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CATALYST AND PROCESS DEVELOPMENT FOR THE
H₂ PREPARATION FROM FUTURE FUEL CELL FEEDSTOCKS

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ABSTRACT

Phase I of this contract, which involved preliminary catalyst and process evaluations, has been completed with a decision to pursue an autothermal type reforming process in which the reactants, steam and oil, are preheated to reacting temperature by partial oxidation of the reactants over a monolithic catalyst upstream of the high temperature steam reformer.

Five commercial steam reforming catalysts were evaluated in short tests to indicate initial aging. Methane leakage in the range of 2.4 to 3.1% was noted with these catalysts in the hydrogen assisted steam reforming of No. 2 oil at about 1650°F. An experimental Engelhard catalyst was slightly more active than the commercial catalysts with a methane leakage of about 1.2% under similar conditions.

The catalytic partial oxidation of No. 2 oil was carried out over a monolithic catalyst containing Pt/Pd/Rh. At the space velocities used, some light hydrocarbon leakage was noted. However, operation without carbon plugging in the monolith was accomplished at an O₂/C molar ratio of 0.31. The results from these runs with No. 2 oil are being used to design an autothermal reactor with a monolithic catalytic partial oxidation preheater.

Pure methanol was steamed reformed over a commercial low temperature shift catalyst at 525°F in a 900 hour aging run. Methanol conversion was essentially 100% throughout the period of the test. In the presence of 5% higher alcohols, the low temperature shift catalyst is rapidly deactivated. The use of Pd/Al₂O₃ catalyst upstream of the shift catalyst was not effective in preventing this deactivation with this very high level of higher alcohols.

TECHNICAL SUMMARY

TASK 1. PROCESS FEASIBILITY STUDIES (G10-10)

A. HYDROGEN ASSISTED STEAM REFORMING

The work on this process was continued during this quarter as a means of evaluating a series of commercial steam reforming catalysts and to compare their activity for steam reforming No. 2 oil with an experimental catalyst made by Engelhard. As was described last quarter, carbon formation was observed in the preheater section of the modified test unit. This buildup of carbon was slow which made it possible to run short aging runs to evaluate catalyst.

Under the conditions selected for testing catalyst, the thermodynamic equilibrium concentration of methane in the dry exit gas should be zero. Test conditions were approximately 1650°F, pressure 10-50 psig, H_2O/C molar ratio 6-9, WHSV of No. 2 oil 0.2-0.65, H_2/C molar ratio 1.2-1.7. Methane leakage for commercial catalysts ranged from 2.4 to 3.1%. The experimental nickel catalyst made by Engelhard was slightly more active as evidenced by a methane leakage of 1.2%.

The physical properties of these used catalyst are being measured. The results from this work will serve as a basis for the catalyst development work to be done under Task 4 of the contract.

B. CATALYTIC PARTIAL OXIDATION

A new catalyst preparation was made consisting of Pd/Pt/Rh loaded onto 3 inch lengths of cordierite monoliths. Two of these were used as a six inch section to partially oxidize No. 2 oil with varying air/fuel ratios and with varying steam to carbon levels. The concentration of H_2 and CO was near that expected from the partial oxidation reaction. The addition of steam did not increase the hydrogen concentration. The gas space velocity of about $100,000 \text{ hrs}^{-1}$ may be too high for steam reforming. The rhodium was added because of its activity for steam reforming. The No. 2 oil was completely converted to C_3 and lower components. Break-through of propane was noted under each test condition. Once again, the space velocity may be too high to convert these less reactive light hydrocarbons. No carbon plugging occurred in the monolith even at the lowest O_2/C ratio of 0.31.

The results with the monolith for catalytic partial oxidation of No. 2 oil are encouraging. It may serve well as a preheat section in combination with a subsequent steam reforming section. Also, it offers promise for handling heavier hydrocarbons either as a preheat part of an autothermal type design or as a processor itself in combination with a molten carbonate type fuel cell.

C. AUTOTHERMAL REFORMING

A flow scheme has been prepared for an autothermal reforming reactor using a monolithic type catalytic partial oxidation zone to preheat the reactants directly to about 1700°F. The required parts have been ordered to modify the reactor now being used for high temperature steam reforming. This test set up will be used to study this process concept supplying design data needed for Task 8 as well as serving as a unit to test new catalyst candidates generated in Task 4.

TASK 2. TECHNICAL ANALYSIS (G10-20)

The heat balance between the partial oxidation and the steam reforming reactions have been added to the computer program ATR-1. This program will be of value in our continued work on the autothermal reforming process.

TASK 3. METHANOL STEAM REFORMING (G10-30)

This work was completed with a 900 hour aging run using pure methanol over a commercial low temperature shift catalyst (ICI 52-1) at 525°F. Even at this higher temperature, which appeared to be the key variable in preventing deactivation, the dry gas CO level was below 1%. Conversion of methanol was essentially 100% over the test period. An IR technique was used to determine the amount of unreacted methanol in the liquid condensate. These qualitative results were in agreement with the routinely made, very precise density measurements. The results show that methanol conversion exceeded 99.98% during the run. The results indicate that pure methanol can be steam reformed effectively for long periods of time to provide hydrogen for the phosphoric acid type fuel cell.

