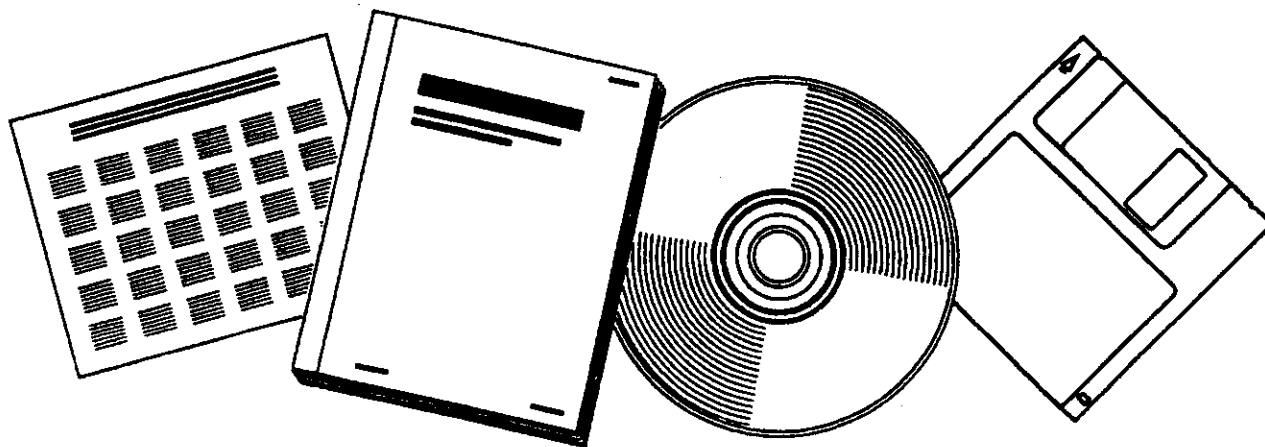DE83004091

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LIQUID-HYDROCARBON FUELS FROM SYNGAS. FIRST ANNUAL REPORT, MARCH 1981-FEBRUARY 1982

UNION CARBIDE CORP., TARRYTOWN, NY.
TARRYTOWN TECHNICAL CENTER

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TECHNICAL PROGRESS REPORT

DE-AC22-81PC40077

First Annual Report.

March 1981 - February 1982

LIQUID-HYDROCARBON FUELS FROM SYNGAS

Molecular Sieve Department, Engineering Products Division

Union Carbide Corporation

Tarrytown Technical Center

Tarrytown, New York

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I.   CONTRACT OBJECTIVE

The objective of the contract is to develop a catalyst and to select operating conditions for the direct conversion of syngas to liquid hydrocarbon fuels, using microporous crystals—"molecular sieves" – in combination with transition metals.

II.   SCHEDULE

The contract work is planned for a thirty-six month period, which started March 6, 1981. The work on the program is divided into four tasks. In Task 1, shape-selective catalysts (SSC's) will be evaluated for converting low molecular weight liquids (e.g. methanol and small olefins) to desired products such as gasoline, turbine and diesel fuel. In Task 2, the feed will be syngas (CO + H_2), and the catalyst will be a combination of transition metal component (MC) and SSC. Task 3 is a study of surface effects and reaction intermediates during the hydrogenation of carbon monoxide, and will be carried out as a subcontract under the direction of Dr. Gabor A. Somorjai, of U.C. Berkeley. Task 4 is a series of management and technical reports.

III. ORGANIZATION

"Liquid Hydrocarbon Fuels from Syngas" is the goal of a research and development program on catalysts to be carried out by the Molecular Sieve Technology Department of the Engineering Products Division, Union Carbide Corporation at their Tarrytown Laboratories. Principal investigator is Dr. Jule A. Rabo. Program manager is Dr. Richard C. Eschenbach.

IV.   PROGRESS SUMMARY
Tasks 1 and 2

A number of catalysts of different structure have been prepared at various levels of acidity to aid in selection of the SSC component. Four selected molecular sieves were sodium ex-changed, then back-exchanged to different degrees with NH_4Cl to give various concentrations of acid sites. The work on SSC

Task 3

Dr. Gabor Somorjai is supervising work on a subcontract to this contract, at the University of California at Berkeley, to characterize catalyst surfaces and study reaction intermediates produced during the conversion of CO and H_2 to liquid hydrocarbon fuels. In one apparatus, photoelectron spectroscopy is being used to determine the oxidation state of transition metal compounds which may be useful as the Fischer-Tropsch component of an LHF catalyst. Another apparatus is being modified to study surface intermediates. Dr. Somorjai's work is reported in Appendix E.

V. CHANGES

During the first year five modifications to the contract were implemented. The first changed the duration from thirty to thirty-six months. The others increased obligated funds and changed the wording of several sections.

VI. FUTURE WORK

An appropriate feedstock and test conditions will be established for Task 1 evaluation of SSC's. Then the effect of catalyst type and acidity and operating conditions on the efficiency of feed conversion to desired products will be determined.

Task 2 tests with syngas feed will start soon.

R. C. Eschenbach
Program Manager

RCE/eh
Encls.

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synthesis and characterization is described in Appendix A.

During the first year of the program, equipment was assembled to enable fairly rapid testing of candidate catalysts at a variety of conditions. Shakedown tests in January and February 1982 disclosed some minor operating problems which have been rectified. Appendix B reports work on the test apparatus.

Fairly complete data are available from two runs made during the second and third quarters of the contract, using a UCC Berty reactor. The first run used methanol feed over a high silica zeolite catalyst, and resulted in making products in the gasoline boiling range. However, the chemical nature of the products (methylated aromatics which are solid at room temperature) is not desirable. Work is planned with feed stocks in Task 1 other than methanol, since methanol is suspected of causing the formation of the undesired products when it coexists with reaction intermediates. When syngas is the feed, the intermediate products on a transition metal catalyst are believed to be mainly small olefins in the absence of methanol. Thus it seems that methanol will not be the best feed for selecting the SSC component.

The second preliminary run used iron as the Fischer-Tropsch active component, supported on a relatively inert amorphous silica-alumina base. This was a Task 2 run, with syngas as the feed. Although the fraction of feed converted to hydrocarbons was rather low, the fraction of that which was undesired solid was much less than with methanol feed.

Recent shakedown tests have confirmed the methanol result and provide further support for trying an alternate feedstock in developing the "standard test" for Task 1.

The development of analytical techniques for evaluating product samples is reported in Appendix C. Results of the catalyst test runs to date are reported in Appendix D.

Appendix A: Synthesis and Characterization   P. K. Coughlin
                                                F. P. Gortsema

Characterization of Shape Selective Catalyst Candidates

Previously it was shown that methanol and syngas can be converted to a high quality gasoline by the use of a catalyst system based on the use of zeolite ZSM-5[1]. This particular zeolite has very desirable shape selective characteristics because of its channel dimensions and channel pathways so that it is able to convert methanol to liquid fuels boiling in the gasoline range with high efficiency. The products obtained are free of oxygenates, and have a high aromatic content along with iso-and n-paraffins. The largest aromatic molecule produced in significant quantities is durene and its concentration must be kept below a critical level in gasoline in order to prevent precipitation of this material in the carburetor of an automobile engine. Liquid fuels with boiling points above the gasoline range (i.e. turbine and jet fuel) are not produced using the Mobil catalysts.

The object of the present work is to evaluate a variety of molecular sieves for use in catalyst systems to convert syngas to liquid hydrocarbon fuels (LHF), with preference to turbine and diesel oil. For this purpose the effect of the molecular sieve composition, structure type, acidity level and strength, and polarity will be investigated in order to determine the effect of these particular molecular sieve properties on the LHF product yield and product composition.

For the initial catalyst synthesis work, various Union Carbide commercial catalysts have been chosen for study. The molecular sieves chosen are: LZ-105-6[2], a medium pore zeolite having a structure similar to ZSM-5 with O_{10} rings and a pore size of approximately 6Å; mordenite[3], a large pore zeolite with O_{12} rings and a one dimensional channel system; Y-62, a

large pore zeolite with a 3 dimensional channel system, O_{12} rings and 8Å pores[3]; silicalite, a microporous silicate with medium size pores[4]; and finally a non-shape selective material, commercial amorphous silica-alumina gel, for comparison.

