYST AND PROCESS EVALUATION

Task 2. Technical Analysis

For an autothermal reactor system, the heat generated by partial oxidation reactions is used to sustain the endothermic steam reforming reactions. Engelhard Industries has proposed to study a system with a monolithic catalyst in the partial oxidation section followed by a steam reforming section using pelleted catalysts.

In order to better understand this system and to compare experimental results with those predicted by equilibrium, a computer program called ATR-6 has been written. The program calculates the thermodynamic equilibrium composition of the reactor product, the temperature after the CPO section, and the exit temperature after the steam reforming section.

The ATR-6 program considers the following chemical reactions:

Catalytic Partial Oxidation (CPO):

$$CnHm + \frac{n}{2} O_2 \longrightarrow nCO + \frac{m}{2} H_2 \quad \ldots\ldots\ldots\ldots (1)$$

Steam Reforming Reaction (SR):

$$CnHm + n H_2O \longrightarrow nCO + (n + \frac{m}{2}) H_2 \quad \ldots\ldots\ldots\ldots (2)$$

Methanation Reaction:

$$CO + 3H_2 \xrightleftharpoons{KME} CH_4 + H_2O \quad \ldots\ldots\ldots\ldots (3)$$

Water Gas Shift Reaction:

$$CO + H_2O \xrightleftharpoons{KWGS} CO_2 + H_2 \quad \ldots\ldots\ldots\ldots (4)$$

Methane Cracking Reaction:

$$CH_4 \xrightleftharpoons{KC} C + 2H_2 \quad \ldots\ldots\ldots\ldots (5)$$

Carbon Monoxide Disproportionation Reaction:

$$2CO \xrightleftharpoons{KCCO} C + CO_2 \quad \ldots\ldots\ldots\ldots (6)$$

Reaction (1) is exothermic and heat (called HPOR) will be generated from this reaction; reaction (2) is endothermic and heat (called HASR) is consumed by this reaction. For reactions (1) and (2), they are treated as irreversible reactions in the ATR-6 programs. To calculate the equilibrium composition, reactions (3), (4), (5) and (6) are considered to be reversible reactions and the final composition must satisfy simultaneously the equilibrium constants KME, KWGS, KC and KCCO as described below. Here, KME, KWGS, KC and KCCO are equilibrium constants for reactions (3), (4), (5), and (6) respectively.

The flow chart of the ATR-6 program is shown in Figure 1. Briefly, the inputs to this program are reactant inlet temperature, reactor pressure, molecular formula of the fuel (CnHm), H_2O/C molar ratio and O_2/fuel molar ratio. Several options are available with this program in the form of a series of questions: (1) Is nitrogen present in the feed? (2) Is excess carbon (graphite) always present in the reactor system? (3) Do you want to calculate the adiabatic reforming exit temperature (TH)? (4) Do you want to calculate the temperature after the CPO reaction (TPOR)? After all the inputs and options are specified, the ATR-6 program will first calculate the equilibrium constants, and then, calculate the first trial value (NMOL) from the inlet O_2/fuel and H_2O/C ratios. Here, NMOL is a concentration vector which consists of moles of H_2O, CH_4, CO_2, CO, H_2, N_2, CnHm and O_2 present in the gas phase. To calculate the equilibrium composition, the ATR-6 program will revise the above initial NMOL by using a step by step correction method with the equilibrium constants KME, KWGS, KC and KCCO as described in the following sections.

To start the calculation, the ATR-6 program first finds a revised NMOL (a new NMOL) which satisfies the equilibrium constant KME. In other words, a new set of concentrations for CO, H_2, CH_4 and H_2O which satisfies the equilibrium constant KME is calculated by a "Regula Falsi" iteration method, and this new set of concentrations is then used to correct for the initial values of NMOL. Secondly, the above new NMOL is further revised by finding another set of NMOL which satisfies the equilibrium constant KWGS, i.e., solves for a new set of concentrations for CO, CO_2, H_2O, and H_2 by a quadratic equation. Thirdly, to check for the carbon formation by reaction (5), the ratio of PH_2^2/PCH_4 (called $CDCH_4$) is calculated from NMOL. If $CDCH_4$ is less than KC, the forward methane cracking reaction is favored and, thus, a new set of NMOL is found by calculating a new set of concentrations for H_2 and CH_4, so that the equilibrium constant KC is satisfied. If $CDCH_4$ is greater than KC, the forward cracking reaction is not favored and NMOL will not be corrected by KC. Similarly, the correction of NMOL by the CO disproportionation reaction is treated the same way as for the methane cracking reaction.

After the concentrations of the initial trial values of NMOL are revised by the equilibrium constants as described previously, the resultant NMOL will be tested by the following two conditions: (1) Test conditions are used to see if the calculated NMOL satisfies simultaneously the equilibrium constants KME and KWGS. (2) If carbon is formed, the values of $CDCH_4$ and CDCO calculated from this NMOL have to be equal to those of KC and KCCO. If carbon is not formed, the values of $CDCH_4$ and CDCO have to be greater than those of KC and KCCO. When the above two test conditions are satisfied, this NMOL would be considered as the thermodynamic equilibrium composition, otherwise, this NMOL is sent back to the iteration loop for further corrections, as shown in the flow chart.

To calculate the temperature after the CPO reaction (TPOR) the heat of the partial oxidation (HPOR) is first calculated from the inlet conditions, and TPOR is calculated by making a heat balance across the CPO catalyst section using a "Regula Falsi" iteration method. Similarly, the adiabatic exit temperature (TH) of the autothermal reactor can be calculated by making overall heat and material balances across the whole ATR reactor, as shown in the flow chart.

Application of the ATR-6 Program:

Although this ATR-6 program is still in the development stage, the present program can be used to do the following calculations:

a) Steam Reforming of Hydrocarbons:

For the conventional steam reforming process, heat is being transferred into the reactor to maintain the steam reforming catalyst at a constant temperature, pressure, type of hydrocarbon and H_2O/C molar ratio, the thermodynamic equilibrium composition of the product gas can be calculated by this ATR-6 program as shown in Table I. Since the carbon monoxide produced from this reforming reactor can later be converted into hydrogen by low temperature and/or high temperature water gas shift catalysts, 1 mole of carbon monoxide produced here can be considered to be equivalent to one mole of hydrogen. Therefore, the equivalent hydrogen ratio, which is defined as the molar ratio of total CO and H_2 produced to the total carbon atoms in the feed is also shown in the table. As indicated in Table I, at higher reforming temperatures the equivalent hydrogen ratio is generally higher.

b) Coke Formation:

The ATR-6 program can be used to predict thermodynamically whether or not coke is formed under a specified condition. For example, at 1600°F, 1 atm, C_9H_{20}, H_2O/C molar ratio of 1 and O_2/C molar ratio of 0, the ATR-6 program predicts coke formation under the above conditions as shown in Table II. However, this program also predicts that coke will not be formed if the reformer temperature is increased from 1600°F to 1800°F.

Although this program is capable of predicting whether or not a given experimental condition is in the coke formation region, the current ATR-6 program does not automatically search for coke boundaries.

c) Catalytic Partial Oxidation:

For the catalytic partial oxidation reaction, the O_2/C ratio is 0.5 as described in reaction (1). Since this process produces heat from this reaction, the exit temperature (TPOR) will be higher than the inlet temperature. As shown in Table III, the exit temperature and the equivalent hydrogen ratio can be calculated by this ATR-6 program if the inlet conditions are specified.

d) Autothermal Reactor:

The autothermal reactor system is to use the heat generated by the upstream partial oxidation reaction for the downstream endothermic steam reforming reactions. For a given preheat temperature, reactor pressure, molecular formula of hydrocarbon (CnHm), O_2/C molar ratio and H_2O/C molar ratio, this ATR-6 program can be used to calculate the temperature after the CPO reaction, the adiabatic temperature after the steam reforming catalyst and also the equivalent hydrogen ratio. The results obtained from several sample calculations for propane (C_3H_8) and n-nonylbenzene ($C_{15}H_{24}$) are listed in Table IV.

