LIQUID HYDROCARBON FUELS FROM SYNGAS. SIXTH TECHNICAL PROGRESS REPORT, JUNE-AUGUST 1982

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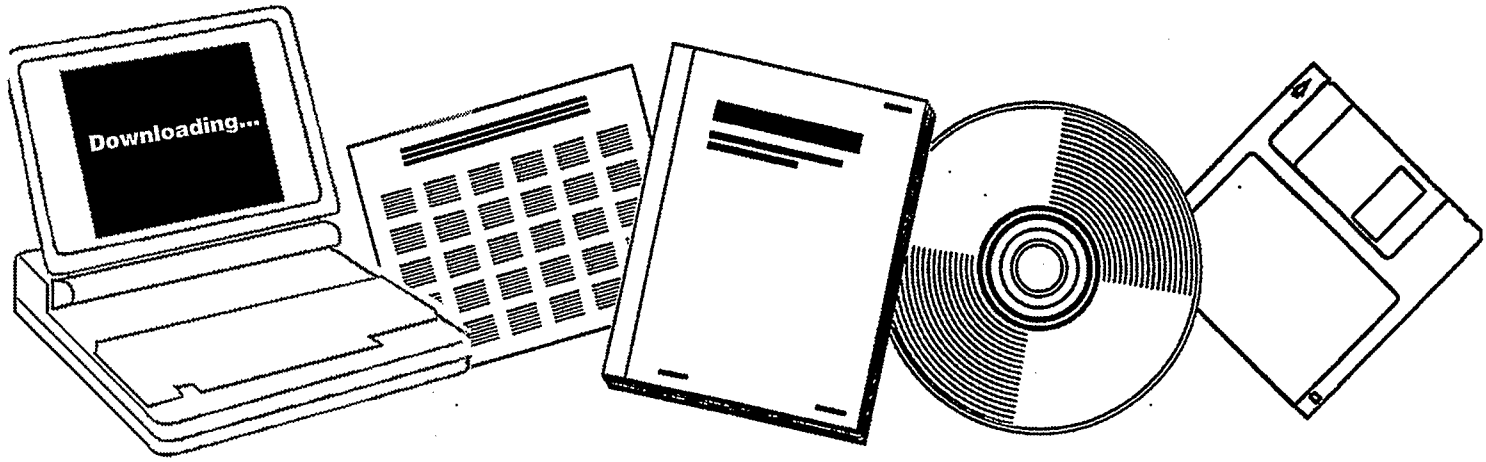

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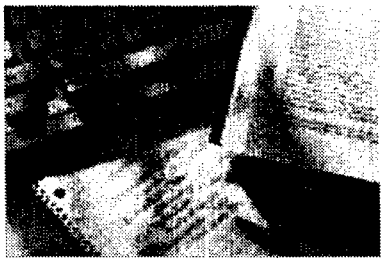

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Sixth Quarterly Report

June - August 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) are being evaluated for converting low molecular weight liquids such as methanol and propylene to desired products like gasoline, turbine and diesel fuel. In Task 2, the feed is syngas ($CO + H_2$), and the catalyst is 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, 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 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

Task 1

Four new aluminophosphate molecular sieves were prepared in test quantities. Chemical modification to increase their catalytic activity is planned. One of these (unmodified), $AlPO_4$-11, was tested and found rather inactive for propylene oligomerization. Appendix A reports synthesis work on both Task 1 and Task 2 catalysts.

Appendix B reports development work on analytical techniques. The on-line G.C. was put into service. Separation procedures for the proposed liquid chromatographic alternative to FIA analysis were found unsatisfactory.

Data from seven tests of propylene oligomerization with several catalysts are reported in Appendix C. Changing from methanol to propylene feed eliminated earlier problems associated with the solid part of methanol reaction products. Tests with UCC-101, a proprietary UCC, large pore molecular sieve of moderate acidity, resulted in reaction products having both gasoline and diesel fractions. Tests with LZ-105-6, similar in properties to Mobil's ZSM-5, resulted in good yield of gasoline range product with very little diesel range product. Feeding water along with the propylene and hydrogen was found to markedly reduce the rate of deactivation of both LZ-105 and UCC-101. Another new UCC proprietary molecular sieve, UCC-104, was active and very selective for the production of gasoline range hydrocarbons (more than 95% selective to C_5^+). At low temperatures, the UCC-104 produces less propane than the LZ-105-6, i.e. the UCC-104 is more selective to liquid product formation than catalysts like ZSM-5.

Also included in Appendix C are some Task 1 screening tests on a microreactor setup.

Task 2

Results of seven Task 2 tests appear in Appendix C. In four runs the catalysts had reasonable activity but were not as selective to liquid products as desired. The very low catalyst activity in the other three tests is believed due to problems with catalyst preparation or activation.

Task 3

The high pressure-low pressure cell in Professor Somorjai's lab has been completed. Preliminary F-T tests were carried out in it. A catalyst, prepared at Tarrytown by decomposing adsorbed metal carbonyl inside the zeolite, showed good selectivity to olefins in a test in this apparatus.

V. CHANGES

No changes in the last quarter.

VI. FUTURE WORK

Promising SSC catalyst types will continue to be evaluated in Task 1 Berty runs. Tests with MC loaded UCC-104 will be done using syngas feed. Exploratory work on metal-loading techniques will continue.

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RCE/eh

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APPENDIX A: CATALYST SYNTHESIS

Synthesis of catalysts to be used in Task 1 testing has proceeded well this quarter. More of the previously synthesized materials were formed as 20% alumina bonded extrudates ready for testing. Sodium exchanged LZ-Y62, was further cation exchanged with rare earth to give a RE(III)Y62. The rare earth accounted for 70% of the ion exchange capacity of the zeolite. This was prepared as a continuation of the series of catalysts prepared last quarter with multivalent cation exchange to create Lewis acid sites in the zeolite. The LZ-Y62 was also cation exchanged with cesium to give a CsY62. The activity of this material for propylene oligomerization will be compared with that of NaY62, which was tested earlier this quarter, to see the effect of cation size on the activity of the catalyst. Zeolite Omega was sodium cation exchanged in preparation for making a partially acid Ω-zeolite catalyst.

Additional scaleup batches of $AlPO_4$-5, 11, 17, 31 have been prepared by hydrothermal techniques using Parr 2L stainless steel autoclaves and the procedures described in the Wilson patent (1). The goal of this synthesis effort is to prepare enough material of the four structure types listed above to provide material both for catalytic testing and to try chemical modification techniques on these new materials to enhance their catalytic activities. The latter materials would also be tested catalytically to determine if the chemical modification techniques were effective in changing the acidity characteristics of the material, or some other property of these new molecular sieves.

The major emphasis in synthesis activity this quarter has been to prepare these materials, phase-pure, in sufficient quantities to permit thorough testing of each structure type. This has meant that synthesis procedures have had to be modified, or in some cases different structure-directing templates have had to

be used. At least one satisfactory 200g batch of each composition has been prepared. One more batch of each will be synthesized to provide material for modification structure of each composition. So far only $AlPO_4$-11 has been tested for propylene oligomerization. Two new Union Carbide molecular sieves labeled UCC-104 and UCC-105 have been introduced into the program and formed as 20% alumina-bonded extrudates. One of them, UCC-104 was tested for propylene oligomerization this quarter.

Synthesis and characterization of metal-loaded molecular sieve catalysts for Task 2 testing has also proceeded well this quarter. A previously synthesized material, with 50% Fe as Fe_2O_3 precipitated on UCC 101, was formed as a catalyst and calcined under different conditions, temp 250°C-500°C, time 2 hours - 16 hours, to see if the form of the Fe_2O_3 and activation procedure affected the catalytic properties of these iron-loaded molecular sieves. It appears that catalyst preparation or contamination muddled the results of this investigation. Many of these materials were completely inactive for Fischer-Tropsch synthesis even though the iron had been reduced. One of the completely inactive catalysts was suspected of massive sintering of the iron during activation, but SEM analysis showed no real differences in the form of the iron after testing between a catalyst which had been active and the one which was suspected of sintering. EDAX showed no sign of sulfur contamination, another possible explanation for inactivity. At the present the cause of the problem with that batch of catalyst is still unclear.

Other catalysts of this type have also been prepared. A catalyst which was to be 20% Fe was synthesized by the stoichiometric addition of 6M aqueous ammonia to a boiling slurry of the zeolite LZ-52, in aqueous ferric nitrate. The chemical analysis showed the anhydrous material to be 20.7% Fe. This analysis shows the material to be 29.6% Fe_2O_3 with the balance being zeolite. This material was tested at the very end of this quarter and found to be active for F-T synthesis. A similar catalyst has been prepared using silicalite (2) as the molecular sieve. Catalysts have

also been prepared by partial ion exchange of F-T metals into molecular sieves. The catalysts of this type synthesized thus far have been Fe(III) and Co(II) ion exchanged into LZ-13X.

The synthesis and characterization of catalysts made by the occlusion of metal carbonyls, $Fe(CO)_5$, $Fe_2(CO)_9$, and $Mn_2(CO)_{10}$ in molecular sieves has begun. The materials prepared thus far are shown below.

		Anhydrous	
Notebook #	Molecular Sieve	% Fe	% Mn
9674-34	Hydrated UCC 101	5.8	---
9674-37	Hydrated UCC 103	6.3	---
9674-40	Dehydrated UCC 103	1.3	8.5
9674-42	Dehydrated UCC 103	1.2	7.8
9673-17	Dehydrated UCC 103	1.1	7.3

The metal carbonyls were adsorbed in the pores of UCC 101 and acid extracted UCC 101, UCC 103. The attempted total metal loading level was 10%. When hydrated molecular sieves were used only 5.8 and 6.3% metal loading were obtained after oxidation decomposition of the metal carbonyls. When the molecular sieves were air calcined to remove the adsorbed water just prior to adsorption of the carbonyls, metal loadings of 8.6 - 9.8% were obtained after oxidation decomposition of the metal carbonyls. In the mixed manganese-iron system the Mn:Fe ratio in the product was greater than the desired 4:1, indicating preferential loss of iron during decomposition. Further characterization of these catalysts using ESCA and TEM is proceeding.

A description of the catalysts tested this quarter is given in Table I.

(1) U.S. Patent 4,310,440

(2) U.S. Patent 4,061,724

TABLE 1

CATALYSTS TESTED THIS QUARTER

TASK 1

NaY-62 10% H-Y62 40% H-Y62	These are a series of large pore zeolites with a three-dimension pore structure, which were first cation exhcanged with sodium and then partially cation exchanged with ammonium. The proton form of the zeolite is produced by calcination.
97% H-Y62	Similar to the above materials except produced by more complete ammonium exchange.
CaY-62	The sodium cation exchanged form of Y was subsequently cation exchanged with calcium.
LZ-105-6	A Union Carbide medium pore molecular sieve with a SiO_2/Al_2O_3 ratio of about 35, having a structure similar to ZSM-5.
$AlPO_4$-11	A new Union Carbide aluminophosphate molecular sieve with a pore size of ~6Å and undetermined structure.
UCC-101	A large pore molecular sieve having moderate acidity.
UCC-103	The acid extracted form of UCC-101.
UCC-104	A Union Carbide proprietary molecular sieve.
UCC-106	A large pore molecular sieve having moderate acidity.

TASK 2

Reference Fe	An unsupported potassium-promoted iron catalyst.
Fe-Y52	20% iron as $Fe_2O_3 \cdot XH_2O$ precipitated on sodium LZ-Y52.
UCC-201	A catalyst with ~40% iron as $Fe_2O_3 \cdot XH_2O$ precipitated from a nitrate solution on UCC-101.
UCC-202	A catalyst made by the oxidative decomposition of manganese and iron carbonyls which had been adsorbed inside UCC-103, resulting in about 8% by weight of ~6:1n:1Fe.

APPENDIX B: ANALYTICAL TECHNIQUES

The new Carle Model 530 gas chromatograph, for on-line gas phase analysis, required several major modifications to the original plumbing scheme to obtain the desired chromatographic separations. These changes were made and the instrument has been in service since mid-June.

The Envirochem/Unacon Model 810B sample concentrating purge and trap G.C., which was ordered to do capillary column analysis of the C_6 to C_{22} carbon range "heart-cut" of the LHF product samples, arrived in early June. The instrument has been set up and work is underway to develop the analytical technique which will be used to fractionate and analyze the heart-cut.

The samples of LHF products which we reported last quarter a) had been separated by Perkin-Elmer into hydrocarbon group-types via liquid chromatography and b) were awaiting efforts by Envirochem to quantitate the fractions via their Unacon Model 810B, showed the following results:

1. The saturates fraction was a lighter cut than the original sample. Higher boiling saturates were missing.
2. Part of the mid to heavy saturates were found in the olefins fraction.
3. Normal paraffins were evident in the aromatics fraction.

All of these results indicate that the highly non-polar character of the freon-type LC solvent cannot accomplish group type separations of wide boiling mixtures.

Perkin-Elmer subsequently tried a pentane solvent system and returned the separated fractions to us for analysis using our newly acquired Unacon Model 810B. The pentane solvent was not able to separate the saturates from the olefins and therefore was not acceptable. Perkin-Elmer expressed a desire to further investigate techniques to accomplish the desired separations. They indicate

that the wide boiling range of our samples is the prime reason why current LC techniques have not been successful.

In the hope that they can resolve these problems, we have placed a conditional purchase order with Perkin-Elmer for an LC system. Delivery of the LC would not be made until we are satisfied with the separation techniques they develop. The conditional purchase order places us on the manufacturing list and is automatically cancelled in four months, if satisfactory techniques have not been developed by that time.

Data on FIA analyses (performed on almost all liquid samples taken this quarter) are not presented in this quarterly report. Significant discrepancies in analyses, submitted as duplicates or from nearly equivalent conditions, have cast doubt on the reliability as well as the accuracy and reproducibility of the techniques as used for our samples. Work to find a reliable way to distinguish olefins and aromatics separately from saturates is starting.

APPENDIX C

CATALYST TESTING OPERATIONS

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G. N. Long
L. F. Elek
P. K. Coughlin

CONTENTS

INTRODUCTION

During the months of June, July and August, 1982, we had three reactor systems in operation - two Berty internal recirculation reactors and one fixed bed micro-reactor. In the two Berty reactors, we made ten runs with propylene feed (Runs 9972-1 to 9972-10) and ten runs with syngas feed (Runs 9710-18, 9710-19, 10011-1 to 10011-6, 9972-11, and 9972-12). In the micro-reactor system, we made five runs with propylene feed. A brief description of the runs is presented in Tables 1, 2 and 3. The catalysts used are described in table I of Appendix A.

In the Task 1 program for evaluation of the shape-selective component of the catalyst, we report on the performance of two new catalysts on propylene feed, one tested both with and without co-fed steam. Steam stabilizes the catalyst performance and slows down catalyst deactivation. The first new catalyst was an $AlPO_4$-11 catalyst, a new microporous crystalline molecular sieve of the aluminophosphate series discovered by Union Carbide Corporation scientists (U.S. patent 4,310,440). It has practically no catalytic activity for propylene reaction. The result is not surprising, since the as-synthesized aluminophosphate materials have perfect electric charge balance in their crystal structure and have no ion exchange capacity. However, this does not preclude utility as a shape selective component in syngas reactions of Task 2. Another new molecular sieve, UCC-104, was also tested. The selectivity of UCC-104 for liquid products (91 to 95% C_5^+) was superior to that of LZ-105-6 or UCC-101.

In the Task 2 program, the results of syngas operation using Fe-loaded UCC-101 catalyst and Mn-Fe-loaded UCC-103 catalyst are reported. None of the catalysts reported here contain promoters and therefore are not expected to have high selectivities to heavier hydrocarbons; they are only preliminary tests of activity. The manganese-iron loaded UCC-103 made by the oxidative decomposition of the metal carbonyls inside the molecular sieve was almost completely inactive for F-T synthesis. The best run on Fe-loaded UCC-101 catalyst (Run 9710-19) was carried out with the reactor pressure at 300 psig and temperatures of 250, 284, and 313°C with 60/30/10 H_2/CO/Argon feed. It achieved syngas conversion levels of 34, 47 and 53% and C_5^+ product selectivity of 40, 13 and 7% at the respective temperatures of 250, 284, and 313°C. One of the product samples (Run 9710-19-5 at 250°C) showed a selectivity of 60% C_1-C_4 light ends, 29% C_5-420°F gasoline range and 10% 420-700°F diesel range products. Simulated boiling point distributions of the collected liquid products are also presented. The performance of each catalyst is also a function of its activation conditions. These are detailed in the descriptions of individual runs.

As noted in Appendix B, FIA results obtained this quarter are not reported.

TABLE 1 OPERATING STATUS

PROPYLENE RUNS IN FIXED BED MICRO-REACTOR

RUN NO.	CATALYST	FEED H2:C3H6	C3H6 WHSV	PSIG	T C	LIQUID HC PRODT
10027-1	LZ-105-6	2:1	1	150	340	NO
10027-2	"	"	"	"	"	YES, 11.3 GM
10027-3	10%H-Y62	2:1	1	150	340	NO
10027-4	"	"	"	"	"	NO
10027-5	97%H-Y62	2:1	1	150	340	YES, 1.89 GM
		"	"	"	"	YES, 0.91 GM
10027-6	40%H-Y62	2:1	1	150	340	YES, 0.66 GM
10027-7	NA-Y62	2:1	1	150	340	NO

TABLE 2 OPERATING STATUS

PROPYLENE RUNS IN BERTY REACTOR

RUN NO.	CATALYST	FEED H2:C3H6:H2O	C3H6 WHSV	PSIG	TEMPERATURE C
9972-1	LZ-105-6	1: 1: 0	1	150 150,75,300 300,150,50	280,310,340,370,280 280 370
9972-2	LZ-105-6	1: 1: 2	0.4	150	410
9972-3	UCC-101	1: 1: 2	0.4	150	410
9972-4	UCC-101	1: 1: 3	0.5	150	280,340
9972-5	ALPO-11	2: 1: 1	0.5	150 300	280,340 340
9972-6	UCC-104	1: 1: 0	0.5	150	280,340
9972-7	UCC-104	2: 1: 1	0.5	150	280,340
9972-8	UCC-103	1: 1: 2	0.5	150	280,340
9972-9	UCC-106	1: 1: 2	0.5	150	280,340
9972-10	CA-Y62	1: 1: 2	0.5	150	280,340

TABLE 3 OPERATING STATUS

SYNGAS RUNS IN BERTY REACTOR

RUN NO.	CATALYST	H2:CO:AR	GHSV	PSIG	T C	%CONV	%C5+	SAMPLE NO & REMARKS
9710-18	UCC-201 (FE-UCC-101)	60:30:10	435	300	250	5	24	
9710-19	UCC-201	60:30:10	435	300	250	34	40	3,4,5
		"	"	297	284	47	13	6,7,8
		"	"	294	313	53	7	9,10
		45:45:10	"	297	313	69	17	
10011-1	UCC-201	60:30:10	435	290	280	44	15	
				"	"	18*	11	*AFTER 113 HRS @410F
10011-2	UCC-201	60:30:10	300	300	220	10	15	
		45:45:10	"	"	219	9	32	
		"	"	"	270	37	29	
		"	"	100	251	15	36	
10011-4	UCC-201	45:45:10	300	100	273	17	19	
		"	"	103	302	35	15	
10011-5	UCC-201	45:45:10	300	105	279	12	17	
10011-3	UCC-202 (MN-FE-UCC103)	45:45:10	300	300	220	3	7	
		"	"	"	252	4	17	
10011-6	REF. CAT. FE203,K20	50:50: 0	300	102	254			BRN OIL TO YLW WAX
		45:45:10	300	98	254			YLW WAX
		60:30:10	300	95	254			YLW WAX
		"	"	"	281			YLW GRN WAX
		"	"	93	309			YLW WAX
		"	"	32	310			YLW WAX
		"	"	"	342			YLW OIL
9972-11	UCC-201	50:50:0	300	101	252			
9972-12	FE-Y52	60:30:10	300	100	251			
		"	"	"	280			

Propylene Runs in Fixed Bed Micro-Reactor System

A fixed bed micro-reactor system owned by UCC was used as an initial screening device on the activity of several catalyst candidates as part of the Task 1 test program. Seven grams of catalyst was used in each test. The feed consisted of a mixture of hydrogen and propylene at 2:1 H_2:C_3H_6 mole ratio; propylene was fed at 1 WHSV (weight hourly space velocity). The reaction was run at 150 psig and 340°C. Propylene was fed during day-time hours only, with hydrogen flowing continuously overnight. A catalyst was usually tested for two days. This is a rough screening test, designed to see if the catalyst has any activity for making of liquid product. If so, the catalyst may be considered for further testing in the Berty reactor.

We tested five catalysts in the micro-reactor system: LZ-105-6 (used as reference) and four modified LZ-Y62 catalysts starting with sodium-exchanged LZ-Y62, of various acidity: NaY62, 10% H-Y62, 40%H-Y62, 97% H-Y62. In these screening tests, the respective liquid product makes were: LZ-105-6, 11.3 gm.; NaY62, none; 10% H-Y62, none; 40% H-Y62, 0.66gm.; 97% H-Y62, 2.8 gm. These runs are listed in Table 1.

Propylene Operation in the Berty Reactor

Hydrogen and steam were co-fed with propylene into the reactor in order to simulate the reactor environment of a syngas operation in an internal recirculation reactor. The feed composition is expressed in terms of mole ratios of H_2:C_3H_6:H_2O. The H_2:C_3H_6 ratio was generally 1 to 1, and on occasion 2 to 1. The ratio of steam co-fed to propylene included values of 0, 1, 2 and 3. In all the reported runs except Run 9972-1, the feed mixture was fed continuously without interruption. For Run 9972-1, the propylene was fed during the daytime hours only, with the hydrogen fed continuously throughout the night.

Seven different types of catalysts were used in this series of operations. For the intermediate pore molecular sieves, we tried LZ-105-6, $AlPO_4$-11, and for the large pore molecular sieves, we tried UCC-101, UCC-103, UCC-106 and Ca-Y62, in addition we used UCC-104. For a description of these catalysts, please refer to the section on Catalyst Synthesis and Characterization in this report and earlier quarterly reports.

Seven propylene runs (Run 9972-1 to 9972-7) will be covered in this report. The product samples for the other three runs have not been fully characterized and will be covered in the next report.

Run 9972-1, Feed 1:1:0 (H_2:C_3H_6:H_2O) on LZ-105-6

In this run, as mentioned earlier, the propylene was fed during daytime hours with hydrogen being fed continuously overnight. Since LZ-105-6 is known to be a stable catalyst, it was tested over an extensive range of temperatures and pressures. The conditions of the operation and results are tabulated in Tables 4A to 4E. The Tables list the results including: material balances; conversion of C_3H_6; product selectivities grouped by light ends, gasoline fraction and diesel fraction; product characterizations, such as iso/normal ratios, paraffin/olefin ratios and boiling range of the

liquid hydrocarbon samples. The operating conditions were 1:1 H_2:C_3H_6 mole ratio fed at 1 C_3H_6 WHSV feed rate, on 30 grams of catalyst of about 50 cc. volume. The pressure and temperature schedule (Figure 1) is briefly repeated below (in chronological order).

PSIG	TEMP. °C
150	280, 310, 340, 370, 280
150, 75, 300	280
300, 150, 50	370

Hence there are data at constant pressure (150 psig) and increasing temperatures, as well as data at constant temperatures (280 and 370°C) with different pressures. These are plotted accordingly in Figures 2 and 3. For each of the conditions tested, a simulated boiling point distribution plot of a representative sample is presented; Samples 1, 3, 5, 7, 12, 14, 16, 17, 20 are shown in Figures 4 through 12.

Figure 2 shows the effect of temperature on conversion and product boiling range. The conversions are high, with a range of 92 to 96%. Higher temperatures resulted in much higher C_1-C_4 light hydrocarbon fractions. The liquid products also become lighter with increased temperature. At 280°C, 82% of the C_5^+ product boils in the gasoline range, that is less than 420°F. At 310°C to 340°C, 88-90% of the C_5^+ product boils in the gasoline range. Comparison of Figures 4 to 7 also shows another trend in the composition of liquid product. As the reaction temperature increases from 280 to 370°C (going from Figure 4 to 7) the distillation curve becomes less smooth. Individual components can be distinguished boiling at 230, 285, and 330°F. These temperatures correspond to the boiling points of toluene, xylenes and C_9 aromatics respectively. The increasing refractive index of the liquid product also supports the conclusion that the product is becoming more aromatic at the higher temperatures. Propane and butane, products of hydride transfer, also increase with temperature, as would be expected with

increased aromatics production. The kinetics of aromatics formation should improve with higher reaction temperature.

Figure 3 shows the effect of pressure at constant temperatures of 280°C (left side column of the plots) and 370°C (right side column of the plots). At 280°C and 75 psig, 86% of the C_5^+ product was in the gasoline range. This amount decreased to 82% at 150 psig and 80% at 300 psig. The higher pressure led to a larger percentage of the liquid product boiling above the gasoline range. Increased pressure, i.e., concentration, would be expected to increase addition reactions, leading to heavier products.

At 370°C, (see the right side column of plots in Figure 3) there was a major increase in C_1-C_4 fraction with increased pressure, mostly in the form of propane and butane (samples 16 and 17). While the absolute amount of C_5^+ markedly decreased with increasing pressure, the C_5^+ that was produced became heavier, just like at 280°C. At 50 psig, 92% of the C_5^+ product was in the gasoline range. At 150 psig this percentage was 89 and at 300 psig it was only 84. The simulated distillation plots also show another trend with increasing pressure (shown in Figures 12, 7, and 10 going from 50 psig to 150 psig to 300 psig). The curve becomes less smooth, i.e. the distillation of individual components becomes more pronounced with increasing pressure. The refractive index also increases with increasing pressure. These observations of the liquid product along with the changes in the propane and butane production are all consistant with greater aromatics production at higher pressures. The propane and butane are the products of the hydride transfer necessary to form the aromatics. This would be a bimolecular reaction, the rate of which would increase with pressure. This was not seen at 280°C because the temperature was too low for the kinetics to allow significant production of aromatics. A total of 21 product collections were made with pressure and temperature conditions as depicted in Figure 1.