The Union Carbide materials selected for this initial study have been characterized by conventional chemical analysis to give the elemental composition as well as impurity content. Surface area measurements were made by conventional BET N_2 adsorption techniques. Pore size dimensions were determined by McBain adsorption measurements using various probe molecules (e.g. xenon, n-butane, isobutane, cyclohexane, neopentane) of known dimensions. These measurements are very important for estimating the pore aperture available for admission of molecules as well as determining pore blockage or structure irregularities.

Oxygen capacity of these materials, measured at -196 or -183°C at 100 Torr pressure in a McBain apparatus, provides a useful measure for estimating the degree of crystallinity.

The materials were selected not only for their range of pore sizes and channel geometry, but also for the range of acid concentration and acid strength available for each sieve type. These factors can greatly influence the conversion of methanol or syngas to LHF products. The acid strength and acid concentration level of each zeolite can be modified by such state of the art techniques as NH_4^+ ion exchange followed by calcination[5]

$$NH_4Z \xrightarrow{\Delta T} HZ + NH_3\uparrow$$
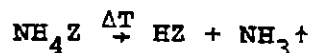
In order to eliminate any H acidity, the four selected molecular sieves were first ion exchanged with NaCl to convert the material totally to the Na^+ exchanged form. Chemical analysis of the

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Na$^+$ exchanged form gives the cation equivalent per Al atom of each composition. The Na$^+$ exchanged materials were then ion exchanged with NH_4Cl solutions to give NH_4^+ exchange corresponding to about 10, 40, and 100% of their total ion exchange capacity. Chemical analysis of the NH_4^+ back exchanged material after calcination, for Na_2O and $(NH_4)_2O$, gives the concentration of ion exchange sites converted to acid sites. For mordenite and Y-62 the back exchange procedure must be repeated several times in order to approach the 100% acid form. The actual degree of ion exchange and the target level are shown in the following table.

Ion Exchange Treatment of Selected Molecular Sieves

Type	Type	SiO_2/Al_2O_3	Target ion exchange level	observed NH4 cation equiv. per Al atom
LZ 105-6	O10	37	10%	12%
			40	36
			100	82
			100	98
Mordenite M-8	O12	17	10	16
			40	45
			100	70
Y-62	O12	5	10	11
			40	32
			100	52
			100	97*

			Alkali content wt-%
S-115HE silicalite (Al_2O_3 impurity = 0.4%)	O10		0.18
			0.1
			0.04

* Obtained with a different batch of Y-62 which had been subjected to a continuous ion exchange.

Because of the high sodium levels in some of the members of the Y-62 acidity series, a possibility existed that the zeolite might not survive the hydrothermal environment in the Berty reactor. With this in mind, the hydrothermal stability of one member of that series, Y-62 which had been sodium exchanged then 50% back-exchanged with NH_4^+, was tested in a 100% steam environment at 400°C for 48 hours. The surface area of the material remained high, >850 m^2/g, and the x-ray powder pattern showed the material to be highly crystalline. This indicates that the crystal structure of the Y-62 should survive the reaction conditions.

Another useful technique for measurement of relative acid strength is the determination of the Bronsted and Lewis acidity by measurement of the infrared spectrum of adsorbed pyridine[6]. Bronsted acid sites show pyridinium ion adsorption at 1540 cm^{-1} while Lewis acid sites show adsorption at 1450 cm^{-1} corresponding to the formation of Lewis type complexes. The use of this technique does not necessarily give the same acidity values as obtained by ion exchange. Adsorption of pyridine by different molecular sieves may be affected greatly by pore size constraints, polarity, degree of hydration, and other factors. However, it is believed that the analytical technique is valuable in showing trends within a given molecular sieve type.

The polarity of each of the four molecular sieves chosen for preliminary testing and screening studies has been measured using a simple shake test with the sample in contact with a water butanol mixture (1 vol % butanol = 0.80 wt-%). This test determines the hydrophilic/hydrophobic character of the sample by the measurement of the weight percent of butanol present in the liquid phase after a four hour shake period. The results for the four selected materials are:

Molecular Sieve (acid form)	Wt-% butanol present in liquid phase
Y-62	0.79
M-8	0.74
S-115	<0.05
LZ-105-6	<0.05

As can be seen from the above results Y-62 and M-8 are hydrophilic. However, S-115 and LZ 105-6 show hydrophobic behavior, removing practically all the butanol from the liquid phase. This observation is in agreement with the known behavior of silica-rich materials.

Zeolite Synthesis

Approximately 200g of ZSM-5 type zeolite with a target SiO_2/Al_2O_3 ratio of 30, and another batch to have $SiO_2/Al_2O_3 = 80$ have been prepared using synthesis procedures developed at Union Carbide. The x-ray diffraction pattern of our synthesized material was excellent, showing highly crystalline material had formed. Chemical analyses of the two materials gave SiO_2/Al_2O_3 ratios of 35 and 86, after air calcination and an NH_4^+ ion exchange treatment to remove the remaining Na^+.

Silica bonded ZSM-5 type zeolite was however not satisfactory in Berty reactor tests because of a failure to form reasonably strong pellets using a tableting press. Tablets of ZSM-5 disintegrated into small particles inside the Berty reactor. This is believed to be due to the difficulty of bonding SiO_2 to the surface of a calcined high silica molecular sieve. Treatment of SiO_2 with base is known to rehydroxylate the surface resulting in better bonding. This treatment was given to calcined ZSM-5 and silicalite to determine how these materials would survive the treatment. The x-ray powder patterns and surface area analyses after the treatment with base at room temperature showed that the structures of these materials were still intact

after this treatment. Tests with the new tablets will be made to see if bonding is satisfactory.

In addition, two samples of UCC 101, a proprietary Union Carbide synthesized molecular sieve, were prepared in tablet form.

References for Appendix A

1. _Development Studies on Selected Conversion of Synthesis Gas from Coal to High Octane Gasoline_ FE-2276-27, Mobil Research and Development Corporation, October 1978, DOE Contract No. EX-76-C-01-2276.
Research Guidance Studies to Assess Gasoline from Coal by Methanol to Gasoline and Sasol-type Fisher Tropsch Technologies FE-2447-13, Mobil Research and Development Corp., Aug. 1978, DOE Contract No. EF-76-C-01-2447.

2. USP No. 4,257,885

3. Linde Molecular Sieve Zeolite Catalyst Data Sheet

4. E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, R. M. Kirchner _Nature_ 271 512 (1978).

5. See, for example, Chapter 3 in ACS Monograph 171, Zeolite Chemistry and Catalysis, J. A. Rabo, Ed.

6. L. H. Little "Infrared Spectra of Adsorbed Species", Academic Press, London 1967. M. L. Hair "Infrared Spectroscopy in Surface Chemistry", Marcel Dekker, N.Y. 1967.

7. USP 3,702,886

Appendix B: Catalyst Testing Facility   L. F. Elek

The laboratory catalyst testing facility was designed to accommodate three Berty recirculating 5" diameter reactors at a time. Three reactor bays were planned in such a way that the reactors could be moved from one bay to another easily. Two bays are to be used for catalyst screening and catalyst evaluation and the third for the activation and/or regeneration of catalyst to be used in task 2 of the program. (Fischer-Tropsch-active components need a special activation treatment).

A schematic diagram of the apparatus for testing catalyst performance is shown in Figure B1. The Berty reactor uses a pressurized fixed bed, with an externally driven impeller which imparts a high degree of back-mixing to the gaseous reaction mixture. Thus the catalyst essentially sees the uniform composition of the product components. The back-mixing helps to control the temperature of the exothermic reaction.

Laboratory modifications were carried out, the test facilities were designed, and capital and other equipment ordered in the first quarter. By the end of the second quarter most of the equipment was received. The construction, assembly and high pressure plumbing started in September and was completed on schedule in December 1981.

Catalyst testing was initiated early in January 1982. During January and February, 9 runs were carried out in catalyst testing bay #1. All the runs completed were with methanol feed using various catalysts at different pressures and temperatures, at 1 WHSV based on methanol and using nitrogen as carrier gas. Preliminary data for these runs are given in Appendix D.