A simulated crude methanol containing 95% methanol, 4% ethanol, and 1% propanol was used to accelerate the aging to be expected with undistilled methanol from a commercial methanol synthesis reactor. Over ICI 52-1 at 525°F, this crude methanol rapidly deactivated the catalyst to give only 90% conversion. Over 1% Pd/Al₂O₃ catalyst at identical conditions, the conversion was about 71%. The product gas from this run with Pd catalyst indicated very little shift reaction occurring, as expected, and that methane, ethane, and propane, were formed from the higher alcohols. The crude methanol was also tested over a dual catalyst bed of Pd/Al₂O₃ followed by ICI 52-1. No advantage was found for this dual bed of catalyst at this high level of higher alcohols. It may be of interest for the lower impurity levels expected commercially.

TECHNICAL REVIEW
BY TASKS

TASK 1. PROCESS FEASIBILITY STUDIES (G10-10)

A. HYDROGEN ASSISTED STEAM REFORMING

Five commercial catalysts together with Engelhard's SF-3 catalyst have been screened for the hydrogen assisted steam reforming (HASR) of No. 2 oil (See Table I for properties of this oil). Experimentally, the water and hydrogen mixture in the feed was first heated to about 800°F and then mixed with No. 2 oil (preheated to 310°F) inside the injector (See Figure 1). The above reactants were subsequently passed through a spiral preheater (Figure 2) to increase their temperature to about 1720°F and then through the steam reforming catalyst. Since the steam reforming reaction is endothermic, the reaction could be monitored by the catalyst bed temperatures, as shown in Figure 3. After the reactor, the water in the product gas was removed by a condenser and the dry gas was analyzed by a gas chromatograph.

For a typical HASR experimental run, about 50 cc of a given catalyst (14-20 mesh) was loaded into the reactor. This sample was first reduced at 932°F at 300 psig in flowing H₂ for about 16 hours. Water was then admitted into the reactor and the temperature was gradually increased to about 1720°F. As the reactor temperature lined out at the above temperature, No. 2 oil was subsequently admitted into the reactor. Typically, the initial feed rates of the reactants for most of the runs were adjusted to be about 20 cc/hr of No. 2 oil, about 1 ft³/hr of H₂ flow and about 200 cc/hr of water.

Since thermal cracking of No. 2 oil occurs when the reactant temperature reached about 1200°F, carbon will be deposited in the preheater and thus block the flow channel. The longer the experiment, the more carbon will be deposited and, thus, the greater the pressure drop across the preheater.

When the pressure drop across the spiral preheater reached about 40 psig, the experiment was terminated.

The catalysts tested are listed in Table II.

The composition of the product gases for the experiments obtained under the conditions given in Table III are summarized in Table IV.

TASK 1. PROCESS FEASIBILITY STUDIES (G10-10)

A. HYDROGEN ASSISTED STEAM REFORMING (CONTINUED)

Under the hydrogen atmosphere and at high temperature, No. 2 oil will be cracked and/or dehydrogenated either thermally or catalytically to hydrocarbons with lower carbon numbers. These in turn will be steam reformed to the end products such as CO, CO₂, H₂, CH₄ and lower hydrocarbons. Under the reaction temperature and pressure, the end products will then equilibrate over the reforming catalyst mainly via the water gas shift and the methane reforming reactions. From this reaction pathway a more active catalyst would crack higher hydrocarbons to methane under the same experimental conditions and the methane leakage from the reactor would approach the value determined by thermodynamic equilibrium. Therefore, the concentration of methane and the other light hydrocarbons in the product gas could be used to determine the activity of a given reforming catalyst.

For each of the experimental conditions given in Table III, the equilibrium methane concentration is zero. Therefore, for a given catalyst, the lower the methane and other light hydrocarbons in the product gas would indicate that the catalyst is a more active one. As shown in Table IV, the data indicate that Engelhard's SF-3 catalyst is the most active one among the catalysts studied. However, the experimental conditions for each of the runs given in Table II were not exactly the same, especially the H₂O/C and H₂/c ratios vary with the increase in pressure drop across the preheater (because of the carbon deposition). Therefore, to rigorously rank the activity of the reforming catalysts studied could not be done at this time. It should be noted that a duplicate test on G56B produced essentially equivalent methane leakage.

The BET surface areas of the six samples tested for HASR are listed in Table V along with the corresponding virgin values. As can be seen, the BET surface area of the used E.I. SF-3 is much higher than the others. By stabilizing the alumina carrier, the surface area remained high indicating that occlusion of the surface nickel by sintering alumina has been retarded. This may explain the higher activity of SF-3.

TABLE I

PROPERTIES OF NO. 2 OIL USED

GRAVITY, API @ 60°F	35.7
FLASH POINT, PM, CC	162°F
VISCOSITY, S.U., @ 100°F	33.9 SEC.
POUR POINT, ASTM	+5°F
SULFUR, ASTM	0.17%
WATER AND SEDIMENTATION	Nil
BTU/POUND	19,736
BTU/GALLON	139,080
C/H WEIGHT RATIO	6.636
NITROGEN	Less than 100 PPM
DISTILLATION	
IBP	356°F
10%	410
50%	482
90%	592
EP	654
Recovery	99%
ASH	Nil
LEAD	3 PPM