TABLE 4A PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-01
CATALYST LZ-105-6 #9939-01 50 CC 30.0 GM (33.16 GM AFTER THE RUN)
FEED C3H6/H2 @ 1/1 MOLE RATIO, 290 CC/MIN H2 FLOW, C3= FLOW 7 HR/D
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)

RUN & SAMPLE NO.	9972-01-1	9972-01-2	9972-01-3	9972-01-4	9972-01-5
C3H6 WHSV	1.1	1.1	1.1	1.1	1.1
HRS ON STREAM5	2.5	7.5	11.0	14.0	17.5
PRESSURE,PSIG	152	148	144	142	143
TEMP. C	278	279	307	307	336
FEED C3H6 CC	131.51	314.0	198.2	195.07	195.07
HOURS FEEDING	2.0	5.0	3.0	3.0	3.0
EFFLNT GAS LITER	45.2	116.9	71.1	70.3	74.3
GM LIQ HYDROCARBON	32.77	93.30	42.13	51.31	32.75
WT FR. LIQ HC/FEED	.4882	.5821	.4165	.5153	.3289
MATERIAL BALANCE WT %	83.99	90.23	80.26	90.80	82.83
C3H6 CONVERSION %	93.70	96.19	94.65	94.65	95.27
PRDT SELECTIVITY WT %					
CH4	0.0509	0.0387	0.1174	0.0911	0.2584
C2 HC'S	0.1635	0.1226	0.0000	0.2999	0.7806
C3H8	6.7851	9.0719	6.4647	4.4276	10.5096
C4H10	5.3615	2.8712	9.2434	6.6405	16.0236
C4H8=	3.5921	3.7820	4.7222	4.6925	4.3213
C5H12	3.9458	2.2712	6.9334	5.3198	10.2667
C5H10=	4.0046	4.2365	4.4360	4.7022	3.3246
C6H14	3.0899	2.1888	4.2713	3.6977	5.0462
C6H12= & CYCLO'S	1.8936	2.0526	1.9870	1.6435	0.9596
C7+ IN GAS	5.2618	4.6779	4.9821	6.3212	5.4495
LIQ HC'S	65.8512	69.1784	56.8424	62.1638	43.0597
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	15.95	15.89	20.55	16.15	31.89
C5 -420 F	70.61	69.14	69.79	73.59	60.51
420-700 F	13.43	14.42	9.38	10.26	7.43
C5 -END PT	84.05	84.11	79.45	83.85	68.11

ISO/NORMAL MOLE RATIO					
C4	1.1577	1.2819	1.7247	1.8769	1.5071
C5	2.7926	2.7286	2.7825	2.8644	2.5075
C6	2.8870	2.1805	3.0477	2.7869	3.5047
C4=	0.4146	0.3881	0.4389	0.4324	0.4413
PARAFFIN/OLEFIN M RATIO					
C3	0.9677	2.1937	1.0930	0.7481	2.0319
C4	1.4408	0.7328	1.8895	1.3660	3.5794
C5	0.9578	0.5211	1.5193	1.0997	3.0018
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLEAR OIL	CLEAR OIL	OIL,LT BL	OIL,LT BL	OIL,YL GR
DENSITY	0.759	0.761	0.777	0.755	0.797
N,REFRACTIVE INDEX	1.4346	1.4337	1.4457	1.4399	1.4684
SIMULATED DISTILLATION					
10 WT % @ DEG F.	172	183	157	162	159
16	204	210	192	193	195
50	315	321	297	300	299
84	445	453	426	423	431
90	492	503	475	468	477
RANGE(16-84%)	241	243	234	230	236
WT % @420 F	79.6	78.2	83.0	83.5	82.4
WT % @700 F	100.0	99.2	99.5	100.0	99.6

TABLE 4B PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-01
CATALYST LZ-105-6 #9939-01 50 CC 30.0 GM (33.16 GM AFTER THE RUN)
FEED C3H6/H2 @ 1/1 MOLE RATIO, 290 CC/MIN H2 FLOW, C3= FLOW 7 HR/D
C3H6 MW= 42.0813 DENSITY= 0.5041 GM/CC (@ 73 F)

RUN & SAMPLE NO.	9972-01-6	9972-01-7	9972-01-8	9972-01-9	9972-1-10
C3H6 WHSV	1.1	1.1	1.1	1.1	1.1
HRS ON STREAMS	21.0	25.0	29.0	32.5	37.5
PRESSURE,PSIG	145	147	145	147	150
TEMP. C	337	370	370	282	282
FEED C3H6 CC	223.39	230.94	247.30	193.81	292.60
HOURS FEEDING	3.5	3.5	4.0	3.0	4.5
EFFLNT GAS LITER	85.4	90.3	101.7	72.9	109.2
GM LIQ HYDROCARBON	49.15	29.72	44.41	58.77	86.62
WT FR. LIQ HC/FEED	.4311	.2521	.3518	.5941	.5800
MATERIAL BALANCE WT %	90.36	85.41	92.38	95.08	93.74
C3H6 CONVERSION %	95.04	95.20	97.06	86.37	89.19
PRDT SELECTIVITY WT %					
CH4	0.2065	0.5748	0.4903	0.0294	0.0276
C2 HC'S	0.6403	1.5026	1.3124	0.0200	0.0762
C3H8	7.1552	17.8821	14.0543	3.0490	8.1101
C4H10	12.1173	21.1874	16.9210	1.1281	1.4564
C4H8=	4.7449	4.1059	4.0579	4.7259	4.1347
C5H12	8.4045	10.2999	9.4264	0.9042	1.0794
C5H10=	3.8333	2.3068	2.8045	4.8598	4.3935
C6H14	4.3723	4.1523	4.2326	1.5975	1.6156
C6H12= & CYCLO'S	1.5794	0.8800	0.8119	2.6501	2.6697
C7+ IN GAS	5.2174	5.2134	5.6469	5.8134	5.2274
LIQ HC'S	51.7287	31.8948	40.2417	75.2225	71.2092
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	24.86	45.25	36.84	8.95	13.81
C5 -420 F	67.17	47.38	56.89	75.10	71.10
420-700 F	7.97	7.24	6.28	15.87	15.03
C5 -END PT	75.14	54.75	63.16	91.05	86.19

ISO/NORMAL MOLE RATIO					
C4	1.6531	1.3480	1.3967	1.1239	0.5756
C5	2.5364	2.7891	2.5174	2.4760	1.5747
C6	2.9060	4.8999	3.6158	1.5029	1.2075
C4=	0.4366	0.4201	0.4834	0.3231	0.3400
PARAFFIN/OLEFIN M RATIO					
C3	1.3100	3.4063	4.4573	0.1845	0.6397
C4	2.4652	4.9813	4.0253	0.2304	0.3400
C5	2.1312	4.3403	3.2672	0.1809	0.2388
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL,YL GR	OIL,YL GR	OIL,YL GR	OIL,YL GR	OIL,YL GR
DENSITY	0.773	0.839	0.815	0.753	0.736
N,REFRACTIVE INDEX	1.4562	1.4972	1.4732	1.4287	1.4305
SIMULATED DISTILLATION					
10 WT %@ DEG F.	155	188	161	188	187
16	191	224	196	212	212
50	294	321	299	324	323
84	416	457	417	449	449
90	463	489	466	494	494
RANGE(16-84%)	225	233	221	237	237
WT % @420 F	84.6	76.9	84.4	78.8	78.8
WT % @700 F	100.0	99.6	100.0	99.9	99.9

TABLE 4C PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-01
CATALYST LZ-105-6 #9939-01 50.CC 30.0 GM (33.16 GM AFTER THE RUN)
FEED C3H6/H2 @ 1/1 MOLE RATIO, 290 CC/MIN H2 FLOW, C3= FLOW 7 HR/D
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)

RUN & SAMPLE NO.	9972-1-11	9972-1-12	9972-1-13	9972-1-14	9972-1-15
C3H6 WHSV	1.1	1.1	1.1	1.1	1.0
HRS ON STREAM	40.5	44.0	48.0	52.0	55.5
PRESSURE,PSIG	147	74	73	299	303
TEMP. C	282	279	281	283	289
FEED C3H6 CC	186.26	188.78	258.63	219.61	210.80
HOURS FEEDING	3.0	3.0	4.0	3.5	3.5
EFFLNT GAS LITER	74.1	77.2	104.2	79.9	80.4
GM LIQ HYDROCARBON	57.36	53.72	69.70	45.24	59.46
WT FR. LIQ HC/FEED	.6034	.5575	.5280	.4036	.5526
				*****	
MATERIAL BALANCE WT %	100.21	97.00	98.24	71.43	91.70
C3H6 CONVERSION %	84.11	80.99	78.37	85.87	89.09
PRDT SELECTIVITY WT %					
CH4	0.0248	0.0167	0.0190	0.0809	0.0688
C2 HC'S	0.0713	0.0594	0.0659	0.1805	0.1589
C3H8	2.6535	2.2477	2.1299	6.6429	4.7074
C4H10	0.7715	0.6357	0.6745	1.9969	1.7005
C4H8=	5.0642	6.2363	6.6248	4.0554	3.6196
C5H12	0.7983	0.5001	0.5482	1.2119	1.1676
C5H10=	4.8852	5.8271	6.2591	4.3761	3.9528
C6H14	1.7032	1.6093	1.7335	1.9060	4.5162
C6H12= & CYCLO'S	3.4710	3.6054	3.5951	3.0626	2.6430
C7+ IN GAS	6.0648	6.7315	8.6878	6.1712	5.0870
LIQ HC'S	74.4924	72.5307	69.6620	70.3155	72.4052
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	8.5852	9.1957	9.5141	12.9566	10.2552
C5 -420 F	75.3244	78.1839	78.7827	68.4098	72.7296
420-700 F	16.0159	12.6204	11.7032	17.8602	16.6532
C5 -END PT	91.4148	90.8043	90.4859	87.0434	89.7448

ISO/NORMAL MOLE RATIO					
C4	1.1515	1.2932	1.4982	0.6539	0.8371
C5	2.3461	2.7149	2.6332	2.1944	2.4042
C6	1.4732	1.2844	1.2987	1.4945	6.2711
C4=	0.2901	0.2939	0.3045	0.3169	0.3289
PARAFFIN/OLEFIN M RATIO					
C3	0.1341	0.0913	0.0737	0.3865	0.3679
C4	0.1471	0.0984	0.0983	0.4753	0.4535
C5	0.1588	0.0834	0.0851	0.2692	0.2891
.IQ HC COLLECTION					
PHYS. APPEARANCE	LT YL OIL	LT YL OIL	LT YL OIL	LT YL OIL	LT YL OIL
DENSITY	0.726	0.719	0.719	0.713	0.783
N,REFRACTIVE INDEX	1.4309	1.4288	1.4289	1.4304	1.4320
SIMULATED DISTILLATION					
10 WT % @ DEG F.	189	178	173	205	193
16	213	209	208	233	217
50	324	308	305	341	328
84	450	427	424	475	461
90	495	469	466	524	509
RANGE(16-84%)	237	218	216	242	244
WT % @420 F	78.4	82.6	83.2	73.5	76.5
WT % @700 F	99.9	100.0	100.0	98.9	99.5

TABLE 4D PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-01
CATALYST LZ-105-6 #9939-01 50 CC 30.0 GM (33.16 GM AFTER THE RUN)
FEED C3H6/H2 @ 1/1 MOLE RATIO, 290 CC/MIN H2 FLOW, C3= FLOW 7 HR/D
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)

RUN & SAMPLE NO.	9972-1-16	9972-1-17	9972-1-18	9972-1-19	9972-1-20
C3H6 - WHSV	1.0	1.0	1.1	1.1	1.1
HRS ON STREAM5	59.0	62.0	65.5	68.5	72.5
PRESSURE,PSIG	307	300	150	153	52
TEMP. C	371	369	363	364	371
FEED C3H6 CC	182.48	183.11	188.78	185.63	221.50
HOURS FEEDING	3.0	3.0	3.0	3.0	3.5
EFFLNT GAS LITER	70.0	70.3	76.0	75.5	96.1
GM LIQ HYDROCARBON	8.81	14.80	30.79	36.92	41.22
WT FR. LIQ HC/FEED	.0946	.1584	.3195	.3897	.3646
MATERIAL BALANCE WT %	90.11	87.50	83.58	95.97	94.02
C3H6 CONVERSION %	98.05	97.25	93.47	94.22	89.16
PRDT SELECTIVITY WT %					
CH4	1.8615	1.3055	0.3256	0.4916	0.0142
C2 HC'S	4.4719	3.1024	0.0000	0.0000	0.9910
C3H8	47.1570	35.5407	10.7354	10.8825	8.1611
C4H10	20.5693	20.6111	15.9695	14.9539	12.5917
C4H8=	1.1714	1.9056	5.7303	5.1026	9.8380
C5H12	6.5860	8.1639	9.5202	8.7946	6.7556
C5H10=	0.4300	1.2504	4.0157	3.4684	5.9569
C6H14	2.6697	3.2520	4.6131	4.3146	3.7071
C6H12= & CYCLO'S	0.3932	0.5338	1.4037	1.4463	1.9894
C7+ IN GAS	3.2135	4.4145	5.3114	5.8777	5.9876
LIQ HC'S	11.4765	19.9201	42.3751	44.6677	44.0073
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	75.23	62.47	32.76	31.43	31.60
C5 -420 F	20.41	32.42	60.03	62.32	63.08
420-700 F	4.18	5.12	7.20	6.25	5.32
C5 -END PT	24.77	37.53	67.24	68.57	68.40

ISO/NORMAL MOLE RATIO					
C4	0.9991	1.0912	1.4695	1.4744	1.7370
C5	2.8005	2.9919	2.5089	2.6507	2.6828
C6	6.3846	5.4527	3.3978	3.6525	3.1930
C4=	0.4617	0.4555	0.4329	0.4290	0.4345
PARAFFIN/OLEFIN M RATIO					
C3	23.3722	12.2638	1.4624	1.6976	0.6412
C4	16.9506	10.4408	2.6902	2.8290	1.2355
C5	14.8880	6.3466	2.3045	2.4648	1.1024
LIQ HC COLLECTION					
PHYS. APPEARANCE	LT YG OIL	LT YG OIL	LT GR OIL	YL GR OIL	YL GR OIL
DENSITY	0.925	0.853	0.786	0.794	0.825
N,REFRACTIVE INDEX	1.5142	1.5004	1.4766	1.4610	1.4651
SIMULATED DISTILLATION					
10 WT % @ DEG F.	232	199	160	155	158
16	265	233	196	193	192
50	363	327	299	292	288
84	488	473	428	407	398
90	528	500	472	451	437
RANGE(16-84%)	223	240	232	214	206
WT % @420 F	62.0	74.3	83.0	86.0	87.9
WT % @700 F	98.4	100.0	100.0	100.0	100.0

TABLE 4E PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-01
CATALYST LZ-105-6 #9939-01 50 CC 30.0 GM (33.16 GM AFTER THE RUN)
FEED C3H6/H2 @ 1/1 MOLE RATIO, 290 CC/MIN H2 FLOW, C3= FLOW 7 HR/D
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)

RUN & SAMPLE NO.	9972-1-21
C3H6 WHSV	1.8
HRS ON STREAM5	75.5
PRESSURE,PSIG	47
TEMP. C	371
FEED C3H6 CC	190.67
HOURS FEEDING	3.0
EFFLNT GAS LITER	80.0
GM_LIQ HYDROCARBON	29.44
WT FR. LIQ HC/FEED	.3025
MATERIAL BALANCE WT %	85.39
C3H6 CONVERSION %	96.77
PRDT SELECTIVITY WT %	
CH4	0.0137
C2 HC'S	0.0000
C3H8	16.2809
C4H10	13.6646
C4H8=	7.8575
C5H12	7.5489
C5H10=	5.3913
C6H14	3.9106
C6H12= & CYCLO'S	1.5540
C7+ IN GAS	6.7336
LIQ HC'S	37.0448
TOTAL	100.00
SUBGROUPING	
C1 -C4	37.82
C5 -420 F	57.70
420-700 F	4.49
C5 -END PT	62.18

ISO/NORMAL MOLE RATIO	
C4	1.2401
C5	2.1048
C6	2.2465
C4=	0.5205
PARAFFIN/OLEFIN M RATIO	
C3	4.6953
C4	1.6787
C5	1.3611

LIQ HC COLLECTION

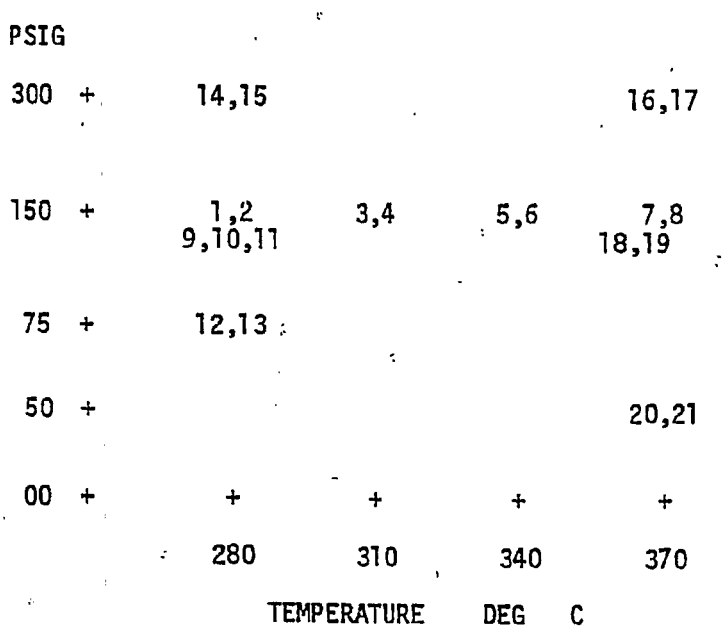
PHYS. APPEARANCE	YL GR OIL
DENSITY	0.772
N,REFRACTIVE INDEX	1.4617
SIMULATED DISTILLATION	
10 WT % @ DEG F.	159
16	192
50	287
84	406
90	438
RANGE(16-84%)	214
WT % @420 F	87.9
WT % @700 F	100.0

FIGURE 1 RUN 9972-1

IDENTIFICATION OF
PRESSURE & TEMPERATURE AT WHICH
PRODUCT SAMPLES WERE TAKEN

CATALYST: LZ-105-6

FEED: H2:C3H6 @1:1 & 1 C3H6 WHSV



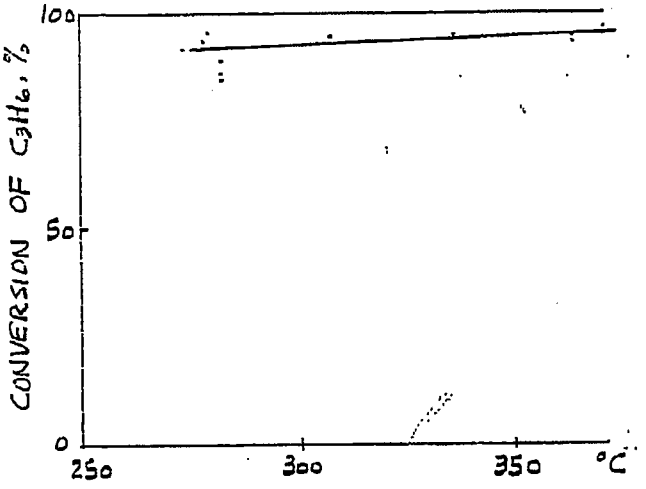
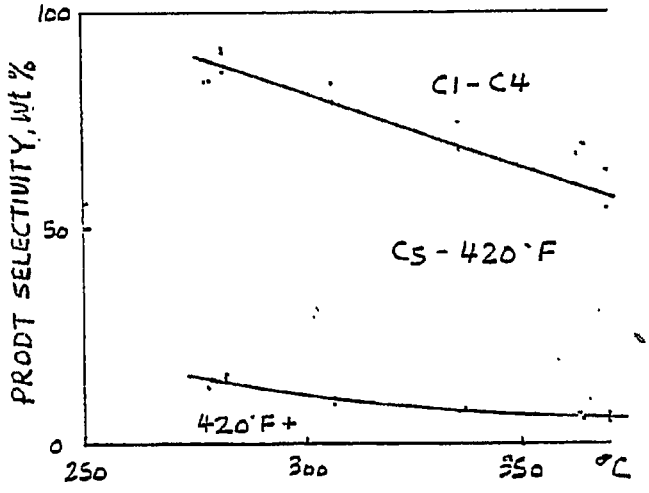


FIGURE 2

EFFECTS OF TEMPERATURE ON PROPYLENE OPERATION WITH LZ-105-6 AT 150 PSIG

RUN 9972-1, LZ-105-6
H_2:C_3H_6 @ 1:1
C_3H_6 WHSV = 0.5
150 PSIG



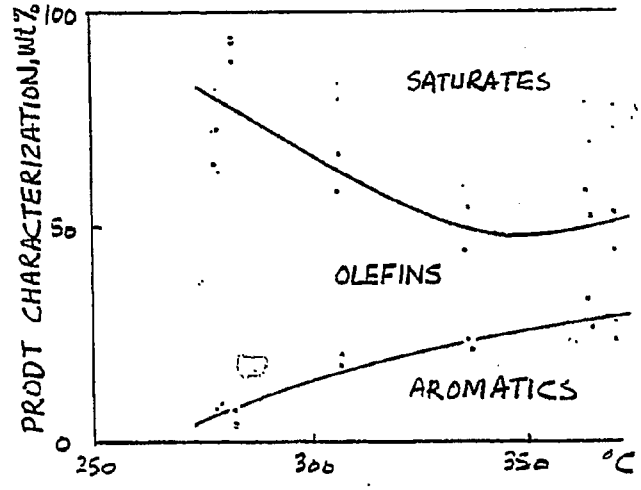
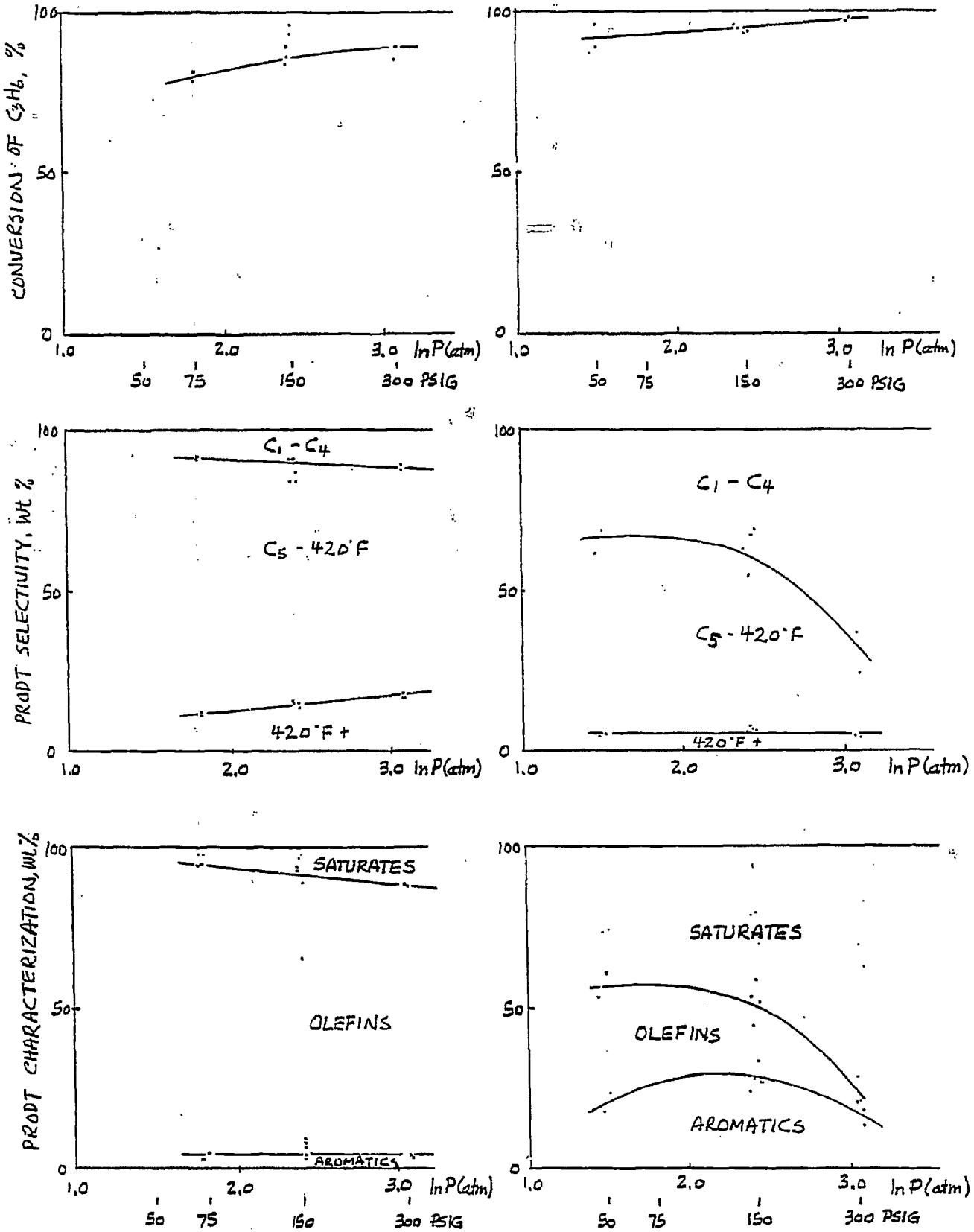