Catalyst testing bay #2 is not complete; a defective low pressure alarm that was shipped back to the manufacturer is not expected to be repaired before the middle of March 1982.
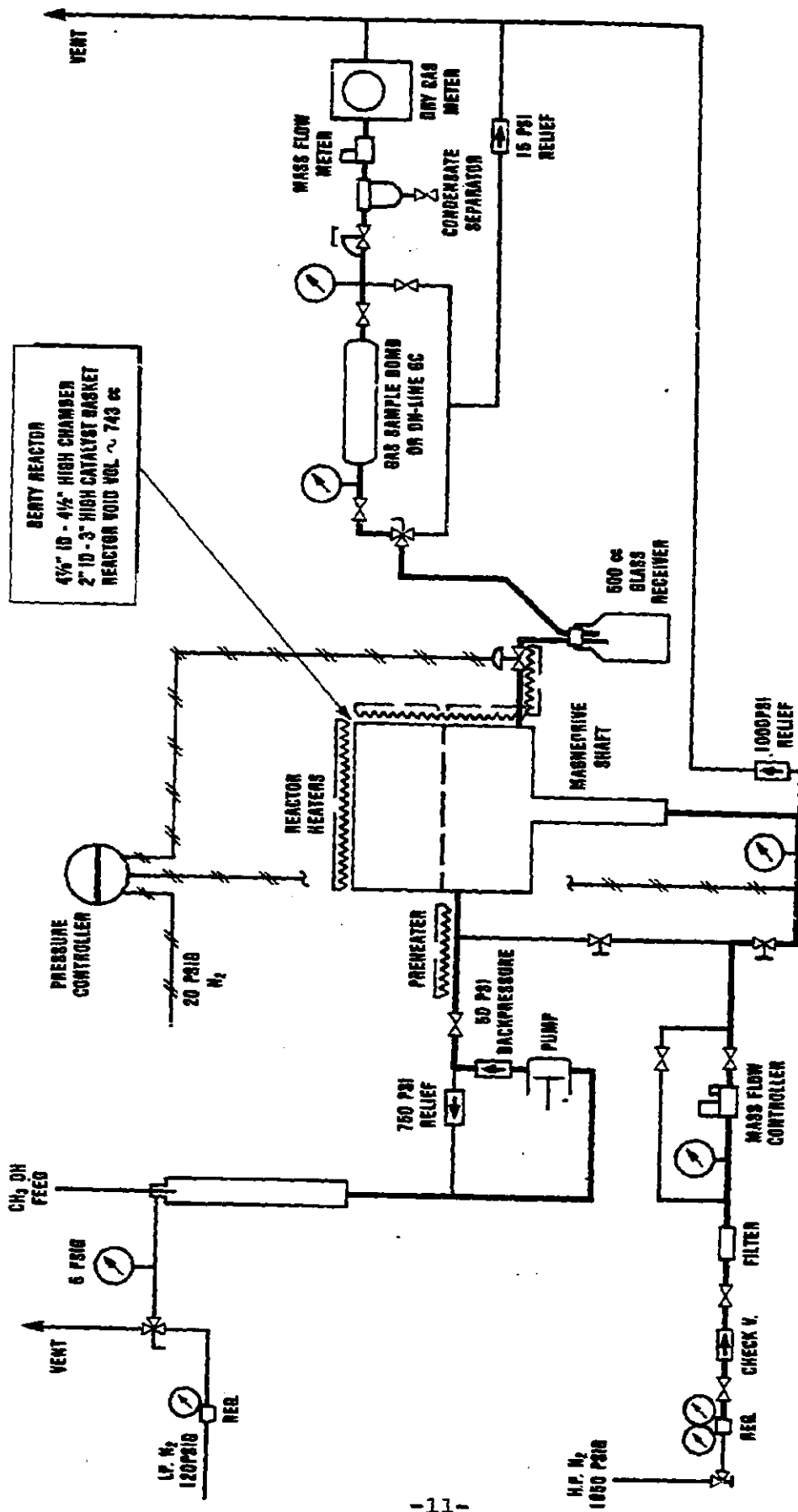
FIGURE B1 SCHEMATIC OF CATALYST TEST STATION

BERTY REACTOR
4½" ID - 4½" HIGH CHAMBER
2" ID - 3" HIGH CATALYST BASKET
REACTOR VOID VOL ~ 743 cc

VENT

MASS FLOW METER

DRY GAS METER

CONDENSATE SEPARATOR

15 PSI RELIEF

GAS SAMPLE BOMB OR ON-LINE GC

500 cc GLASS RECEIVER

MAGNEDRIVE SHAFT

1000 PSI RELIEF

REACTOR HEATERS

PRESSURE CONTROLLER

20 PSIG N₂

PREHEATER

50 PSI BACKPRESSURE

PUMP

750 PSI RELIEF

CH₃ OH FEED

6 PSIG

VENT

L.P. N₂ 120 PSIG

REG

MASS FLOW CONTROLLER

FILTER

CHECK V.

REG

H.P. N₂ 1850 PSIG

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During the month of January, we experienced a reactor bearing failure. This Berty reactor was shipped back to the manufacturer for repair under warranty.

The liquid feed system is presently being modified to allow pumping of propylene and other olefins in liquid form, under a pressure higher than their vapor pressure. An apparatus has been built to allow continuous monitoring of liquid level and thus liquid feed rate in a stainless steel pressurized container equipped with a sight-glass. This feed system is being installed and calibrated. It is expected that it will be operational by the end of March 1982.

All the necessary equipment including a temperature programmer for the activation bay to be used in Task 2 has been ordered. Task 2 shakedown testing will start in the next quarter.

Appendix C: Analytical Techniques

J. M. Basile
D. J. Cadden

In order to evaluate LHF experiments, the following analytical procedures are planned. Some have already been implemented.

A. The gaseous phase of the experimental product will be analyzed on-line by gas chromatography. Equipment has been specified and ordered which is capable of identifying C_1 through C_6 saturated and olefinic hydrocarbons, with components heavier than C_6 detected as a single backflush peak. In addition, fixed gases such as H_2, CO, CO_2, N_2 and polar compounds such as CH_3OH, H_2O and dimethylether will also be detected.

Delivery of the specially modified Model 530 gas chromatograph from Carle Instruments, to be used for on-line gas phase analysis, is still pending. Scheduled arrival for January 1982 has now slipped to April. In the interim period, experimental gas phase samples are being collected in 300 cc. steel cylinders and analyzed off-line via another gas chromatograph

B. The liquid products are separated into their aqueous and hydrocarbon portions. Quantitative phase separation of the aqueous layer from the mixed oil and solid hydrocarbon portion has been a major bottleneck which is just now being resolved. Almost every sample has to be handled differently, due to the grossly varying amounts of hydrocarbon present as two phases in a large quantity of aqueous phase. After phase separation the aqueous portion is analyzed by gas chromatography for CH_3OH, dimethylether and water content. The hydrocarbon portion is submitted for ASTM simulated distillation and FIA hydrocarbon group-type analysis. Preparations are under way to analyze the C_5 to C_{20} fraction of liquid hydrocarbon products via a glass capillary G.C. technique. In order to fractionate the C_5 to C_{20} portion from the overall liquid product prior to injection into the glass capillary column, an Envirochem/Unacon Model 810B concentrating purge and trap system has been ordered. Delivery is expected in June 1982.

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Efforts to use liquid chromatography to replace the standard FIA analysis for hydrocarbon group-type separations have proven unsuccessful to date. Although hydrocarbon group-type separations are easily accomplished by LC, quantitative results using standard LC detectors have been unacceptable. This project had, therefore, been shelved. However, the introduction of the Envirochem/Unacon Model 810B (mentioned above) has opened new possibilities. We are now investigating using LC to do the physical separation of the hydrocarbon group-types, collecting each separate group-type fraction, and using the Envirochem concentrating purge and trap instrument both to separate the LC solvent away from the hydrocarbon group-type and quantitate each fraction via its FID detector.

C. After data reduction the analytical data are transmitted to the UCC time-share computer for storage and/or further manipulation.

A Varian Vista 401 data system was ordered for use with the Carle on-line gas chromatograph and has been delivered. A computer program has been written for our Apple II computer, to be used in conjunction with the Vista 401, which facilitates the storage of the DOE chromatographic data on our time-share computer.