FIGURE 1
REACTOR FOR
HYDROGEN ASSISTED
STEAM REFORMING

RMV

FIGURE 2
PREHEATER AND INJECTOR

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FIGURE 3

TEMPERATURE PROFILE IN THE
REACTOR DURING HYDROGEN-
ASSISTED STEAM REFORMING

RUN 7108
SF-3 CATALYST

THERMOCOUPLES

- o- #1 PREHEATER
- #2 TOP OF BED
- △- #3 MID-BED
- ▽- #4 BOTTOM BED
- #5 POST BED

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TABLE II
SAMPLES TO BE EVALUATED FOR HIGH-TEMPERATURE
HYDROGEN ASSISTED STEAM REFORMING

<u>CATALYST</u>	<u>NOMINAL COMPOSITION</u>
ENGELHARD SF-3	19 WT. % NiO BALANCE STABILIZED Al_2O_3
ICI 54-1 (KATALCO)	19-25 WT. % NiO 10-16 WT. % CaO BALANCE Al_2O_3
ICI 23-2 (KATALCO)	6-10 WT. % NiO BALANCE Al_2O_3
GIRDLER G56B	32 WT. % NiO BALANCE Al_2O_3
GIRDLER G90	19 WT. % NiO BALANCE Al_2O_3
PICKFORD-HOLLAND NUA-21	14 WT. % NiO 8.3 WT. % U_3O_8 1.8 WT. % BaO BALANCE $\alpha-Al_2O_3$

TABLE III

EXPERIMENTAL CONDITIONS FOR HYDROGEN
ASSISTED STEAM REFORMING OF NO. 2 OIL

CATALYST	TEMP °F	PRE PSIG	OIL RATE CC/HR	H ₂ O/C	H ₂ /C	WHSV	RUN NO.
SF-3	1640	19.5	34	5.9	1.67	0.65	7108
G-56B	1662	14	22	8.1	1.39	0.36	7113
G-56B	1661	11.5	24	7.5	1.51	0.40	7130
Kataco 54-1	1660	14	22	8.5	1.44	0.32	7118
Kataco 23-2	1670	10	20	8.7	1.46	0.24	7123
NUA-21	1680	11	20	9.4	1.69	0.23	7139
G-90C	1666	10	25	6.7	1.25	0.30	7144

TABLE IV

DRY GAS COMPOSITION OF THE
PRODUCT GAS FOR HASR OF NO. 2 OIL

CATALYST	% COMPOSITION								
	H ₂	CO	CH ₄	CO ₂	C ₂	C ₃	i-C ₄	n-C ₄	C ₅
SF-3	82.49	7.86	1.15	8.49	T	T	T	0.01	---
G-56B	79.17	7.86	3.20	9.74	0.02	---	---	0.01	0.01
G-56B	80.86	7.22	3.12	8.79	0.02	T	T	T	T
K-54-1	76.92	10.35	3.02	9.69	0.01	T	---	T	---
K-23-2	79.61	9.02	3.46	7.89	0.02	---	---	---	---
NUA-21	81.80	6.17	2.95	9.06	0.02	T	---	T	T
G90-C	81.23	7.99	2.41	8.36	0.01	---	---	---	---

* T TRACE

TABLE V

BET SURFACE AREAS OF
SAMPLES TESTED FOR HIGH TEMPERATURE
STEAM REFORMING

SAMPLE	BET SA M ² /G		HASR
	VIRGIN	USED	RUN NUMBER
SF-3	140.2	75.5	7098
G-56B	88.5	5.6	7113
G-90C	27.5	3.8*	7144
ICI 23-2	3.1	1.6*	7123
ICI 54-1	139.1	26.0	7118
NUA-21	33.1	2.1*	7139

* The error function associated with these measurements were higher than expected. More accurate values can be obtained using Krypton.

TASK 1. PROCESS FEASIBILITY STUDIES (G10-10) (CONTINUED)

B. CATALYTIC PARTIAL OXIDATION

Commissioning runs with pure propane were made to check out the system. The results were reported last quarter. The test rig set up for catalytic partial oxidation is shown in Figure 4. The runs with propane used six one inch segments of catalyst consisting of Pt/Pd on Torvex. One run was also made with No. 2 oil (same composition as used in the HASR work reported previously) using these one inch segments which are shown schematically in Figure 5. The results for this test run (No. 4) are listed in Table VI. Use of the six 1 inch segments at low air/fuel ratios resulted in low hydrogen make due to an inadequate temperature rise. Loss of heat occurs radially at the junctions between these segments. In a straight segment, radial transport is minimal. Also, a continuous length of monolith assures a higher average temperature because of heat conduction along its length.

To overcome this problem, a second composition was prepared on 3 inch segments of cordierite monolith. Two segments were used in the subsequent tests. In addition, rhodium was added to the Pt/Pd composition as a potential catalyst for steam reforming.

For this series of tests (Run 5 to 8), the air flow was held constant while fuel and steam flows were varied to attempt to maximize H_2 plus CO production. Run 5 yielded 26.3% hydrogen in the dry exit gas at the air/fuel ratio of 4.91 (O_2/C molar ratio of 0.489). The water/carbon molar ratio was 2.55. The desired steam reforming was not taking place, but no catalyst blockage by coking was evident. In Run 6 the water/carbon molar ratio was lowered to 1.73 and the hydrogen concentration increased to a maximum of 27.0%.

In order to explain these results a comparison is made between a hypothetical case and the results of Run 6. This comparison is listed in Table VII. Since the chromatograph used was not capable of resolving CO in the presence of N_2 , the CO level was determined by carbon balance. The results from the experiment are in fair agreement with the hypothetical case. Some CO_2 was formed indicating some shift reaction occurring. A small amount of hydrocarbons were also observed. Hydrocarbons were measured by a total hydrocarbon analyzer which used a flame ion detector to measure all hydrocarbon species. The instrument is calibrated with propane and the results are reported as propane. In addition, samples were analyzed by an available GC. This indicated the presence of C1 to C3 hydrocarbons with methane as the main component.