FIG. 3 EFFECT OF PRESSURE ON PROPYLENE OPERATION WITH LZ-105-6

AT 280 °C RUN 9972-1 AT 370 °C



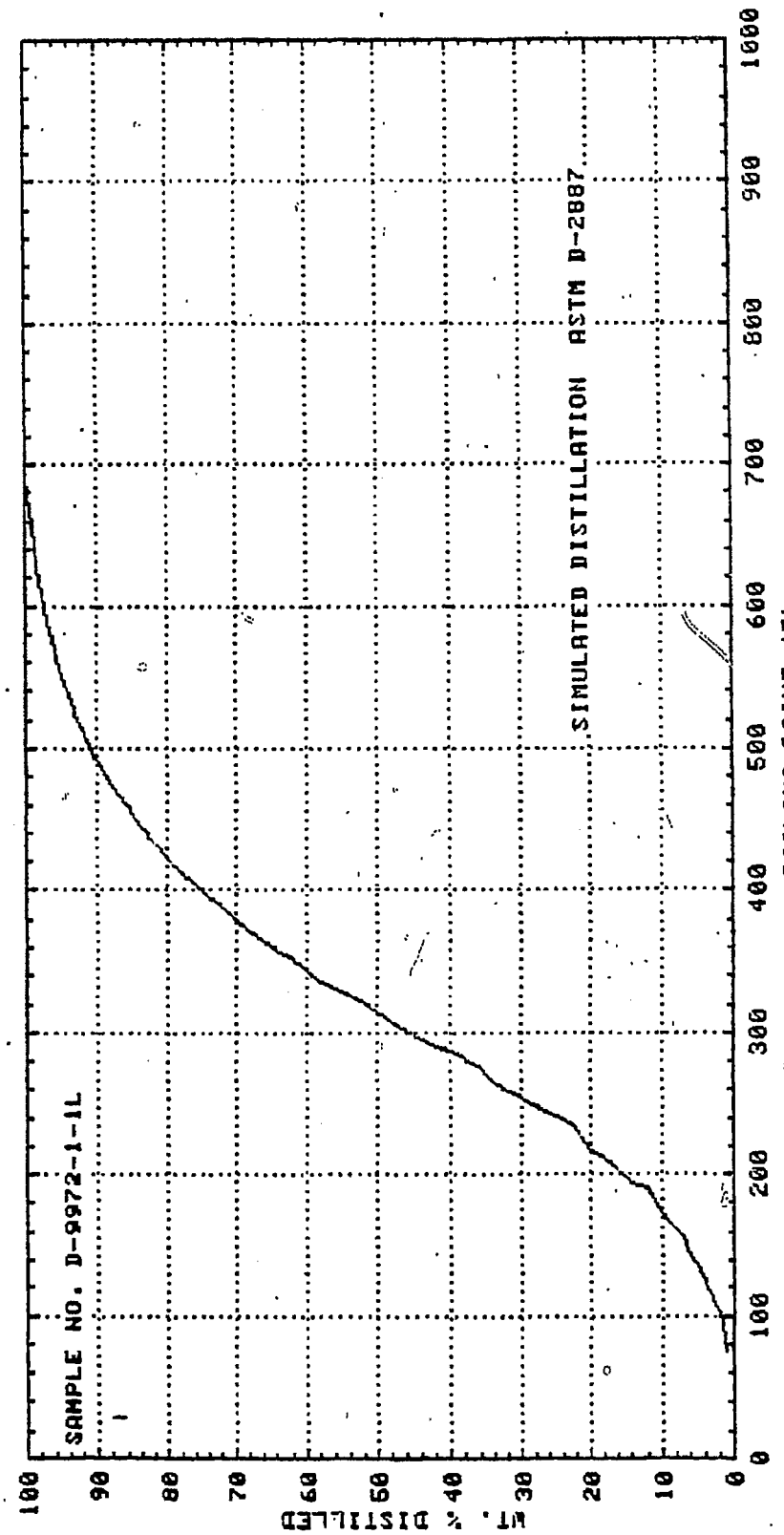

SAMPLE NO. D-9972-1-1L
SIMULATED DISTILLATION ASTM D-2887
WT. % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 4

FIG. 5

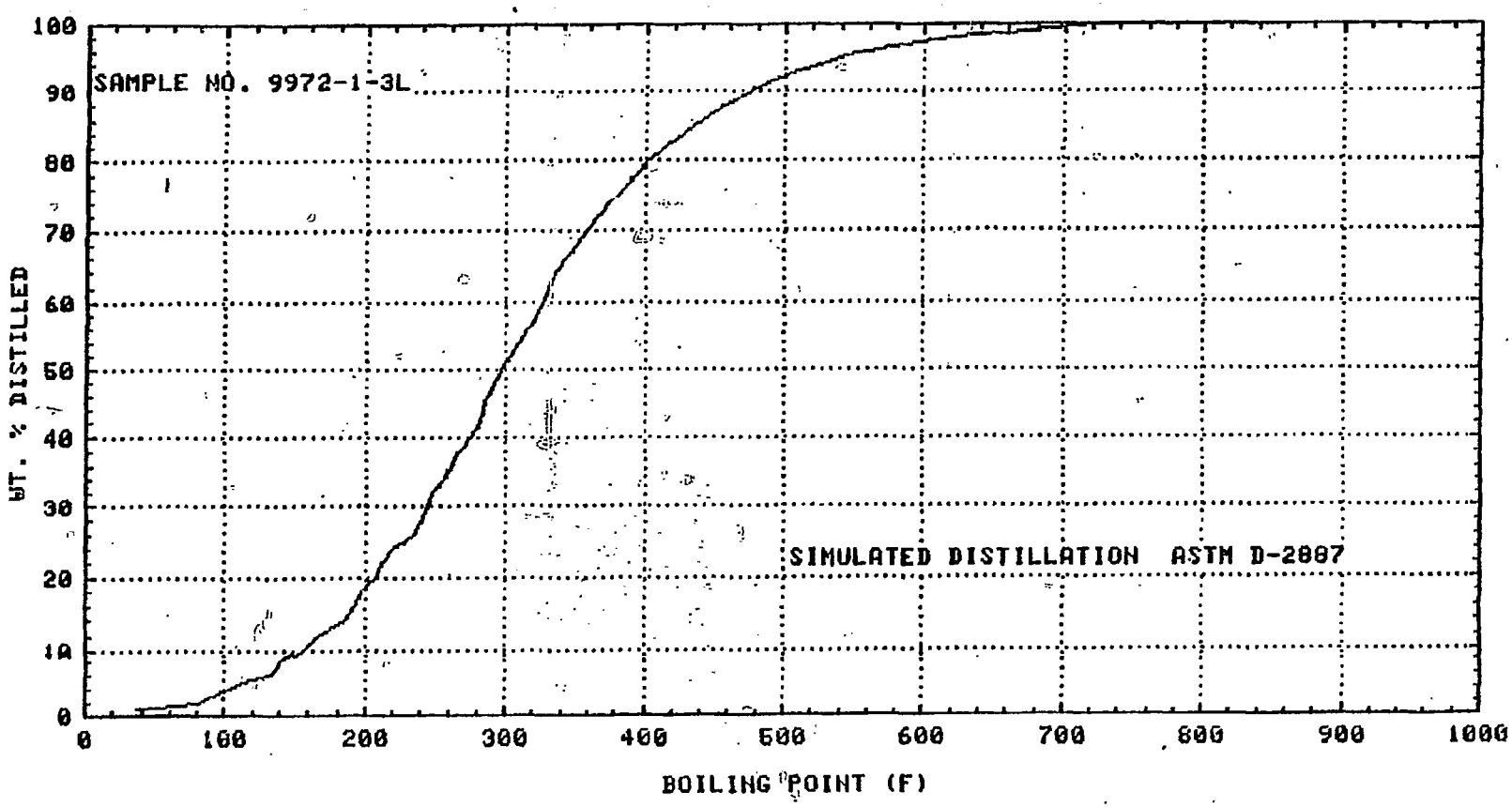

SAMPLE NO. 9972-1-3L
SIMULATED DISTILLATION ASTM D-2887
WT. % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 6

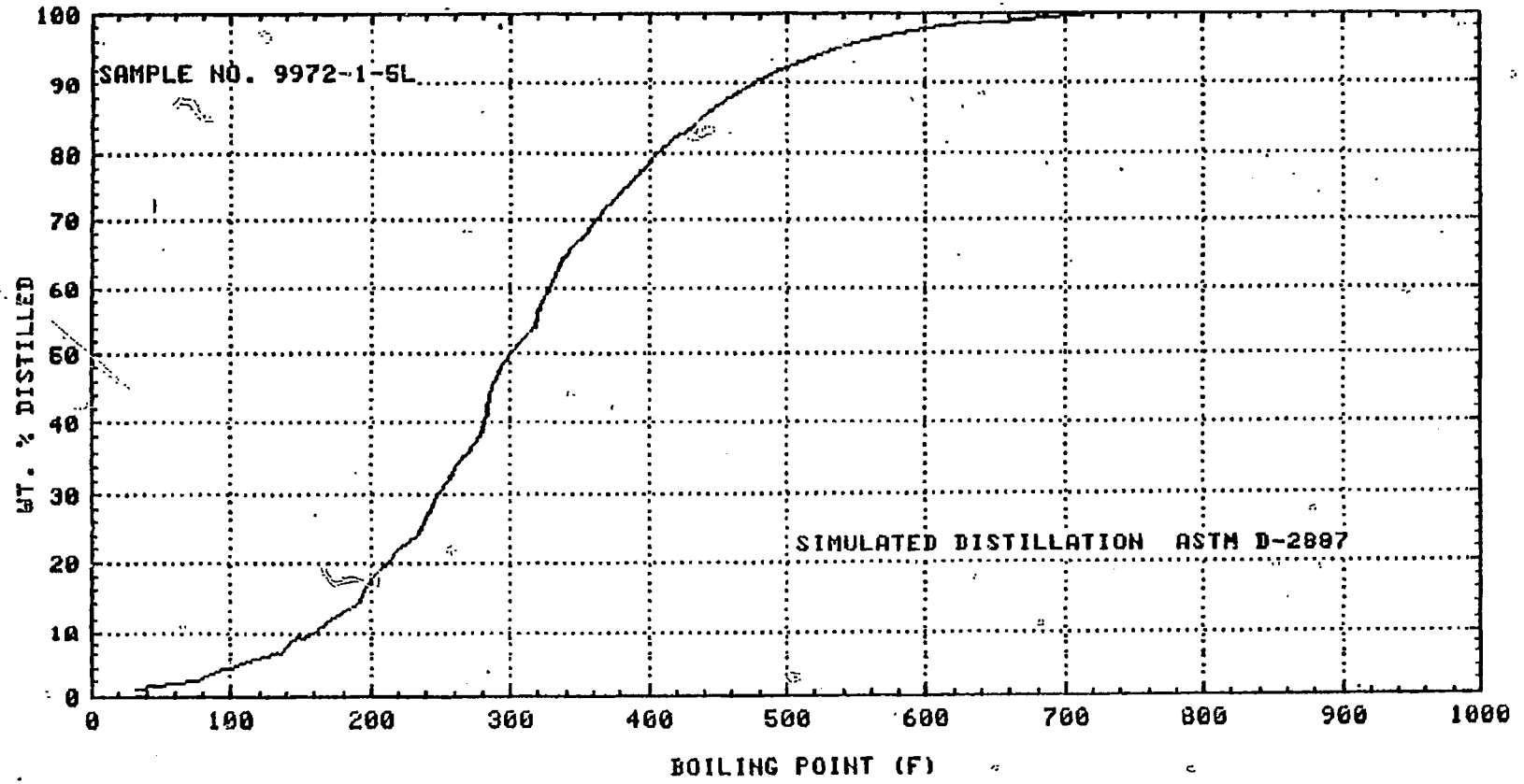

SAMPLE NO. 9972-1-5L
SIMULATED DISTILLATION ASTM D-2887
WT. % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 7

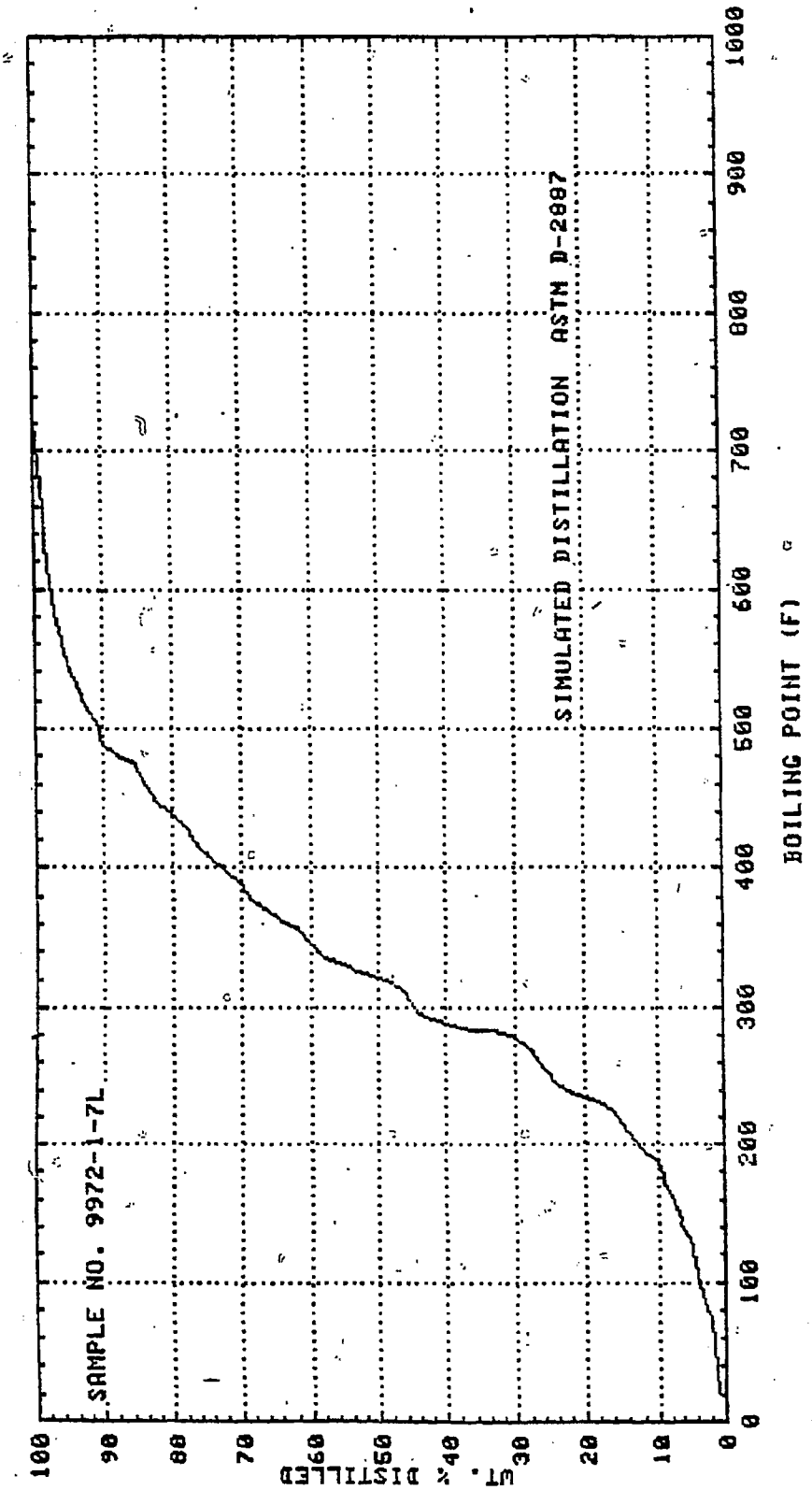

SAMPLE NO. 9972-1-7L
SIMULATED DISTILLATION ASTM D-2887
WT. % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 8

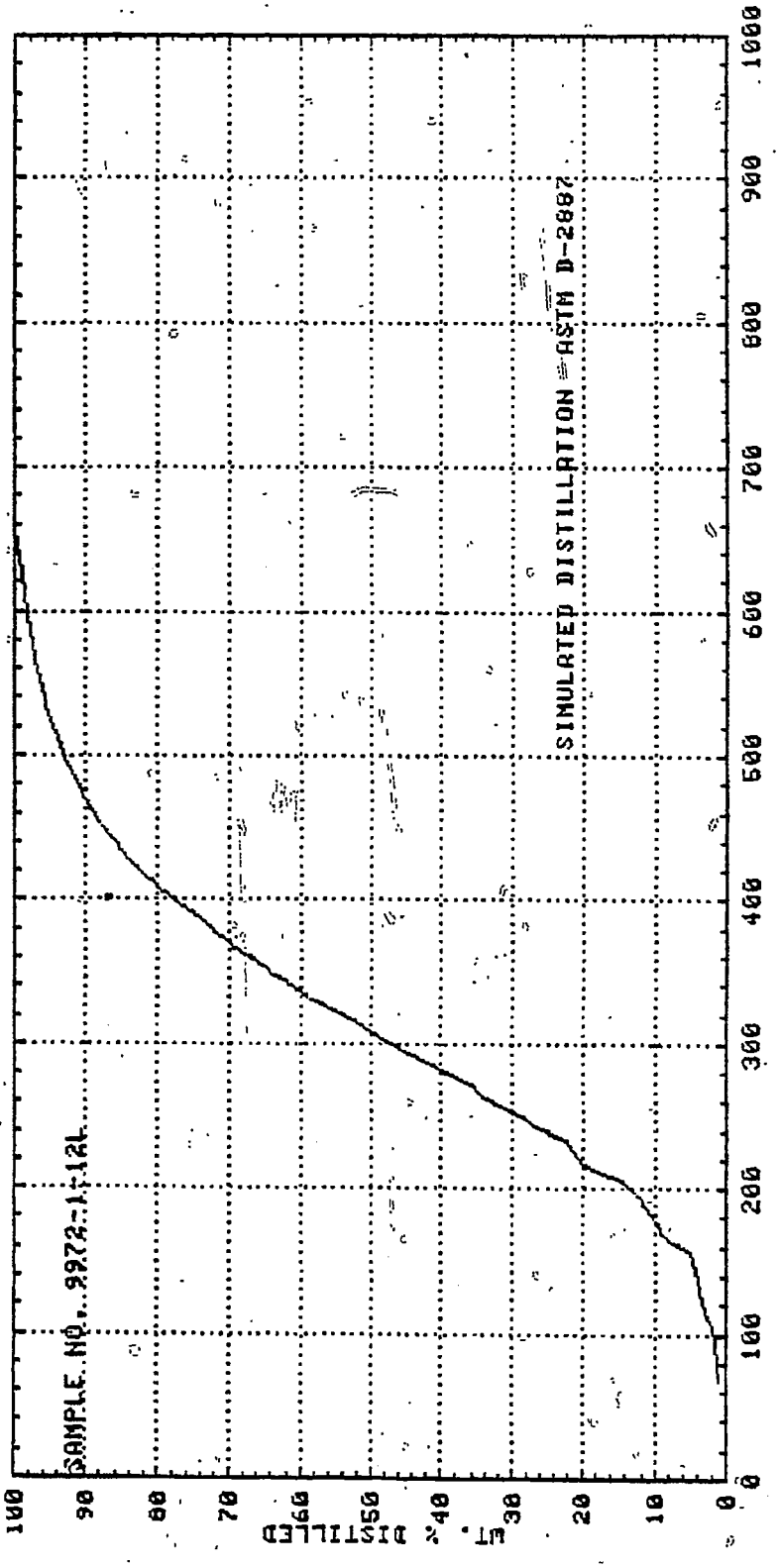

SAMPLE NO. 9972-1-12L
SIMULATED DISTILLATION - ASTM D-2887
WT. % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 9

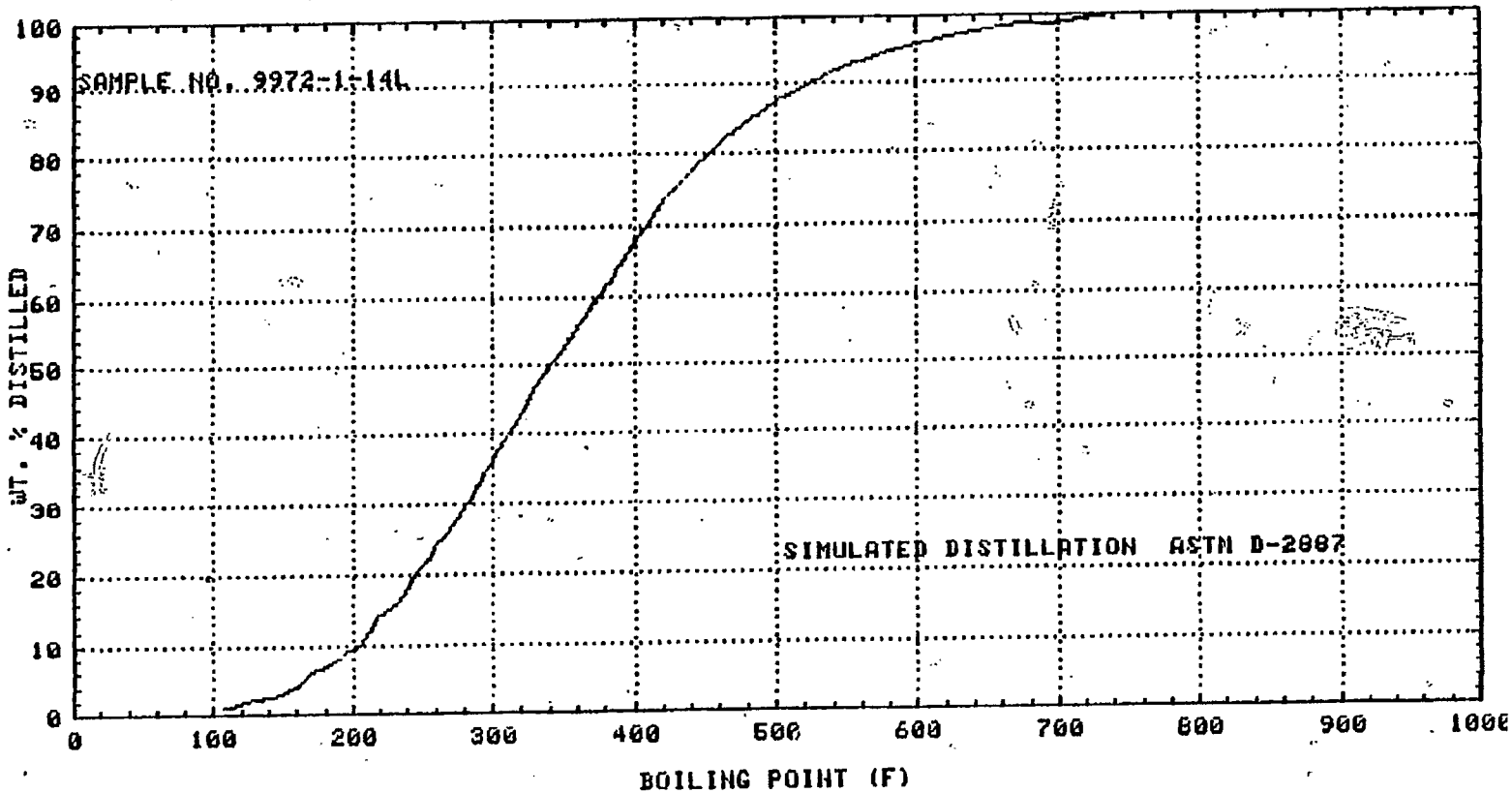

SAMPLE NO. 9972-1-14L
SIMULATED DISTILLATION ASTM D-2887
WT. % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 10

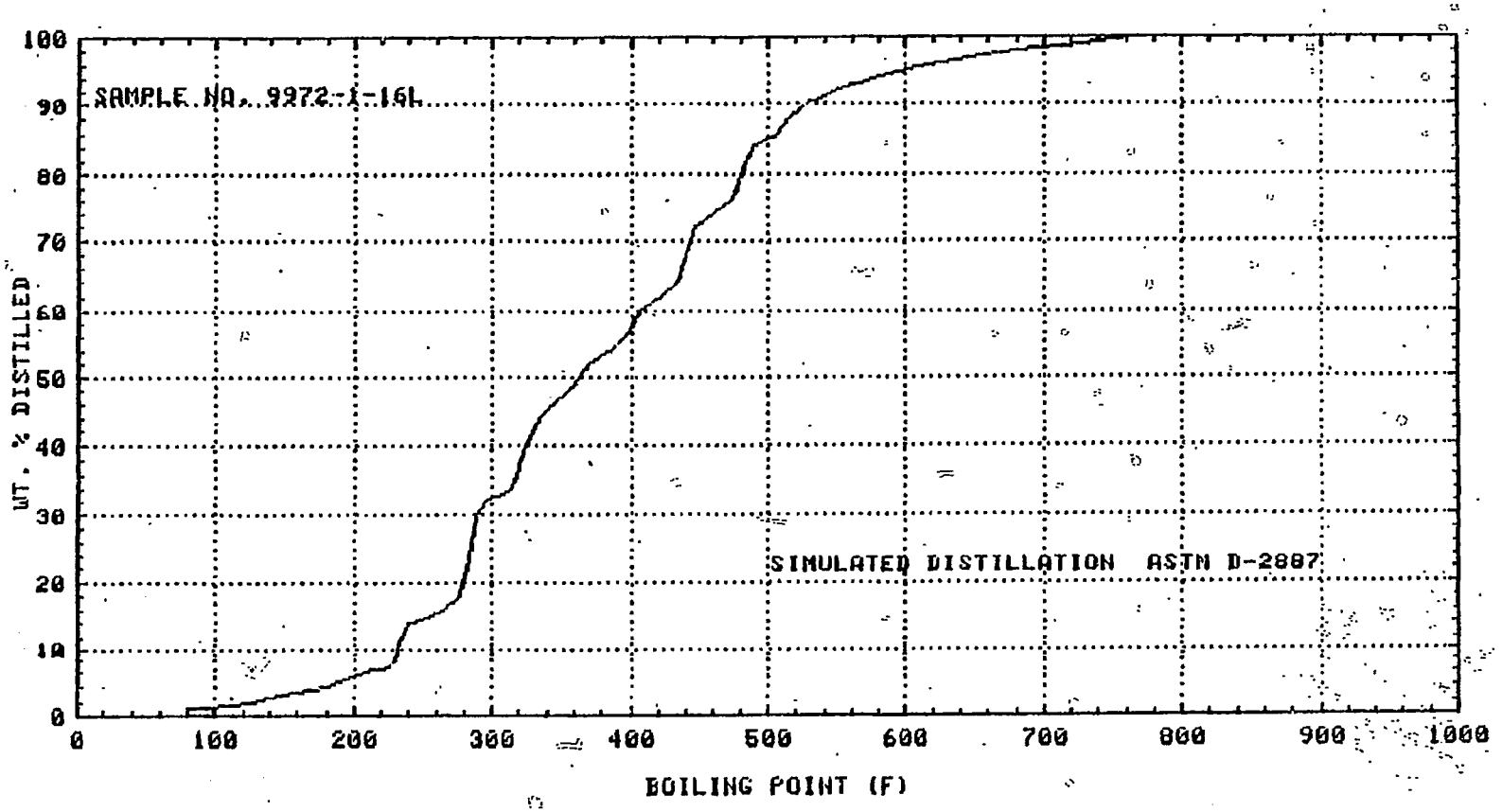
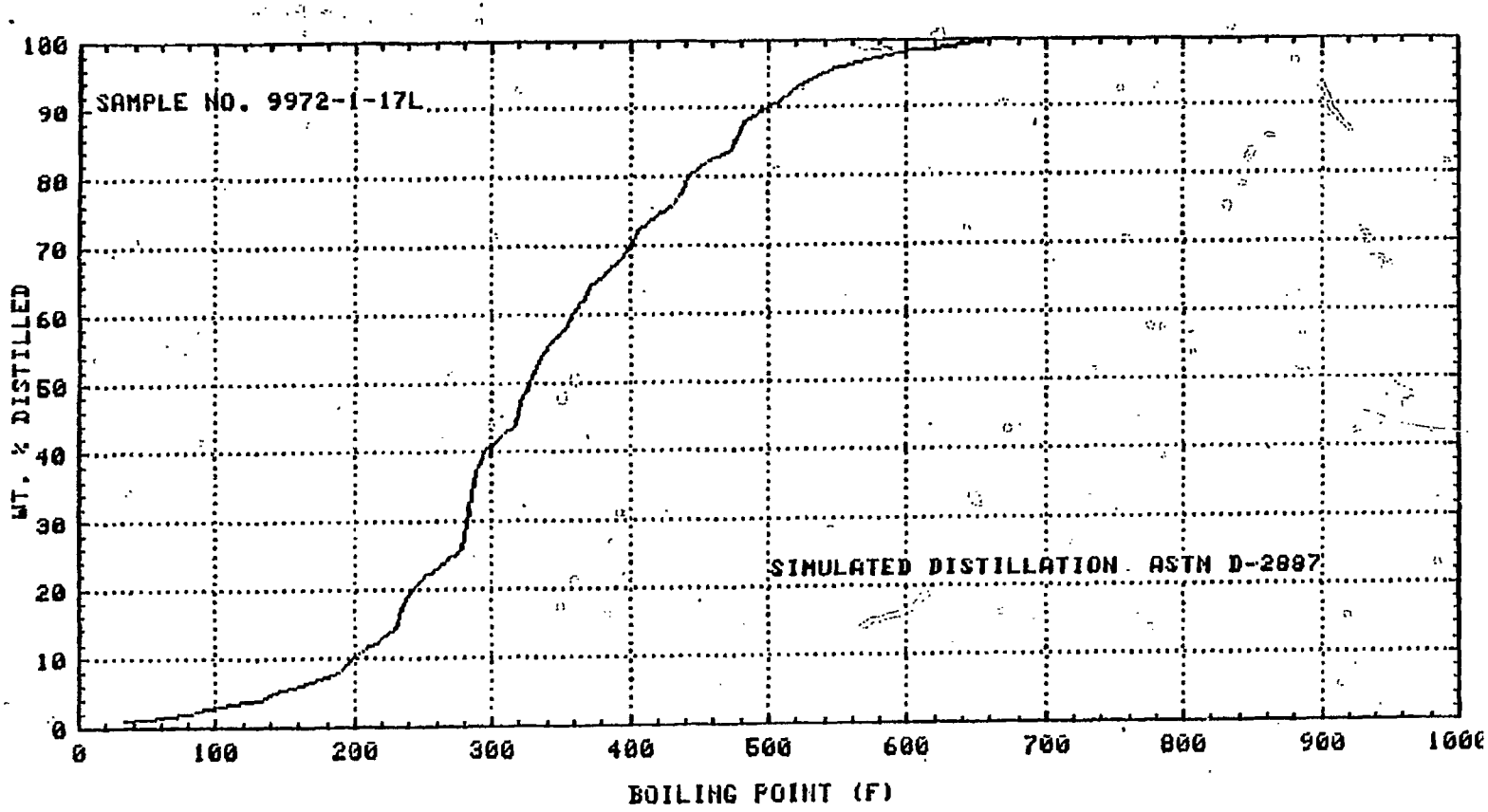

SAMPLE NO. 9972-1-16L
SIMULATED DISTILLATION ASTM D-2887
WT. % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 11


SAMPLE NO. 9972-1-17L
SIMULATED DISTILLATION ASTM D-2887
WT. % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

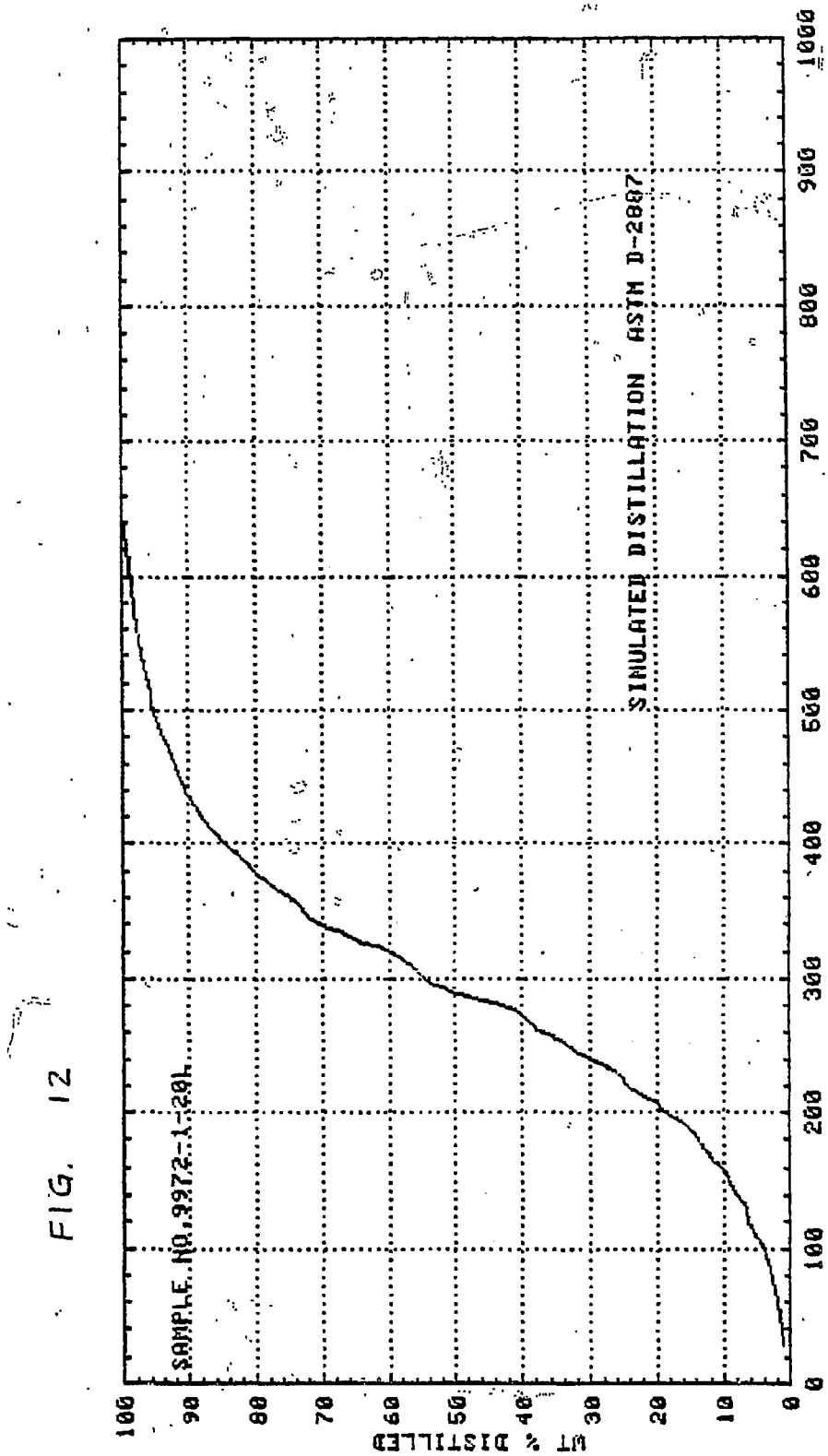

SAMPLE NO.9972-1-20L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 12

Run 9972-2 Feed 1:1:2 (H_2:C_3H_6:H_2O) on LZ-105-6

Mobil Oil in U.S. Patent 4,150,062 previously disclosed the effect of steam on the propylene oligomerization activity of ZSM-5 in a fixed bed reactor. The conversion of propylene was stable with and without steam. The steam gave lower hot spots leading to a more favorable product distribution, less coking of the catalyst and less C_{10} and C_{11} aromatics as a fraction of the total aromatics.

The effect of steam on the propylene oligomerization activity of LZ-105-6 can easily be seen by comparing the present test, 9972-2, with one reported last quarter, 9710-13. The process conditions for 9972-2 were 150 psig, 410°C and 0.4 WHSV of C_3H_6 with a H_2:C_3H_6:H_2O equal to 1:1:2. Tables 5A and 5B and Figure 13 show the results of this test. Table 5C and figure 14 repeats the results of test 9710-13, which had process conditions similar to 9972-2 except that the propylene was fed at 1.0 WHSV with no co-fed water.

The present test gave very constant operation with little change in either the conversion or product selectivity. This was not true for run 9710-13 which showed both decreasing conversion and changes in product distribution with time. To examine the effect of steam on product selectivity, the products of the present run should be compared to the initial products of 9710-13, that is before the effects of deactivation dominated the selectivity. The initial conversions were very similar at approximately 97%. The C_1 and C_2 selectivities were slightly higher without steam. The sum of the propane and butane production, the products of hydride transfer to the olefins, was constant with and without steam but the individual concentrations were different. The C_5^+ selectivities were also very close. The refractive indices of 9710-13-1 and the samples from run 9972-2 are all close to 1.5. This fact along with the high propane and butane production again implies a highly aromatic liquid product. The distillation of the individual aromatic components can again easily be seen in the simulated distillation plots. This is consistent with what was seen in the

previous run, that aromatics are produced at the higher temperatures. The addition of steam to the reactor does not seem to significantly affect this aromatization process. The simulated distillation of 9972-2-2L or 6L (Figures 15A and 15B) looks like that of 9710-13-1L (Figure 16A). The major difference is at ~450°F and ~475°F where the distillation of individual compounds can clearly be seen in 9710-13-1L and not in 9972-2-2L. This is consistent with the findings of Mobil where heavier compounds are decreased upon the addition of steam. For run 9972-2 an average of 93% of the C_5^+ products boiled in the gasoline range. The simulated distillation curve for the later sample in the run without steam (Figure 16B) clearly differs from the other three curves.

When all the aspects of the samples are considered, the samples of 9972-2 are very much like 9710-13-1. It can easily be seen that 9710-13-1 is much more like 9972-2-2 than like 9710-13-2. Unlike what Mobil found with ZSM-5, the major effect of steam with LZ-105-6 in the Berty reactor system is simply to lock the catalyst into its initial reactivity and not allow deactivation. The slight changes in the product selectivities seem secondary effects.