C-L Yang
G. N. Long

Appendix D: Catalyst Test Operations

In the past year, while waiting for the installation of the three new Berty reactor systems for this project, we ran two tests in a Union Carbide owned Berty reactor system. Analytical data on products are nearly complete; the runs will be described below in considerable detail.   One run was made with methanol feed over an LZ-105-6 catalyst, and the other with syngas feed over an iron-loaded amorphous silica-alumina gel catalyst.

Early in January 1982, one of the new Berty reactor units became ready for operation.   Nine runs were made with methanol feed on four different types of molecular sieve. These runs will be described very briefly as little analytical data on the products are yet available.

The first test: Task 1 type

The first Berty run (9502-1) was made with methanol feed over an LZ-105-6 catalyst (the acid form of LZ-105, mentioned in Appendix A).   Catalyst weight was 20 gm.   Methanol was fed at 1.0 WHSV (weight hourly space velocity = gm/hr methanol divided by grams catalyst), in a methanol/nitrogen mixture of 0.8/0.2 mole ratio.   Nitrogen was introduced to help in controlling the reactor pressure at 300 psig. Methanol was fed during day-time hours only for about 7 hours, with nitrogen flowing continously overnight.   Two liquid product collections and an effluent gas collection were made each day. The liquid product samples contained an aqueous layer, an oil layer and a solid hydrocarbon phase.   These three layers were separated by centrifugation and submitted for various analyses. The gas samples were analyzed by gas chromatography.

Methanol conversion and hydrocarbon product selectivity data are presented in Table D1.   The conversion and selectivity results for product samples 1,2 and 7,8 have been revised to correct an earlier data entry error to the computer program. The revised result is also shown in Figure D1.   (Table 1 and Figure 1 in the third quarter Progress Report have errors and are superseded by this report).

TABLE D1

Run 9502-1
Catalyst: LZ-105-6, 20 grams
Feed: Methanol/N_2 mole ratio 0.8/0.2
       Methanol WHSV 1.0 hr.$^{-1}$

| Sample No.	1,2	5,6	7,8	9,10
Hours on Stream	3,6	18,21	22,27	30,34
Pressure, psig.	300	300	300	95
Temperature, °C	369	311	279	374
Mat'l Balance on: Carbon	0.93	.90	0.77	.76
(product/feed) Hydrogen	0.86	.90	0.80	.80
Oxygen	0.79	.94	0.82	.79
Consistency Ratio	1.19	0.95	0.91	0.96
CH_3OH Conversion, %	99.96	99.96	90.95	99.21
Primary Product Distribution, % C-atoms				
Dimethyl Ether	0.00	38.71	94.21	0.00
Hydrocarbons	98.37	61.18	5.76	98.56
Others (CO,CO_2)	1.63	0.11	0.03	1.44
HC Selectivity, % C-atoms				
CH_4	0.78	0.96	4.76	1.09
C_2 hydrocarbons	2.30	6.45	17.58	3.41
C_3^o	23.52	4.94	9.44	23.87
$C_3^=$	0.40	3.40	12.86	0.87
C_4^o	19.00	6.34	9.04	25.37
$C_4^= + C_4^=$	0.21	1.51	4.53	0.47
C_5^o	6.97	7.94	11.50	3.58
$C_5^=$	0.01	.05	0.78	0.04
C_6H_{14}	2.85	4.60	5.85	6.05
C_6H_{12} (& cyclo-C_6)	0.12	.10	0.12	0.22
C_7^+	43.84	63.40	23.54	35.02
Subsum C_5^+	53.79	76.09	41.79	44.92
Fraction of Feed C-atoms as C_5^+HC's	0.53	0.47	0.02	0.44

Supplemental Data:

Solid Sample 1 (NMR): 62.66% of C-atoms are in aromatic rings.

Solid Sample 2 (NMR): 85% Durene

Oil Sample 6 (FIA): 52.5% aromatics, 4.7% olefins,
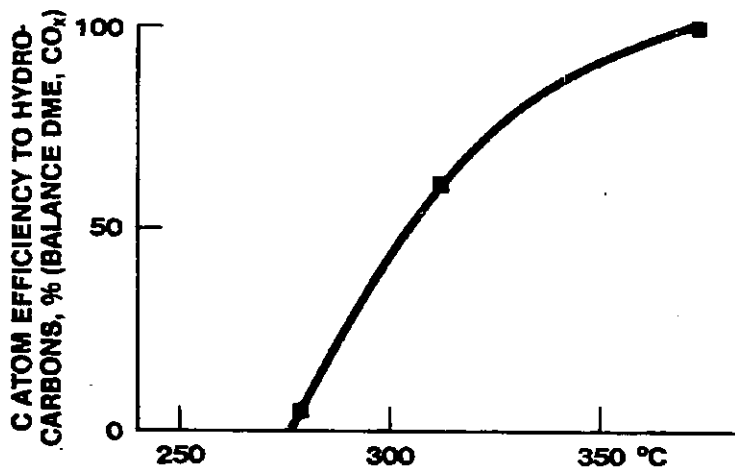   43.1% saturates

FIGURE D1

RUN: 9502-1
CATALYST: LZ-105-6
BERTY REACTOR
FEED: 80-20 CH_3 OH-N_2
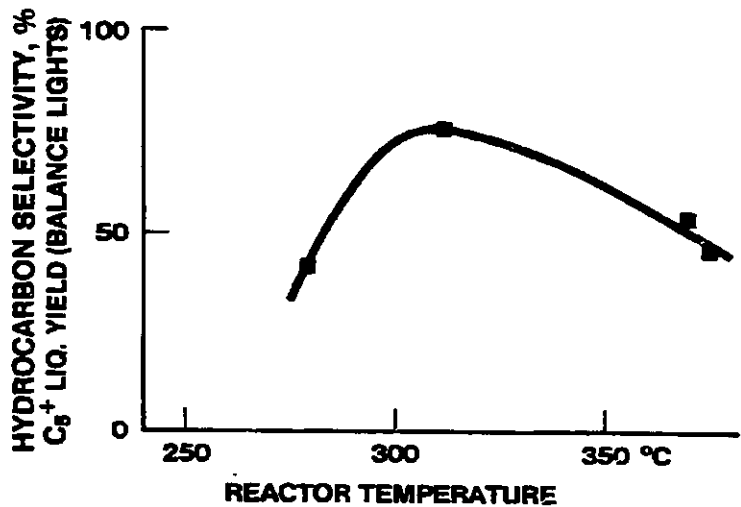@ WHSV on CH_3 OH = 1.0
PRESSURE: 300 PSIG
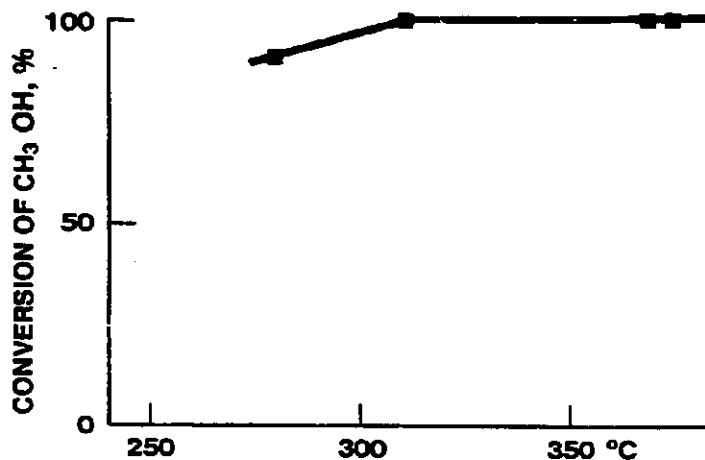
a) % CONVERSION

b) C-ATOM EFFICIENCY

c) HC SELECTIVITY

It is believed that the conversion of methanol proceeds sequentially, with dehydration of methanol to produce dimethylether (DME) and water as the first step. This step proceeds readily over the temperature range studied. Subsequently dimethylether is converted to hydrocarbon products, probably through small olefin intermediates. The second step, the conversion of DME to hydrocarbon products requires temperatures in the upper part of the range tested. The conversion to hydrocarbons varies between 6 and 98% over the range tested.