In Run 7 the O_2/C molar ratio was lowered to 0.346 (to correspond to values used by United Technologies Corporation). The H_2 level dropped below 10% and the propane level increased. No coking was observed. In Run 8 the O_2/C molar ratio was further lowered to 0.31 without carbon pluggage even though the H_2/C ratio was only 0.46. The propane level increased to 5.6% with 13.5% H_2 produced.

The following summary concludes this exploratory investigation of catalytic partial oxidation:

1. No. 2 oil was converted to a synthesis gas containing a total of about 46% of hydrogen plus carbon monoxide using a Pt/Pd/Rh monolithic catalyst with an O_2/C molar ratio near to 0.5.
2. No catalyst blockage due to carbon forming was observed in these runs even with O_2/C ratios as low as 0.31.
3. No evidence of steam reforming was noted even in the presence of rhodium. This is believed due to the very high space velocities used.
4. Some propane leakage was noted which was also attributed to the high space velocity.
5. The absence of carbon blockage is apparently related to the partial oxidation being done with the precious metal catalyst supported in the small channels of the monolith in the presence of steam.
6. Further experimentation is suggested to take advantage of these observations. The results are encouraging in respect to handling fuels heavier than No. 2 oil.

FIGURE 4

SCHEMATIC OF ENGELHARD LABORATORY
TEST RIG FOR CATALYTIC PARTIAL OXIDATION

(FI) FLOW INDICATOR

(FRC) FLOW RECORDER CONTROLLER

(ΔP) PRESSURE DROP

FIGURE 5
MONOLITHIC CATALYSTS
USED FOR CATALYTIC PARTIAL
OXIDATION

TABLE VI
EXPERIMENTAL RESULTS - CATALYTIC PARTIAL OXIDATION

RUN NO. FUEL	CAT. TYPE	INLET TEMP (°C)	AIR/FUEL RATIO (BY WEIGHT)	O ₂ /C (MOLAR RATIO)	H ₂ O/C (MOLAR RATIO)	CATALYST GAS SPACE VELOCITY (hr ⁻¹) [⊗]	OUTLET GAS COMPOSITION (VOLUME DRY BASIS)	H ₂ (%)	CO* (%)	CO ₂ (%)	C ₃ ** (%)	O ₂ (%)	NO _x (PPM)
1 Propane	I	310	6.71	0.714	0	163,500	22.15			2.99	2.85	.07	14.3
2 Propane	I	305	6.71	0.714	0.92	"	19.90			2.09	---	---	---
3 Propane	I	317	5.83	0.620	0	"	22.59			2.77	2.89	.07	16.4
4+ No. 2 Oil	I	370	5.84	0.583	0	"	10.21			3.72	2.70	6.76	34.8
5 No. 2 Oil	II	266	4.91	0.491	2.55	109,000	26.30			7.71	2.77	---	---
6 No. 2 Oil	II	362	4.90	0.489	1.73	"	27.00			4.00	1.30	0.30	---
7+ No. 2 Oil	II	350	3.46	0.346	1.23	"	9.51			4.00	3.00	---	---
8+ No. 2 Oil	II	358	3.09	0.308	0.46	"	13.5			3.50	5.60	---	---

+ Hydrocarbon breakthrough accounts for the low H₂ levels

⊗ Vol Air/Hr/Vol Catalyst

* Chromatograph available could not resolve CO in the presence of N₂.

** By total Hydrocarbon Analyzer Calibrated with propane and reported as propane.

TABLE VII
CATALYST PARTIAL OXIDATION

COMPARISON BETWEEN HYPOTHETICAL AND EXPERIMENTAL
RESULTS

1. HYPOTHETICAL

AIR CONTAINS $\sim 4 \text{ N}_2 / 1 \text{ O}_2$

COMPONENT	INLET		EXIT	
	MOLES	%	MOLES	%
-CH ₂ -	1.0	28.6	0	0
O ₂	0.5	14.3	0	0
N ₂	2.0	57.1	2	50
CO	---	---	1	25
H ₂	---	---	1	25
TOTAL	3.5	100	4	100

2. EXPERIMENTAL (RUN 6)

OIL C_{13.93} H_{24.7} CH_{1.77}

O₂/C = 0.489

H₂O/C = 1.73

EXIT GAS COMPOSITION

O ₂	0.3
N ₂	48.3 (BAL)
CO	19.1 (C BAL)
H ₂	27.0
CO ₂	4.0
C ₃ H ₈	1.3
	<u>100.0</u>

HYPOTHETICAL

	0
	50
	25
	25
	0
	0
	<u>100</u>

TASK 1. PROCESS FEASIBILITY STUDIES (G10-10) (CONTINUED)

C. AUTOTHERMAL REFORMING

An Engelhard autothermal reactor system has been designed. The schematic flow diagram is shown in Figure 6. Note that the catalyst bed consists of a Pd/Pt/monolith catalyst in front of a conventional high temperature steam reforming catalyst. After proper mixing of the reactants, the feed is passed through a catalytic partial oxidation (CPO) catalyst, where partial oxidation reaction of No. 2 oil will occur and the heat released from this oxidation reaction will be used to increase the reactant temperature to about 1700°F. When this preheated reaction mixture is subsequently passed through the following reforming catalyst, the steam reforming reaction of the remaining No. 2 oil will take place adiabatically. It is clear from this diagram that the reforming temperature will be controlled by the inlet temperature and the total heat released from the oxidation reaction. The total heat of oxidation will in turn be controlled by the amount of O₂/C ratio present in the feed.