TABLE 5A PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-2
CATALYST LZ-105-6 #9939-01 50 CC 35.0 GM (34.27 GM AFTER THE RUN)
FEED H2:C3H6:H2O @ 1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINOUS OVERNITE
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN, 10.08 L/HR H2O 15 CC/HR
ACTUAL FLOW: 27.77 CCHR EFFLUENT 10.70 L/HR 10.63 CC/HR

RUN & SAMPLE NO.	9972-2-1	9972-2-2	9972-2-3	9972-2-4	9972-2-5
C3H6 WHSV	0.4	0.4	0.4	0.4	0.4
HRS ON STREAMS	7.5	24.5	29.5	47.5	53.
PRESSURE,PSIG	174	154	162	158	176
TEMP. C	410	410	408	409	409
FEED C3H6 CC	213.95	487.67	132.14	503.4	138.44
HOURS FEEDING	7.5	16.83	5.17	18.0	5.5
EFFLNT GAS LITER	82.0	187.5	47.3	198.0	47.9
GM AQUEOUS LAYER	73.59	176.58	50.10	182.02	57.73
GM LIQ HYDROCARBON	25.02	63.46	18.87	69.68	20.61
WT FR. LIQ HC/FEED	.2291	.2549	.2798	.2712	.2917
MATERIAL BALANCE WT %	94.99	96.22	97.55	97.05	94.42
C3H6 CONVERSION %	97.90	96.00	96.97	97.03	97.19
PRDT SELECTIVITY WT %					
CH4	0.7609	0.3632	0.3466	0.3315	0.3093
C2 HC'S	2.2081	1.4594	1.3206	1.3695	1.2670
C3H8	30.7507	22.1348	21.0171	21.3033	19.4161
C4H10	25.4877	28.4025	27.4300	28.3054	26.3262
C4H8=	1.2135	2.3285	2.0277	2.0841	2.0393
C5H12	6.9660	9.7110	9.8116	10.1027	9.7838
C5H10=	0.0228	0.0533	0.0408	0.0458	0.0467
C6H14	1.1132	1.7058	1.7949	1.7990	1.9180
C6H12= & CYCLO'S	0.2425	0.4559	0.4736	0.5002	0.5593
C7+ IN GAS	5.8875	5.4898	4.9319	5.0625	5.1790
LIQ HC'S	25.3472	27.8960	30.8052	29.0959	33.1554
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	60.4208	54.6884	52.1421	53.3939	49.3579
C5 -420 F	34.3830	42.4941	44.0997	44.1912	47.1974
420-700 F	5.1962	2.8175	3.7582	2.4150	3.4447
C5 -END PT	39.5792	45.3116	47.8579	46.6061	50.6421

ISO/NORMAL MOLE RATIO					
C4	2.0769	2.4555	2.3613	2.4110	2.3919
C5	5.4191	5.6217	5.3059	5.6500	5.5687
C6	7.6082	7.6459	7.3716	7.7657	7.4144
C4=	0.4614	0.4953	0.4677	0.4910	0.4850
PARAFFIN/OLEFIN M RATIO					
C3	13.8700	5.1500	6.5519	6.8021	6.5335
C4	20.2750	11.7749	13.0582	13.1106	12.4617
C5	297.3053	177.1607	233.8688	214.3594	203.8476
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	0.888	0.863	0.862	0.849	0.852
N,REFRACTIVE INDEX	1.5114	1.4996	1.4957	1.4975	1.4906
SIMULATED DISTILLATION					
10 WT % @ DEG F.	231	231	221	218	209
16	236	235	233	234	233
50	293	289	289	290	290
84	439	389	396	372	387
90	475	430	435	405	425
RANGE(16-84%)	203	154	163	138	154
WT % @420 F	79.5	89.0	88.0	91.7	89.6
WT % @700 F	100.0	100.0	100.0	100.0	100.0

TABLE 5B PROPYLENE(WITH H2) OPERATION

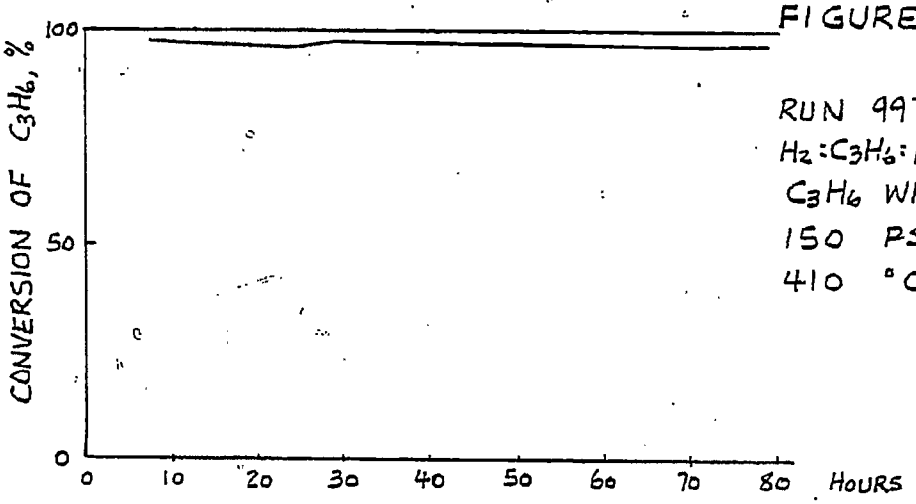
RUN NO. 9972-2
CATALYST LZ-105-6 #9939-01 50 CC 35.0 GM (34.27 GM AFTER THE RUN)
FEED H2:C3H6:H2O @ 1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINOUS OVERNITE
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN, 10.08 L/HR H2O 15 CC/HR
ACTUAL FLOW: 27.76 CCHR EFFLUENT 10.70 L/HR 10.63 CC/HR

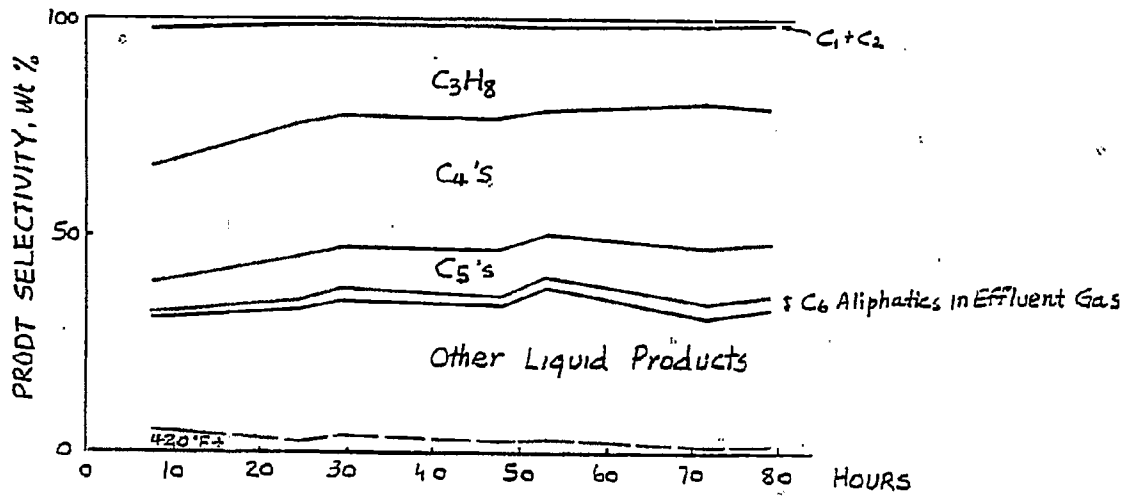
RUN & SAMPLE NO.	9972-2-6	9972-2-7
C3H6 WHSV	0.4	0.4
HRS ON STREAM5	71.8	79.1
PRESSURE,PSIG	168	168
TEMP. C	410	409
FEED C3H6 CC	516.62	223.37
HOURS FEEDING	18.75	7.417
EFFLNT GAS LITER	205.3	80.4
GM AQUEOUS LAYER	194.21	75.49
GM LIQ HYDROCARBON	75.98	30.74
WT FR. LIQ HC/FEED	.2953	.2696
MATERIAL BALANCE WT %	109.24	99.83
C3H6 CONVERSION %	96.47	96.39
PRDT SELECTIVITY WT %		
CH4	0.2351	0.2629
C2 HC'S	1.1456	1.2075
C3H8	17.7434	18.8471
C4H10	30.3359	28.7799
C4H8=	2.8610	2.7738
C5H12	13.1666	11.5828
C5H10=	0.0674	0.0600
C6H14	2.2889	2.3055
C6H12= & CYCLO'S	0.6315	0.6871
C7+ IN GAS	3.8993	4.7166
LIQ HC'S	27.6253	28.7768
TOTAL	100.00	100.00
SUBGROUPING		
C1 -C4	52.3210	51.8712
C5 -420 F	46.1596	46.2583
420-700 F	1.5194	1.8705
C5 -END PT	47.6790	48.1288

ISO/NORMAL MOLE RATIO		
C4	2.2820	2.3460
C5	5.5353	4.9806
C6	7.5869	6.7056
C4=	0.4842	0.4699
PARAFFIN/OLEFIN M RATIO		
C3	4.7488	4.9172
C4	10.2355	10.0159
C5	189.8147	187.8043
LIQ HC COLLECTION		
PHYS. APPEARANCE	OIL	OIL
DENSITY	0.837	0.840
N,REFRACTIVE INDEX	1.4841	1.4920
SIMULATED DISTILLATION		
10 WT % @ DEG F.	180	197
16	230	234
50	287	291
84	354	358
90	385	392
RANGE(16-84%)	124	124
WT % @420 F	94.5	93.5
WT % @700 F	100.0	100.0

FIGURE 13

RUN 9972-2, LZ-105-6
$H_2:C_3H_6:H_2O$ @ 1:1:2
C_3H_6 WHSV = 0.4
150 PSIG
410 °C





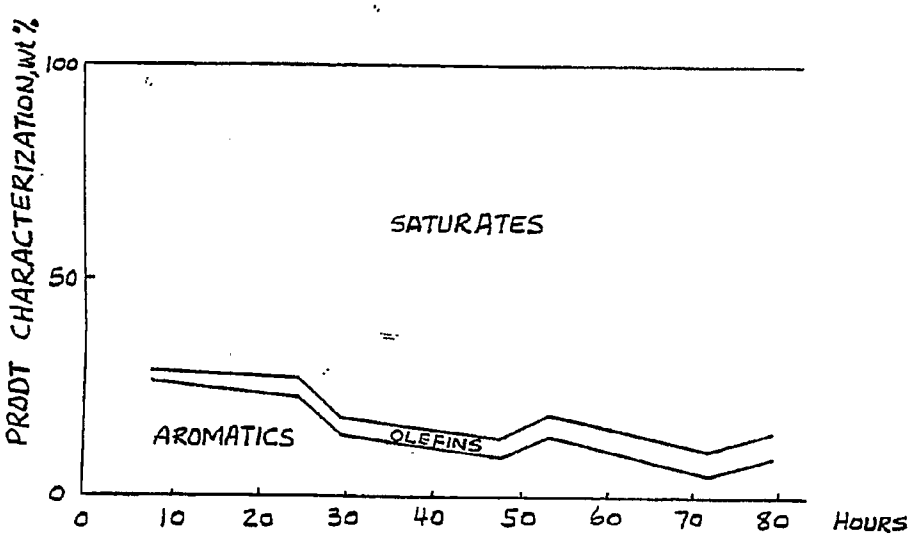


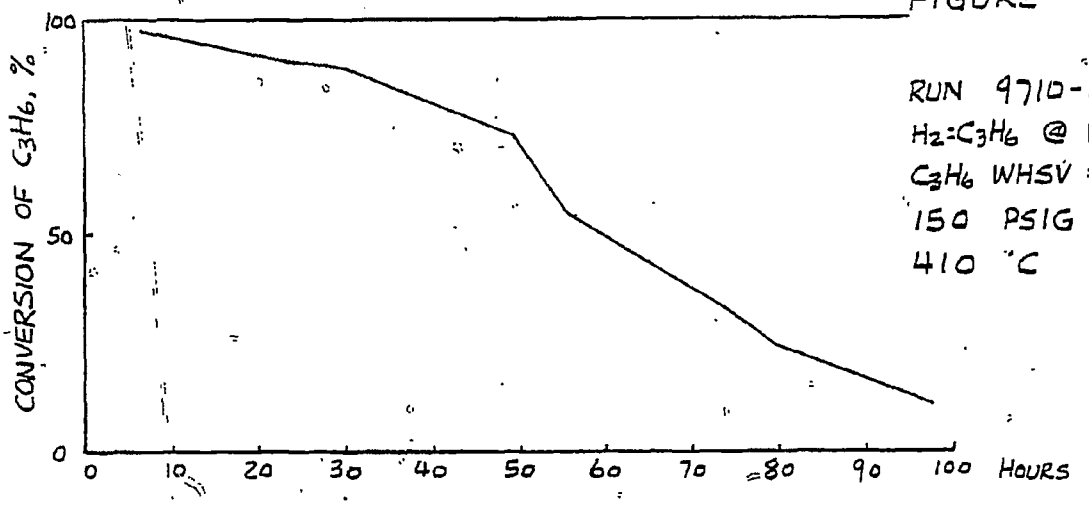
TABLE 5C - PROPYLENE(WITH H2) OPERATION

RUN NO. 9710-13
CATALYST LZ-105-6 #9939-01 43 CC 30.00 GM (34.05 GM AFTER THE RUN)
FEED C3H6/H2 @ 1/1 MOLE RATIO, 285 CC/MIN H2 FLOW
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)

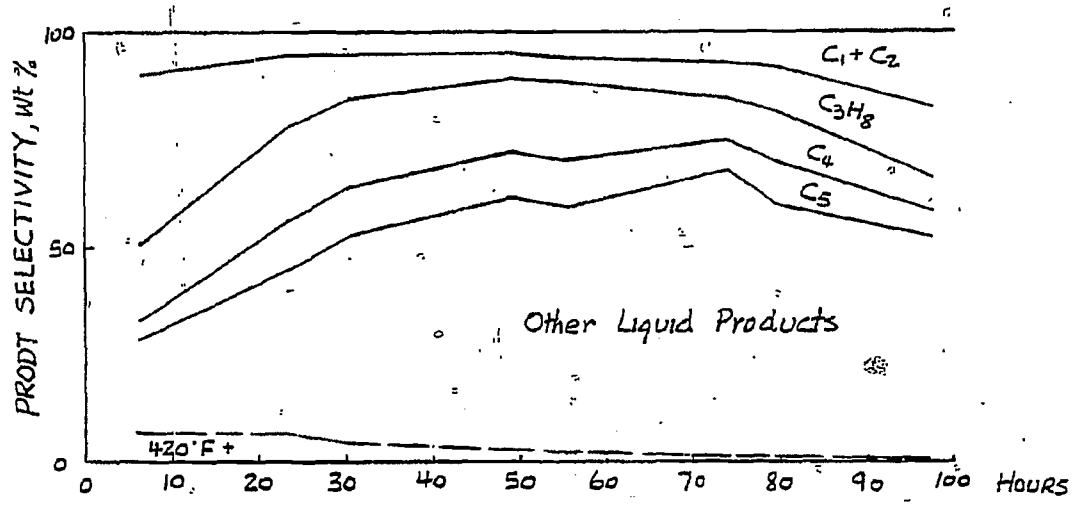
RUN & SAMPLE NO.	9710-13-1	9710-13-2	9710-13-3	9710-13-4	9710-13-5
C3H6 WHSV	1.0	1.0	1.0	1.0	1.0
HRS ON STREAM5	6.5	23.5	30.5	49.3	55.5
PRESSURE,PSIG	149	149	149	149	149
TEMP. C	410	410	410	410	410
FEED C3H6 CC	393.3	1076.0	440.8	1071.6	394.46
HOURS FEEDING	6.5	16.833	7.167	16.833	6.50
EFFLNT GAS LITER	174.9	456.1	197.2	488.89	202.60
GM LIQ HYDROCARBON	33.42	129.66	70.38	146.32	33.20
WT FR. LIQ HC/FEED	.1665	.2361	.3128	.2675	.1649
MATERIAL BALANCE WT %	86.78	79.47	91.58	89.54	94.07
C3H6 CONVERSION %	97.23	90.51	86.69	72.82	55.63
PRDT SELECTIVITY WT %					
CH4	2.9546	1.6485	1.5167	1.6234	1.5844
C2 HC'S	6.7002	3.3402	2.9545	2.6541	3.4606
C3H8	39.2707	16.2012	10.9699	6.3160	6.6522
C4H10	16.6900	15.4444	10.4359	2.8838	1.9024
C4H8=	1.1912	7.1262	10.2218	14.5296	16.3015
C5H12	4.2091	6.8590	5.2173	1.6728	1.0093
C5H10=	0.4215	3.8409	5.8190	8.8444	9.6614
C6H14	1.1600	3.4388	3.2288	2.6794	3.6413
C6H12=	0.0624	1.7218	1.9208	5.2912	9.5745
C7+ IN GAS	7.3186	7.4208	7.8250	12.2993	14.3439
LIQ	20.0216	32.9583	39.8915	41.2062	31.685
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	66.81	43.76	36.10	28.01	29.90
C5 -420 F	26.37	49.81	59.59	69.11	68.51
420-700 F	6.83	6.43	4.31	2.88	1.59
C5 -END PT	33.19	56.24	63.90	71.99	70.10

ISO/NORMAL MOLE RATIO					
C4	1.1081	1.5723	1.6006	1.3520	1.1954
C5	3.0558	2.5625	2.3316	1.9811	1.7615
C6	6.5967	3.5364	2.6188	1.2322	1.2927
C4=	0.4641	0.4116	0.4069	0.3560	0.3379
PARAFFIN/OLEFIN M RATIO					
C3	13.4417	1.4833	0.6843	0.1621	0.0801
C4	13.5250	2.0921	0.9855	0.1916	0.1127
C5	9.7059	1.7359	0.8716	0.1838	0.1015
LIQ HC COLLECTION					
PHYSICAL APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	0.904	0.843	0.789	0.763	0.735
N,REFRACTIVE INDEX	1.5358	1.4972	1.4646	1.4485	1.4340
SIMULATED DISTILLATION					
10 WT % @ DEG F.	235	191	160	158	160
16	238	231	192	178	181
50	335	317	286	266	261
84	481	441	391	365	350
90	499	480	427	397	381
RANGE(16-84%)	243	210	199	187	169
WT % @420 F	65.9	80.5	89.2	93.0	95.0
WT % @700 F	100.0	100.0	100.0	100.0	100.0

FIGURE 14



RUN 9710-13, LZ-105-6
H_2:C_3H_6 @ 1:1, No water
C_3H_6 WHSV = 1.0
150 PSIG
410 °C



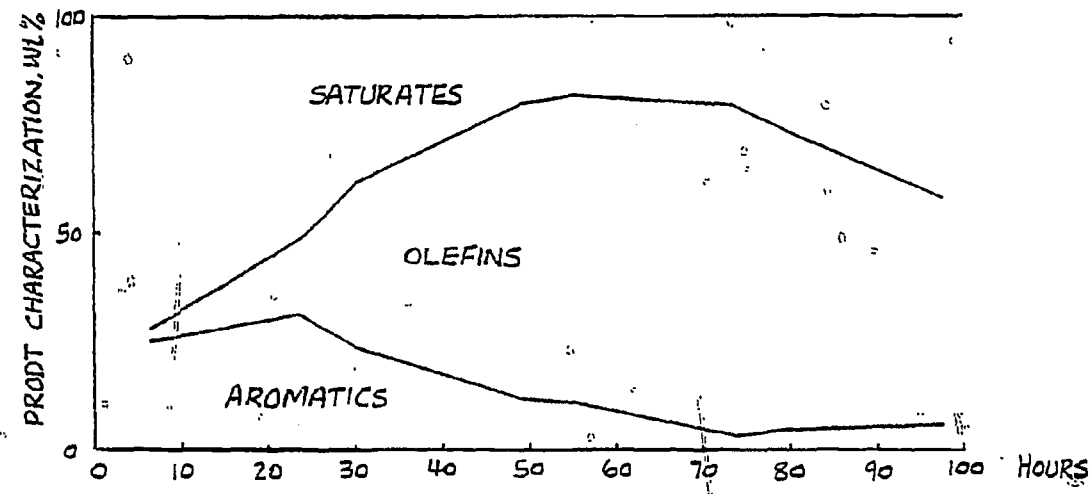


FIGURE 15A

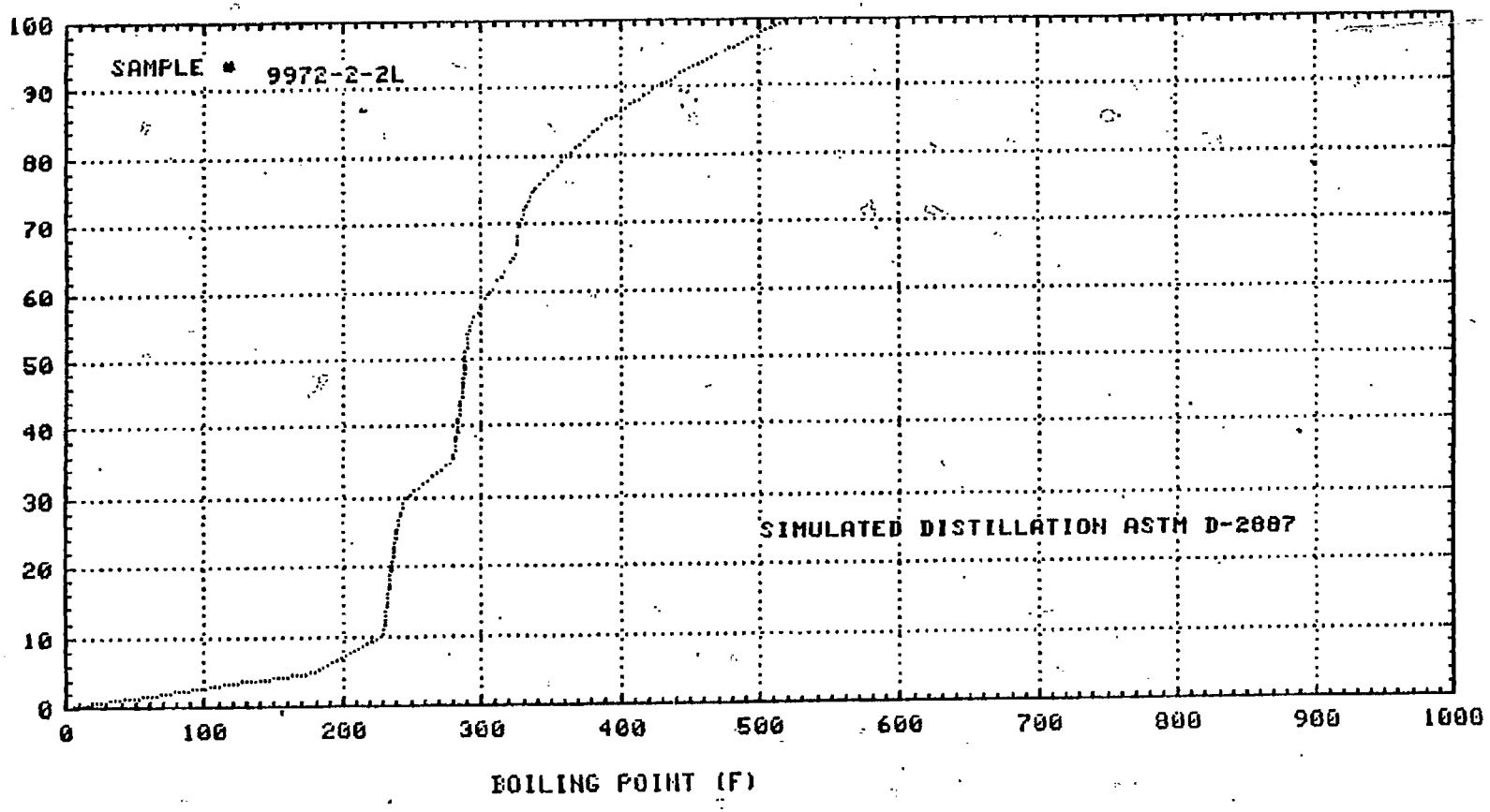
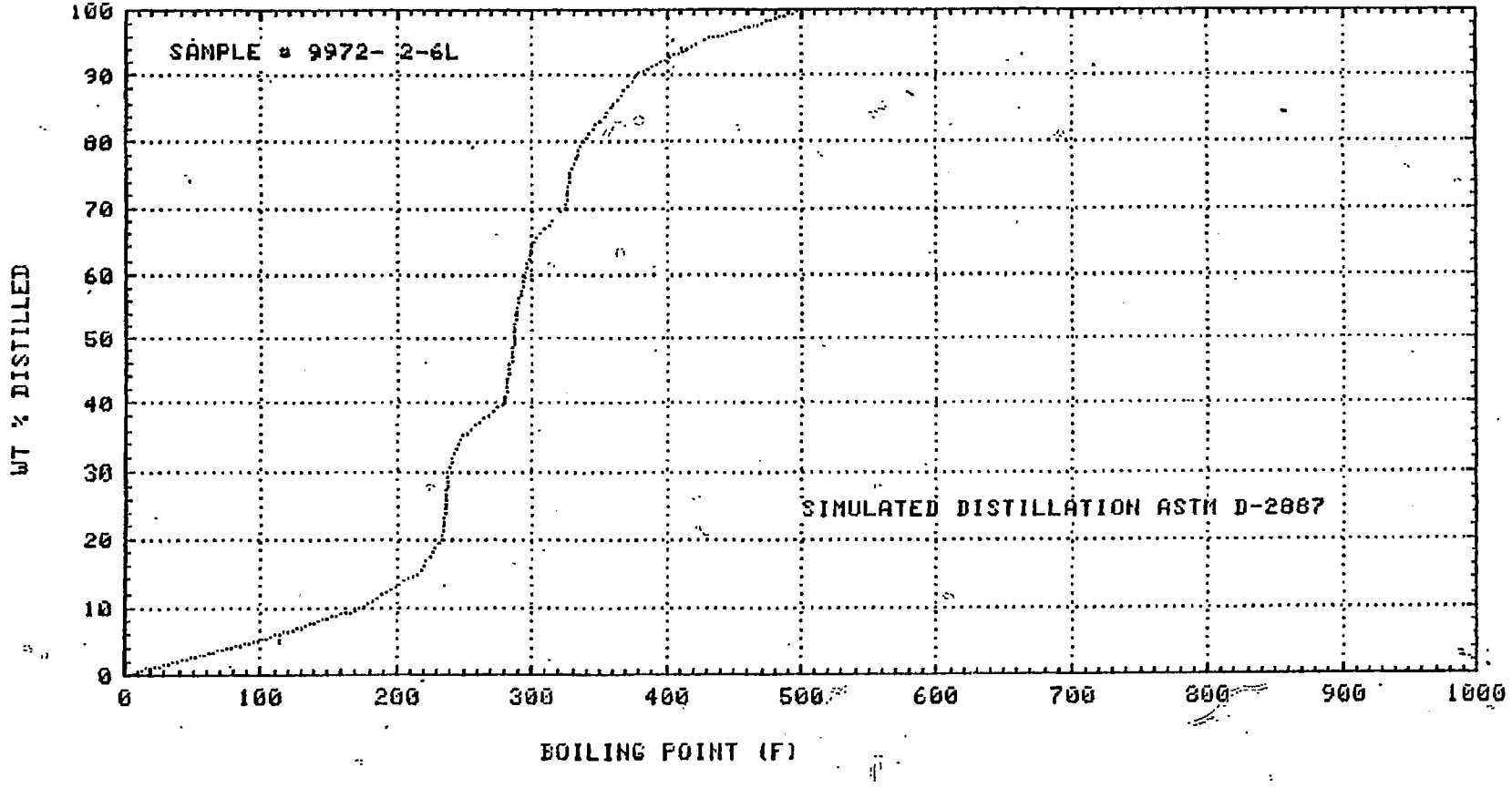

SAMPLE # 9972-2-2L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIGURE 15 B


SAMPLE = 9972- 2-6L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

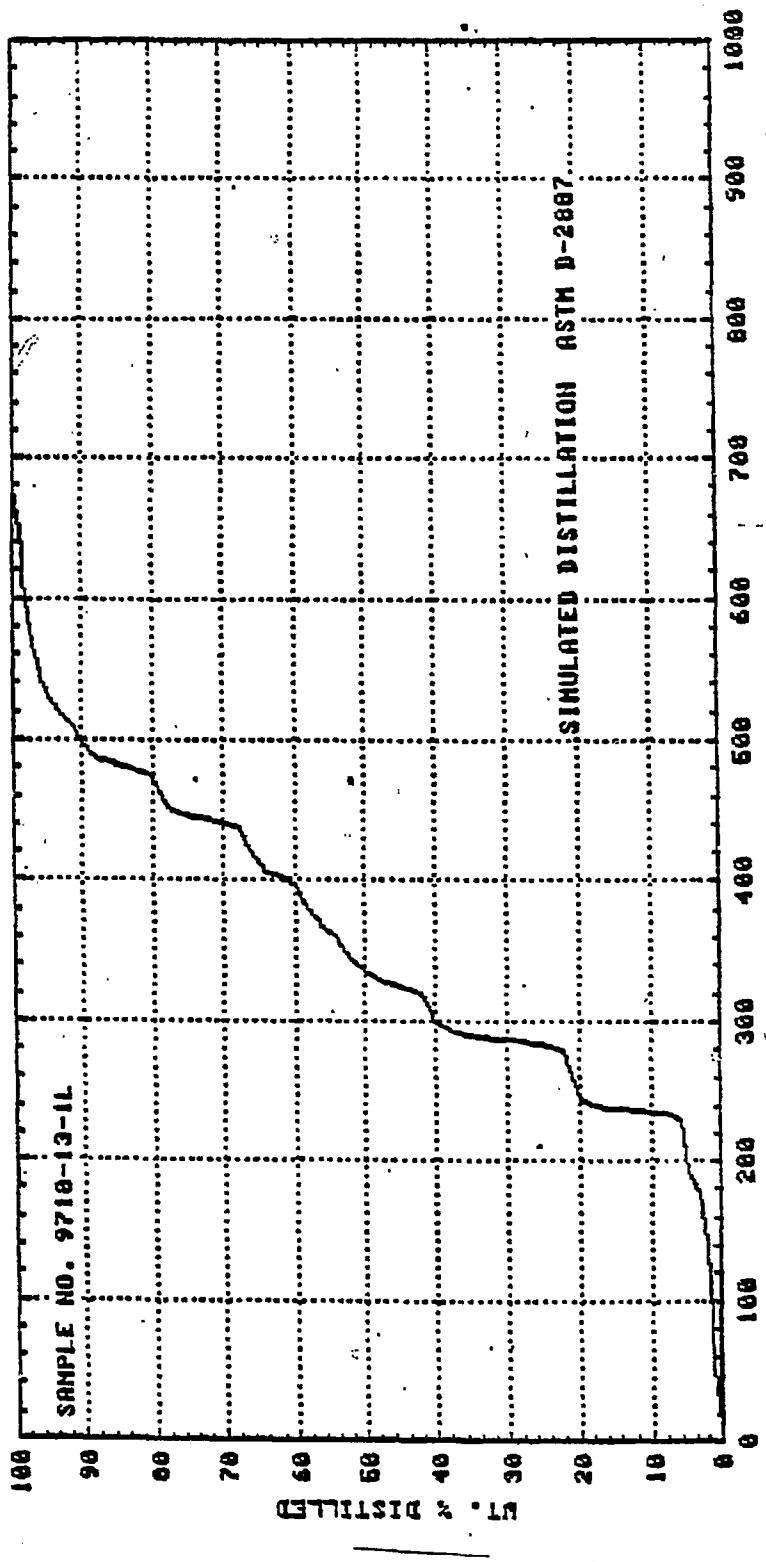

SAMPLE NO. 9710-13-1L
SIMULATED DISTILLATION ASTM D-2887
BOILING POINT (F)
WT. % DISTILLED
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

FIG. 16A

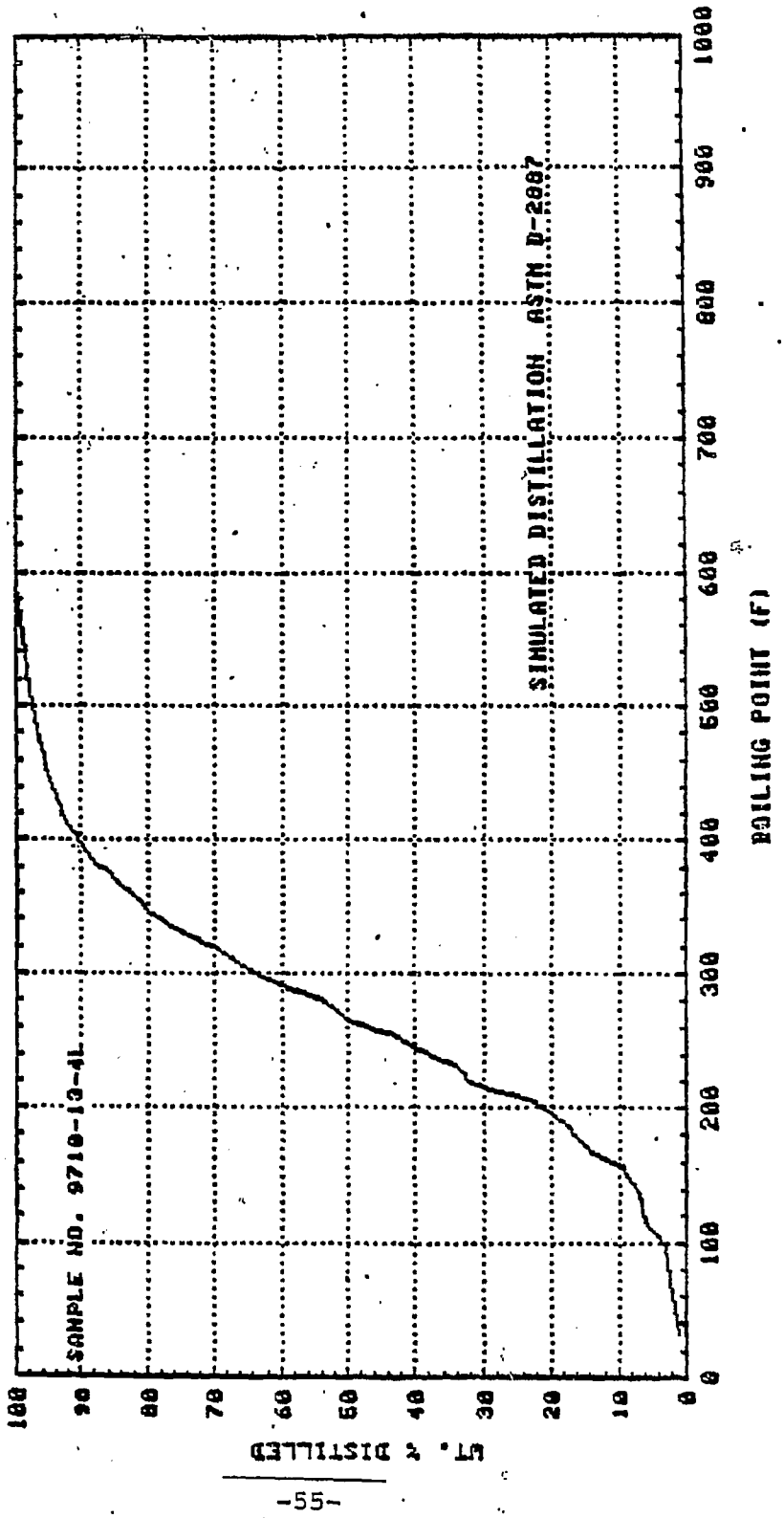

SIMULATED DISTILLATION ASTM D-2887
SAMPLE NO. 9710-13-4L
BOILING POINT (F)
WT. % DISTILLED
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

FIG. 16B

Run 9972-3, 9972-4, Feed H_2:C_2H_6: Steam on UCC-101

In these two runs, the catalyst UCC-101 was used with hydrogen-propylene feed plus co-fed steam. The pressure levels were similar, but the temperatures were different: 408°C for Run 9972-3 and 280° and 340°C for Run 9972-4. The detailed results are tabulated in Tables 6, 7A and 7B, and the conversions and selectivities are plotted in Figures 17 and 18. The catalyst still deactivated with time on stream, though the presence of steam stabilized the catalyst to some extent and helped to slow down the deactivation rate compared to tests reported last quarter (tests 9710-14, 16 and 17) particularly at high temperature. The initial conversion level increased with temperature as expected (Figure 19), but was much lower than that of LZ-105-6 at corresponding temperatures. The conversions are 11%, 23% and ∿40% and C_5^+ selectivities are 55%, 47% and 44% for the respective temperatures of 278, 338 and 408°C. The simulated boiling point distribution plots (Figures 20 to 24) have a smoother appearance than those with LZ-105-6 as the catalyst.