The hydrocarbon products obtained contain substantial amounts of crystalline solids. Supplemental information on these solids showed that the products consist mostly of durene (1,2,4,5-tetra-methyl benzene), with more than 60% of the carbon atoms in unsaturated bonding.

Additional simulated boiling point distribution data (ASTM D-2887-70T) of the oil and solid product samples (one of which, sample 6, oil and solid, is reproduced here as Figure D2) supported the findings of FIA and NMR in that large peaks of hydrocarbons appeared at the boiling point range of tetra-methyl benzene isomers. It is envisioned that the strong acidity of LZ-105-6 molecular sieve contributed to the multiply-methylated aromatics; however, the very high yield of the multiply-methylated aromatics is probably caused by the total-backmixing feature of the Berty Reactor and the moderately high pressures (300 psig) under which the reaction is carried out, together with the known effectiveness of CH_3OH as a methylating reagent. The cutoff product carbon number at durene has been explained by Mobil Oil (in reference 1 of Appendix A) as due to the size-limiting molecular sieve character of this zeolite structure.
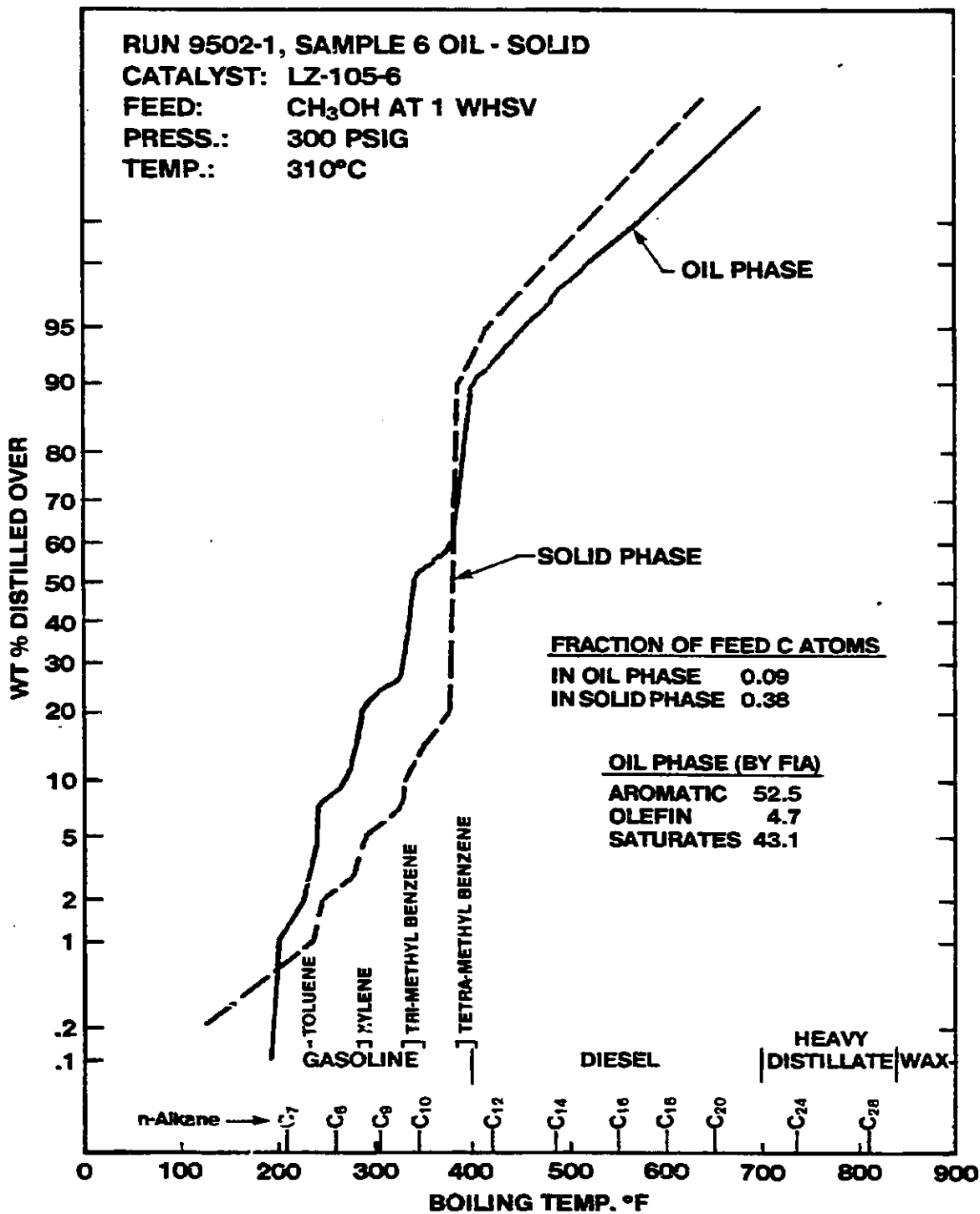
FIGURE D2   SIMULATED DISTILLATION CURVES

The paraffin/olefin ratio of the C_3, C_4 and C_5 hydrocarbon products is plotted in Figure D3. Zeolite catalysts are well known to aid hydrogen transfer, catalyzing the conversion of olefins to a mixture of paraffins and aromatics.

The second test: Task 2 type

Syngas feed of a H_2-CO-Argon mixture (at 60-30-10 mole ratio) was fed at 400 GHSV (gas hourly space velocity) to the Berty Reactor over an iron-loaded (45 wt-%) amorphous SiO_2/ Al_2O_3 gel catalyst (Run 9502-2). The reaction was carried out at 300 psig pressure at temperatures between 250 and 310°C. The conversion of the syngas feed, the transformation of the carbon atoms to either hydrocarbon or CO_2, and the selectivity among the hydrocarbon fractions are tabulated in Tables D2 and D3 and are plotted in Figure D4.

The syngas conversion ranges from 21-59% and increases with reaction temperature as expected. The second plot in Figure D4 shows the percentage of reacted carbon atoms converted to hydrocarbons, the balance being CO_2. Thermodynamically, for the reaction to proceed, the oxygen in CO must be reduced and rejected to a lower free energy level, either as water or as CO_2.
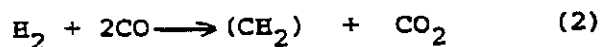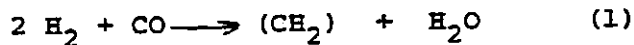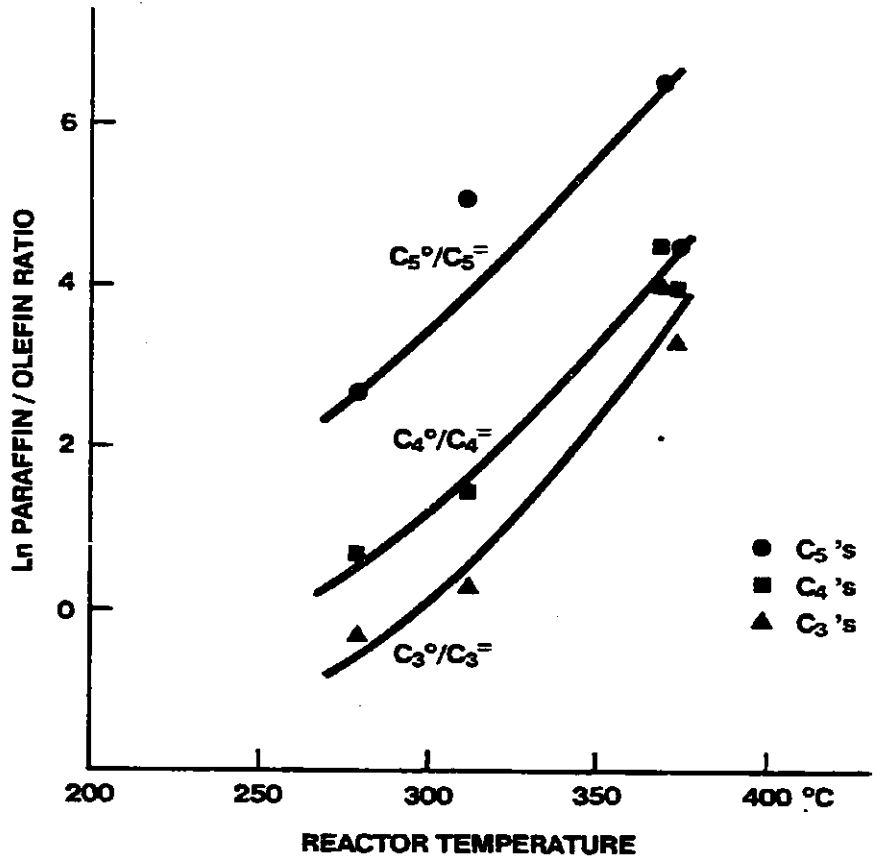
$$2 H_2 + CO \longrightarrow (CH_2) + H_2O \qquad (1)$$

$$H_2 + 2CO \longrightarrow (CH_2) + CO_2 \qquad (2)$$

$$H_2O + CO \longrightarrow H_2 + CO_2 \qquad (3)$$

RUN: 9502-1
CATALYST: LZ-105-6
BERTY REACTOR
FEED: 80-20 CH_3 OH–N_2
                @ WHSV on $CH_3OH = 1.0$
PRESSURE: 300 PSIG