1

TASK 2. TECHNICAL ANALYSIS (G10-20)

The coke line for the steam reforming of methane predicted by the ATR-1 computer program agrees with the results published by Schlatter (California Research Corporation, NTIS AD 456740 (1965)). Now the heat balance between partial oxidation and the steam reforming reactions has been added to the Engelhard computer program ATR-1. This program can be used to calculate the adiabatic reaction temperature as well as the equilibrium compositions for a given set of inlet conditions such as O_2/C molar ratio, H_2O/C molar ratio, inlet temperature, and pressure. This program will be of value in our continuing work on the autothermal reforming system.

TASK 3. METHANOL STEAM REFORMING (G10-30)

The work during the quarter consisted of an aging run with pure methanol and a series of runs with a simulated crude methanol containing higher alcohols.

1. STEAM REFORMING PURE METHANOL

Experiments on steam reforming of pure methanol (reagent grade) were continued in this quarter. Previously, the percentage methanol conversion over both ICI 52-1 and T-2130A at 400°F, about 6 psig, 1.5 H_2O/CH_3OH molar ratio with a space velocity based on hydrogen of 440 hrs^{-1} were found to decline below 100% after only a few hundred hours on stream. During this quarter, the aging rate was studied at a higher temperature. The results are discussed below.

At 525°F, H_2O/CH_3OH molar ratio of 2.6 psig, and a hydrogen space velocity of 300 hr^{-1} , 100% methanol conversion was observed throughout the period of 647 hours. After 647 hours, the temperature and pressure of the reactor were maintained constant, while the space velocity and H_2O/CH_3OH ratio were varied according to the following table:

- (a) 0~647 hours: 300 hr^{-1} , 2.0 H_2O/CH_3OH
- (b) 648~817 hours: 440 hr^{-1} , 2.0 H_2O/CH_3OH
- (c) 818~886 hours: 440 hr^{-1} , 1.5 H_2O/CH_3OH
- (d) 887~899 hours: 1780 hr^{-1} , 1.5 H_2O/CH_3OH

At the end of the run, the methanol conversion was still at 100% as shown in Figure 7. The amount of gas produced during this run equals that calculated from 100% methanol conversion. Therefore, it can be concluded that the deactivation rate of the ICI 52-1 catalyst at 525°F, 2.0 H_2O/CH_3OH and space velocity of 300 hr^{-1} is much slower than that found and reported earlier at 400°F, 1.5 H_2O/CH_3OH and space velocity of 440 hr^{-1} . The difference in the

deactivation rate at various experimental conditions indicate a necessity to optimize the experimental temperature, $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ ratio and space velocity.

Although the gas make is approximately equivalent to that for 100% conversion, the density of the liquid product condensed is lower than that of water. To check the amount of methanol present in the condensate, a differential infrared technique was used.

This technique used a Perkin-Elmer 521 grating infrared spectrometer and a matched pair of International Crystal Laboratories SL-3 liquid cells with BaF_2 windows. The reference beam cell is filled with water and sample cell with 1 vol.% methanol in water. After scanning the entire spectrum of 1% $\text{MeOH}-\text{H}_2\text{O}$ versus H_2O , the absorption band centered at 1020 cm^{-1} was most pronounced and chosen for the semi-quantitative work. The results are shown in Figure 8. Other samples which contained 5 vol.%, 2 vol% and 0.1 vol.% (1000 PPM) methanol were used as standards.

Two samples of the liquid product condensate from the aging run over ICI 52-1 (Run 7101, 525°F , $\text{H}_2\text{O}/\text{MeOH}$ molar ratio = 2, 300 hr^{-1} space velocity) were analyzed using the infrared technique.

These samples are:

<u>RUN NO.</u>	<u>SAMPLE NO.</u>	<u>HOURS</u> <u>PRODUCT COLLECTED</u>	<u>DENSITY</u>
7101	1	24-28	0.9973 gms/cc
7101	2	116-120	0.9966

The IR data from the standards do not follow a Beer-Lambert relationship, i.e., a linear dependance of absorbance versus concentration. Hence the actual amount in these two samples could not be calculated. However, when sample 2 was run versus a 1000 ppm $\text{MeOH}-\text{H}_2\text{O}$ rather than a H_2O reference, no band at 1020 cm^{-1} was recorded (See Figure 9). Hence sample 2 contains about 1000 ppm MeOH . (If sample 2 contained only water, the base line would have deflected in the opposite direction, i.e., higher percent transmittance). Sample 1 run versus a water reference shows a weak band at 1020 cm^{-1} indicating a methanol concentration <1000 ppm and, from the percent transmittance decrease, a reasonable guess is that sample 1 contains about 500 ppm methanol. Thus density and infrared data of the condensates agree indicating that some methanol does not react although gas volume make is equal to the theoretical amount calculated for 100% MeOH conversion. (1000 ppm CH_3OH in the condensate corresponds to 99.98% conversion).