The high propane selectivity for all the samples and the 1.52 refractive index for the one sample measured implies an aromatic product. The smooth distillation plots show no signs of toluene and little sign of the other aromatics which were so easily seen in the distillation of samples from previous runs. The distillation data also shows that the condensed liquid collected from these runs is much higher boiling than that from the previous runs with LZ-105-6 as the catalyst. This heavier product is less marked when the entire C_5^+ product is considered. Deactivation of the catalyst seems to increase selectivity to gas phase hydrocarbons at the expense of the condensed liquid. Sample 2 of 9972-3 (408°C) had half of the C_5^+ as condensed liquid, while by sample 5 the condensed liquid amounted to less than a tenth of the total C_5^+.

TABLE 6 PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-3
CATALYST UCC-101 #9939-27 60 CC 35.0 GM (44.3 GM AFTER THE RUN, +9.3 GM)
FEED H2:C3H6:H2O @ 1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINOUS OVERNITE
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN, 10.08 L/HR H2O 15 CC/HR
ACTUAL FLOW: 28.92 CCHR EFFLUENT 17.13 L/HR 10.42 CC/HR

RUN & SAMPLE NO.	9972-3-1	9972-3-2	9972-3-3	9972-3-4	9972-3-5
C3H6 WHSV	0.4	0.4	0.4	0.4	0.4
HRS ON STREAM5	4.1667	7.6667	25.1667	31.9167	48.5833
PRESSURE,PSIG	172	178	179	178	179
TEMP. C	408	408	408	409	408
FEED C3H6 CC	132.14	99.423	523.54	165.49	484.53
HOURS FEEDING	4.1667	3.50	17.50	6.75	16.6667
EFFLNT GAS LITER	64.60	57.30	302.10	114.40	294.00
GM AQUEOUS LAYER	0.0	72.37	175.12	67.37	167.36
GM LIQ HYDROCARBON	0.0	3.51	1.40	0.29	0.13
WT FR. LIQ HC/FEED	.0000	.0692	.0052	.0034	.0005
MATERIAL BALANCE WT %	69.13	96.42	84.12	102.30	86.81
C3H6 CONVERSION %	50.37	31.06	9.47	7.86	5.16
PRDT SELECTIVITY WT %					
CH4	1.2558	0.8444	1.3219	1.4112	1.6555
C2 HC'S	1.9387	1.5031	2.3223	2.6226	3.8195
C3H8	62.9995	47.4961	62.3689	62.2339	63.0845
C4H10	4.5238	1.1010	1.2465	2.6253	4.2017
C4H8=	7.1352	4.4865	3.7899	5.6893	7.1939
C5H12	2.5906	0.6025	0.6040	0.6929	0.8256
C5H10=	0.2053	0.1618	0.1890	0.2343	0.3750
C6H14	4.9462	3.0185	3.5826	3.7124	4.2668
C6H12= & CYCLO'S	4.6688	7.9576	9.6325	8.5573	7.8029
C7+ IN GAS	9.7360	8.6442	8.4847	7.9335	6.6254
LIQ HC'S	0.0000	24.1844	14.1610E	4.2874E	1.1490E
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	77.8530	55.4312	71.0495	74.5822	78.9552
C5 -420 F	22.1470	33.9277	23.8295	23.5314	20.5392
420-700 F	0.0000	9.6979	4.3266	1.7192	0.4608
C5 -END PT	22.1470	44.5688	28.9505	25.4178	21.0448

ISO/NORMAL MOLE RATIO					
C4	2.0584	1.1355	0.3955	0.1466	0.0833
C5	2.9107	1.0894	0.4038	0.4839	0.2442
C6	3.7536	2.0800	1.7256	1.8657	1.4759
C4=	0.4142	0.4460	0.4075	0.3768	0.3553
PARAFFIN/OLEFIN M RATIO					
C3	0.6321	0.2098	0.0644	0.0524	0.0340
C4	0.6120	0.2369	0.3175	0.4454	0.5638
C5	12.2640	3.6197	3.1064	2.8750	2.1400
LIQ HC COLLECTION					
PHYS. APPEARANCE		OIL			
DENSITY		0.879			
N,REFRACTIVE INDEX		1.5171			
SIMULATED DISTILLATION					
10 WT % @DEG F.	0	295	386	0	0
16	0	325	408	0	0
50	0	407	511	0	0
84	0	564	659	0	0
90	0	604	729	0	0
RANGE(16-84%)		239	251		
WT % @420 F	0	56	20.7	0	0
WT % @700 F	0	96.1	87.6	0	0

TABLE 7A PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-4
CATALYST UCC-101 #9939-27 60 CC 35.0 GM (37.11GM AFTER THE RUN, +2.1 GM)
FEED H2:C3H6:H20 @ 1:1:3 MOLE RATIO, 0.5 C3H6 WHSV, CONTINOUS OVERNITE
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN, 10.11 L/HR H20 22.5 CC/HR
ACTUAL FLOW: 29.8 CCHR EFFLUENT 14.99 L/HR 24.67 CC/HR

RUN & SAMPLE NO.	9972-4-1	9972-4-2	9972-4-3	9972-4-4	9972-4-5
C3H6 WHSV	0.4	0.4	0.4	-0.4	0.4
HRS ON STREAM	7.8	23.8	28.1	31.2	48.1
PRESSURE,PSIG	160	154	156	157	160
TEMP. C	278	278	278	340	338
FEED C3H6 CC	215.84	488.93	125.85	86.21	521.03
HOURS FEEDING	7.75	16.00	4.25	3.17	16.92
EFFLNT GAS LITER	108.70	244.40	63 80	45.80	258.30
GM AQUEOUS LAYER	187.46	390.30	104.88	77.11	412.63
GM LIQ HYDROCARBON	0.0	1.43	0.00	1.12	2.00
WT FR. LIQ HC/FEED	0.000	0.0057	0.000	0.0255	0.0075
MATERIAL BALANCE WT %	85.07	83.96	88.49	97.09	83.91
C3H6 CONVERSION %	10.99	7.14	6.51	22.76	11.81
PRDT SELECTIVITY WT %					
CH4	0.0453	0.0837E	0.0925	0.2210	0.1835
C2 HC'S	0.1854	0.1178E	0.1303	0.3156	0.2482
C3H8	34.9861	35.4022E	39.1240	37.1714	38.9291
C4H10	3.6021	2.2243E	2.4581	4.9234	3.6059
C4H8=	5.9033	10.0413E	11.0969	10.2263	13.2319
C5H12	2.9608	1.3998E	1.5470	2.9490	0.7180
C5H10=	0.2288	0.1971E	0.2178	0.2826	0.3462
C6H14	15.2585	8.4234E	9.3089	7.3512	3.7970
C6H12= & CYCLO'S	7.9238	9.6847E	10.7028	6.2292	12.0398
C7+ IN GAS	28.9061	22.9128E	25.3217	18.1121	19.3498
LIQ HC'S	0.0000	9.5128E	0.0000	12.2182	7.5507
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	44.7221	47.8693E	52.9018	52.8577	56.1986
C5 -420 F	55.2779	47.8499E	47.0982	41.8274	39.8977
420-700 F	0.0000	3.9954E	0.0000	4.8751	3.6243
C5 -END PT	55.2779	52.1307E	47.0982	47.1423	43.8014

ISO/NORMAL MOLE RATIO					
C4	5.8252	---	1.7902	2.2263	0.3878
C5	------	---	10.6000	5.9028	0.0973
C6	18.4058	---	7.3011	6.8580	1.8226
C4=	0.5287	---	0.4669	0.4643	0.4480
PARAFFIN/OLEFIN M RATIO					
C3	0.0422	0.0265	0.0265	0.1070	0.0508
C4	0.5890	0.2138	0.2138	0.4647	0.2631
C5	12.5811	6.9048	6.9048	10.1429	2.0163
LIQ HC COLLECTION					
PHYS. APPEARANCE		OIL		OIL	OIL
DENSITY					
N,REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F.	0	291	0	275	303
16	0	330	0	290	335
50	0	409	0	405	425
84	0	508	0	531	555
90	0	556	0	592	609
RANGE(16-84%)	0	178	0	241	220
WT % @420 F	0	55.0	0	56.5	48.3
WT % @700 F	0	97.0	0	96.4	96.3

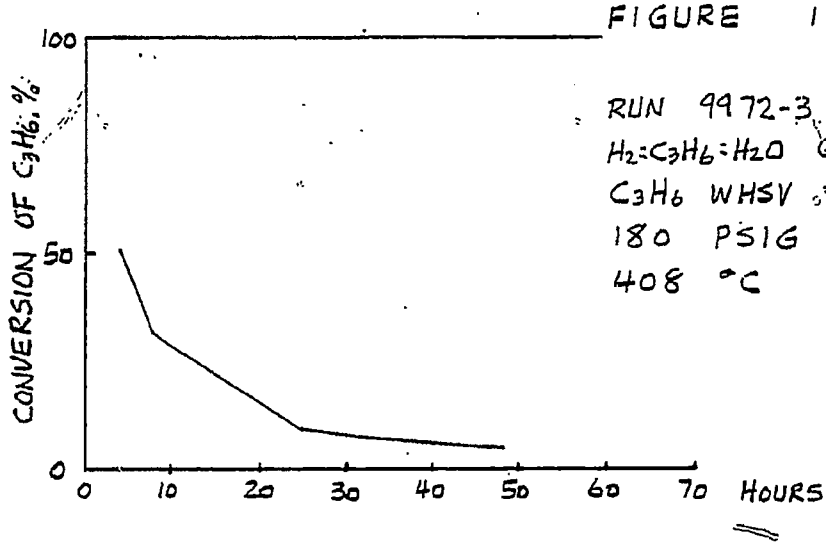
TABLE 7B PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-4
CATALYST UCC-101 #9939-27 60 CC 35.0 GM (37.11GM AFTER THE RUN, +2.1 GM)
FEED H2:C3H6:H20 @ 1:1:3 MOLE RATIO,0.5 C3H6 WHSV,CONTINOUS OVERNITE
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN, 10.08 L/HR H20 22.5 CC/HR
ACTUAL FLOW: 29.8 CC/HR EFFLUENT 14.89 L/HR 24.7 CC/HR

RUN & SAMPLE NO.	9972-4-6
C3H6 WHSV	0.4
HRS ON STREAM5	55.0
PRESSURE,PSIG	155
TEMP. C	338
FEED C3H6 CC	201.36
HOURS FEEDING	6.92
EFFLNT GAS LITER	103.50
GM AQUEOUS LAYER	167.84
GM LIQ HYDROCARBON	0.790
WT FR. LIQ HC/FEED	0.0020
MATERIAL BALANCE WT %	87.55
C3H6 CONVERSION %	9.81
PRDT SELECTIVITY WT %	
CH4	0.1694
C2 HC'S	0.4297
C3H8	39.4476
C4H10	3.1567
C4H8=	10.9984
C5H12	0.8183
C5H10=	0.3326
C6H14	3.7366
C6H12= & CYCLO'S	13.4696
C7+ IN GAS	18.3737
LIQ HC'S	9.0675
TOTAL	100.00
SUBGROUPING	
C1 -C4	54.2018
C5 -420 F	41.7179
420-700 F	3.8083
C5 -END PT	45.7982

ISO/NORMAL MOLE RATIO	
C4	0.3321
C5	1.3918
C6	1.4639
C4=	0.4805
PARAFFIN/OLEFIN M RATIO	
C3	0.0419
C4	0.2771
C5	2.3918
LIQ HC COLLECTION	
PHYS. APPEARANCE	OIL
DENSITY	.
N,REFRACTIVE INDEX	.
SIMULATED DISTILLATION	
10 WT % @ DEG F.	
16	0
50	0
84	0
90	0
RANGE(16-84%)	0
WT % @420 F	0
WT % @700 F	0

FIGURE 17



RUN 9972-3, UCC-101
H_2:C_3H_6:H_2O @ 1 : 1 : 2
C_3H_6 WHSV = 0.4
180 PSIG
408 °C

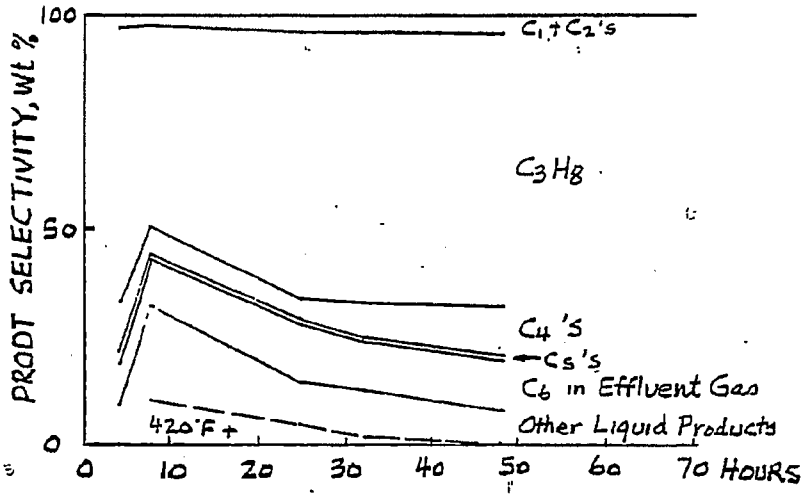
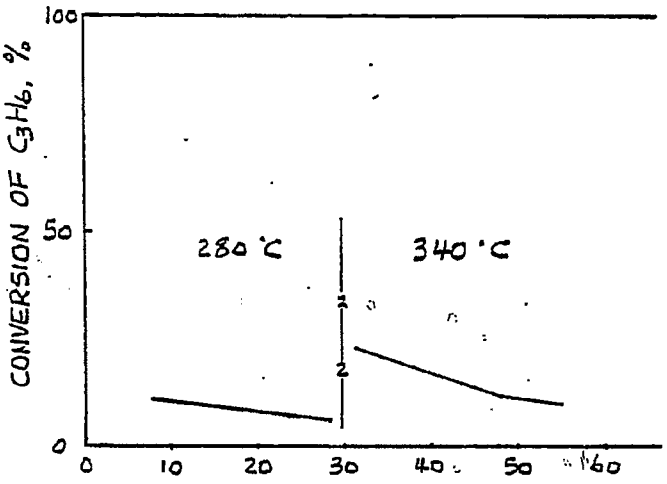