Comparison of the equivalent hydrogen ratios calculated by this ATR-6 program for catalytic partial oxidation and for the autothermal reactor system can be made from both Tables III and IV. Under the same (reactor) inlet conditions, the equivalent hydrogen ratios produced by autothermal reactor are higher than those produced by catalytic partial oxidation. Therefore, the results indicate that autothermal reforming is a more efficient process than partial oxidation.

e) Future Improvements:

As described previously, the equilibrium composition predicted by this ATR-6 program are calculated by a trial and error method. Occasionally, problems have been found in converging to the final solution during one of the iteration steps. Therefore, to assure obtaining final solutions all the time, these covergence problems should be minimized.

Although this ATR-6 program can predict thermodynamically whether or not coke will form under a given set of experimental conditions, it does not automatically search for the coke boundaries. To search for the coke boundaries, iterations on one of the parameters such as reactor temperature or H_2O/C ratio must be included in this program. Therefore, further improvements have to be made in order to use this program to predict the coke boundaries.

PHASE II. CATALYST DEVELOPMENT

Task 4. Catalyst Preparation

The catalysts in the subsequent tasks were prepared by Engelhard as part of their cost contribution to this contract.

Task 5.1.A Catalyst Screening Using a Microreactor

Work continued in our effort to develop a prescreening test using pure compounds. The steam reforming of ethane was selected as preliminary method of screening samples which had been previously treated with a steam/hydrogen mixture at high temperatures.

To differentiate the differences in activity among samples, a five fold increase in space velocity was selected. That is, the space velocity was increased from 1900 hr^{-1} to 10,000 hr^{-1}. The effect of this increase was demonstrated on an experimental catalyst, FP-13, which contains 15% by weight of nickel on stabilized alumina. The conversion of ethane, as monitored by gas chromatography, was measured and reported in Table V.

These results show that higher space velocity converts less ethane as expected for this first order reaction. However, the amount of hydrogen produced remains nearly constant as space velocity varies five-fold.

The effect upon other gases produced showed methane and carbon monoxide concentration decreased as VHSV is increased while CO_2 remains relatively constant. The lower C_2H_6 conversion is expected since at higher VHSV the reactant contact time over the catalyst is shorter. A temperature rise of 30-45°F was also noted as the VHSV was lowered which is unexpected since more ethane is reacting and steam reforming is an endothermic reaction. The temperature rise may be caused by the lower gas velocity passing over the sample which removes less heat and/or the rapid increase in methane production which is exothermic.

The results in Table V show the importance of monitoring the amount of ethane and gaseous products. Determination of just the hydrogen produced does not differentiate catalyst activity.

Increasing the percentage of hydrogen used during the PMR reduction procedure (2 to 100% after the bed temperature reached 960°F) showed slightly higher amount of hydrogen produced. Unfortunately, this observation was noted prior to the GC being on line and no other gaseous products were analyzed. This result, however, does indicate that more strigent reduction techniques prior to steam reforming may be necessary to assure that all catalysts are fully reduced before deactivating and testing.

Sample SF-3B (15 wt% Ni/stabilized Al_2O_3, 1/16 inch extrudate) was evaluated for ethane conversion via the PMR after being reduced and steam aged (960°F/3 hours 100% H_2/1700°F/16 hours at $H_2O/H_2=3$). Product gas was analyzed via gas chromatography after thermal equilibration at 540, 640, and 740°F as shown in Table VI. Assuming a first order rate equation ($-dc/dt = kc$) and considering t as space time (reciprocal space velocity) the activation energy (Ea) was calculated from the Arrhenius plot shown in Figure 2. The slope of the line in Figure 2 is -12000 and Ea has a value of 24Kcal/mole as determined by slope = -Ea/R. This activation energy, within our reaction temperature range (540-740°F) is typical of a catalyst having large pores in which diffusion through the pores is not rate limiting as pointed out by Wheeler[1]. The reaction can be considered intrinsically controlled when slope values are large as described by Wicke's[2] for kinetic regimes of an Arrhenius type diagram.

A carbon atom mass balance for SF-3B at 540, 640, and 740°F showed 84, 90 and 83 percent respectively for carbon accountability as reported in Table VI. Products from the dehydrogenation of ethane such as acetylene or ethylene were not detected, therefore the unaccounted carbon most likely is catalyic coke forming on the sample or in the preheat section. No attempt was made at this time to analyze for coke on the used sample.

[1] Wheeler, A., Advances in Catalysis, Vol. III, (1951)

[2] Wicke, E., Chem.-Ing.-Tech., <u>29</u>, 305 (1957)

Results on FP-13 (15 wt% Ni on stabilized Al_2O_3) evaluated after thermal equilibration at 740, 810 and 905°F (Table VII) showed a slope equal to -5540 as derived from the Arrhenius plot in Figure 3. The activation energy determined from the slope is 11 Kcal/mole and is similar to that observed by Wheeler[1] for catalysts having small pores. Hence, we can consider the reaction to be pore diffusion controlled within the limits of our temperature range (740 to 905°F). Ideally to prove pore diffusion in the above case, an experiment using smaller particle size material should be performed.

Task 5.1.B. Catalyst Screening Using an ATR Test Unit

The work on this task during the quarter centered on developing a test procedure whereby catalyst samples could be screened for the steam reforming section of the proposed Engelhard ATR system. In the testing to be described, the composition of the monolithic CPO catalyst remained constant. The steps taken to develop a test procedure were as follows:

1. Start-up procedures involving the fuel rich mode.
2. Determine the products after the CPO section using:
    a) propane
    b) No. 2 oil
3. Preliminary tests comparing a nickel catalyst with a rhodium catalyst.
4. Modifications to increase the temperature in the steam reforming section.
5. Selection of test conditions.

Details of each step are described below.

The experimental set-up used is illustrated in Figures 4, 5 and 6. Figure 4 is the schematic flow diagrams. More details are shown in Figure 5 which shows the injector used for admitting the vaporized No. 2 oil into a stream of a hot mixture of water and air. Figure 6 shows the location of the catalytic partial oxidation (CPO) catalyst and the steam reforming catalyst inside the ATR reactor. In this design, CPO catalyst is equivalent to about 22 channels of a 400 channels per square inch monolith. The total feed rate of the reactants is adjusted so that the mass velocity across this CPO catalyst is approxmately the same as the velocity used previously for the CPO experiments. After the CPO catalyst, the CPO product gas and the residual reactants are further steam reformed to produce CO and H_2 over a steam reforming catalyst in the second stage of the ATR catalyst bed. Again, the mass velocity across this steam reforming catalyst is approximately the same as the one reported previously in our hydrogen assisted steam reforming experiments.

1. Start-Up Procedures

Since the commercial steam reforming catalysts are mostly Ni/Al_2O_3 catalysts, the presence of oxygen in the reacting stream could possibly cause the metal to form nickel spinel and thus cause the loss of its original activity. Therefore, the oxygen leakage from the CPO catalyst should be kept at a minimum level. For this reason, the commissioning runs for this ATR unit were used to develop a reliable start-up procedure, so that all commercial steam reforming catalysts can be tested in this ATR unit.

The start-up procedure developed is listed in Table VIII. By starting with a light hydrocarbon like propane, some hydrogen is produced by steam reforming. Thus rich conditions are assured as air is admitted slowly. Oil flow is established before the propane is shut off to assure a steady transition.

2. Determining the Products of Reaction in the CPO Section

During these preliminary runs the products formed in the CPO section were determined for both propane and NO. 2 oil. This information provides a rough indication of the composition that must be reformed by the steam reforming catalyst.