EXPERIMENTAL RATIO OF $C_n^o/C_n^=$

RUN 9502-2

Catalyst: 45% Fe on amorphous SiO_2/Al_2O_3 gel: 80 cc., 70.93 gm.

Feed: Syngas 60-30-10, H_2-CO-Argon, 400 GHSV hr.$^{-1}$

| Sample No.	1	2	4
Hours on Stream	25	48	96
Pressure, psig.	300	300	300
Temperature, °C	279	279	311
Mat'l Balance on: Carbon	.94	.94	.95
(product/feed) Hydrogen	1.04	1.10	1.08
Oxygen	.98	.97	.96
Consistency Ratio	.94	.945	.99
H_2/CO Usage, from products	1.21	1.24	1.19
H_2/CO Usage, from feed	1.10	1.16	1.04
Conversion on CO, %	71.29	66.92	84.90
Conversion on H_2, %	40.60	40.03	45.77
Conversion on (CO+H_2), %	51.05	49.19	59.09
Primary Product Distribution, % C-atoms			
Hydrocarbons	61.08	62.05	58.93
CO_2	38.92	37.95	41.07
HC Selectivity, % C-atoms			
CH_4	36.72	35.80	54.54
C_2 hydrocarbons	19.47	19.86	20.3
C_3^o	18.93	18.89	12.56
$C_3^=$	2.70	2.91	.45
C_4^o	8.59	8.24	4.69
$C_4^=(+C_4^{==})$	2.91	3.13	.42
C_5^o	3.96	3.81	1.86
$C_5^=$	1.17	1.11	.23
C_6H_{14}	2.38	2.14	.94
C_6H_{12} (& cyclo-C_6)	.06	.04	.00
C_7^+	3.11	4.06	4.01
Fraction of Feed C-atoms as C_5^+HC's	0.065	0.069	0.041
Effluent K for Water-: Gas Shift $\dfrac{[H_2] \cdot [CO_2]}{[CO] \cdot [H_2O]}$	6.01	4.81	15.55
Equilibrium K, at above T	53.6	53.6	33.3

Catalyst: 45% Fe on amorphous SiO_2/Al_2O_3 gel: 80cc., 70.93 gms.

Feed: Syngas 60-30-10, H_2-CO-Argon, 400 GHSV hr.$^{-1}$

Sample No.		7	8	9
Hours on Stream		168	192	216
Pressure, psig.		300	300	300
Temperature, °C		250	281	279
Mat'l Balance on:	Carbon	.74	.92	.94
(product/feed)	Hydrogen	1.22	.99	1.18
	Oxygen	.77	.94	.95
Consistency Ratio		.95	.96	.98
H_2/CO Usage, from products		1.82	1.30	1.29
H_2/CO Usage, from feed		1.10	1.21	1.03
Conversion on C, %		30.26	61.47	64.41
Conversion on H_2, %		17.21	38.46	34.08
Conversion on (CO+H_2), %		21.65	46.29	44.40
Primary Product Distribution, % C-atoms				
Hydrocarbons		81.02	64.04	64.00
CO_2		18.98	35.96	36.00
HC Selectivity, % C-atoms				
CH_4		24.29	36.11	36.33
C_2 hydrocarbons		16.06	20.50	20.19
C_3^O		16.06	18.08	17.56
$C_3^=$		6.89	3.11	2.69
C_4^O		8.24	7.64	7.40
$C_4^=$		6.83	3.06	2.94
C_5^O		4.96	3.48	3.57
$C_5^=$		3.43	1.52	.74
C_6H_{14}		4.22	2.28	2.43
C_6H_{12} (& cyclo-C_6)		.93	.31	.09
C_7^+		8.09	4.11	6.04
Subsum C_5^+		21.63	11.50	12.87
Fraction of Feed C-atoms as C_5^+HC's		0.175	0.074	0.082
Effluent K for Water-Gas Shift : $\dfrac{[H_2] \cdot [CO_2]}{[CO] \cdot [H_2O]}$		0.655	3.65	4.45
Equilibrium K at T above		86.4	52.0	53.6

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FIGURE D4

RUN: 9502-2

CATALYST: 45% Fe on
Amorphous SiO_2–Al_2O_3

BERTY REACTOR

FEED: 60-30-10 H_2–CO–Ar
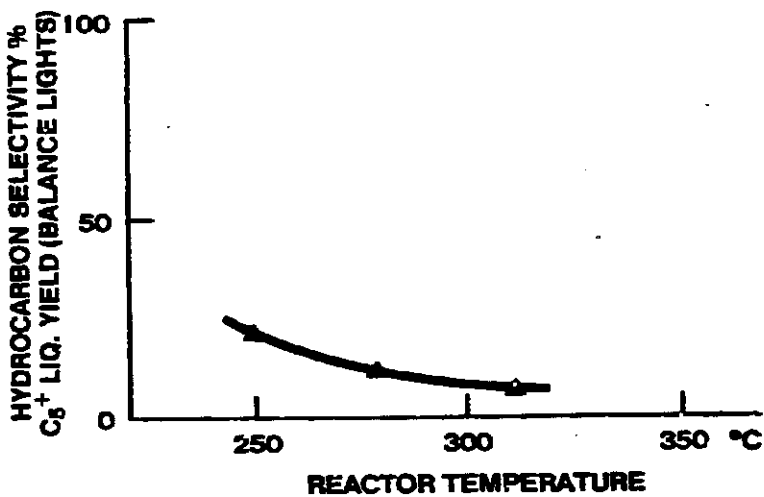@ 400 GHSV

PRESSURE: 300 PSIG

a) % CONVERSION
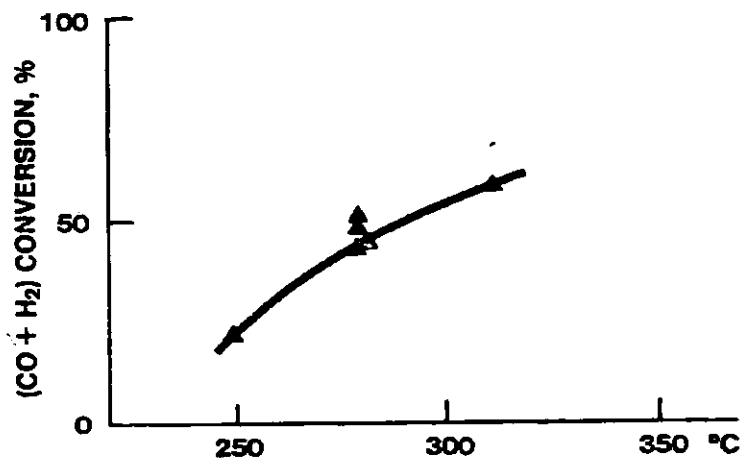
## b) C-ATOM EFFICIENCY
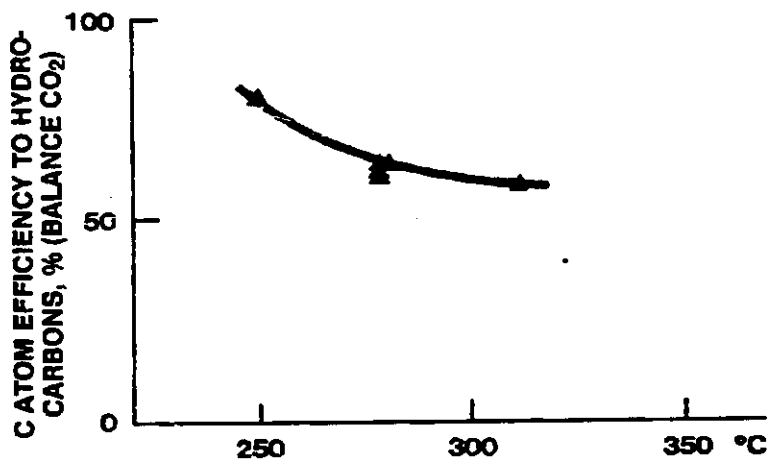
c) HC SELECTIVITY