FIGURE 18

RUN 9972-4, UCC-101
$H_2 : C_3H_6 : H_2O$ @ 1 : 1 : 3
C_3H_6 WHSV = 0.5
150 PSIG
280 & 340 °C



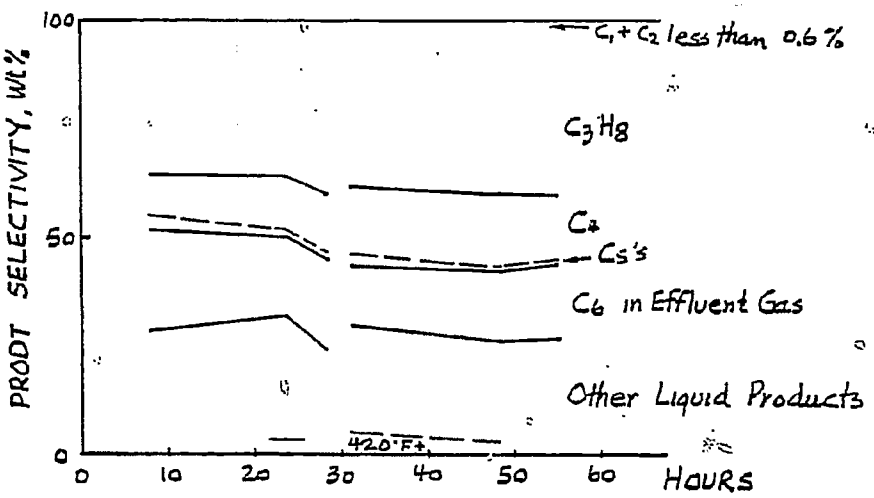


FIGURE 19

RUN 9972-3, -4
UCC-101
$H_2 : C_3H_6 : H_2O$ @ 1:1:2
1:1:3
150 - 180 PSIG
INITIAL CONVERSIONS

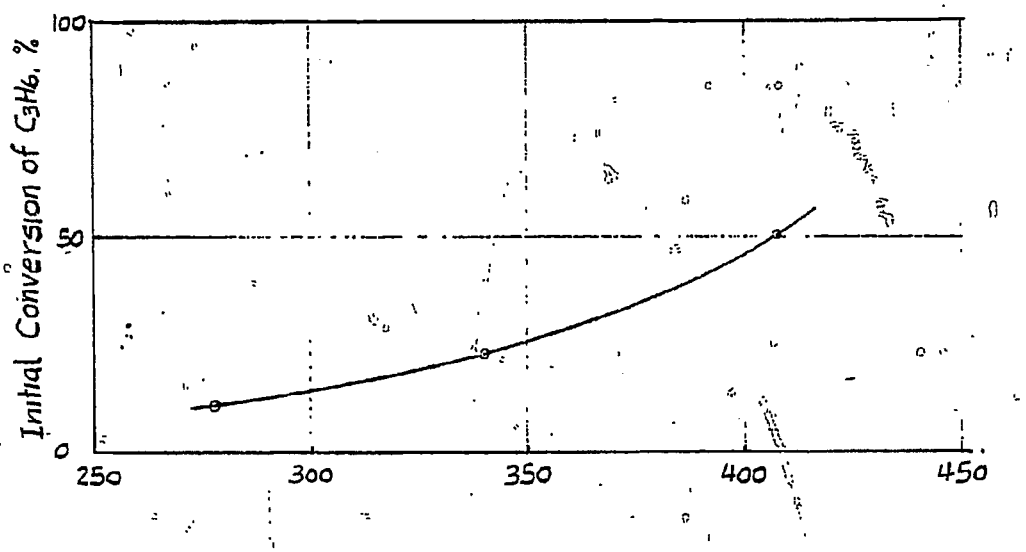


FIGURE 20

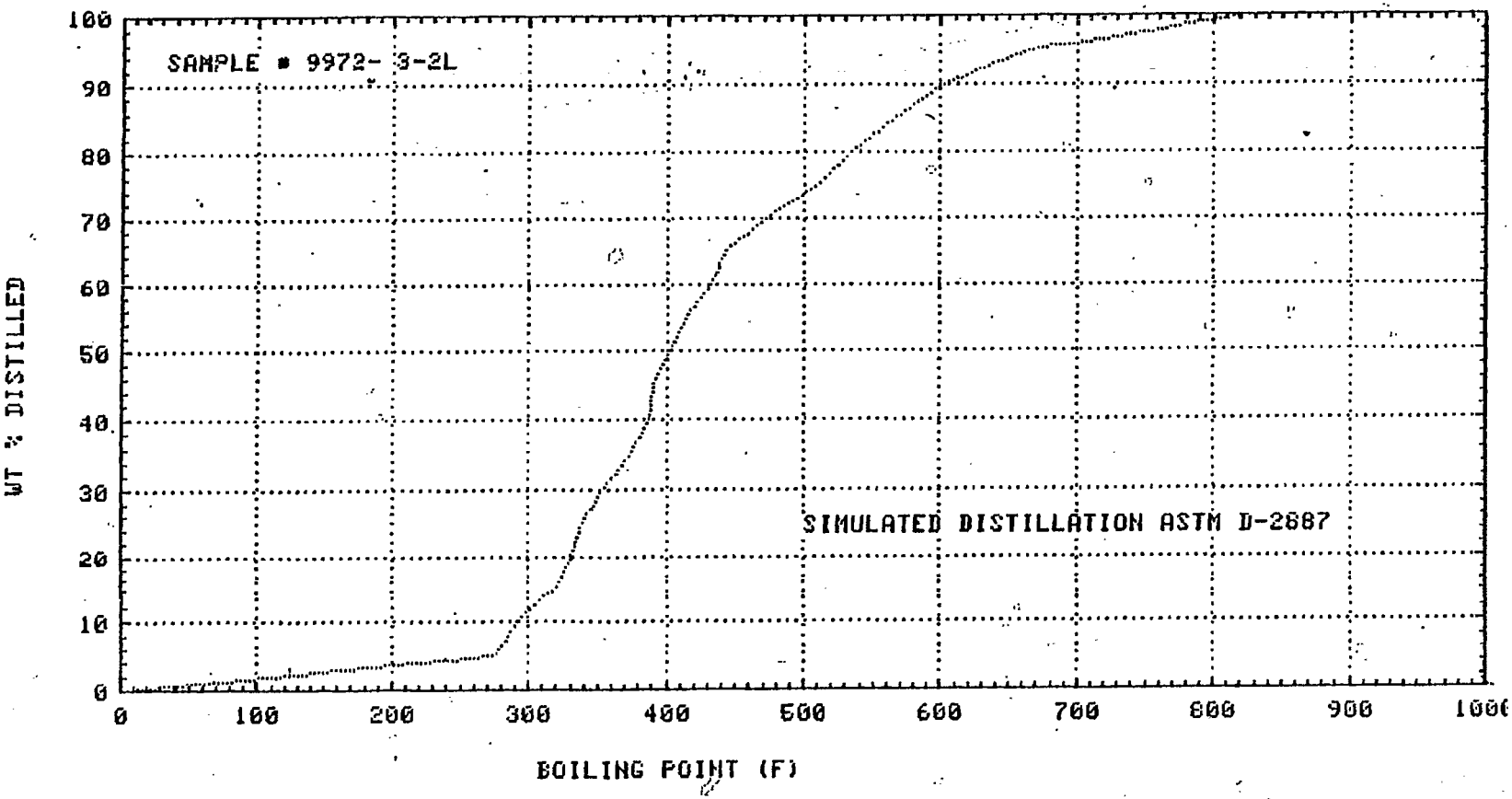

SAMPLE # 9972- 3-2L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIGURE 21

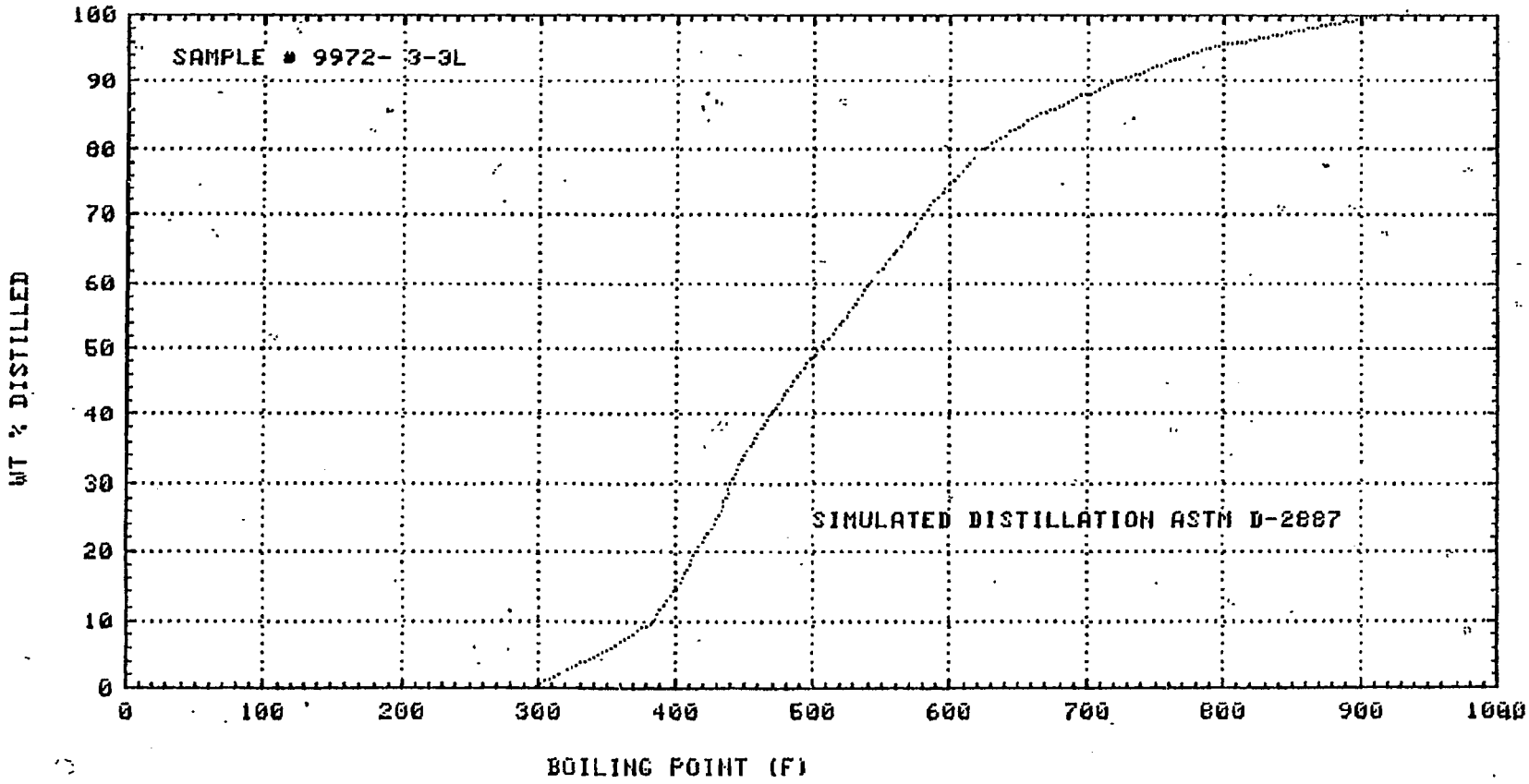

SAMPLE # 9972- 3-3L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIGURE 22

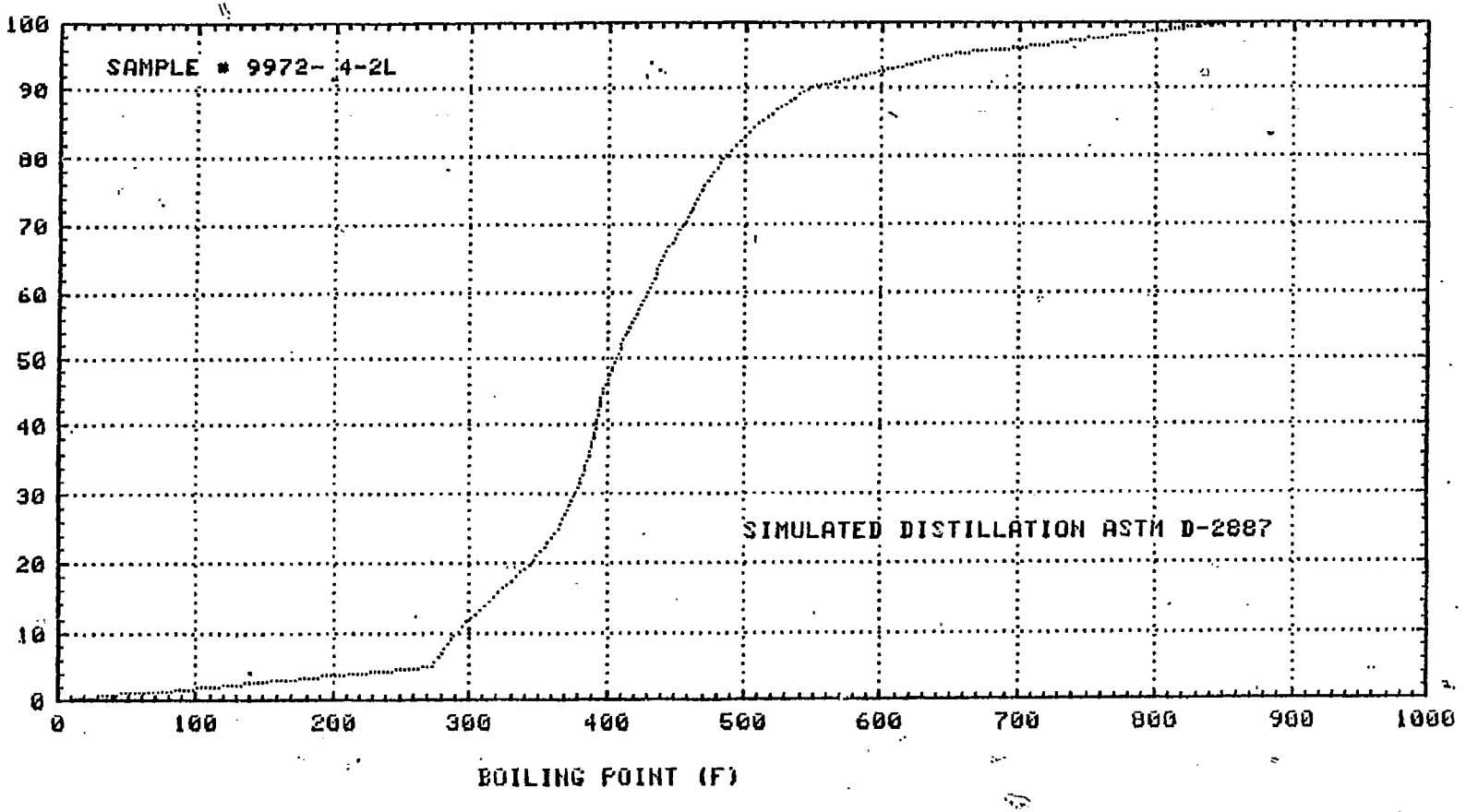

SAMPLE # 9972- 4-2L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIGURE 25

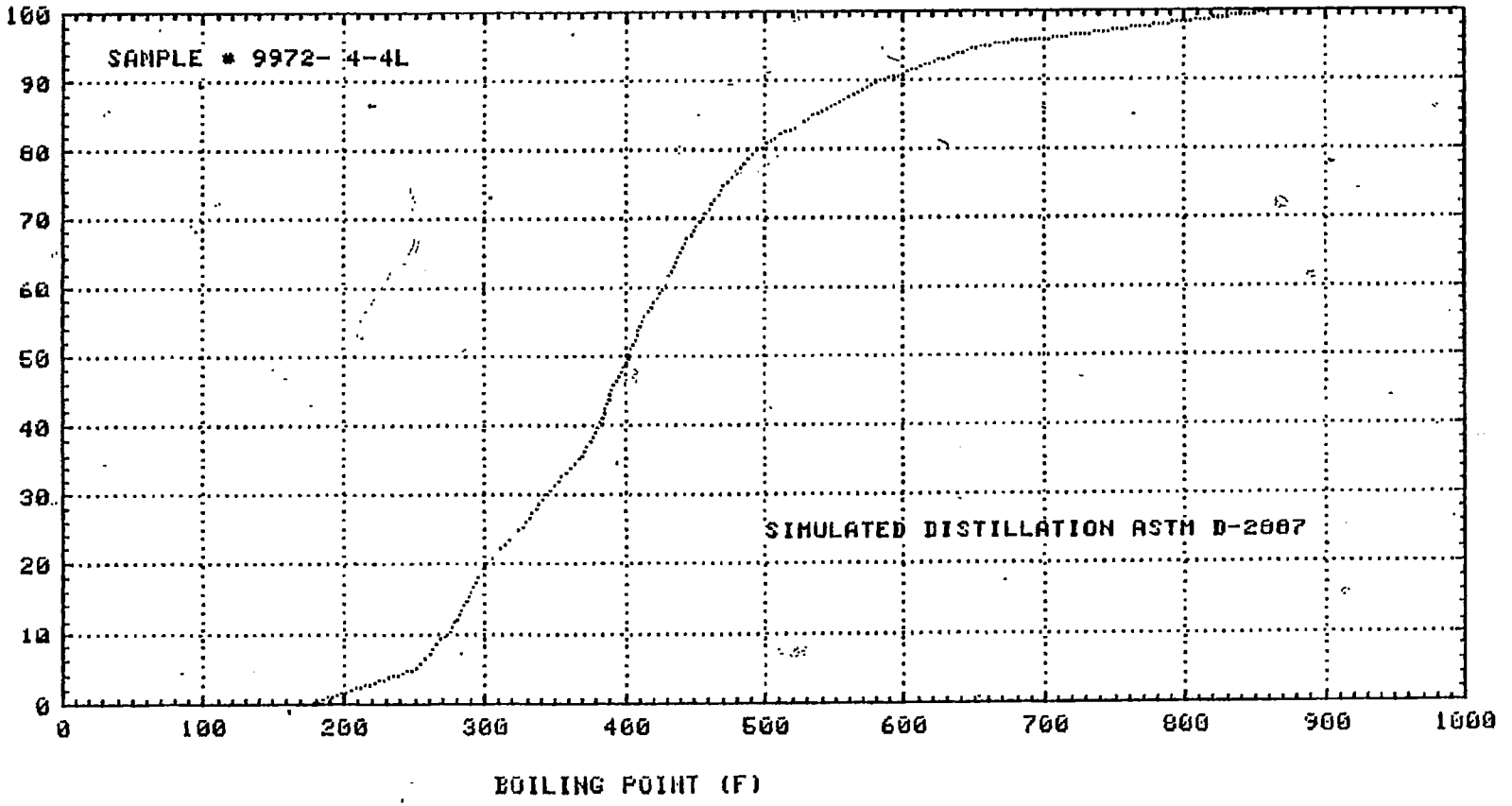
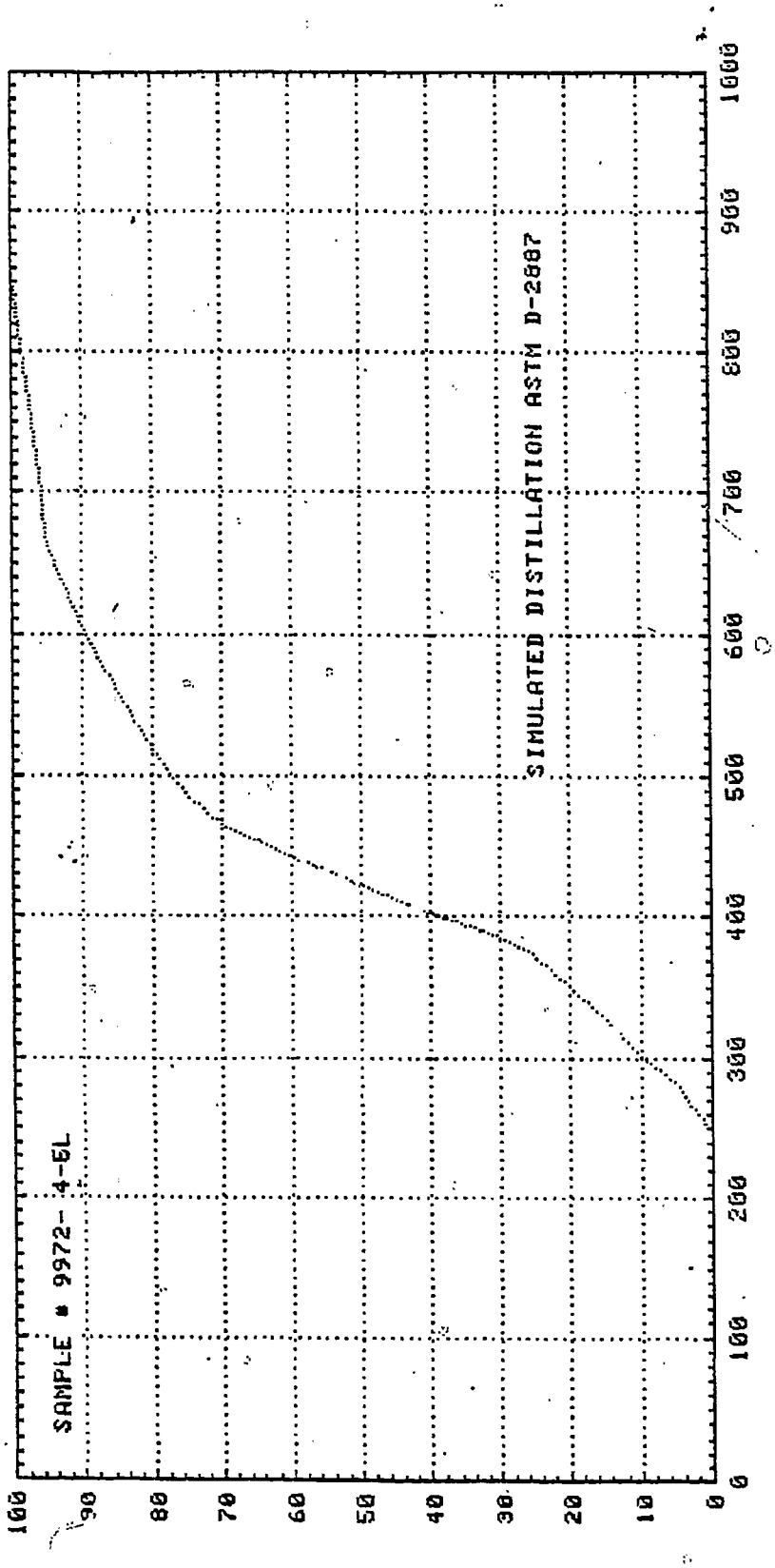

SAMPLE # 9972- 4-4L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIGURE 24


SAMPLE # 9972- 4-EL
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Run 9972-5, Feed 2:1:1 (H_2:C_3H_6:H_2O) on $AlPO_4$-11

A new class of aluminophosphate molecular sieves has been discovered by Union Carbide scientists (U.S. Patent No. 4,310,440). One member of this class, $AlPO_4$-11, was tested and showed almost no activity for propylene conversion at 280 and 340°C and pressures of 150-300 psig. $AlPO_4$-11 is an intermediate pore size (~6Å) molecular sieve. The results are reported in Table 8. The small amount of converted products present in the react effluent (up to 7% at 337°C of propane and C_6 hydrocarbons) is attributed to the (20% by weight) alumina binder used in making the catalyst tablets. This as-synthesized aluminophosphate molecular sieve had perfect charge balance in the crystal structure, and no ion exchange capacity. This implies it should show no catalytic activity with respect to propylene, but does not rule out its use as a shape-selective component in syngas operation.

TABLE 8 PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-5
CATALYST ALPO-11 (20% AL203) #9939-67, 63 CC 30 GM,30.05G AFTER THE RUN
FEED H2:C3H6:H20 @ 2:1:1 MOLE RATIO,0.5 C3H6 WHSV,DAY-TIME FEED
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 29.4 CC/HR H2 290 CCMN, 17.4 L/HR H20 6.4 CC/HR
ACTUAL FLOW: 29.1 CCHR EFFLUENT 22.55 L/HR 6.0 CC/HR

RUN & SAMPLE NO.	9972-5-1	9972-5-2	9972-5-3	9972-5-4	9972-5-5
C3H6 WHSV	0.4	0.5	0.5	0.5	0.5
HRS ON STREAM5	7.0	24.6	32.0	38.8	46.4
PRESSURE,PSIG	150	148	149	304	301
TEMP. C	278	278	339	337	336
FEED C3H6 CC	182.48	534.87	207.66	218.35	203.88
HOURS FEEDING	7.0	17.6	7.4	6.8	7.5
EFFLNT GAS LITER	159.3	409.0	168.6	145.5	162.3
GM AQUEOUS LAYER	32.2	92.86	39.67	37.55	40.51
GM LIQ HYDROCARBON	0.0	0.0	0.0	0.0	0.0
WT FR. LIQ HC/FEED	0.000	0.000	0.000	0.000	0.000
MATERIAL BALANCE WT %	97.30	84.55	86.29	83.46	86.91
C3H6 CONVERSION %	3.80	0.91	5.48	6.75	6.87
PRDT SELECTIVITY WT %					
CH4	0.4707	2.2457	0.0000	0.3702	0.0000
C2 HC'S	0.0000	0.0000	0.0000	0.1877	0.0000
C3H8	72.9831	0.0000	27.0770	18.7602	15.0155
C4H10	5.3347	12.7855	0.0000	3.0310	0.8574
C4H8=	2.6909	10.3224	0.0000	9.2956	0.4543
C5H12	0.0000	0.0000	0.0000	1.4880	0.7122
C5H10=	0.0000	0.0000	0.0000	0.1102	0.0000
C6H14	1.6208	7.1690	0.0000	7.8285	6.5284
C6H12= & CYCLO'S	11.6183	45.1719	54.0272	34.0115	48.9986
C7+ IN GAS	5.2815	22.3054	18.8958	24.9170	27.4336
LIQ HC'S	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL	100.00	100.00	100.00	100.0	100.00
SUBGROUPING					
C1 -C4	81.4794	25.3536	27.0770	31.6449	16.3272
C5 -420 F	18.5206	74.6464	72.9230	68.3551	83.6728
420-700 F	0.0000	0.0000	0.0000	0.0000	0.0000
C5 -END PT	18.5206	74.6464	72.9230	68.3551	83.6728

ISO/NORMAL MOLE RATIO					
C4	2.2752	0.6871	------	0.0684	0.2430
C5	------	------	------	0.4384	0.3284
C6	0.5152	0.5522	0.0000	0.9392	1.0449
C4=	0.5255	0.4739	0.0000	0.4861	0.0000
PARAFFIN/OLÉFIN M RATIO					
C3	0.0286	------	0.0152	0.0131	0.0107
C4	1.9137	1.1957	------	0.3148	1.8219
C5	------	------	------	13.1250	------

Run 9972-6, 9972-7 on UCC-104

These two runs were made on UCC-104 catalyst with hydrogen-propylene feed, with and without steam. The feed composition and other operating variables are tabulated below:

RUN	H_2:C_3H_6:H_2O	C_3H_6 WHSV	PSIG	TEMP, °C
9972-6	1:1:0	0.5	150	280, 340°C
9972-7	2:1:1	0.5	150	280, 340°C

The details of the results are reported in Tables 9 to 11 and summarized in Figures 25 to 27.

The results of the propylene oligomerization reaction of runs 9972-6 and 7, using UCC-104 as the catalyst are shown in Figures 25 and 26 respectively. Without steam, the catalyst shows good initial conversions; 70% at 280°C and 96% at 340°C. The presence of steam lessons the deactivation rate but also lessens the initial rate of conversion being only 43% at 280°C and 60% at 340°C. The lower conversion rate could be due to the steam moderating the acidity of the catalyst or it could be due to the higher total feed rate, thus lower residence time of the run. Run 9972-7 was operated at twice the real space velocity of run 9972-6. This effect on conversion was not seen in the cases of LZ-105-6 or UCC-101. In the case of UCC-101, the faster deactivation rates may have hidden the effect.

The UCC-104 produces only negligible amounts of C_1, C_2, C_4 and C_5 hydrocarbon products. These are the products of cracking reactions. The catalyst also shows low selectivity to propane. The total selectivity to C_1-C_4 products averages only 10%. The addition of steam has little effect on the C_1, C_2, C_3H_8, C_4 and C_5 product selectivities, although the sum of these products is even less (9% at 280°C and 5% at 340°C). The heavier products, which are the great majority of the hydrocarbon inside the reactor, are affected by the steam and temperature changes. Simulated distillation data are presented in Figure 27 comparing UCC-104 with LZ-105-6 and UCC-101.

TABLE 9A PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-6
CATALYST UCC-104 #9939-74 58 CC 35.0 GM (35.1 GM AFTER THE RUN, +0.1 GM)
FEED H2:C3H6:H20 @ 1:1:0 MOLE RATIO,0.5 C3H6 WHSV,CONTINOUS OVERNITE
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 151 CCMN, 9.06 L/HR(NOTE: H2 MASS FLOW)
ACTUAL FLOW: 29.6 CCHR EFFLUENT 9.20 L/HR(METER OFF)

RUN & SAMPLE NO.	9972-6-1	9972-6-2	9972-6-3	9972-6-4	9972-6-5
C3H6 WHSV	0.4	0.4	0.4	0.4	0.1
HRS ON STREAM5	7.1	24.9	30.3	48.9	53.5
PRESSURE,PSIG	150	150	150	150	151
TEMP. C	280	280	280	341	340
FEED C3H6 CC	171.79	532.98	160.46	457.47	36.5
HOURS FEEDING	7.2	17.8	5.7	16.6	4.5
EFFLNT GAS LITER	52.4	157.3	52.6	138.5	26.6
GM AQUEOUS LAYER	0.0	0.0	0.0	0.0	0.0
GM LIQ HYDROCARBON	32.28	65.31	17.94	85.97	3.07
WT FR. LIQ HC/FEED	0.3681	0.2401	0.2190	0.3682 *CHANGING T	0.1648
MATERIAL BALANCE WT %	98.37	85.35	95.81	53.86*	100.19
C3H6 CONVERSION %	71.64	61.85	58.56	96.12	86.25
PRDT SELECTIVITY WT %					
CH4	0.0055	0.0233	0.0331	0.0570	0.1624
C2 HC'S	0.0131	0.0128	0.0119	0.0818	0.2907
C3H8	10.7970	8.6405	8.5733	1.3926	11.5642
C4H10	0.4168	0.3198	0.4008	0.6145	2.6316
C4H8=	0.9287	1.0057	1.1858	0.9235	5.0197
C5H12	0.3429	0.1991	0.1919	0.6497	2.3623
C5H10=	0.0350	0.0314	0.0334	0.0530	0.1989
C6H14	4.4915	3.1704	3.2983	3.4234	9.7053
C6H12= & CYCLO'S	22.7645	36.8818	36.0544	13.5246	35.3949
C7+ IN GAS	6.1001	3.6835	9.5362	7.1864	12.1123
LIQ HC'S	54.1051	46.0317	40.6807	72.0935	20.5578
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	12.1611	10.0021	10.2050	3.0695	19.6685
C5 -420 F	84.9173	82.1265	84.9540	82.7281	76.7955
420-700 F	2.9217	7.6873	4.8410	12.8326	3.4948
C5 -END PT	87.8389	89.9979	89.7950	96.9305	80.3315

ISO/NORMAL MOLE RATIO					
C4	4.5111	1.3601	0.7807	3.1973	4.1134
C5	13.7753	3.5489	5.5301	4.1335	4.3052
C6	3.5023	1.6072	1.4850	2.8733	3.3221
C4=	0.7314	0.6984	0.6417	0.5267	0.5336
PARAFFIN/OLEFIN M RATIO					
C3	0.2636	0.1342	0.1165	0.3292	0.7012
C4	0.4332	0.3069	0.3263	0.6423	0.5061
C5	9.5290	6.1735	5.5876	11.9241	11.5426
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL CLEAR	OIL CLEAR	OIL CLEAR	OIL YLW	OIL YLW
DENSITY	0.724	0.728	0.710	0.720	0.742
N,REFRACTIVE INDEX	1.4169	1.4166	1.4164	1.4165	1.4277
SIMULATED DISTILLATION					
10 WT % @ DEG F.	147	157	155	169	155
16	156	160	159	177	159
50	222	291	278	300	282
84	362	433	397	453	433
90	392	485	447	521	499
RANGE(16-84%)	106	273	238	276	274
WT % @420 F	94.6	82.9	88.1	80.3	82.8
WT % @700 F	100.0	99.6	100.0	98.1	99.8

TABLE 9B PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-6
CATALYST UCC-104 #9939-74 58 CC 35.0 GM (35.1 GM AFTER THE RUN, +0.1 GM)
FEED H2:C3H6:H2O @ 1:1:0 MOLE RATIO,0.5 C3H6 WHSV,CONTINOUS OVERNITE
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 151 CCMN, 9.06 L/HR(NOTE: H2 MASS FLOW)
ACTUAL FLOW: 29.6 CC/HR EFFLUENT 9.23 L/HR(METER OFF)

RUN & SAMPLE NO.	9972-6-6	9972-6-7
C3H6 WHSV	0.5	0.6
HRS ON STREAM5	72.3	79.0
PRESSURE,PSIG	155	152
TEMP. C	340	340
FEED C3H6 CC	648.76	288.83
HOURS FEEDING	18.8	7.0
EFFLNT GAS LITER	197.6	89.1
GM AQUEOUS LAYER	0.0	0.0
GM LIQ HYDROCARBON	101.69	39.11
WT FR. LIQ HC/FEED	0.3071	0.2653
MATERIAL BALANCE WT %	99.90	96.72
C3H6 CONVERSION %	63.60	59.77
PRDT SELECTIVITY WT %		
CH4	0.0396	0.0401
C2 HC'S	0.0571	0.0590
C3H8	4.3172	4.4432
C4H10	0.4310	0.4564
C4H8=	1.8769	1.9106
C5H12	0.3204	0.2821
C5H10=	0.0724	0.0726
C6H14	3.0862	3.1971
C6H12= & CYCLO'S	32.1118	30.9868
C7+ IN GAS	8.9782	11.5794
LIQ HC'S	48.7092	46.9727
TOTAL	100.00	100.00
SUBGROUPING		
C1 -C4	6.7218	6.9093
C5 -420 F	93.2782	91.7755
420-700 F	0.0000	1.3152
C5 -END PT	93.2782	93.0907

ISO/NORMAL MOLE RATIO		
C4	1.1860	0.8344
C5	2.2386	1.8553
C6	1.0160	0.7396
C4=	0.5779	0.5840
PARAFFIN/OLEFIN M RATIO		
C3	0.0727	0.0636
C4	0.2217	0.2306
C5	4.3019	3.7787
LIQ HC COLLECTION		
PHYS. APPEARANCE	OIL CLEAR	OIL CLEAR
DENSITY	0.716	0.713
N,REFRACTIVE INDEX	1.4132	1.4331
SIMULATED DISTILLATION		
10 WT % @ DEG F.	146	150
16	155	156
50	168	173
84	294	306
90	305	368
RANGE(16-84%)	139	150
WT % @420 F	100	97.2
WT % @700 F	100	100

TABLE 10A PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-7
CATALYST UCC-104 #9939-74 59 CC 35.0 GM (33.9 GM AFTER THE RUN, -1.1 GM)
FEED H2:C3H6:H2O @ 2:1:1 MOLE RATIO,0.5 C3H6 WHSV,CONTINOUS OVERNITE
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 310 CCMN, 18.60 L/HR H2O 7.5 CC/HR
ACTUAL FLOW: 32.5 CC/HR EFFLUENT 19.15 L/HR 7.15 CC/HR

RUN & SAMPLE NO.	9972-7-1	9972-7-2	9972-7-3	9972-7-4	9972-7-5
C3H6 WHSV	0.5	0.5	0.5	0.5	0.5
HRS ON STREAMS	7.3	24.4	31.4	47.5	55.3
PRESSURE,PSIG	150	149	147	142	146
TEMP. C	277	276	276	277	339
FEED C3H6 CC	229.68	560.04	195.70	565.70	242.89
HOURS FEEDING	7.4	17.1	6.9	16.1	7.75
EFFLNT GAS LITER	135.0	326.3	133.8	321.1	141.9
GM AQUEOUS LAYER	46.80	115.32	46.15	107.69	50.99
GM LIQ HYDROCARBON	11.31	16.30	4.87	10.30	23.42
WT FR. LIQ HC/FEED	0.0965	0.0570	0.0488	0.0357	0.1889
MATERIAL BALANCE WT %	96.39	91.47	108.66	87.52	105.78
C3H6 CONVERSION %	49.56	41.19	43.11	37.06	64.51
PRDT SELECTIVITY WT %					
CH4	0.0321	0.0312	0.0305	0.0373	0.0350
C2 HC'S	0.0144	0.0133	0.0086	0.0345	0.0916
C3H8	9.9002	7.8514	6.0165	6.1979	3.8257
C4H10	0.2975	0.5607	0.0954	0.5177	0.8287
C4H8=	0.9039	1.0424	0.5315	1.1562	2.8463
C5H12	0.3234	0.1898	0.0973	0.1279	0.8844
C5H10=	0.0361	0.0299	0.0271	0.0298	0.1172
C6H14	4.9220	4.1218	4.1261	4.6897	9.4567
C6H12= & CYCLO'S	48.6190	56.5851	61.2512	52.6780	34.5065
C7+ IN GAS	14.3996	14.3668	17.4462	23.4749	19.2499
LIQ HC'S	20.5518	15.2077	10.3698	11.0566	28.1579
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	11.1481	9.4989	6.6825	7.9437	7.6275
C5 -420 F	85.6253	88.4024	91.5962	90.4753	90.1199
420-700 F	3.2266	2.0987	1.7214	1.5810	2.2526
C5 -END PT	88.8519	90.5011	93.3175	92.0563	92.3725

ISO/NORMAL MOLE RATIO					
C4	1.4853	0.2644	6.0000	0.2031	2.0866
C5	4.2235	4.5263	3.4848	3.3103	3.6684
C6	1.6207	1.0549	1.2931	1.1376	3.5866
C4=	0.7431	0.6352	0.7673	0.5520	0.5275
PARAFFIN/OLEFIN M RATIO					
C3	0.0934	0.0528	0.0437	0.0350	0.0664
C4	0.3177	0.5192	0.1733	0.4322	0.2811
C5	8.7059	6.1765	3.4848	4.1667	7.3361
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL YL GN	OIL YL GN	OIL YL GN	OIL YL GN	OIL YL GN
DENSITY	0.732	0.738	0.754	0.723	0.729
N,REFRACTIVE INDEX	1.4267	1.4274	1.4292	1.4310	1.4256
SIMULATED DISTILLATION					
10 WT % @ DEG F.	158	158	160	159	0
16	163	163	172	164	0
50	296	297	302	299	0
84	418	407	424	409	0
90	472	457	472	460	0
RANGE(16-84%)	255	244	252	245	0
WT % @420 F	84.3	86.2	83.4	85.7	92.0
WT % @700 F	100.0	100.0	100.0	100.0	100.0

TABLE 10B PROPYLENE(WITH H2) OPERATION

RUN NO. 9972-7
CATALYST UCC-104 #9939-74 59 CC 35.0 GM (33.9 GM AFTER THE RUN, -1.1 GM)
FEED H2:C3H6:H2O @ 2:1:1 MOLE RATIO,0.5 C3H6 WHSV,CONTINOUS OVERNITE
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 310 CCMN, 18.60 L/HR H2O 7.50 CC/HR
ACTUAL FLOW: 32.5 CC/HR EFFLUENT 19.15 L/HR 7.15 CC/HR

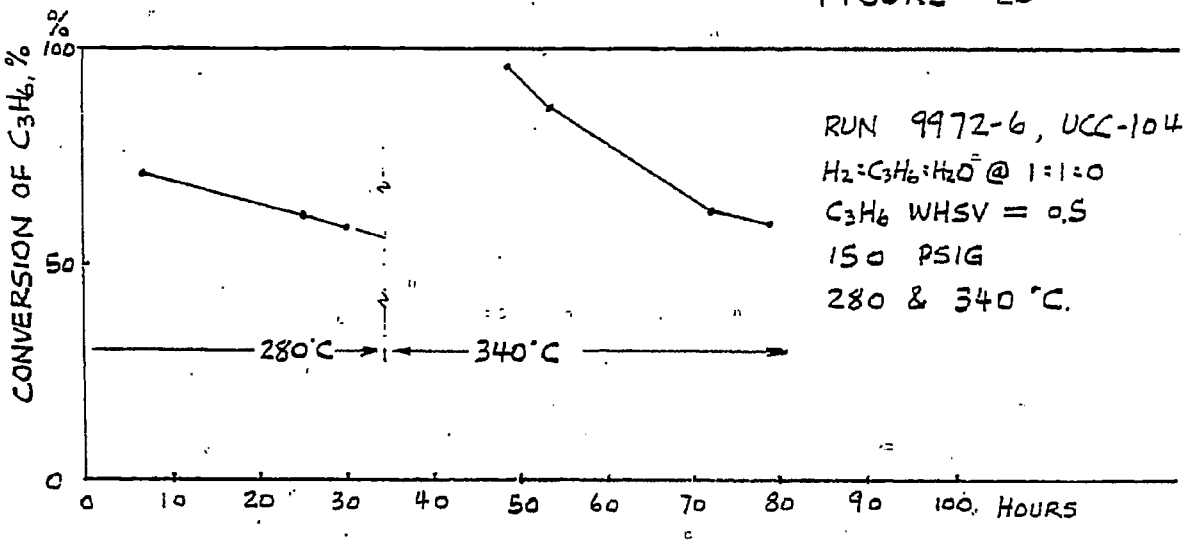
RUN & SAMPLE NO.	9972-7-6	9972-7-7	9972-7-8
C3H6 WHSV	0.5	0.4	0.5
HRS ON STREAM5	70.7	78.0	94.3
PRESSURE,PSIG	155	155	153
TEMP. C	337	337	337
FEED C3H6 CC	508.44	198.22	547.45
HOURS FEEDING	15.3	7.4	16.3
EFFLNT GAS LITER	303.9	146.1	328.8
GM AQUEOUS LAYER	103.80	48.27	109.62
GM LIQ HYDROCARBON	35.85	14.28	29.68
WT FR. LIQ HC/FEED	0.1381	0.1411	0.1062
MATERIAL BALANCE WT %	101.35E	123.39	123.42
C3H6 CONVERSION %	64.10E	63.17	50.45
PRDT SELECTIVITY WT %			
CH4	NO	0.0000	0.0539
C2 HC'S	GAS	0.0000	0.0514
C3H8	SAM	2.6718	2.6813
C4H10	PLE	0.1980	0.1904
C4H8=	---	1.5425	1.4552
C5H12	---	0.1768	0.2437
C5H10=	---	0.7216	0.0737
C6H14	---	5.6123	5.4110
C6H12= & CYCLO'S	---	52.4359	56.1453
C7+ IN GAS	---	18.1686	16.5006
LIQ HC'S	---	18.4725	17.3626
TOTAL	---	100.00	100.00
SUBGROUPING	ESTIMATED		
C1 -C4	4.2499E	4.4123	4.4323
C5 -420 F	93.9678E	94.0175	94.1923
420-700 F	1.7824E	1.5702	1.3755
C5 -END PT	95.7501E	95.5877	95.5677