Table IX summarizes the results obtained for the CPO reaction between propane and air. During the experiment, the flow rates of the above two reactants were monitored by rotameters (but the rates were not calibrated at that time), the water feed rate by a volumetric burette and the dry gas composition by a gas chromatograph. Except for sample 2, the oxygen leakage from the CPO unit was below the detectable limit of the GC analysis as listed in Table IX. These results indicate that under various feed ratios all oxygen was approximately reacted either with propane or with the H_2 and CO produced by the CPO reactions. Furthermore, the outlet temperature could be increased from the inlet temperature of about 420°C to a temperature above 820°C. Therefore, these preliminary results indicate that starting the CPO reaction of propane under fuel rich conditions can be accomplished.

Table X shows the results obtained from a CPO reaction of No. 2 oil with air (in the presence of steam). The experiment was first started with a CPO reaction of propane. When the CPO product temperature was increased from about 420°C to 700°C, No. 2 oil was admitted into the reactor and, subsequently, propane was stopped. For this experiment, the CPO reaction of No. 2 oil was run for about 5½ hours with no apparent increase in pressure drop across the CPO catalyst bed, and the outlet temperature was gradually increased to 775°C when the feed rates were maintained constant. The dry gas compositions as analyzed by a gas chromatograph were approximately the same during the whole run, indicating that the reaction was close to the steady state condition. However, about 0.8% of oxygen breakthrough was monitored from this CPO catalyst bed, and the product temperature was still too low for the downstream reforming reaction (the inlet temperature to the steam reforming zone should be at about 930°C). Hence, higher feed rates for each reactant were used in subsequent experiments so that higher heat input could be produced.

During this run, some smoke-like product was observed in the exit gas (probably unreacted oil aerosol droplets), and the residual C_1 to C_5 hydrocarbons are as listed in Table X. Note that the major gaseous C_1 to C_5 hydrocarbons from this CPO reaction of No. 2 oil were ethylene, propylene, butadiene and methane. Similar product compounds were also observed for the CPO reaction of propane operated under the fuel rich conditions. Therefore, the downstream steam reforming catalyst in this ATR reactor should have good activity for a broader range of hydrocarbons including C_1 to C_5 compounds as well as unreacted oil.

Although it would be desirable to monitor the exit stream from the CPO unit all the time, the small size of this test unit precludes inserting a proble. This will be considered during the design of a larger, adiabatic rig.

3. Prelminary ATR Tests to Compare a Nickel Catalyst with a Rhodium Catalyst

Due to reactant channeling through the monolithic catalyst, it is possible to have oxygen breakthrough from the CPO unit. This trace oxygen can probably cause the activity decline for the downstream supported nickel catalyst. To prevent damage to the Ni catalyst, a 0.5% Pt/Al_2O_3 catalyst was loaded between the CPO and the SR catalysts and was used as a oxygen scrubber. For example, for run #7205, three catalysts (i.e., CPO, Pt/Al_2O_3 and 1% Rh/Al_2O_3) were loaded into the ATR reactor. To start the run, the SR catalyst was first reduced in situ for about ½ hour with the gases produced from the upstream CPO reaction of propane, and the No. 2 oil was subsequently admitted into the reactor to replace propane when the SR catalyst temperature was at about 700°C. The reaction was allowed to reach a steady state condition. The feed rates for water and oil under steady state conditions are reported in Table XI, but the air flow rate was not reported because the rotometer had not been calibrated at that time.

After the reactor, the condensable products were collected and the volume of total dry product gases measured by a dry test meter and its composition by gas chromatography. The experimental conditions and results are reported in Table XI and XII respectively.

During this run, the pressure drop across the catalyst bed was not increased, indicating that coking was not significant during the 7 hour run. Furthermore, except for two temporary disturbances due to fluctuation of the feed rates, the temperature profiles for the catalyst bed were constant and, thus, a steady state operation was obtained.

For run #7208, Engelhard's SF-3B catalyst was used to replace the Rh/Al_2O_3 sample as the steam reforming catalyst. In this run, the same start up procedure as the one described previously was used, and the experimental conditions and dry gas composition are reported in Tables XI and XIII, respectively. Again, constant reactor temperature profiles with no apparent coke build up were observed over about an 8 hour period, and thus a steady state reaction condition was obtained.

For run #7205 (as shown in Table XII), about 39% of CO plus H_2 was measured in the product stream. Some hydrocarbon breakthrough was detected and a trace of wax was found in the collector. For run #7208 (Table XIII), about 45% of CO plus H_2 was measured, some hydrocarbon breakthrough was detected and a trace of oil was found in the collector. By comparing the results (Table XIV) these preliminary data indicate that, as compared to SF-3B catalysts, the Rh/Al_2O_3 catalyst was found to produce smaller amounts of total CO and H_2, a smaller amount of olefins (C_2H_4 and C_3H_6) and a larger amount of paraffins (CH_4 and C_2H_6).

Although some interesting observations were made during these two runs concerning nickel and rhodium catalysts, the conditions are not favorable for screening catalysts for the steam reforming section. The O_2/C level was too high (0.47) and the steam reforming bed temperature was too low (1400°F). Because of the danger of cracking No. 2 oil before it enters the CPO section, it was considered prudent not to increase the preheat temperature. With higher steam reforming bed temperatures the trace amount of unconverted oil could be reacted and the equivalent hydrogen content (i.e., H_2 + CO) could be increased.

4. Modifications Required and Made

The two preliminary runs described above demonstrated a limitation with the small test unit being used. The temperatures were far below those predicted for an adiabatic reactor and the desire was to lower O_2/C ratio in order to increase the amount of conversion done in the steam reformer. Comparing the data from run #7205 (Table XI) with the values predicted by computer program ATR-6 shows the extent of heat loss from the small test unit:

Parameter	Test Data Run #7205	Predicted ATR-6
O_2/C	0.47	0.47
H_2O/C	2.54	2.54
Feed	No. 2 oil	$C_{15}H_{24}$
Injector Temp, °F	≈900	1200
Temperatures: °F		
After CPO	1485	1951
Mid SR Bed	1418	-
Exit SR Bed	1296	1980

The ATR-6 program would not converge below 1200°F. However, the results indicate roughly that the inlet to the SR bed (temperature after CPO) may be as much as 200°F low.

To prevent this heat loss, electrical heating was applied to the steam reforming zone.

5. Selection of Test Conditions

Following modifications to the unit, two runs were made. In run 7228, three catalysts [monolithic CPO, pelleted CPO (0.5% Pt/Al_2O_3) and SF-3B (15% Ni/Al_2O_3, 50 ml)] were loaded into the reactor as shown in Figure 6. The catalysts were reduced overnight in flowing hydrogen at about 500°C. After reduction, the reactor temperature was brough to about 900°C in the reducing condition with air, propane and water as the reactants. After the temperature stabilized, No. 2 oil was then admitted into the reactor and the reactions were allowed to reach steady state. The composition of the dry product was analyzed each hour by a gas chromatograph and the total amount of dry gas product was measured by a dry test meter.

The pelleted CPO catalyst used in these experiments was positioned above the steam reforming section to act as a safeguard in case some oxygen broke through the monolithic CPO unit. The 5ml of Pt/Al_2O_3 used in this section would not likely contribute to the steam reforming reaction due to the high space velocity in this zone (108,000 hrs^{-1} VHSV based on exit gas).

At an O_2/C ratio of 0.368 (calculated from the N_2 balance), H_2O/C ratio of 2.34, 1 atm, injector temperature of ≈860°F (≈460°C) and steam reforming temperature of ≈1600°F, approximately steady state reaction condition were achieved for about 9 hours with no noticable pressure increase in the reactor inlet, as indicated by the dry gas composition (see Table XV). However, some coke was found on the surfaces of the flow distributor (i.e., the expansion cone) and the thermocouple well located in the steam reforming section, and also on the top portion of the steam reforming catalyst bed in between the catalyst particles.

In run 7230 (Table XVI), a 25ml sample of SF-3B was diluted with the same amount of T-61 alpha Al_2O_3, and was loaded into the reactor as described in run 7228. At an O_2/C ratio of 0.375, H_2O/C ratio of 2.28, approximately steady state reaction conditions were achieved initially, but the inlet pressure started to increase after about three hours on stream. The pressure increase was due to coke formation found at the top of the steam reforming bed. As compared to run 7228, more severe coke formation in this run was found, which most likely was due to temperatory feed rate fluctuations and also poor temperature control associated with this run.