There are two major reactions which can produce hydrogen from methanol, i.e. decomposition reaction: $\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$ (1)
steam reforming reaction: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$ (2)

A comparison of the free energy change for reactions (1) and (2) indicate that reaction (2) is favored thermodynamically in the temperature range studied. The free energy changes for the above two reactions are shown in Figure 10 as a plot of the $\ln K$ versus temperature in degrees Kelvin.

Since both ICI 52-1 and T-2130A catalysts are good for the low temperature water gas shift reaction, the water gas shift reaction will occur under the experimental condition. (water gas shift reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$). (3)

At a given temperature, pressure and a $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ ratio, a computer program (called METHANOL) has been written to calculate the thermodynamic equilibrium compositions for reactions (2) and (3). Some results of these calculations are shown in Table VIII.

The dry gas compositions as determined experimentally (given in Table IX) were close to the equilibrium compositions given in Table VIII. Therefore, it may be concluded that the product composition (dry gas) from methanol reforming over Cu/Zn oxide catalysts are close to the thermodynamic equilibrium composition, though it is not in actual equilibrium.

2. STEAM REFORMING SIMULATED CRUDE METHANOL

Previously, it has been shown that, for steam reforming of pure methanol over ICI 52-1 catalyst, the activity could be maintained at 100% conversion for about 900 hrs, and that the deactivation rate at 525°F was much slower than that found at 400°F. To test the deactivation rate as well as the poisoning effect of higher alcohols on the decomposition catalysts, three experiments for steam reforming of a simulated crude methanol were performed. The catalysts used in these experiments were ICI 52-1, Engelhard 1% Pd/ Al_2O_3 and a dual catalyst system containing 1% Pd/ Al_2O_3 and ICI 52-1. The simulated crude methanol used in the preparation of the feed for these runs contained 95% CH_3OH , 4% $\text{C}_2\text{H}_5\text{OH}$ and 1% $i\text{-C}_3\text{H}_7\text{OH}$ (% by volume), and the experimental conditions were chosen to be the same as those used for the pure methanol work, i.e., 525°F, ~6 psig, 2.0 $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (molar ratio, and hydrogen space velocity of 300 hr^{-1}).

After the sample was reduced, the feed containing pure methanol was used initially to assure proper reduction of the sample and also to establish a reference activity, the feed containing the above simulated crude methanol was then admitted into the reactor and

the % CH₃OH conversion calculated from the amount of gas measured by the wet-test meter. The results of these three runs are summarized in Table X and Figures 11 and 12.

For ICI 52-1 catalyst, the initial conversion for pure methanol was 100% and, thus, the sample was properly reduced. However, after the simulated crude methanol was admitted into the reactor, the methanol conversion sharply declined to 90% after only a few hours on stream, and the conversion could subsequently be maintained at the same level for another 40 hours. As shown in Figure 11, the results indicate that higher alcohols present in the feed acted as a poisoning agent for steam reforming of methanol over ICI 52-1 catalyst.

The gas chromatographic analysis for the dry product gas is shown in Figure 13 and 14. For the feed containing pure methanol, the major products were H₂, CO, and CO₂ as shown in Figure 13, but for the feed containing the simulated crude methanol an additional two peaks appeared in the heavy end of the gas chromatogram (Figure 14). These two peaks were not identified in this work. However, they are probably due to either and/or aldehyde type of compounds and are probably related to the decline in the decomposition activity of ICI 52-1 catalyst.

For 1% Pd/Al₂O₃ catalyst, the activity for the steam reforming of pure methanol under the above experimental conditions was found to be 74%, but this activity declined to 71% after a few hours on stream. The dry gas composition as analyzed by a gas chromatograph (See Figure 15) was found to be H₂ (67.9), CO (31.2%), CH₄ (Trace), CO₂ (0.9%) and an unidentified peak (probably CH₃OH). Upon the admittance of the simulated crude methanol to the reactor, the methanol conversion gradually declined from 71% to 64%. As shown in Figure 16, CH₄, ethane, and propane were found in the product gas, indicating that the alcohols were first dehydrated and then hydrogenated to their respective saturated hydrocarbons over the 1% Pd/Al₂O₃ sample. Furthermore, the unidentified peaks found in the heavy ends of the gas chromatogram (Figure 16) were probably due to the unconverted alcohols and/or some other reaction by-products.

Since the decline in methanol conversion was found with both feedstocks, this activity decline was not caused by the higher alcohols in the simulated crude methanol, it is most likely caused by either unknown impurities and/or by sintering of the palladium crystallite. The dispersion of palladium decreased from 18% to 11% during this test as measured by CO chemisorption. Further experiments would be necessary to identify the reasons of this activity decline.

As shown in Figure 12, the ratio of CO to H₂ in the dry gas product was about 1:2, indicating the reaction mechanism is most likely following the decomposition route, ie., CH₃OH → CO + 2H₂.

Furthermore, the CO_2 concentration in the product gas was low; it may thus be concluded that this palladium catalyst has a very low activity for the water gas shift reaction.

As discussed previously, the ICI 52-1 catalyst can be poisoned by the presence of higher alcohols in the feed. The Pd catalyst is capable of converting these higher alcohols to their respective saturated hydrocarbons.

Reducing the concentration of the higher alcohols in crude methanol feed should minimize their poisoning effect and therefore a dual catalyst was used with the simulated crude methanol feedstock. This dual bed consisted of 40 ml of $\text{Pd}/\text{Al}_2\text{O}_3$ followed by 60 ml of ICI 52-1. The results with this dual bed are shown in Figure 11. As can be seen from this plot, there was no advantage of using this dual bed (with this feed containing very high levels of higher alcohols) over that obtained using a single bed of ICI 52-1.