Water is the primary product observed in our operation; CO_2 is made through the water-gas shift reaction (3). In either case, it takes one mole of CO and two moles of H_2 to produce one mole of hydrocarbon species, symbolized as (CH_2) in the equations above. At lower temperatures, the apparent high selectivity of CO to hydrocarbons rather than CO_2 is a reflection of low water-gas shift activity at these temperatures. The extent of the shift reaction over the catalyst can be measured by computing the shift reaction constant from effluent concentrations of the relevant components ($K = (H_2) \cdot (CO_2)/(CO) \cdot (H_2O)$), and comparing these with the equilibrium shift reaction constant at the reaction temperature, as shown in Figure D5. The plot in Figure D5 (log scale) clearly shows that the water-gas shift reaction is kinetically controlled by the catalyst (Fe) as well as by the reaction temperature.

The last plot in Figure D4 shows higher selectivity for C_5^+ liquid yield (vs. C_1-C_4 light hydrocarbons) at lower temperatures. This is expected from thermodynamics. The C_5^+ yield includes both the condensed oil layer product collected from the product receivers and the C_5^+ product found in the gas phase. Unfortunately the amount of condensed oil product was too small to further characterize the nature of the product. Amorphous silica-alumina gel in combination with iron metal does not show much promise for converting syngas to C_5^+ liquid fuel product.

The ratio of paraffins to olefins in the light hydrocarbon fraction is of some interest and is therefore plotted in Figure D6. Hydrogenation equilibrium constants for the reaction of light olefins to paraffins are shown in Figure D7. (calculated using free energy data from Stull, Westrum, Sinke: "The Chemical Thermodynamics of Organic Compounds", John Wiley, 1969). The fact that increasing temperature lowers the ratio of paraffins to olefins at equilibrium (Figure D7), while the data show that increased temperature raises the ratio (Figure D6) indicates that the conversion is kinetically controlled by the catalyst at test conditions.

FIGURE D5

RUN: 9502-2

CATALYST: 45% Fe on
Amorphous SiO_2–Al_2O_3

BERTY REACTOR

FEED: 60-30-10 H_2–CO–Ar
@ 400 GHSV
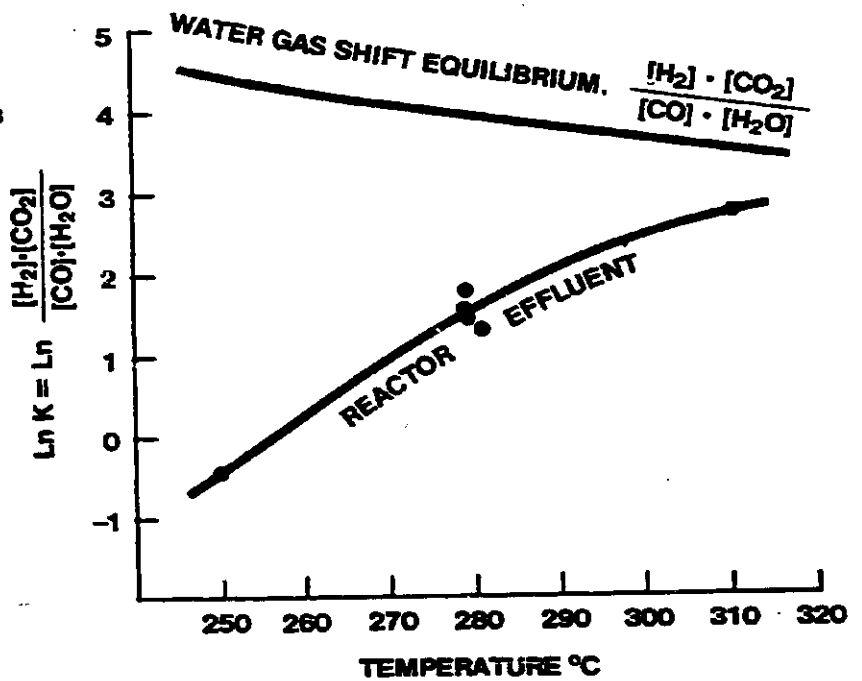
PRESSURE: 300 PSIG

WATER GAS SHIFT CONVERSION

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FIGURE D6

RUN: 9502-2

CATALYST: 45% Fe on Amorphous $SiO_2-Al_2O_3$

BERTY REACTOR

FEED: 60-30-10 $H_2-CO-Ar$ @ 400 GHSV

PRESSURE: 300 PSIG

EXPERIMENTAL RATIO OF $C_n^\circ/C_n^=$

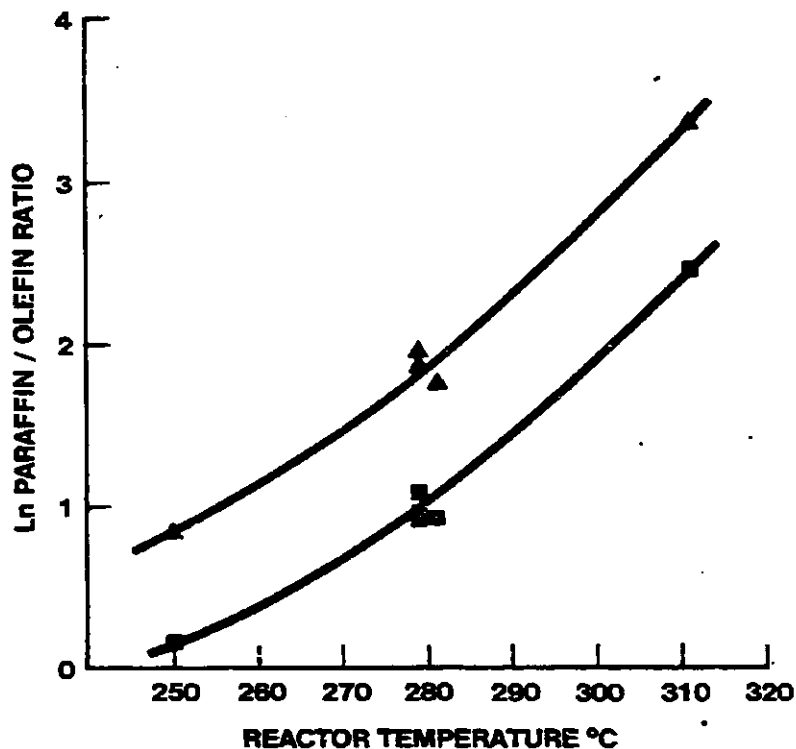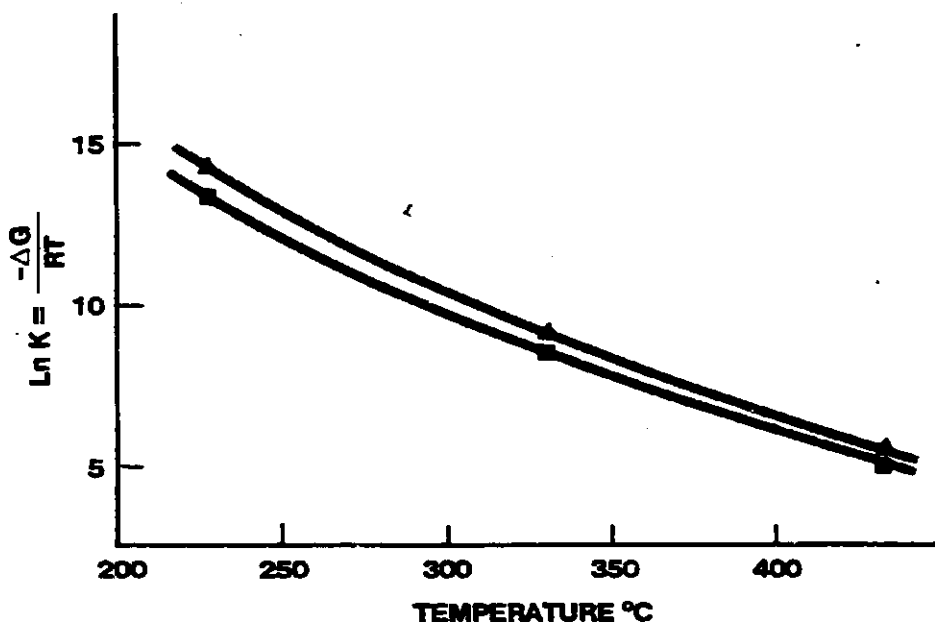## FIGURE D7