The results of the two runs can be summarized as follows:

	Run # 7228	Run # 7230
Volume SR Catalyst, ml	50	25
Catalyst	SF-3B	SF-3B
O_2/C	0.368	0.375
H_2O/C	2.34	2.28
Space Velocities:* V/Hr/Vc		
Through CPO Section	112,000	112,000
Through SR Section	10,800	21,600
Injector Temperature, °F	860	860
Mid SR Bed Temperature, °F	1584	1602
Dry Gas Composition, %		
H_2	37.2	35.4
CO	15.5	16.5
(H_2 + CO)	52.7	51.9
CO_2	11.7	10.9
CH_4	0.78	1.22
C_2H_4	0	0.02
Carbon Conditions	In ½ SR Bed	Plugged
Hydrocarbon Conversion	97.2	95.6

*Based on the dry exit gas rate of 540 lph. Oil feed rate in both cases about 105ml/hr (88g/hr). The WHSV through the SR section is about 2.0 and 4.0 hrs^{-1} for runs 7228 and 7230, respectively.

With about 30ml of steam reforming catalyst it should be possible to distinguish among catalysts by the following criteria:

1. Yield of $(H_2 + CO)/C_F$ or equivalent hydrogen.

2. Hydrocarbon conversion, $(CO + CO_2)/(CO + CO_2 + CH_4 + nC_nH_m)$.

3. Coke formation by:

   observation after the run;
   pressure drop increase

4. Tendency to age over 5 hours.

GOALS FOR NEXT QUARTER

1. Continue to define a prescreening test suitable for the ATR type system.

2. Using the ATR screening test described above, search for catalysts to operate coke free with minor residual hydrocarbon breakthrough.

TABLE I

EQUILIBRIUM COMPOSITION FOR STEAM REFORMING OF HYDROCARBONS

(1 ATMOSPHERE, H_2O/C MOLAR RATIO = 2.0)

Hydrocarbon	Temp. (°F)	% Composition					Equivalent Ratio
		H_2O	CH_4	CO_2	CO	H_2	$(CO + H_2)/C_F$
CH_4	800	48.19	23.96	5.35	0.27	22.23	0.76
	1400	15.98	0.39	4.57	15.20	63.87	3.92
	1600	16.53	0.03	3.51	16.47	63.46	3.99
	2000	17.65	0.00	2.35	17.65	62.35	4.0
C_3H_8	800	47.41	23.48	9.99	0.44	18.68	0.56
	1400	17.53	0.32	6.01	16.90	59.25	3.28
	2000	19.83	0.00	3.25	19.83	57.09	3.33
$C_{15}H_{24}$	800	45.51	22.46	15.08	0.60	16.35	0.45
	1400	18.98	0.25	7.72	18.48	54.58	2.76
	1600	20.15	0.02	6.20	20.11	53.53	2.80
	2000	21.93	0.00	4.38	21.93	51.75	2.80

TABLE II

PREDICTION OF COKE FORMATION DURING STEAM REFORMING OF HYDROCARBONS

Hydrocarbon	Temp. (°F)	H_2O/C	Pressure Atm	O_2/C	Coke Formation
C_3H_8	1600	1.0	1	0	Yes
	1800	1.0	1	0	No
C_9H_20	1600	1.0	1	0	Yes
	1800	1.0	1	0	No

TABLE III

EQUIVALENT HYDROGEN YIELD FOR THE PARTIAL OXIDATION OF HYDROCARBONS AS PREDICTED BY THERMODYNAMIC EQUILIBRIUM

Hydrocarbon	O_2/C	H_2O/C	Preheat Temp. (°F)	TPOR* (°F)	Equivalent H_2 $(CO + H_2)/C_F$
C_3H_8	0.5	2.0	1000	1577	2.33
	0.5	2.0	1400	1954	2.33
	0.5	2.0	1800	2343	2.33
$C_{15}H_{24}$	0.5	2.0	1400	2255	1.8
	0.5	2.0	1800	2636	1.8

* TPOR is the temperature after partial oxidation reaction.

TABLE IV

THE EQUIVALENT HYDROGEN FOR THE AUTOTHERMAL REACTION OF PROPANE AND n-NONYLBENZENE

Hydrocarbon	O_2/C	H_2O/C	Preheat Temp. (°F)	TPOR* (°F)	TH* (°F)	Equivalent H_2 $(CO + H_2)/C_F$
C_3H_8	0.433	2.0	1000	1526	1455	2.46
	0.433	2.0	1400	1903	1803	2.47
	0.433	2.0	1800	2293	2170	2.47
	0.333	2.0	1600	2014	1590	2.67
$C_{15}H_{24}$	0.38	2.54	1200	1845	1686	2.04
	0.38	2.54	1400	2041	1862	2.04
	0.38	2.54	1600	2231	2045	2.04
	0.35	2.54	1200	1813	1576	2.10

*TPOR and TH ~~or~~ are the temperature after partial oxidation and the adiabatic reformer exit temperature respectively.

TABLE V

Space Velocity Effect and Reproducibility Check for FP-13 (15 wt% Ni on Stabilized Al_2O_3)

VHSV $Hr.^{-1}$	Temp. °F	Ethane Converted Percent	Percent Product Gas Composition			
			H_2	CH_4	CO	CO_2
10,000	740	72.3	12.5	9.0	.14	4.54
10,000	740	74.3	12.1	9.4	.15	4.52
1,900	785	99.1	10.3	12.4	.24	4.41
10,000	740	73.2	12.2	9.0	.13	4.40
1,900	770	97.8	11.9	11.7	.22	4.75

Conclusions:

- Good Reproducibility
- Increased severity (lower VHSV) shows expected trend in conversion.
- Must monitor C_2H_6 converted plus gaseous products, not just H_2 produced.

TABLE VI

Ethane Steam Reforming of SF-3B
(15 wt% Ni on Stabilized Al_2O_3)

Reaction Temp. °F	C_2H_6 Feed* Converted Percent	Percent Product Gas Composition				Carbon-Atom Balance Percent
		H_2	CH_4	CO	CO_2	
540	4.8	0.6	0.76	-	0.03	84
640	39.0	4.5	5.2	-	1.7	90
740	84	11.3	10.7	0.12	3.1	83

Reactor Conditions

In situ reduction @ 930-970°F/3-4 hrs. 100% H_2
Steam aging @ 1700°F/17 hrs., $H_2O/H_2 = 3$
Activity @ VHSV = 10,000 hr^{-1}, $H_2O/C = 4$

* Feed Gas ≈ 10% C_2H_6 + 2% H_2 + N_2 Balance

TABLE VII

Ethane Steam Reforming of FP-13
(15 wt%Ni on Stabilized Al_2O_3)

Reaction Temp. °F	C_2H_6 Feed* Converted Percent	Percent Product Gas Composition H_2	CH_4	CO	CO_2	Carbon-Atom Balance Percent
740	72.3	12.5	9.0	0.14	4.5	93
810	87.8	19.4	8.9	0.44	6.2	87
905	97.0	28.1	6.4	1.59	7.6	79

Reactor Conditions

In situ reduction @ 930-970°F/3-4 hrs. 100% H_2
Steam aging @ 1700°F/17 hrs., $H_2O/H_2 = 3$
Activity @ VHSV = 10,000 hr^{-1}, $H_2O/C = 4$

* Feed Gas = 10% C_2H_6 + 2% H_2 + N_2 Balance

TABLE VIII

START UP PROCEDURES FOR THE ATR CATALYST SCREENING UNIT

1. Load CPO catalyst in the first stage and steam reforming catalyst in the second stage of the reactor tube.

2. Insert the reactor tube into the furnace block and pressure test with nitrogen.

3. Purge the reactor with nitrogen at 2CFH for about 10 minutes.

4. With nitrogen flowing, increase the reactor temperature to 350°C. Then gradually increase the temperature to 500°C at 50°C per hour. Line out at 500°C for ½ hour.