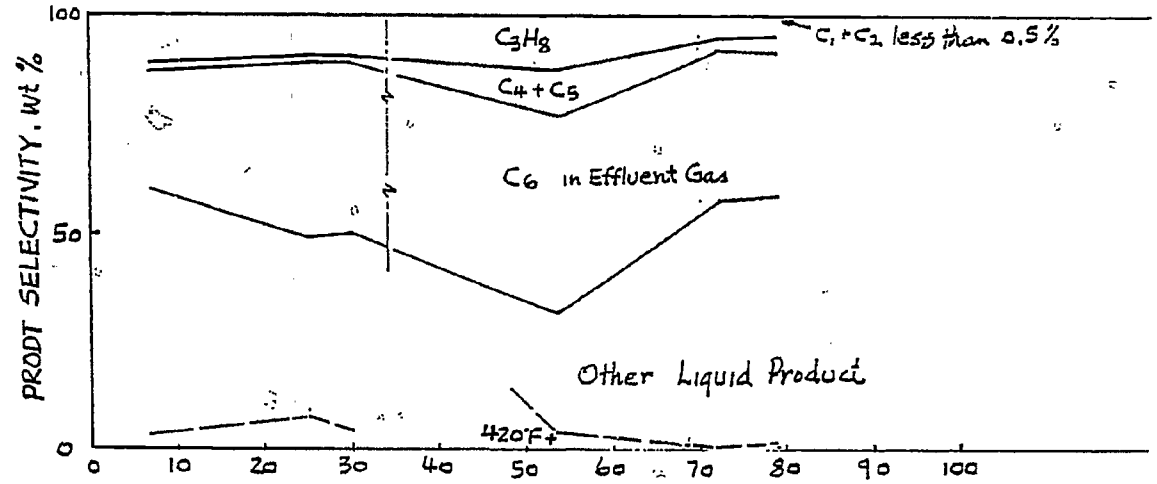
ISO/NORMAL MOLE RATIO			
C4	---	------	3.3093
C5	---	------	1.9320
C6	---	1.7710	1.4756
C4=	---	0.6102	0.5887
PARAFFIN/OLEFIN M RATIO			
C3	---	0.0438	0.0261
C4	---	0.1239	0.1263
C5	---	0.2381	3.2164
LIQ HC COLLECTION			
PHYS. APPEARANCE	OIL YLW	OIL YLW	OIL YLW
DENSITY	0.720	0.710	0.710
N,REFRACTIVE INDEX	1.4286	1.4302	1.4248
SIMULATED DISTILLATION			
10 WT % @ DEG F.	156	157	-
16	159	160	-
50	282	285	-
84	384	387	-
90	407	408	-
RANGE(16-84%)	225	227	-
WT % @420 F	91.7	91.5	-
WT % @700 F	100.0	100.0	-

TABLE 11 COMPARISON OF C3H6 OPERATION AT 340 C TEMPERATURE
UCC-104 VS LZ-105-6

RUN	---9972-1--		-----9972-6------			-----9972-7------		
CATALYST	--LZ-105-6-		-----UCC-104-----			-----UCC-104-----		
FEED H2:C3H6:W	---1:1:0---		------1:1:0------			2:1:1(WITH STEAM)		
SAMPLE	S-5	S-6	S-5	S-6	S-7	S-5	S-7	S-8
C3H6 WHSV	1.0	1.0	0.5	0.5	0.5	0.5	0.5	0.5
HOURS ON STREAM	17.5	21.0	53.5	72.3	79.0	55	78	94
C3H6 LOAD'G G/G	17.5	21.0	26.8	36.2	39.5	27.6	39	47
PSIG	143	145	151	155	155	146	155	153
TEMP C	336	337	340	340	340	339	337	337
MAT'L BAL'CE,%	82.87	90.36	100.19	99.90	96.70	106.0	123.0	123.4
C3H6 CONV,%	95.27	95.04	86.25	63.60	59.77	64.4	63.1	50.4
SELECTIVITY								
C3H8 WT %	10.51	7.16	11.56	4.32	4.44	3.83	2.67	2.68
C4H10	16.02	12.11	2.63	0.43	0.46	0.83	0.20	0.19
C1 -C4 WT %	31.89	24.86	19.67	6.72	6.91	7.62	4.41	4.43
C5 -420 F	60.51	67.17	76.80	93.28	91.78	90.12	94.02	94.19
420-700 F	7.43	7.97	3.49	0.00	1.31	2.25	1.57	1.38
700-END PT	0.17	0.00	0.04	0.00	0.00	0.00	0.00	0.00
C5+ WT %	68.11	75.14	80.33	93.28	93.09	92.37	95.59	95.57

FIGURE 25


CONVERSION OF C_3H_6, %
100
50
0
0 10 20 30 40 50 60 70 80 90 100. HOURS
280°C
340°C
RUN 9972-6, UCC-104
$H_2:C_3H_6:H_2O$ @ 1:1:0
C_3H_6 WHSV = 0.5
150 PSIG
280 & 340 °C.


PRODT SELECTIVITY, Wt %
100
50
0
C_3H_8
C_1+C_2 less than 0.5%
C_4+C_5
C_6 in Effluent Gas
Other Liquid Product
420°F+
0 10 20 30 40 50 60 70 80 90 100

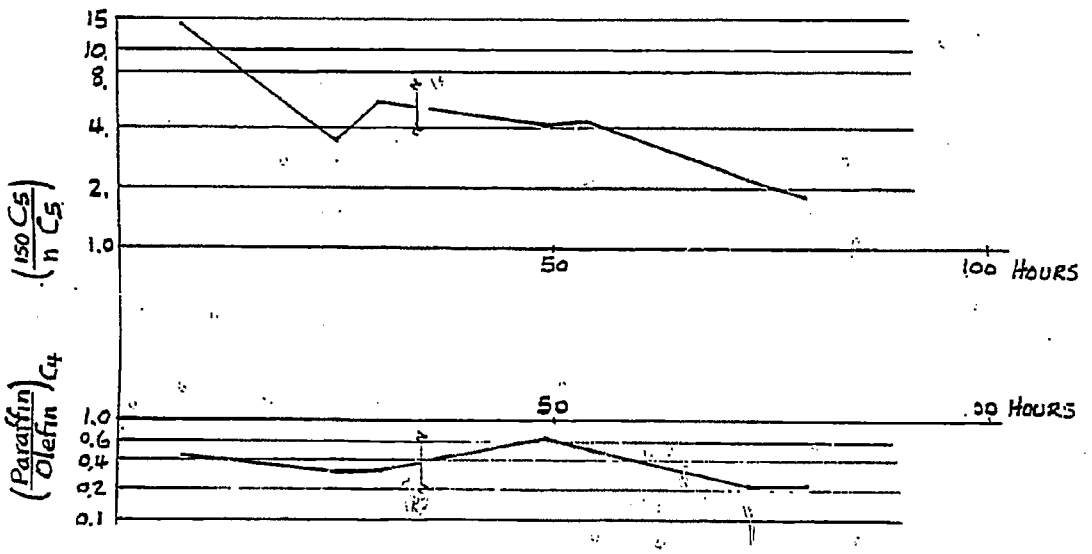

$\left(\frac{150\ C_5}{n\ C_5}\right)$
15
10
8
4
2
1.0
50
100 HOURS
$\left(\frac{Paraffin}{Olefin}\right)_{C_4}$
1.0
0.6
0.4
0.2
0.1
50
100 HOURS

FIGURE 26

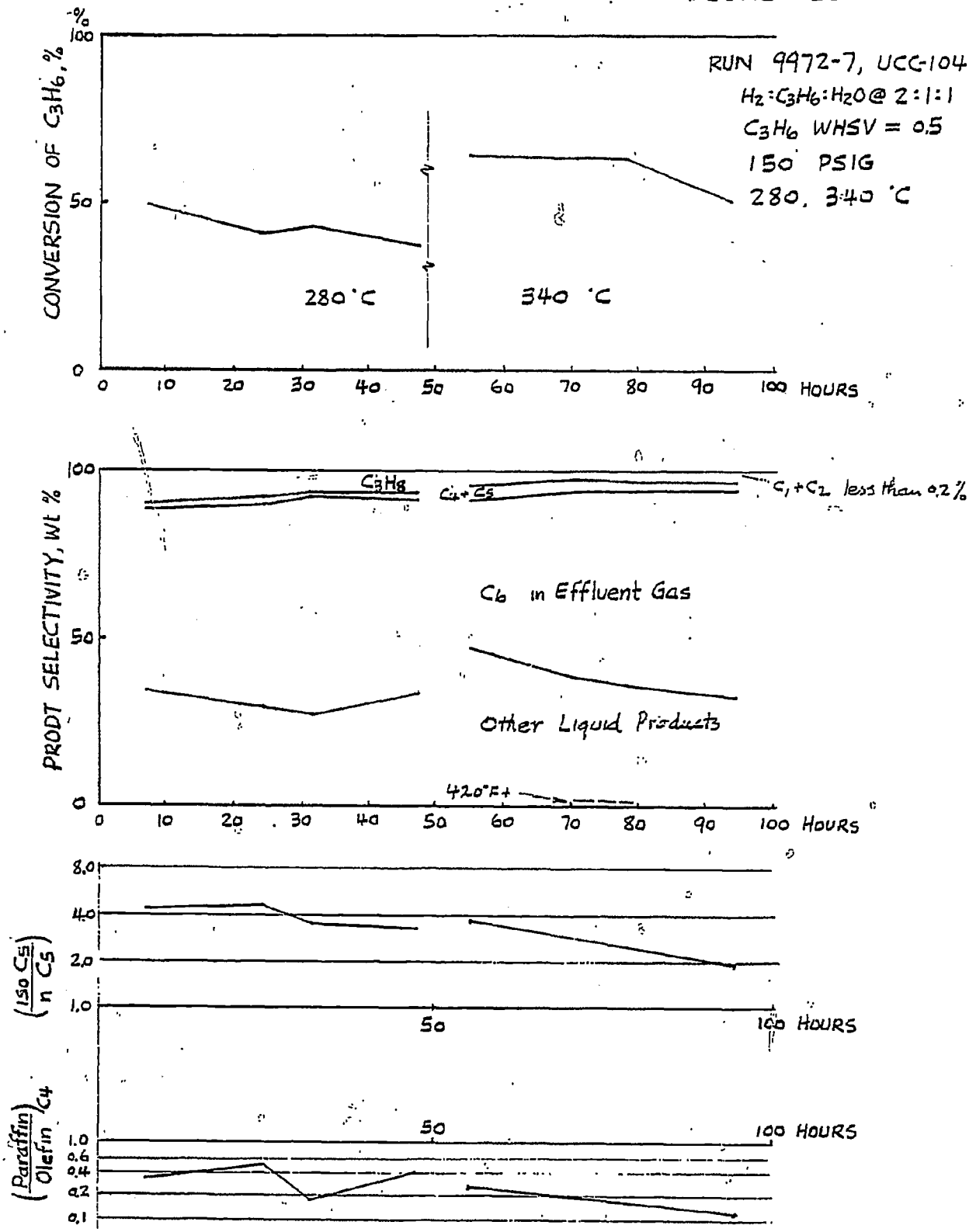
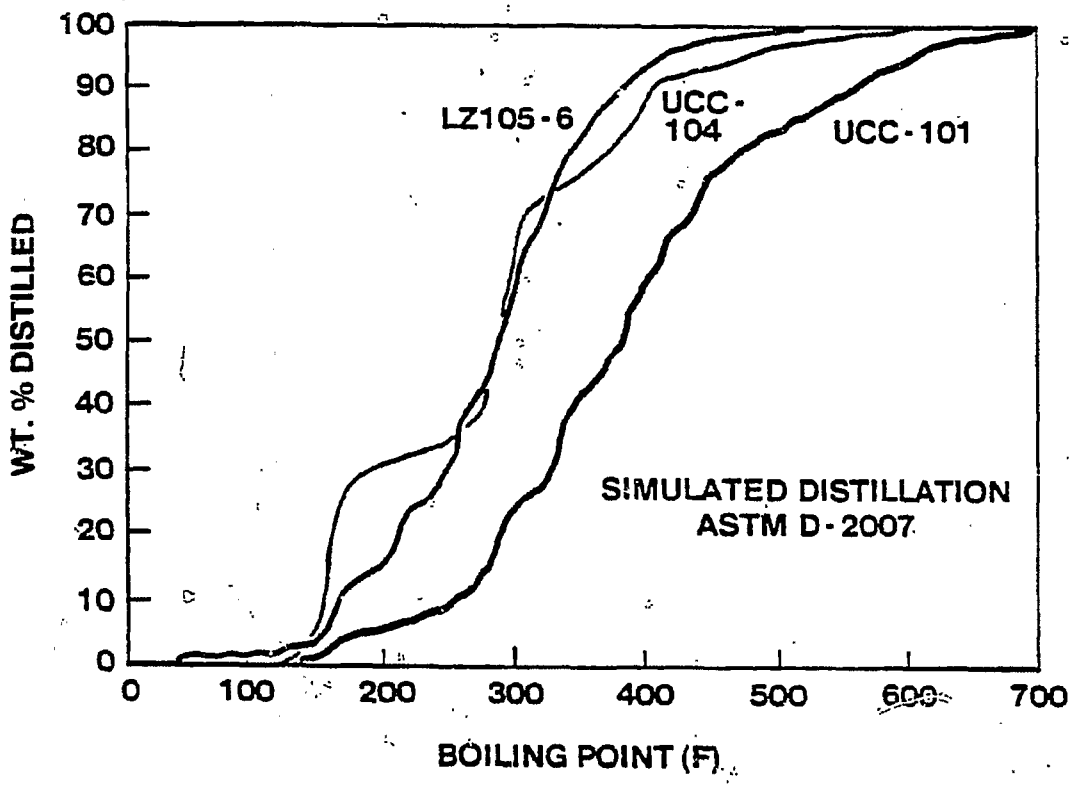

CONVERSION OF C_3H_6, %
100
50
0
0 10 20 30 40 50 60 70 80 90 100 HOURS
280 °C
340 °C
RUN 9972-7, UCC-104
$H_2:C_3H_6:H_2O$ @ 2:1:1
C_3H_6 WHSV = 0.5
150 PSIG
280, 340 °C
PRODT SELECTIVITY, Wt %
C_3H_8
C_4+C_5
C_1+C_2 less than 0.2%
C_6 in Effluent Gas
Other Liquid Products
420°F+
$\left(\frac{iso\ C_5}{n\ C_5}\right)$
8.0
4.0
2.0
1.0
$\left(\frac{Paraffin}{Olefin}\right)_{C_4}$
1.0
0.6
0.4
0.2
0.1

FIGURE 27

BOILING POINT DISTRIBUTION OF THE LIQUID PRODUCT OF PROPYLENE OLIGOMERIZATION USING LZ105-6, UCC 101, AND UCC 104 AS CATALYSTS.



SUMMARY OF THE PROPYLENE OPERATION

LZ-105-6 is a very good catalyst for propylene oligomerization. Its medium pore size leads to most of the C_5^+ product being in the gasoline range. Changes in reaction temperature and pressure have pronounced effects on the product selectivity particularly the composition of the liquid product. Steam addition keeps the catalyst from deactivating at the condition tested, 410°C, and has only a slight effect on the product selectivity.

UCC-101 shows good initial conversion of propylene and reasonable C_5^+ yields. The condensed product has a significant fraction in the diesel range, in contrast to that from LZ-105-6. The catalyst still deactivates even in the presence of steam. The increased stability with added steam is most evident at higher temperature.

$AlPO_4$-11 (unmodified) is almost completely inactive as a catalyst.

UCC-104 is an excellent catalyst for propylene oligomerization. It has very high selectivity to C_5^+ products, >95%, with nearly all the C_5^+ in the gasoline range. The propylene conversion and product selectivity are both affected by the addition of steam to the reaction. The good conversion and desirable selectivity make UCC-104 the best catalyst tested thus far in Task 1 and a promising candidate for Shape selective component in planned Task 2.

Syngas Operation in Berty Reactor

As mentioned earlier, we made ten Fischer-Tropsch syngas runs during the quarter, using UCC-201 (an Fe-loaded UCC-101) catalyst, UCC-202 (a Mn-Fe-loaded UCC-103) catalyst, a reference potassium-promoted, iron-oxide F-T catalyst and an Fe-loaded LZ-Y52 catalyst. In this report, data from the first seven of these runs will be reported: 9710-18, 9710-19 and 10011-1 to 10011-5. One of these (Run 10011-3) is with Mn-Fe-UCC-101 catalyst; all others are on Fe-loaded UCC-101 catalyst. In two of the runs (9710-19, 10011-2), enough oil was produced for characterization by simulated boiling point distribution. In the other runs, not enough liquid oil product was made for characterization. All of the low activity runs used catalyst from a particular preparation batch. Problems with preparation procedures or contamination probably caused the low activity.

Normally the reactor was loaded with 80 cc of catalyst with weights varying from 39 to 63 grams. The catalyst was usually precalcined in air at 250 or 500°C. Two different activation procedures were used: procedure A calls for carburization first and hydrogenation later. Procedure B calls for hydrogenation first and carburization later. The catalyst is then brought into contact with feed gas. Unless otherwise indicated, the feed gas always contains 10% argon as inert carrier. The argon will appear intact in both feed gas and reactor effluent gas and aids in checking material balances. Two different feed gases were used: one with a 2/1 H_2/CO ratio, designated "60/30/10" mixture (for $H_2/CO/Argon$), the other with 1/1 H_2/CO ratio, designated "45/45/10" mixture. The feed gas flow was controlled by a mass flow controller which works very well; one can literally dial a desired feed rate in cc/minute. The effluent gas was measured by a dry test meter and analyzed by on-line G.C. The condensed product was collected in a glass container; the aqueous layer and the organic layer were separated and weighed. Selected samples of aqueous layer were submitted for chemical analysis for CH_3OH and total organic content.

A few aqueous samples showed 2-3% CH_3OH and 0.2-1.5% C_2H_5OH. These minor amounts of organic substance in the aqueous layer have been ignored in the material balance calculations. The organic layer was submitted for characterization by simulated distillation. The material balance analysis consists of a computation of the reaction output/input ratios of carbon, hydrogen and oxygen. A consistency ratio was also computed among the products from the reactor. For the Fischer-Tropsch reaction, it is defined by

$$\text{Consistency Ratio} = \frac{\text{g. atoms of CHx}}{\text{g. moles of } (H_2O + CO_2)}$$

If formation of alcohol is ignored, stoichiometry requires the consistency ratio to be 1.0. Other parameters also computed are:

1. Usage ratio of H_2/CO from the product: the ratio of the moles of H_2 to moles CO required to produce the products.
2. Extent of water gas shift reaction (by calculating an experimental value of the composition ratio corresponding to the shift equilibrium equation):

$$K = \frac{[CO_2] \cdot [H_2]}{[CO] \cdot [H_2O]}$$

On occasion when a gas sample may have leaked out of a sample bomb, or the G.C. analyzer malfunctioned, then the G.C. analysis of the closest sample was used to estimate conversions and selectivities; in such cases, the results have a letter E included in the tabulation. Because the Berty reactor is an internal recirculation reactor and operates at a steady state, surprisingly good material balances can still be obtained using these "second best" gas analysis data.

Conversions of more than 20% were achieved in only three of the seven runs. Some of the problems with low activity are believed to be associated with the activation procedures. It is

thought that some as yet unknown factor in preparation of the catalyst batch used for most of the tests may be responsible for the low activity.

Run 9710-18 on UCC-201 (Fe on UCC-101) Catalyst

This was the first run conducted in the Bay 1 Berty reactor and therefore served as a shake-down run. There was reason to expect the catalyst to perform reasonably well; however, the results were very poor, with only 5% conversion on 60/30/10 (H_2/CO/Argon) syngas at 250°C and 300 psig. The results are tabulated in Table 12. About 73-79% of the product was in the C_1-C_4 light hydrocarbon range. The material balances consistency ratio for both samples was very poor (.50 and .56).

TABLE 12 RESULT OF SYN GAS OPERATION

RUN NO. 9710-18 (INADEQUATE CO TREATMENT DURING ACTIVATION)
CATALYST UCC-201 #9673-11C 80 CC 62.61GM (. G AFTER THE RUN, . GM)
FEED H2:CO:ARGON OF 60/30/10 @ 580 CC/MIN OR 435 GHSV

RUN & SAMPLE NO.	9710-18-1		9710-18-2	9710-18-3
FEED H2:CO:AR	60:30:10			60:30:10
HRS ON STREAM	24.7			48.2
PRESSURE,PSIG	299			298
TEMP. C	250			249
FEED CC/MIN	580			580
HOURS FEEDING	25.0			3.5
EFFLNT GAS LITER	984.2			142.2
GM AQUEOUS LAYER	0.0			0.0
GM OIL	0.0			0.0
MATERIAL BALANCE				
GM ATOM CARBON %	107.86			110.47
GM ATOM HYDROGEN %	111.46			113.47
GM ATOM OXYGEN %	111.46			113.71
RATIO CHX/(H2O+CO2)	0.5015			0.5594
RATIO X IN CHX	2.8415			2.8062
USAGE H2/CO PRODT	1.9423			2.0083
K EFFLT SHIFT REACTN	0.1929			0.1591
CONVERSION %				
ON CO	3.94			4.21
ON H2	5.28			5.55
ON CO+H2	5.02			5.29
PRDT SELECTIVITY,WT %				
CH4	30.85	GAS		29.38
C2 HC'S	23.26	SAM-		12.68
C3H8	8.90	PLE		9.05
C3H6=	4.12	LEA-		10.49
C4H10	7.38	KED		6.56
C4H8=	4.23			4.58
C5H12	7.35			6.62
C5H10=	0.00			1.32
C6H14	6.44			6.69
C6H12= & CYCLO'S	0.00			0.00
C7+ IN GAS	7.47			12.64
LIQ HC'S	0.00			0.00
TOTAL	100			100
SUBGROUPING				
C1 -C4	78.74			72.74
C5 -420F	21.26			27.26
420-700F	0.00			0.00
700-END PT	0.00			0.00
C5 -END PT	21.26			27.26

ISO/NORMAL MOLE RATIO		
C4	.5760	.4222
C5	2.4348	1.1972
C6	4.0435	2.5676
C4=	---	---
PARAFFIN/OLEFIN M RATIO		
C3	2.0592	0.8231
C4	1.6838	1.3813
C5	---	4.8750

Run 9710-19 on UCC-201 (Fe-UCC-101) Catalyst

This catalyst started rather poorly. After it has gone through an activation procedure (pure CO treatment at ambient to 270°C, 3 psig, 400 cc/min. 40 hrs. and H_2 treatment at 270°C, 3 psig, 400 cc/min. 26.5 hours), the conversion on 60/30/10 (H_2/CO/Argon) syngas was only 7-8% at 250°C 300 psig (Samples 1 and 2 of the run). The catalyst was then subjected to a second activation of pure CO treatment (16 hours at 270°C, 4 psig, 400 cc/min. and 7 hours at 300°C, 4 psig, 400 cc/min.) and H_2 treatment (23 hours at 300°C, 4 psig, 400 cc/min). The conversion on 60/30/10 syngas was dramatically improved to about 34% (on average) at 250°C, 300 psig (samples 3, 4, 5). The product selectivity also changed following the second activation. The methane-make declined from 41% to 22%, while the C_5^+ fraction increased from 12% to 34% and the diesel fraction increased from zero to 10%, all at the same temperature level of 251°C and 300 psig. The liquid hydrocarbon collection showed a boiling point range of 399°-638°F (range defined as temperature for 16-84 wt.% cut points, or two-thirds of the liquid sample 5) with 50 wt.% having distilled at 488°F.

When the temperature was raised to 284° and 313°C, the conversions increased to 47% and 53% respectively (samples 6, 7, 8 and 9, 10). At higher temperatures, although the conversion increased the C_5^+ product selectivity decreased to 13% at 284°C and 6.5% at 313°C.

At this point, the feed was switched from 60/30/10 (H_2/CO/Agon) syngas to 45/45/10 syngas. At 313°C, the conversion increased from 52.5% to 69.5% and C_5^+ selectivity increased from 6.3% to 17% (samples 10 and 14). The results are tabulated in Table 13 and the conversion selectivities and simulated distillations are plotted in Figures 28 to 32.

TABLE 13A RESULT OF SYN GAS OPERATION

RUN NO. 9710-19
CATALYST UCC-201 #9939-53 80 CC 43.5 GM (41.15 G AFTER THE RUN, -2.4 GM)
FEED H2:CO:ARGON OF 60/30/10 & 45/45/10 @ 580 CC/MN OR 435 GHSV

RUN & SAMPLE NO.	9710-19-1	9710-19-2	9710-19-3	9710-19-4	9710-19-5
FEED H2:CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAMS	2.7	4.5	24.2	28.8	30.8
PRESSURE,PSIG	296	304	322	298	298
TEMP. C	250	250	251	251	252
FEED CC/MIN	580	580	580	580	580
HOURS FEEDING	2.7	1.97	19.67	4.92	1.92
EFFLNT GAS LITER	96.1	74.9	577.0	150.7	58.7
GM AQUEOUS LAYER	0.0	0.0	30.43	0.0	10.95
GM OIL	0.0	0.0	1.77	0.0	0.66
MATERIAL BALANCE					
GM ATOM CARBON %	98.26	107.04	101.19	101.42	109.61
GM ATOM HYDROGEN %	98.38	107.62	100.71	94.01	131.06
GM ATOM OXYGEN %	101.70	108.89	104.58	87.65	157.33
RATIO CHX/(H2O+CO2)	0.5753	0.7926	0.8991	1.9829 ?	0.4186 ?
RATIO X IN CHX	3.1780	3.0883	2.6402	2.6774	2.5370
USAGE H2/CO PRODT	1.5722	1.6427	1.4981	1.4221	1.7364
K EFFLT SHIFT REACTN	0.7145	0.8074	1.0043	3.8826 ?	0.2696 ?
CONVERSION %					
ON CO	6.91	8.97	40.09	36.15	39.54
ON H2	6.80	8.04	31.43	22.52	44.52
ON CO+H2	6.82	8.22	33.17	25.42	43.66
PRDT SELECTIVITY,WT %					
CH4	43.22	38.57	22.37	23.48	19.43
C2 HC'S	18.24	17.32	13.29	13.99	11.35
C3H8	15.74	14.95	9.22	9.13	7.86
C3H6=	0.00	2.79	8.42	8.94	7.92
C4H10	8.89	8.44	5.33	5.47	4.81
C4H8=	3.78	3.91	9.19	9.69	8.80
C5H12	4.38	6.57	5.02	5.28	4.55
C5H10=	0.00	0.00	1.49	1.67	1.49
C6H14	0.00	3.68	3.93	3.82	3.58
C6H12= & CYCLO'S	0.00	0.00	1.47	2.13	1.36
C7+ IN GAS	5.75	3.76	15.91	16.40	14.11
LIQ HC'S	0.00	0.00	4.35	0.00	14.74
TOTAL	100	100	100	100	100
SUBGROUPING					
C1 -C4	89.87	85.98	67.82	70.71	60.16
C5 -420F	10.13	14.02	29.52	29.29	28.68
420-700F	0.00	0.00	2.55	0.00	10.45
700-END PT	0.00	0.00	0.10	0.00	0.71
C5 -END PT	10.13	14.02	32.18	29.29	39.84

ISO/NORMAL MOLE RATIO					
C4	.1348	.0948	.0673	.0628	.0594
C5	.5393	.1647	.1331	.1241	.1219
C6	---	---	.2413	.1655	.1616
C4=	---	.1503	.0788	.0776	.0799
PARAFFIN/OLEFIN M RATIO					
C3	---	5.1137	1.0446	0.9738	0.9481
C4	2.2697	2.0811	0.5599	0.5488	0.5281
C5	---	---	3.2747	3.0780	2.9595
LIQ HC COLLECTION					
PHYS. APPEARANCE			OIL		OIL
DENSITY			-		-
N, REFRACTIVE INDEX			-		-
SIMULATED DISTILLATION					
10 WT % @ DEG F	---	---	336	---	369
16	---	---	350	---	399
50	---	---	456	---	488
84	---	---	596	---	638
90	---	---	629	---	676
RANGE(16-84 %)	---	---	246	---	239
WT % @420 F			38.5		24.7
WT % @700 F			97.4		93.4

TABLE 13B RESULT OF SYN GAS OPERATION

RUN NO. 9710-19
CATALYST UCC-201. #9939-53 80 CC 43.5 GM (41.15 G AFTER THE RUN, -2.4 GM)
FEED H2:CO:ARGON OF 60/30/10 & 45/45/10 @ 580 CC/MN OR 435 GHSV

RUN & SAMPLE NO.	9710-19-6	9710-19-7	9710-19-8	9710-19-9	9710-19-10
FEED H2:CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAM	47.3	49.7	55.5	71.4	95.4
PRESSURE,PSIG	295	297	297	294	294
TEMP. C	284	284	284	312	313
FEED CC/MIN	580	580	580	580	580
HOURS FEEDING	16.5	2.42	5.83	16.0	23.92
EFFLNT GAS LITER	462.5	68.8	168.4	443.4	629.7
GM AQUEOUS LAYER	22.9	0.0	11.13	17.09	14.07
GM OIL	0.9	0.0	0.0	0.0	0.57
MATERIAL BALANCE					
GM ATOM CARBON %	105.12	108.02	113.54	109.13	104.35
GM ATOM HYDROGEN %	107.75	101.27	116.08	109.26	101.87
GM ATOM OXYGEN %	106.40	93.77	116.30	109.88	99.54
RATIO CHX/(H2O+CO2)	0.9731	1.4521?	0.9486	0.9855	1.1092
RATIO X IN CHX	3.0404	3.0734	3.0122	3.3804	3.3731
USAGE H2/CO PRODT	1.2511	1.1485	1.3334	1.2093	1.1870
K EFFLT SHIFT REACTN	4.7108	20.1352?	3.2581	9.4233	13.6506
CONVERSION %					
ON CO	69.03	67.15	67.50	77.95	77.99
ON H2	42.50	37.09	44.81	47.29	46.02
ON CO+H2	47.70	43.42	49.27	53.41	52.54
PRDT SELECTIVITY,WT %					
CH4	37.06	38.18	34.24	54.82	54.59
C2 HC'S	18.16	18.62	16.66	19.65	19.62
C3H8	15.71	16.29	14.83	12.70	12.57
C3H6=	3.39	3.33	3.22	1.08	1.07
C4H10	6.35	6.49	15.65	4.41	4.36
C4H8=	4.06	4.00	3.59	1.08	1.07
C5H12	4.43	4.29	4.02	2.61	2.57
C5H10=	0.31	0.26	0.25	0.04	0.07
C6H14	3.12	2.53	2.45	1.37	1.42
C6H12= & CYCLO'S	0.54	0.43	0.39	0.08	0.07
C7+ IN GAS	5.19	5.58	4.70	2.15	1.92
LIQ HC'S	1.68	0.00	0.00	0.00	0.68
TOTAL	100	100	100	100	100
SUBGROUPING					
C1 -C4	84.74	86.91	88.19	93.74	93.28
C5 -420F	13.91	13.09	11.81	6.26	6.30
420-700F	1.24	0.00	0.00	0.00	0.37
700-END PT	0.11	0.00	0.00	0.00	0.06
C5 -END PT	15.26	13.09	11.81	6.26	6.72