Figure 17 and 18 show the gas chromatograms for pure methanol and crude methanol, respectively, using this dual bed system. On pure methanol a methane peak and an unreacted methanol peak is observed in addition to the expected H_2 , CO , and CO_2 . On crude methanol, peaks are observed corresponding to methane, ethane, and propane. In addition, unidentified peaks are shown in Figure 18.

After the activity of this dual catalyst bed had been maintained at 87% conversion in the feed containing crude methanol, the feed was switched to the one containing pure methanol and water mixture; the steam reforming activity of this deactivated sample was restored to its original activity level in a few hours. Therefore, for a feed containing low level of higher alcohols in another simulated crude methanol (0.04% $\text{C}_2\text{H}_5\text{OH}$, 0.03% $i\text{-C}_3\text{H}_7\text{OH}$ and balance CH_3OH), the steam reforming activity of this dual bed catalyst was not affected by the presence of these higher alcohols. As shown in Figure 12, it could be concluded that the deactivation caused by the presence of higher alcohols in the feed was a temporary and a reversible effect. In addition, the degree of deactivation depended on the impurity level present in the feed.

As shown in Figure 11, the presence of higher alcohols does not affect the activity for the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst, the above reversible deactivation found in the dual bed catalyst system could be attributed to the influence of higher alcohols on ICI 52-1 sample alone. If this is true, the nature of deactivation can be speculated to be due to the blocking of a portion of the active sites by reversible surface adsorption of the deactivating species such as higher alcohols and/or their reaction by-products (especially ethers and aldehydes). As the crude methanol was admitted into the reactor, the surface concentration on the above deactivating species

started to build up and, thus, the total numbers of the active sites available for reforming started to decrease. When the degree of surface coverage reached the level defined by the adsorption equilibrium, no more surface accumulation of the deactivating species are possible and, thus, the total number of the unblocked sites and also the reforming activity could be maintained at a given level. When the impurity level in the feed changes a new degree of surface coverage of the deactivating species can be expected because of the reversibility of the surface adsorption and also the establishment of a new adsorption equilibrium. Thus, the reforming activity will be changed according to this new adsorption coverage. Similar reversible poisoning effect on the activity of T-2130 catalyst by different levels of ethanol has been reported previously by United Technologies (May 19, 1978, contract No. DAAK70-77-C-0195).

3. CONCLUSIONS ON THE METHANOL/STEAM REFORMING TASKS

At a temperature below 440°F, space velocity above 400 hr⁻¹ and a feed containing 1.5 H₂O/CH₃OH (molar ratio), the activity for steam reforming of pure methanol over both ICI 52-1 and T-2130A catalysts was dropped below 100% methanol conversion after only a few hundred hours on stream. Therefore, under the above experimental conditions, these two catalysts can not meet the reformer requirement for a prototype fuel cell system. To do steam reforming of pure methanol under the above experimental conditions, other types of catalysts, such as methanol synthesis catalysts and/or other mixed oxide catalysts, should be explored. Hopefully, some catalysts which are more active than these two low temperature shift catalysts (i.e., ICI 52-1 and T-2130) can be selected for this reforming process under the above specified conditions.

However, at 525°F, ~6 psig, 2.0 H₂O/CH₃OH and space velocity of 300 hr⁻¹, the activity for ICI 52-1 could be maintained for 647 hours at 100% methanol conversion. Subsequent variation of the feed to 1.5 H₂O/CH₃OH ratio and hydrogen space velocity up to 1780 hr⁻¹ did not decrease the activity, and the conversion remained at 100% after a total of 900 hours on stream. Therefore, the results obtained in this work indicated that long catalyst life could possibly be obtained for this process at a slightly different reaction conditions, and the ICI-52-1 catalyst could possibly meet the reformer requirements for the prototype fuel cell system. At 525°F, the CO level was about 0.7% versus about 0.3% at 400°F. Since the experimental parameters chosen here, i.e., 525°F, ~6 psig 2.0 H₂O/CH₃OH and 300 hr⁻¹, have not been optimized, further experiments should be done to optimize the reforming conditions.

In this study, the activity for steam reforming of methanol over ICI 52-1 catalyst was found to be poisoned by the presence of higher alcohols in the feed. This poisoning effect was found to be temporary and reversible, and also strongly dependent upon the

impurity level. For example, for the methanol containing 5% (by volume) higher alcohols, the activity decreased from 100% to 90% conversion, while for the methanol containing 700 ppm higher alcohols, the poisoning effect was not significant. Since purification of methanol by distillation to remove higher alcohols is relatively cheap, it would be a good choice at the present time to use the purified methanol as the reformer feed.