5. Stop the N_2 flow and start H_2 flow at 2 CFH. Reduce the catalyst in pure H_2 for 4 hours at 500°C.

6. Turn all the heaters on and set as follows:

Water Heater	205°C (400°F)
Air Heater	320°C (600°F)
Oil Heater	410°C (750°F)
Main Preheater	710°C (1310°F)

7. Increase the main preheater to 900°C (1652°F)

8. Admit water to the reactor at the required rate.

9. Admit propane to the reactor while H_2 is still flowing.

10. Stop H_2 flow and quickly start N_2 flow at 2 CFH. After 5 minutes, slowly admit air into the reactor. Watch the temperature rise across the CPO unit. Stop N_2 flow and slowly increase air flow to the specified level.

11. When temperatures line out at 900°C (1652°F) start the No. 2 oil pump.

12. Cut off propane feed.

13. Line out operations at the desired level.

TABLE IX

DRY GAS COMPOSITION FROM THE CATALYTIC PARTIAL OXIDATION OF PROPANE

Sample No.	Temp.	Dry Gas Composition, Mole %									
	(°C)	H_2	CO	CO_2	N_2	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	O_2
1	725	1.48	3.31	14.82	79.98	0.22	-	0.05	0.06	0.08	-
2	760	0.45	4.36	11.43	81.32	0.62	-	0.10	0.25	0.09	1.37
3	890	2.46	4.75	12.90	79.27	0.45	-	-	0.10	0.06	-
4	870	3.80	10.65	10.25	73.69	1.30	-	-	0.26	0.05	-
5	865	6.55	15.68	7.10	67.16	2.43	-	0.05	0.95	0.08	-
6	845	6.65	17.11	5.83	64.26	3.60	-	0.08	2.29	0.15	-
7	820	7.32	17.54	4.87	60.88	4.65	0.19	0.25	3.86	0.39	-

Feed Rate: The rotometer reading for each sample were:

(1) Air @ 6.5 (100 psig), C_3H_8 @ 6.7 (60 psig)
(2) Air @ 11.5 " " C_3H_8 @ 4.5, H_2O @ 200c.c/hr.
(3) Air @ 10.5 " " C_3H_8 @ 4.5, H_2O @ 200c.c./hr.
(4) Air @ 10.5 " " C_3H_8 @ ≈8.0, H_2O @ 200c.c./hr.
(5) Air @ 10.5 " " C_3H_8 @ 10.0, H_2O @ 200c.c./hr.
(6) Air @ 10.5 " " C_3H_8 @ 12.0, H_2O @ 200c.c./hr.
(7) Air @ 8.5 " " C_3H_8 @ 15.0, H_2O @ 200c.c./hr.

TABLE X

DRY GAS COMPOSITION FROM THE CATALYTIC PARTIAL OXIDATION OF NO. 2 OIL

Sample No.	Temp. (°C)	C_5^- Dry Gas Composition, Mole %													
		H_2	CO	CO_2	O_2	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4	C_3H_6	$C_4^=$	C_4H_6	C_5^+
1	725	1.46	7.57	9.82	1.23	74.27	1.57	0.11	0.24	0.01	2.43	0.83	0.21	0.25	a
2	750	1.98	10.68	8.86	0.80	71.89	1.91	0.12	0.05	0.02	2.67	0.69	0.12	0.21	a
3	755	2.12	11.98	8.35	0.71	71.06	2.03	0.13	0.04	0.02	2.68	0.60	0.10	0.19	a
4	770	2.33	12.68	8.07	0.79	70.45	2.13	0.12	0.04	0.01	2.61	0.54	0.06	0.16	a
5	775	2.48	14.11	7.48	0.80	69.69	2.24	0.10	0.03	0.01	2.46	0.43	0.05	0.12	a
6															

a - Unreacted oil present in exit gas

Flow Rates: Air @ 8.0 (≈ 120° psig), oil @ 67 c.c./hr. and
H_2O @ 176 c.c./hr.

TABLE XI

Preliminary Results and Operating Conditions for Autothermal Reactor System

Catalysts	Temperatures(1) (°C)				Feed Rate (cc/hr)			Product
	Injector	CPO	SR	Exit	Oil	H_2O	Air	(Ft^3/hr)
Run 7205 (1) CPO + Pt/ Al_2O_3 + Rh/ Al_2O_3	470	807	770	702	97	263	NA(3)	19.95
(2) CPO + Pt. Al_2O_3 + SF-3B Run 7208	463	765	750	690	95	254	NA(3)	20.31(2)

(1) Temperatures measured at oil injector, after CPO catalyst, middle of SR catalyst and 1" after SR catalyst.

(2) Recalibration of dry test meter required.

(3) The feed rate for air was note calibrated.

TABLE XII

Product Composition for Autothermal Reaction Over 1% Rh/Al_2O_3 and CPO Catalysts (#7205)

Sample No.	Temp.(3) (°C)	% Dry Gas Composition(2) H_2	CO	CO_2	O_2(1)	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4	C_3H_6	C_4	C_4H_6
1	662	20.8	6.3	13.6	0.8	58.3	0.2							
2	740	23.0	3.9	15.1	0.8	57.4								
3	760	29.2	10.3	14.5	0.6	44.0	1.3	0.03						
4	765	28.3	10.5	14.2	0.6	44.9	1.3	0.06			0.04	0.01		
5	770	27.7	11.4	13.8	0.6	45.3	1.3	0.07			0.07	0.02		
6	775	27.7	11.3	13.8	0.6	45.3	1.2	0.06			0.05	0.01		
7	775	27.6	11.7	13.4	0.6	45.2	1.3	0.08			0.08	0.02		

(1) An oxygen analyzer will be used in future work.

(2) Trace of wax was observed in the condenser.

(3) Temperature after CPO was ≈810°C.

TABLE XIII

Product Composition for Autothermal Reaction Over SF-3B (15%Ni/Al_2O_3) and CPO Catalysts (#7208)

Sample No.	Temp(3)	% Dry Gas Composition(2)												
	(°C)	H_2	CO	CO_2	O_2(1)	N_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4	C_3H_6	C_4	C_4H_6
1	710	23.8	15.8	10.4	0.6	48.0	1.0	0.05			0.26	0.05		
2	735	24.6	15.8	10.6	0.6	47.3	0.9	0.06			0.17	0.02		
3	746	24.8	15.5	10.6	0.6	47.2	1.0	0.07			0.3	0.05		
4	750	25.8	15.5	11.1	0.6	45.5	1.0	0.08			0.3	0.05		
5	756	25.9	15.7	11.1	0.6	45.3	1.0	0.05			0.28	0.05		
6	760	26.2	15.6	11.2	0.6	45.2	1.0	0.03			0.17	0.03		
7	764	26.3	15.8	11.1	0.6	45.0	1.0	0.03			0.19	0.03		

(1) An oxygen analyzer will be used in future work.

(2) Trace of oil breakthrough from the reactor.

(3) Temperature after CPO was ≈ 775°C.