HYDROGENATION EQUILIBRIUM FOR $C_n^= + H_2 \rightarrow C_n^\circ$

(DATA FROM STULL, WESTRUM, SINKE)

Current Operations

One of the new Berty Reactor units for this project is ready for operation. We have been operating the unit with methanol feed. Nine runs were made on four different types of catalysts: LZ-105-6, "ZSM-5", Y-82 and UCC-101. The feed consisted of CH_3OH-N_2 mixture in approximately 63-37 mole ratio, with methanol fed at about 1 WHSV and a catalyst charge in each run of about 20 grams. Operating problems were encountered in some runs due to a large amount of solid made in the product, which resulted in plugging of the discharge line and valve, pressure build-up in the system and automatic shutdown by the built-in safety devices. In two of the runs, we did not have an effluent gas sample to make a material balance. In the rest of the runs, material balances will be made when analytical data on the product become available. Most of the runs were made at 300 psig and 370°C. Because of the excessive amount of the solid in the product, two of the later runs were operated at lower pressures of 50 and 25 psig with the hope of producing more liquid hydrocarbon product and less solid. A higher reaction temperature (408°C) was also tried. Table 4 lists the runs we made during the current quarter.

Table D4

DOE METHANOL RUNS AT 1 WHSV CH$_3$OH

CATALYST AND PROCESS CONDITIONS

RUN NO.	CATALYST	PSIG	T^{O}C
9710-1	LZ-105-6	332	370
9710-2	LZ-105-6	307	369
9710-3	ZSM-5*	303	369
9710-4	UCC-101	322	377
9710-5	UCC-101	298 299	372 401
9710-6	Y-82	294	373
9710-7	Y-82	300	402
9710-8	UCC-101*	50 50 50	373 373 403
9710-9	UCC-101*	25 28	370 408

* Synthesized at Tarrytown (see Appendix A)

Appendix E: Study of Structure and Chemistry of Relevant
Catalyst Surfaces during the Hydrogenation of CO.

G. A. Somorjai

The low-pressure-high-pressure apparatus that is to
be used to study the structure and catalytic activity of low
surface area metal components, for use in combination with
the shape-selective catalyst for the hydrogenation of carbon
monoxide, has been completed (see Figure El for a schematic
representation). Testing and troubleshooting of its various
components is under way.

Several rhodium compounds that are the combination of
rhodium ions incorporated in refractory oxide matrices have
been synthesized: Na_2RhO_3, $GdRhO_3$, $CuRh_2O_4$, WRh_2O_4 and $TbRhO_3$.

The composition and valency of these compounds will be
studied by photoelectron spectroscopy. In work thus far, the
oxidation states of the Rh ions in gadolinium and tungsten
rhodates were successfully determined. The valence of the Rh
in both cases was +3, as expected. Also, scanning Auger
spectroscopy determined that the surface composition of these
compounds is homogeneous.

Iron-manganese and molybdenum-sulfur catalysts are also
being prepared. All of the compounds will subsequently be
tested for carbon monoxide hydrogenation activity and selectivity.

Another apparatus is being modified to study surface
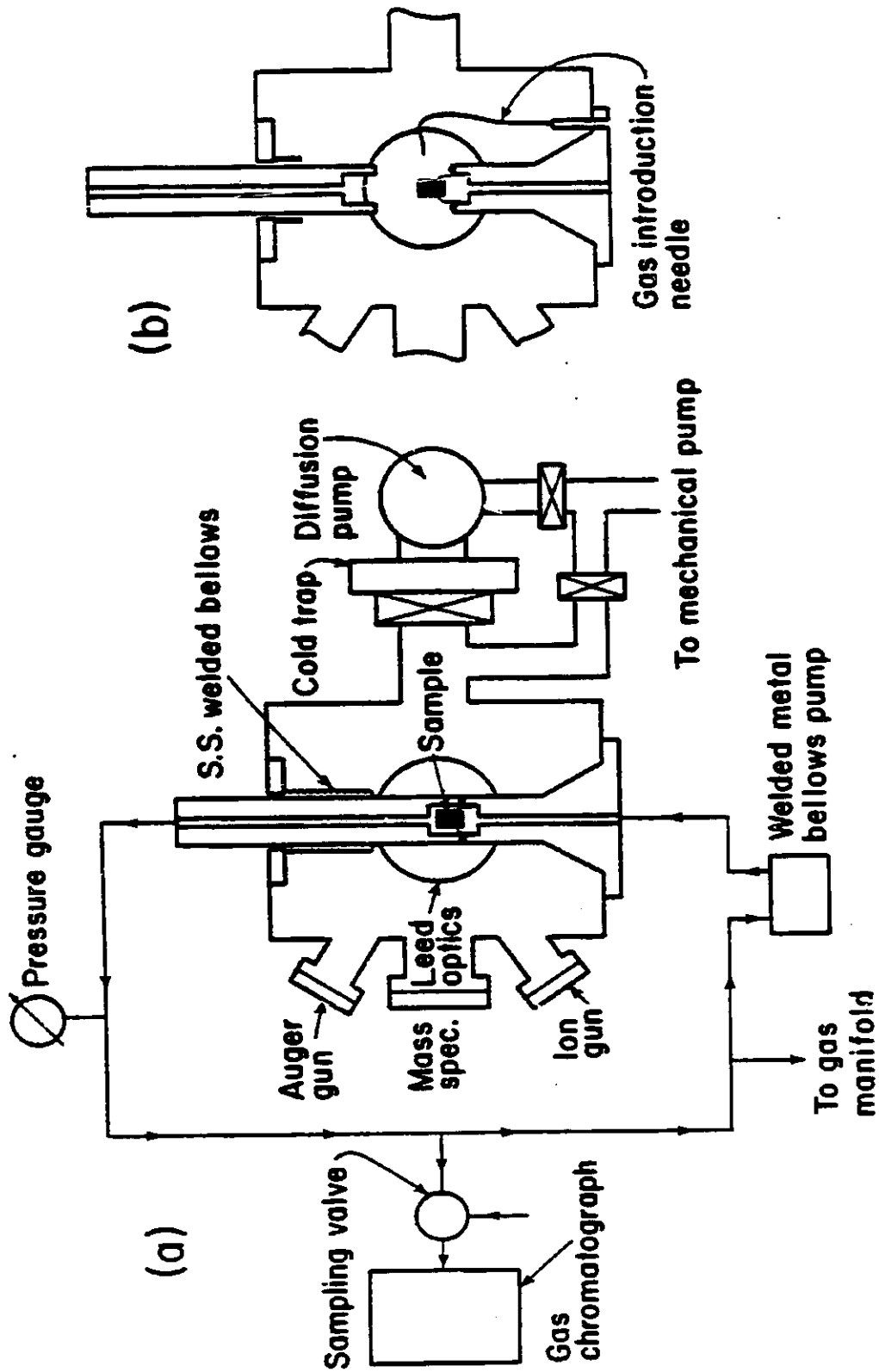intermediates by electron loss spectroscopy.

(a)

(b)

Figure E1   Schematic representation of the low pressure – high pressure apparatus