FIGURE 7

STEAM REFORMING OF PURE METHANOL
AGING RUN WITH ICI 52-1

FIGURE 8
IR RUNS IN WATER AND METHANOL-WATER MIXTURES
USING MATCHED BaF₂ SL-3 LIQUID IR CELLS

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2 February 1979

Phyllis Pappas
2/2/79

FIGURE 9

COMPOSITE INFRARED DATA FOR RUN 7101
SAMPLES 1 AND 2

A. 1000 ppm MeOH
in H₂O versus
H₂O -
Run from 1050 cm⁻¹
to 960 cm⁻¹

B. Sample 1, Run 7101
versus H₂O

C. Sample 2, Run 7101
versus H₂O

a. Sample 2, Run 7101
vs 1000 ppm MeOH-H₂O

b. Sample 1, Run 7101
vs H₂O

c. 1000 ppm MeOH - H₂O
vs. H₂O

d. Sample 1, Run 7101
vs H₂O

RM 4 9/20/79

FIGURE 10

COMPARISON OF METHANOL
DECOMPOSITION TO REFORMING

Rmg 4/30/79

TABLE VIII

EQUILIBRIUM COMPOSITION OF THE PRODUCT GAS
FROM STEAM REFORMING OF METHANOL AND WATER
GAS SHIFT REACTION (1.5: H₂O/CH₃OH FEED)

Temp. °F	Pressure psig	H ₂ O/CH ₃ OH *	% CH ₃ OH Conversion	% Dry Gas Composition		
				H ₂	CO	CO ₂
400	30	1.50	100	74.73	1.01	24.24
		2.14	70	74.87	0.48	24.64
		3.75	40	74.95	0.21	24.85
400	6	1.50	100	74.82	0.67	24.49
		2.14	70	74.92	0.31	24.77
		3.75	40	74.97	0.13	24.90

* The values given in this column is the ratios of total moles of water in feed to the total moles of methanol converted.

TABLE IX
DRY GAS COMPOSITION

Catalyst	Run No.	Hours on Stream	% CH ₃ OH Conversion	Pressure Temperature		% Gas Composition		
				psig	°F	H ₂	CO	CO ₂
G66-B	6989	24	70	30	440	73.95	0.26	25.79
		73	40	30	440	73.79	0.53	25.68
	6996	8	100	30	440	73.76	0.38	25.86
		147	92	30	440	73.75	0.35	25.86
ICI 52-1	7058	72	100	6	400	74.12	0.65	25.23
		142	100	6	400	74.42	0.30	25.28
		271	100	6	400	74.46	0.26	25.27
		339	97	6	400	74.71	0.26	25.03
		414	96	6	400	74.84	0.23	24.93

TABLE X

ACTIVITY FOR STEAM REFORMING OF
METHANOL

(525°F, 6 PSIG, 2.0 H₂O/CH₃OH (molar ratio) and 300 hr⁻¹)

CATALYST	% CONVERSION		COMMENT
	PURE	CRUDE	
ICI 52-1	100	90	WHSV * = 0.20
1% Pd/Al ₂ O ₃	71	70	ACTIVITY DECLIED TO 65% at 105 HRS ON STREAM, WHSV= 0.13
1% Pd/Al ₂ O ₃ + ICI 52-1	100	88	40 CC Pd/Al ₂ O ₃ + 60 CC ICI 52-1, WHSV= 0.15

* WHSV BASED ON MeOH IN THE FEED.

TABLE XI
% COMPOSITION IN (DRY) GAS PRODUCT

CATALYST	% DRY GAS COMPOSITION							TYPE OF CH ₃ OH IN FEED
	H ₂	CO	CO ₂	C ₁	C ₂	C ₃	C ₄ +	
ICI 52-1	75.21	.74	24.05					Pure
	74.79	.43	24.44	0.1	---	---	T	Crude
1%Pd/Al ₂ O ₃	67.9	31.2	.9	T				Pure
	67.1	32.1	1.15	1.32	.04	.07	T	Crude
1% Pd/Al ₂ O ₃ + ICI 52-1	75.19	.49	24.30	.02				Pure
	73.67	5.70	19.56	.97	.02	.03	T	Crude

T = TRACE

FIGURE 11

CATALYST AGING RATE

(525°F, 6 PSIG, 2.0 H₂O/CH₃OH, 300 HR⁻¹ H₂ SPACE VELOCITY)

HSH 3/20/78

FIGURE 12

STEAM REFORMING OF METHANOL OVER DUAL
CATALYSTS

(525°F, 6 PSIG, 2 H₂O/CH₃OH, 300 HR⁻¹)

FIGURE 13

GAS CHROMATOGRAM
OF DRY PRODUCT GAS USING
PURE MeOH

FIGURE 14

GAS CHROMATOGRAM OF
DRY PRODUCT GAS USING
SIMULATED CRUDE MeOH

catalyst : 1% Pd/Al₂O₃
 Condition : 273°C. ~6 psig
 ~85% CH₃OH
 conversion
 Feed : 2.0 H₂O/CH₃OH (pure)

RUN 712 L
 15-16 HRS

Run 7/30/74

FIGURE 15

GAS CHROMATOGRAM OF DRY
 PRODUCT GAS USING PURE MeOH

Catalyst : 1% Pd/Al₂O₃

Condition : 273°C; ~6 psig
~70% CH₃OH
conversion

Feed : 2.0 H₂O/CH₃OH
(Crude)

RUN 7121

98-99 HOURS

FIGURE 16

GAS CHROMATOGRAM OF PRODUCT
GAS USING CRUDE MeOH

FIGURE 17

GAS CHROMATOGRAM OF DRY
PRODUCT GAS USING PURE MeOH
OVER DUAL CATALYSTS

Feed : 2.0 H₂O/CH₃OH (Crude)

FIGURE 18

GAS CHROMATOGRAM OF DRY
PRODUCT GAS USING CRUDE
MeOH OVER DUAL CATALYSTS