TABLE XIV

COMPARISON OF THE STEAM REFORMING CATALYSTS TESTED IN THE ATR UNIT

COMPOSITION MOL%	SR CATALYST TYPE NONE	Rh	Ni	CALCULATED AT EQUILIBRIUM
H_2	2.5	27.6	26.3	34.0
CO	14.1	11.7	15.8	9.3
H_2 + CO	16.1	39.3	42.1	43.3
CO_2	7.5	13.4	11.1	13.6
N_2	70.5	45.8	45.6	43.1
METHANE	2.2	1.3	1.0	0.01
ETHANE	0.1	0.08	0.03	-
PROPANE	0.03	-	-	-
BUTANE	0.01	-	-	-
ETHYLENE	2.5	0.08	0.19	-
PROPYLENE	0.4	0.02	0.03	-
BUTYLENE	0.05	-	-	-
BUTADIENE	0.12	-	-	-
C_6+	YES	YES	YES	NO
PROCESS CONDITIONS:				
TEMP, °C	775	775	764	770

$H_2O/C = 2.5$, $O_2/C = 0.47$, 7-8 HRS ON FEED

TABLE XV

Autothermal Reforming of No. 2 Oil Using 15% Ni/Al_2O_3 as the Steam Reforming Catalyst

50 ml of SF-3B

(Run 7228 Catalysts: CPO + SF-3B)

(H_2O/C = 2.34 O_2/C = 0.368)

Hours on Stream	Injector Temp. °C	SR Temp. (°C)	Dry Gas Composition, Mole %					
			H_2	CO	CO_2	O_2**	N_2	CH_4*
1	457	860	36.59	15.64	11.66	0.20	35.05	0.85
2	460	860	37.16	15.32	11.84	0.17	34.69	0.81
3	460	862	37.24	15.52	11.67	0.18	34.60	0.78
4	460	866	36.91	15.83	11.45	0.18	34.87	0.75
5	463	866	36.97	16.12	11.32	0.17	34.69	0.72
6	463	870	36.98	16.03	11.34	0.18	34.74	0.72
7	463	872	36.99	16.00	11.39	0.18	34.69	0.73
8	466	881	36.60	16.41	11.19	0.18	34.89	0.72
9	465	885	36.67	16.15	11.28	0.20	34.95	0.74

* Methane is the highest hydrocarbon detected

** O_2 not yet calibrated on chromatograph

TABLE XVI

Autothermal Reforming of No. 2 Oil Using 15% Ni/Al_2O_3 as the Steam Reforming Catalyst

25 ml of SF-3B (Diluted)
(Run 7230 Catalysts: CPO + SF-3B)
(H_2O/C = 2.28 O_2/C = 0.375)

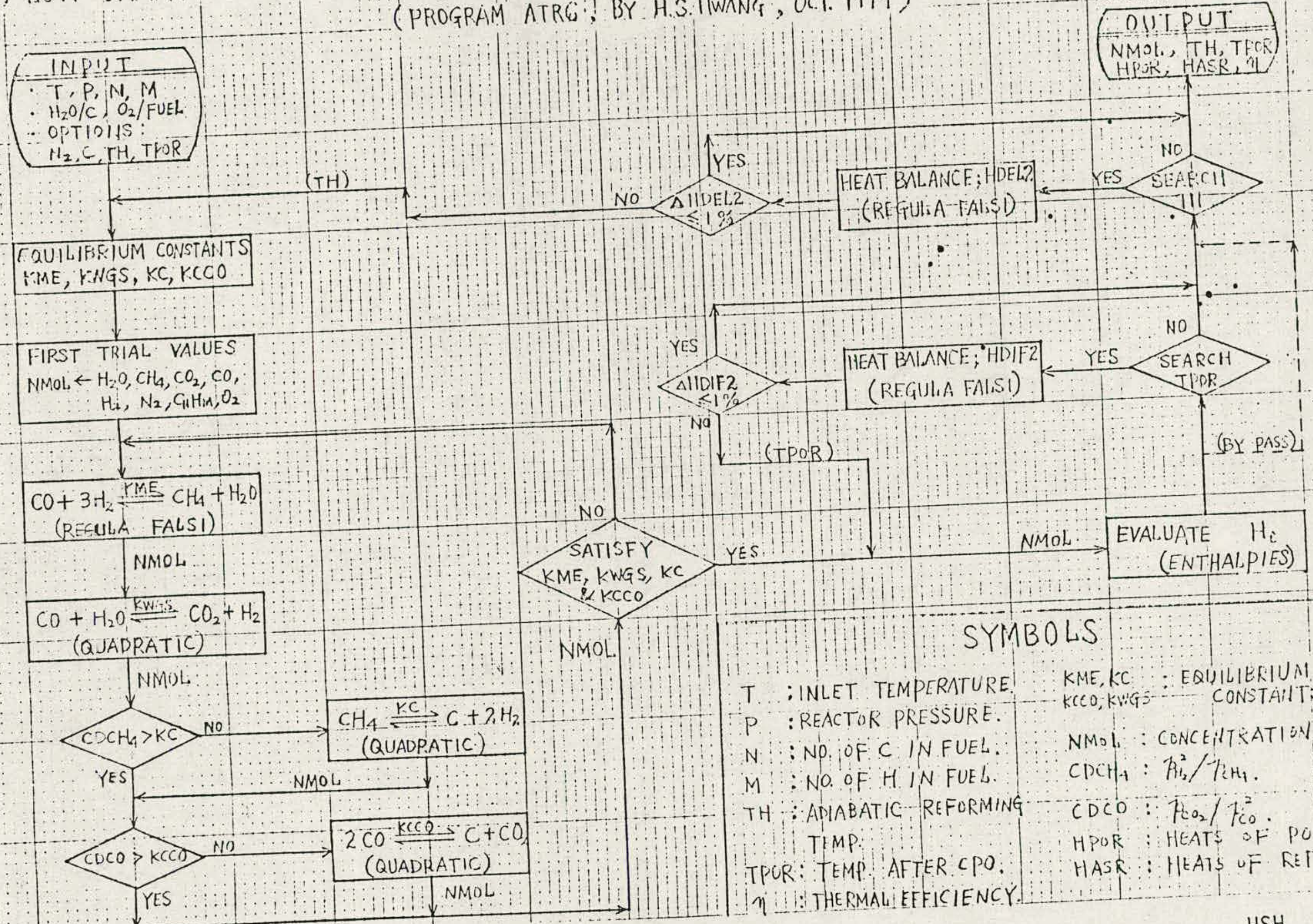
Hours on Stream	Injector Temp. °C	SR Temp. (°C)	Dry Gas Composition, Mole %						
			H_2	CO	CO_2	O_2**	N_2	CH_4	C_2H_4*
1	443	866	35.59	16.47	10.93	0.09	35.66	1.23	0.01
2	454	867	35.14	16.56	10.94	0.09	35.99	1.53	0.01
3	460	872	35.38	16.51	10.90	0.09	35.87	1.22	0.02
4	460	885	34.72	16.49	10.88	0.21	36.49	1.20	0.02

* Ethylene is the highest hydrocarbon detected

** O_2 not yet calibrated on the chromatograph

FLOW CHART FOR CALCULATING AUTOTHERMAL EQUILIBRIUM COMPOSITION OF C-H-O SYSTEM

(PROGRAM ATRG ; BY H.S. HWANG , OCT. 1979)



SYMBOLS

T : INLET TEMPERATURE.

P : REACTOR PRESSURE.

N : NO. OF C IN FUEL.

M : NO. OF H IN FUEL.

TH : ADIABATIC REFORMING TEMP.

TPOR : TEMP. AFTER CPO.

η : THERMAL EFFICIENCY.

KME, KC, KCCO, KWGS : EQUILIBRIUM CONSTANTS.

NMOL : CONCENTRATION VECTOR.

CDCH4 : $P_{H_2}^2 / P_{CH_4}$.

CDCO : P_{CO_2} / P_{CO}^2.

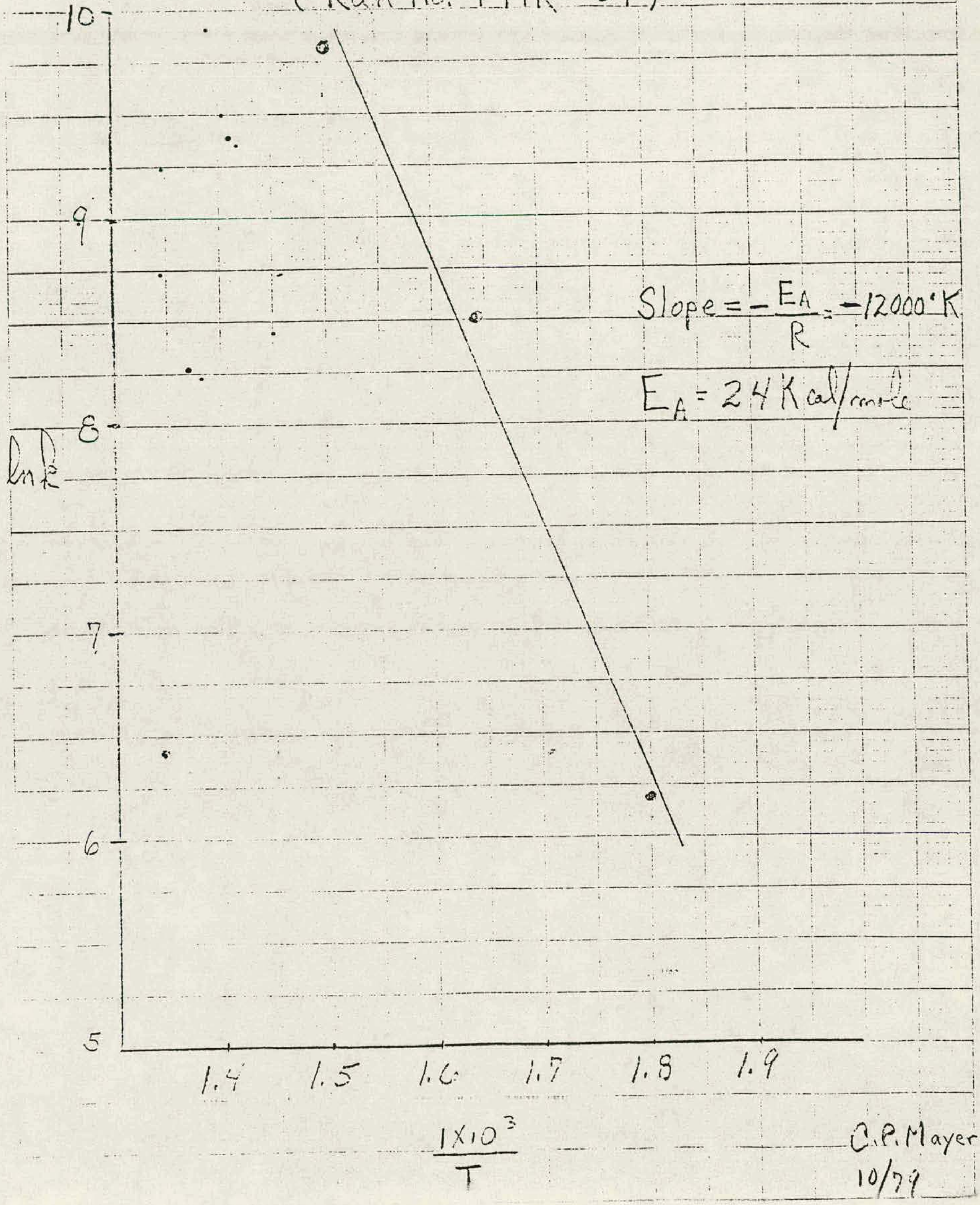
HPOR : HEATS OF POR.

HASR : HEATS OF REFORMING

HSH
10/29/79

Figure 2

Arrhenius Plot of SF-3B
(Run No. PMR-39)



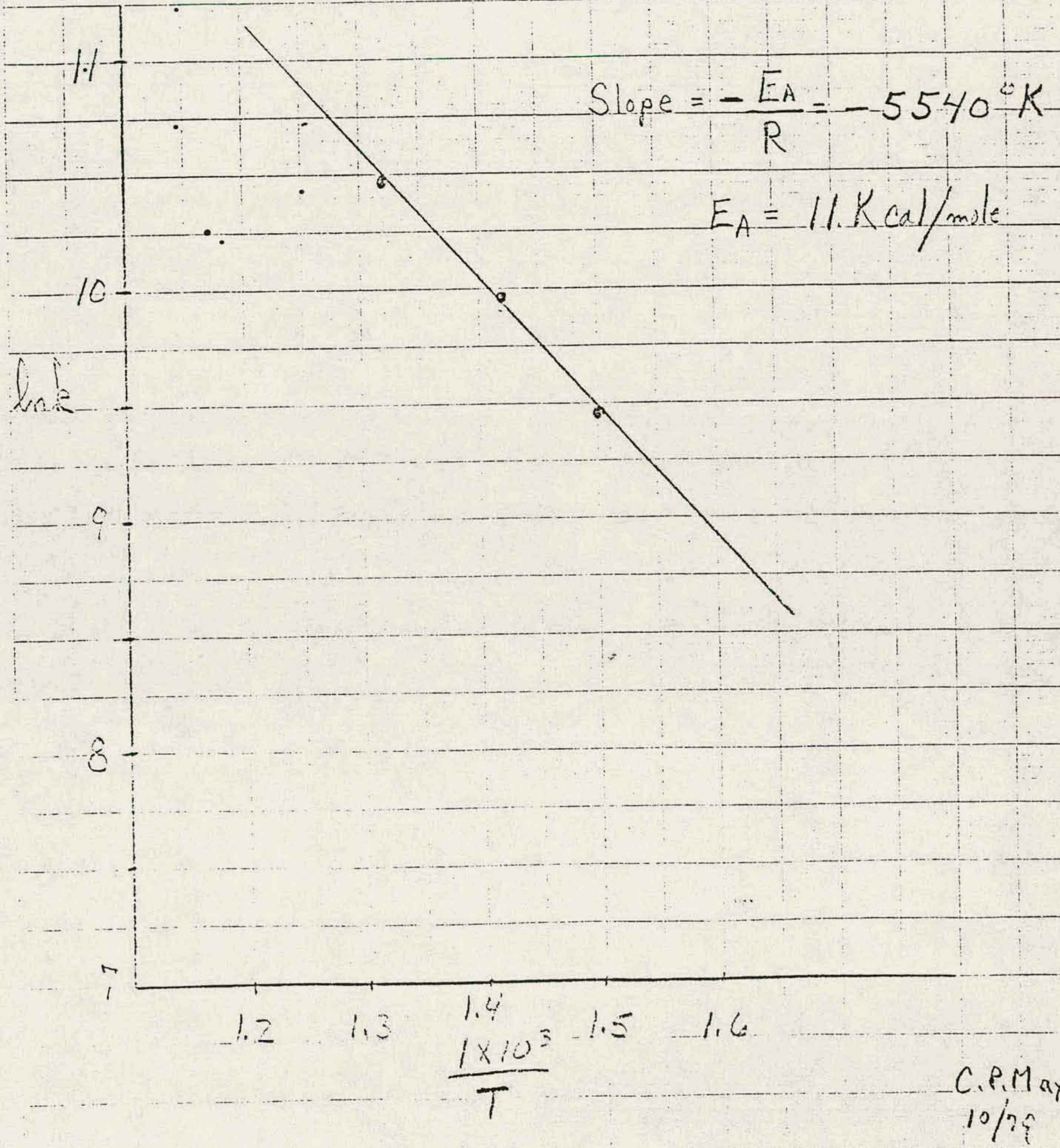
$\text{Slope} = -\frac{E_A}{R} = -12000°K$

$E_A = 24$ Kcal/mole

C.P. Mayer
10/79

Figure 3

Arrhenius Plot of FP-13
(Run No. PMR-38)



C.P. Mayer
10/75

Figure 4

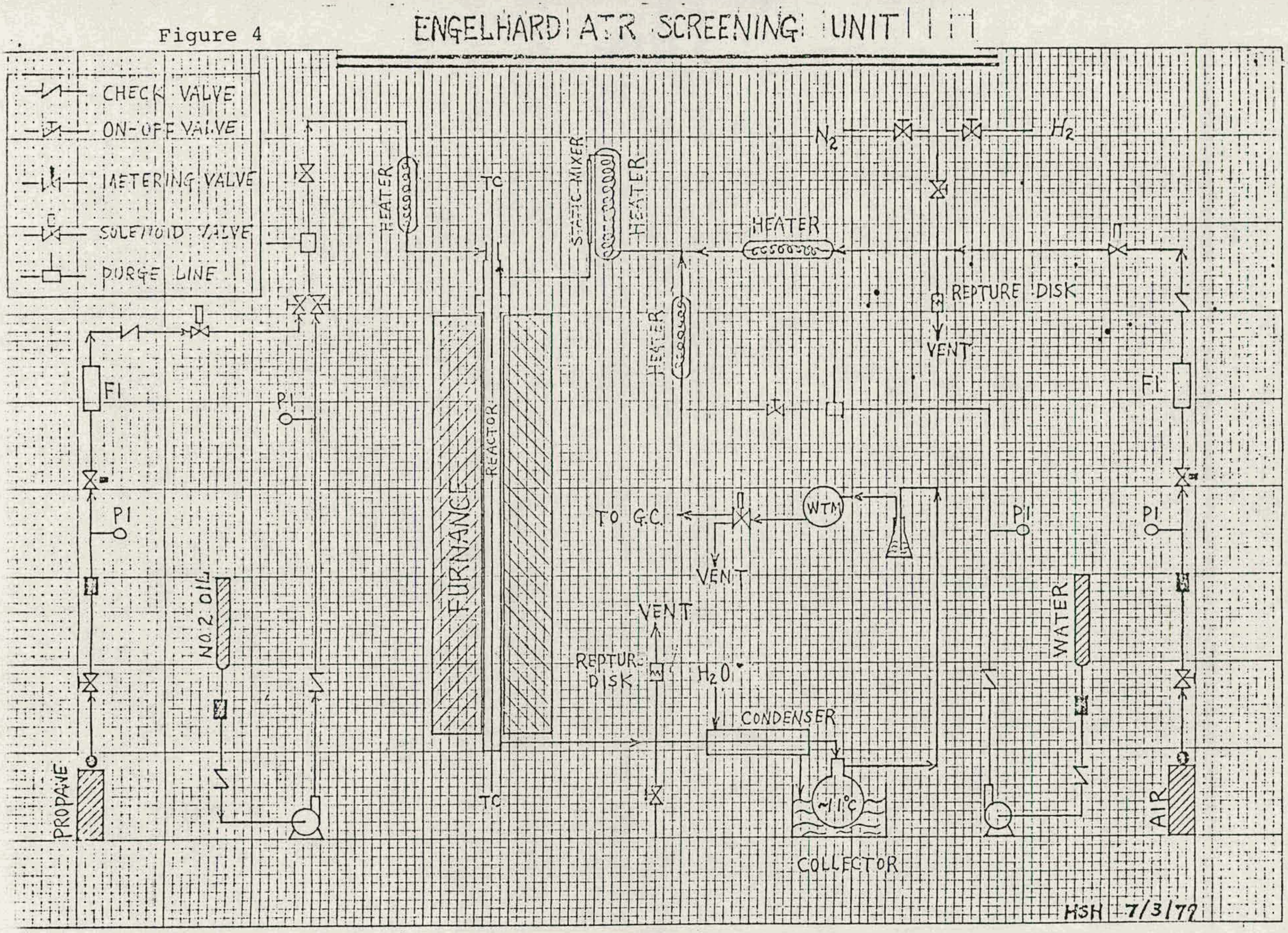
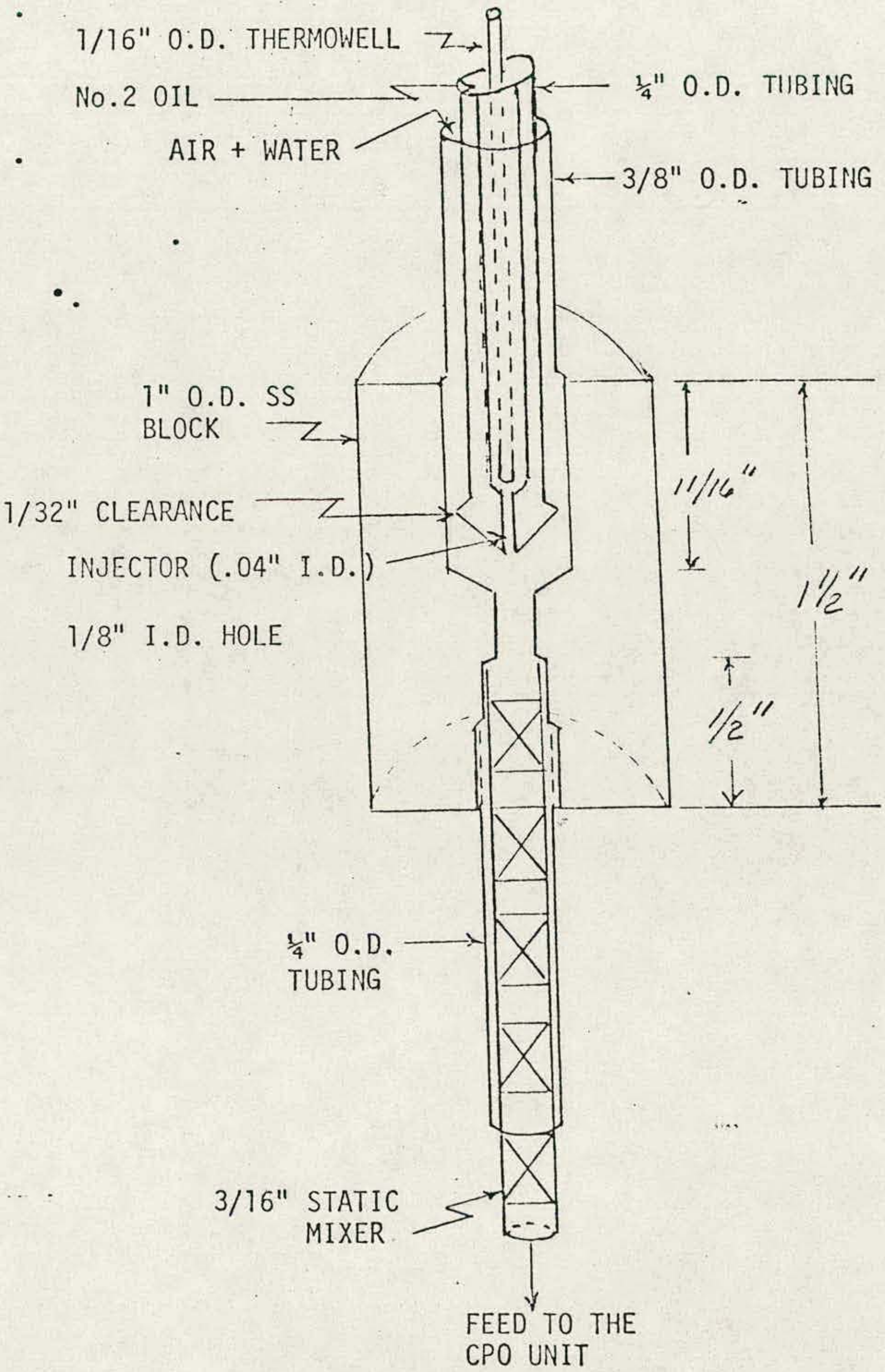

ENGELHARD ATR SCREENING UNIT
CHECK VALVE
ON-OFF VALVE
METERING VALVE
SOLENOID VALVE
PURGE LINE
N2
H2
HEATER
TC
STATIC MIXER
HEATER
HEATER
REPTURE DISK
VENT
HEATER
FI
PI
REACTOR
FURNANCE
FI
PI
TO G.C.
WTM
VENT
PI
PI
NO.2 OIL
VENT
REPTURE DISK
H2O
CONDENSER
WATER
PROPANE
TC
~11°C
AIR
COLLECTOR
HSH 7/3/79

Figure 5

INJECTOR/MIXER DESIGN FOR

THE ATR CATALYST SCREENING UNIT



RMY
10/29/79