ISO/NORMAL MOLE RATIO					
C4	.1092	.1062	.0391	.1687	.1719
C5	.2513	.2466	.2568	.6134	.6194
C6	.4509	.4283	.4741	1.1702	1.3117
C4=	.1087	.1060	.1018	.0784	.0807
PARAFFIN/OLEFIN M RATIO					
C3	4.4233	4.6674	4.3977	11.1770	11.2439
C4	1.5093	1.5671	4.2063	3.9289	3.9399
C5	14.0488	15.9029	15.8952	58.0000	38.4333
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLEAR OIL				OIL
DENSITY					
N, REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	395	-	-	-	343
16	412	-	-	-	371
50	512	-	-	-	451
84	656	-	-	-	599
90	694	-	-	-	677
RANGE(16-84 %)	244	-	-	-	228
WT % @420 F	19.5				37.0
WT % @700 F	91.1				91.2

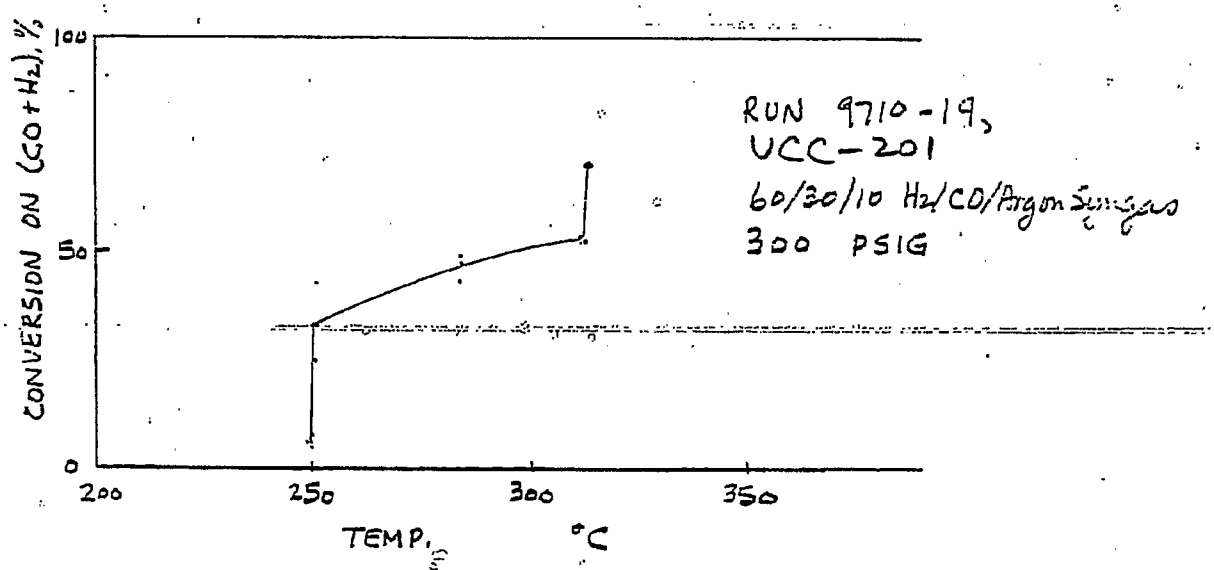
TABLE 13C RESULT OF SYN GAS OPERATION

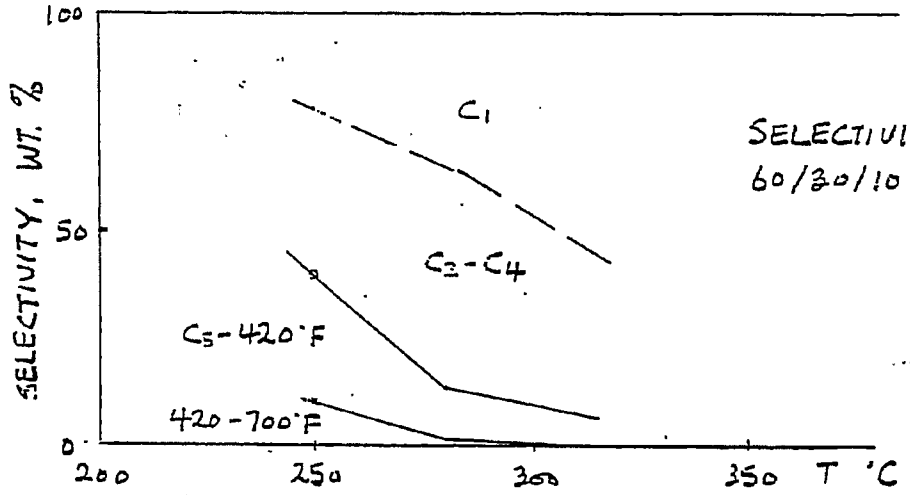
RUN NO. 9710-19
CATALYST UCC-201 #9939-53 80 CC 43.5 GM (41.15 G AFTER THE RUN, -2.4 GM)
FEED H2:CO:ARGON OF 60/30/10 & 45/45/10 @ 580 CC/MN OR 435 GHSV

RUN & SAMPLE NO.	971019-14
FEED H2:CO:AR	45:45:10
HRS ON STREAM	102.3
PRESSURE,PSIG	296
TEMP. C	313
FEED CC/MIN	580
HOURS FEEDING	7.08
EFFLNT GAS LITER	178.6
GM AQUEOUS LAYER	3.31
GM OIL	0.0
MATERIAL BALANCE %	
GM ATOM CARBON	108.61
GM ATOM HYDROGEN	107.61
GM ATOM OXYGEN	110.12
RATIO CHX/(H2O+CO2)	0.9666
RATIO X IN CHX	2.9527
USAGE H2/CO PRODT	0.8544
K EFFLT SHIFT REACTN	8.3004
CONVERSION %	
ON CO	76.04
ON H2	66.17
ON CO+H2	69.48
PRDT SELECTIVITY,WT %	
CH4	31.36
C2 HC'S	17.22
C3H8	18.24
C3H6=	3.75
C4H10	7.95
C4H8=	4.63
C5H12	5.95
C5H10=	0.30
C6H14	3.52
C6H12= & CYCLO'S	0.45
C7+ IN GAS	6.73
LIQ HC'S	0.00
TOTAL	100.00
SUBGROUPING	
C1 -C4	83.05
C5 -420F	16.95
420-700F	0.00
700-END PT	0.00
C5 -END PT	16.95

ISO/NORMAL MOLE RATIO	
C4	0.1733
C5	0.5846
C6	1.1124
C4=	0.0519
PARAFFIN/OLEFIN M RATIO	
C3	4.6372
C4	1.6569
C5	19.1737
LIQ HC COLLECTION	
PHYS. APPEARANCE	
DENSITY	
N, REFRACTIVE INDEX	
SIMULATED DISTILLATION	
10 WT % @ DEG F	-
16	-
50	-
84	-
90	-
RANGE(16-84 %)	-

FIGURE 28


CONVERSION ON (CO+H2), %
100
50
0
200
250
300
350
TEMP, °C
RUN 9710-19,
UCC-201
60/30/10 H2/CO/Argon Syngas
300 PSIG


SELECTIVITY, WT. %
100
50
0
200
250
300
350
T °C
C1
C2-C4
C5-420°F
420-700°F
SELECTIVITY WITH
60/30/10 (H2/CO/Ar) Syngas

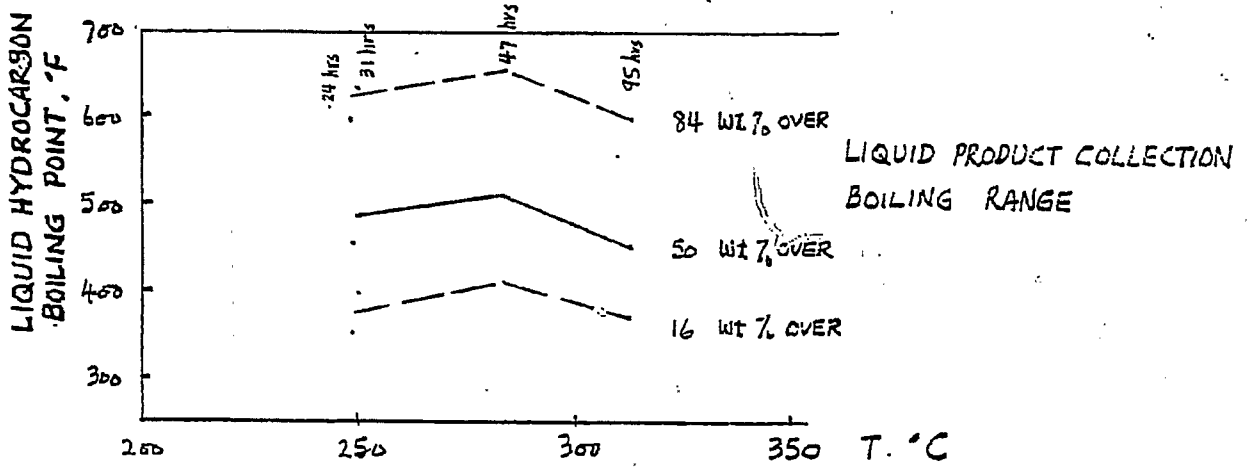

LIQUID HYDROCARBON
BOILING POINT, °F
700
600
500
400
300
200
250
300
350
T. °C
24 hrs
31 hrs
47 hrs
95 hrs
84 WT% OVER
50 WT% OVER
16 WT% OVER
LIQUID PRODUCT COLLECTION
BOILING RANGE

FIG. 29

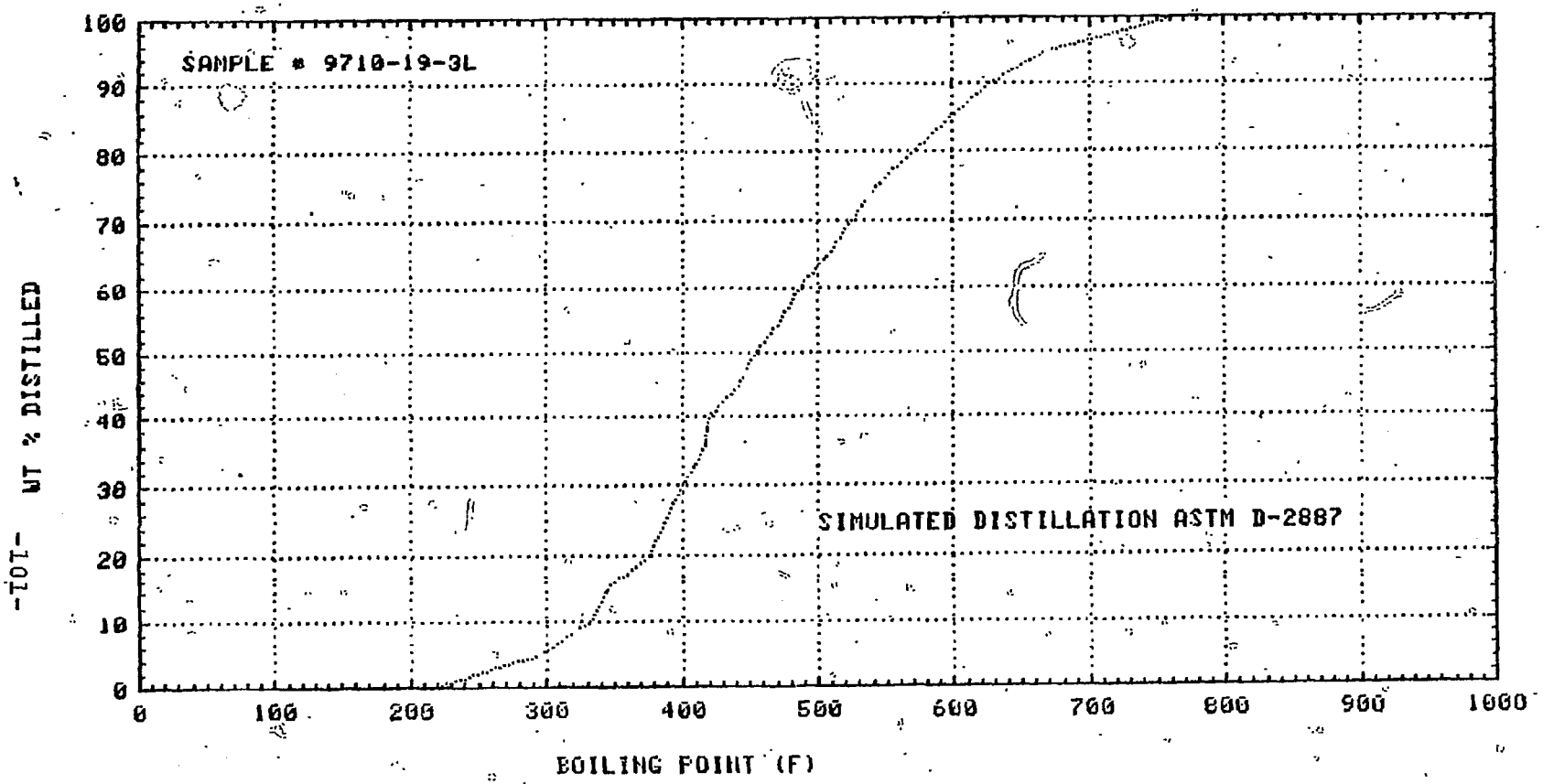

SAMPLE # 9710-19-3L
SIMULATED DISTILLATION ASTM D-2887
-TOT- WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 30

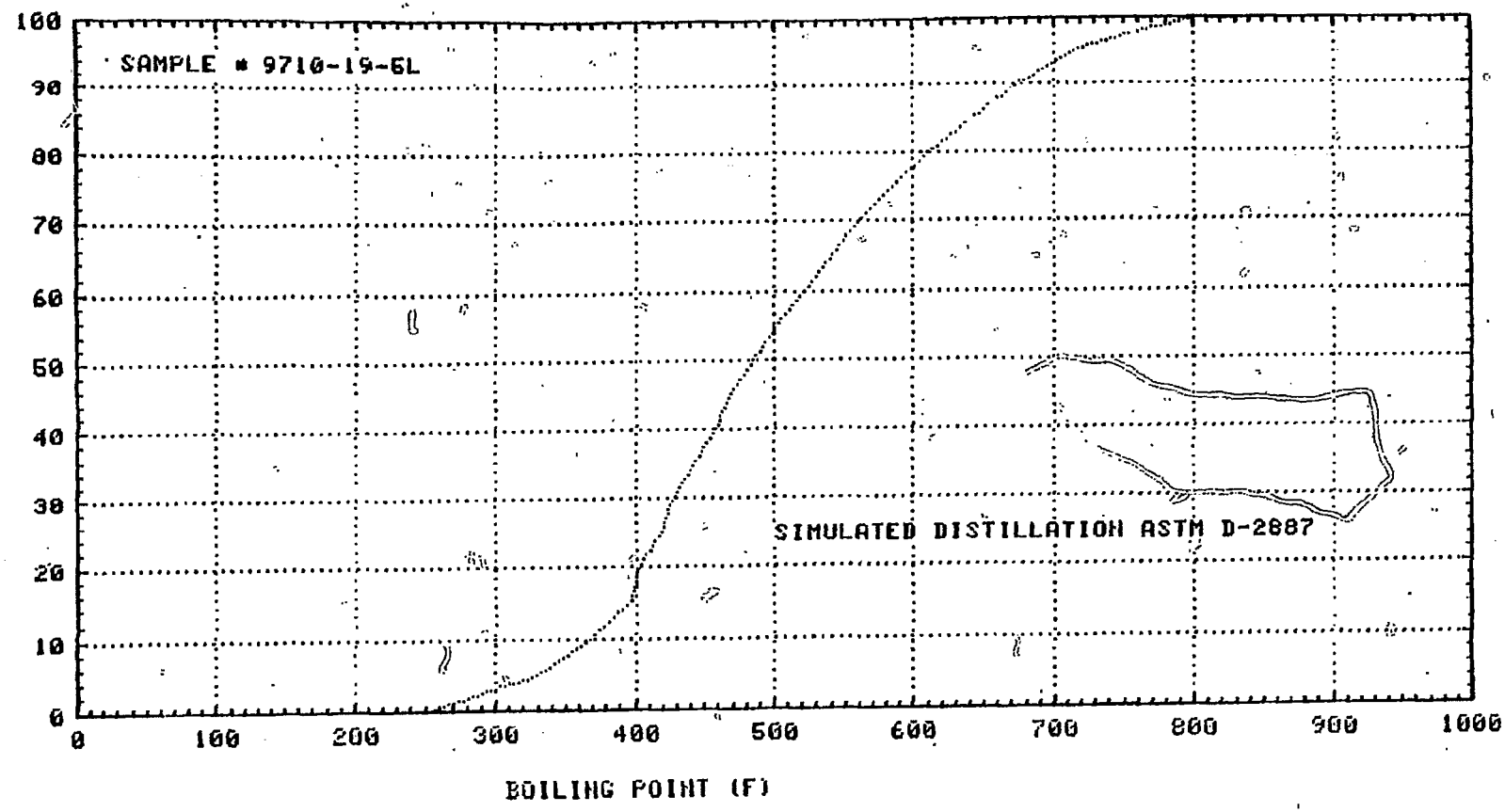

SAMPLE # 9710-19-6L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG 31

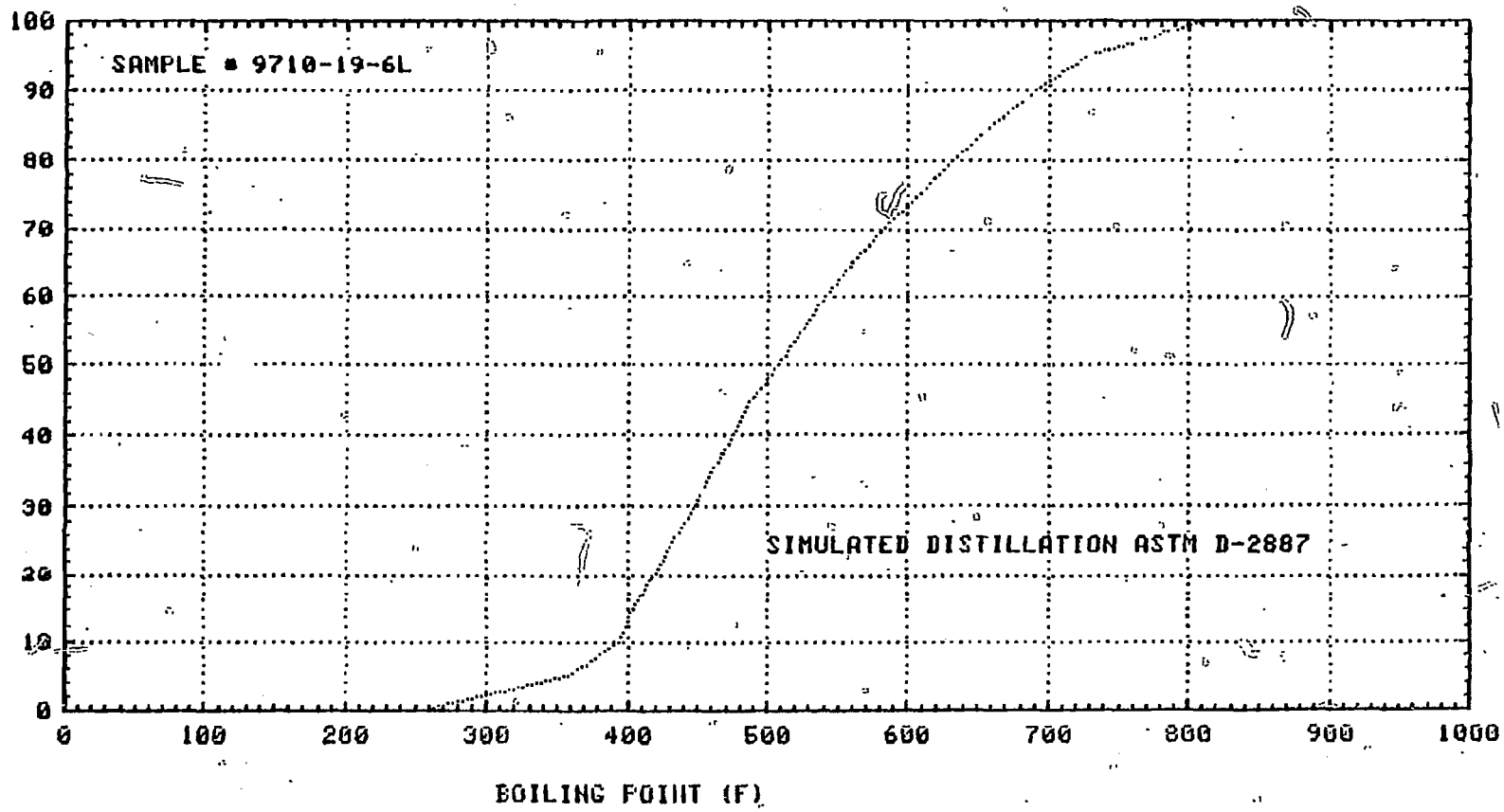
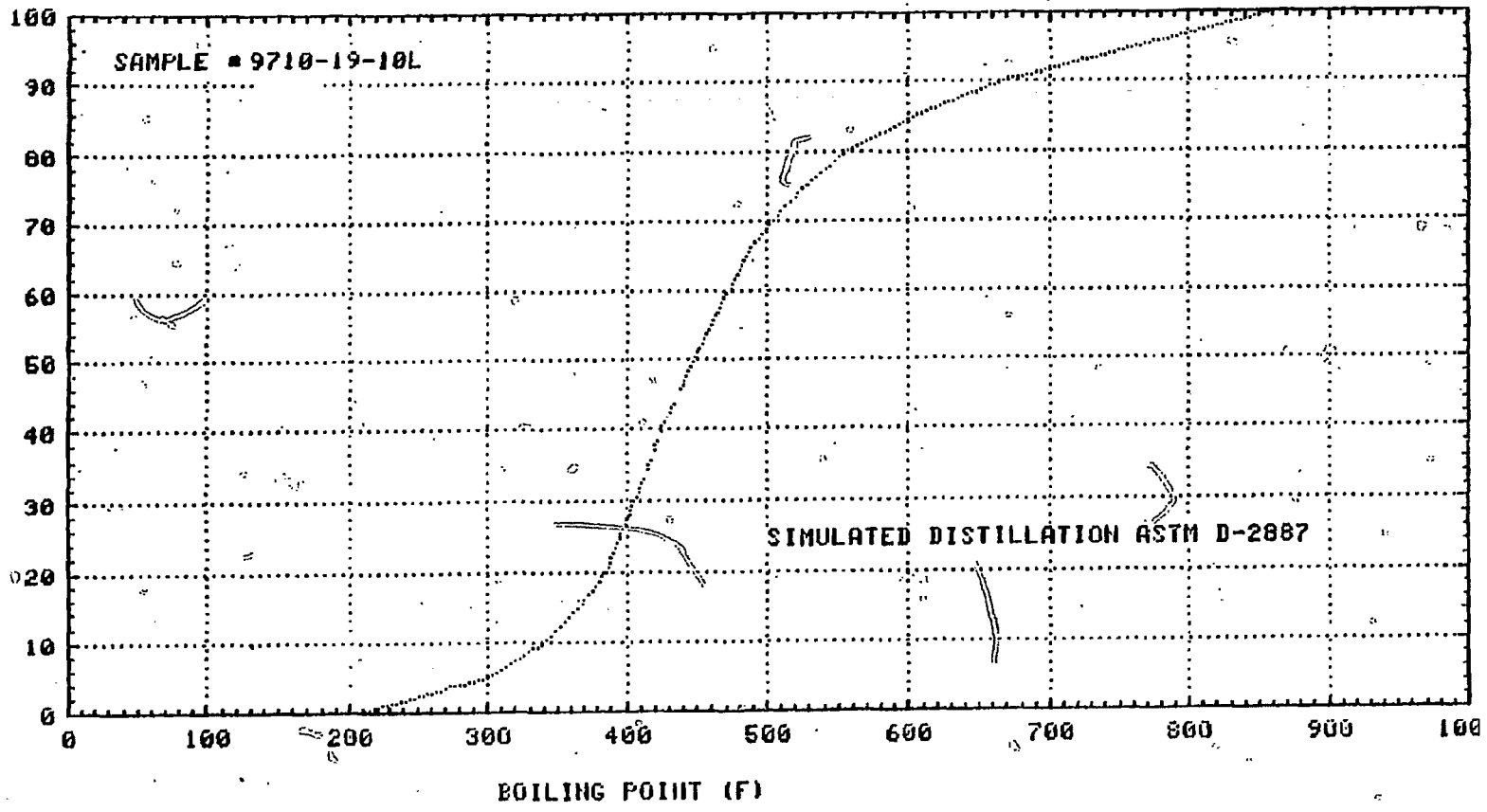

SAMPLE # 9710-19-6L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 32


SAMPLE # 9710-19-10L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
800
900
100

Run 10011-1 on UCC-201 (Fe-UCC-101) Catalyst

This catalyst was activated by the same procedure used in Run 9710-19, i.e., 24 hour CO treatment at 270°C, 3 psig, 400 cc/min. and 24 hour H_2 treatment at 270°C, 3 psig, and 400 cc/min. Ascarite and Drierite traps were installed to monitor the CO_2-make during the CO treatment (6.6 gm. weight gain was observed) and H_2O-make during the H_2 treatment (0.6 gm weight gain was observed). The catalyst was then brought into contact with 60/30/10 syngas feed at 280°C and 290 psig. The conversion was found to be 44% with 15% selectivity for C_5^+ product (samples 1, 2, 3, Table 14). This performance was comparable to the previous run (9710-19) at 280°C. Because the drierite trap weight gain was only 0.6 grams, we thought the H_2 treatment was not adequate. Therefore, the catalyst was subjected to a second H_2 treatment at 400°C (diluted with nitrogen, 300 cc/min N_2, 150 cc/min. H_2) under 300 psig. This happened to be a July 4th weekend when the reactor was run unattended, so the treatment lasted for 113 hours. The 60/30/10 syngas feed was then brought on stream again at 283°C and 303 psig. The result was worse, with the conversion decreased to 16-21% (Samples 4,5). It is believed that the active carbon species on the catalyst surface may have been rendered inactive through graphitization by the high temperature exposure. High temperature exposure after CO treatment should probably be avoided. The results are given in Table 14. Obvious inconsistencies in data from Sample 1 mean that results of this sample should be disregarded.

TABLE 14 RESULT OF SYN GAS OPERATION

RUN NO. 10011-1
CATALYST UCC-201 #9939-56 80 CC 49.7 GM (45.82 G AFTER THE RUN, -3.88GM)
FEED H2:CO:ARGON OF 60/30/10 @ 580 CC/MIN OR 435 GHSV

RUN & SAMPLE NO.	10011-1-1	10011-1-2	10011-1-3	10011-1-4	10011-1-5
FEED H2:CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAM	4.0	21.0	25.6	31.2	57.7
PRESSURE, PSIG	292	290	292	303	303
TEMP. C	281	281	280	283	284
FEED CC/MIN	580	580	580	580	580
HOURS FEEDING	4.0	17.0	4.6667	5.6	25.5
EFFLNT GAS LITER	115.8	483.6	132.2	199.7	899.3
GM AQUEOUS LAYER	0.0	28.48	7.49	0.0	8.98
GM OIL	0.0	0.42	0.0	0.0	0.0
MATERIAL BALANCE					
GM ATOM CARBON %	60.40	104.06	103.25	104.54	105.55
GM ATOM HYDROGEN %	103.59	105.24	104.25	101.36	105.30
GM ATOM OXYGEN %	29.80	110.37	109.15	105.13	107.52
RATIO CHX/(H2O+CO2)	5.7068	0.8621	0.8681	0.9627	0.9071
RATIO X IN CHX	3.3339	3.0583	3.0701	3.0975	3.0299
USAGE H2/CO PRODT	2.8455	1.3381	1.3325	1.1700	1.2544
K EFFLT SHIFT REACTN	2.1904	2.4338	0.2504	3.5296	2.4923
CONVERSION %					
ON CO	64.14	58.01	56.49	23.75	28.70
ON H2	32.19	40.38	37.51	14.50	18.63
ON CO+H2	36.26	43.87	43.84	16.40	20.65
PRDT SELECTIVITY, WT %					
CH4	51.20	36.24	36.57E	33.22	29.72
C2 HC'S	19.34	19.04	19.22E	27.49	25.66
C3H8	13.96	16.43	16.58E	18.30	20.17
C3H6=	0.55	2.54	2.57E	1.16	1.49
C4H10	6.18	7.58	7.65E	7.80	8.78
C4H8=	0.54	2.97	3.00E	1.14	2.16
C5H12	4.42	6.22	6.28E	4.62	5.20
C5H10=	0.00	0.15	0.15E	0.51	0.63
C6H14	235	3.65	3.69E	2.41	2.74
C6H12= & CYCLO'S	0.00	0.23	0.23E	0.20	0.50
C7+ IN GAS	1.46	4.05	4.08E	3.14	2.96
LIQ HC'S	0.00	0.89	0.00	0.00	0.00
TOTAL	100	100	100	100	100
SUBGROUPING					
C1 -C4	91.76	84.81	85.57E	89.12	87.98
C5 -420F	8.24	14.48	14.43E	10.88	12.02
420-700F	0.00	0.65	0.00	0.00	0.00
700-END PT	0.00	0.06	0.00	0.00	0.00
C5 -END PT	8.24	15.19	14.43E	10.88	12.02

ISO/NORMAL MOLE RATIO					
C4	0.2799	0.1641	-	.0714	.0653
C5	1.4631	0.8445	-	.1482	.1223
C6	1.9707	1.6747	-	.3013	.1800
C4=	---	0.0195	-	.2759	.1401
PARAFFIN/OLEFIN M RATIO					
C3	24.0034	6.1657	-	14.9901	12.9210
C4	11.0186	2.4609	-	6.5878	3.9218
C5	---	39.2308	-	8.7736	8.0723
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	---	---	---	---	---
16	---	---	---	---	---
50	---	---	---	---	---
84	---	---	---	---	---
90	---	---	---	---	---
RANGE(16-84 %)	---	---	---	---	---
WT % @420 F					
WT % @700 F					

Run 10011-2 on UCC-201 (Fe-UCC-101) Catalyst

This catalyst (same as the one for Run 10011-1), was activated by similar procedure (but with slight variation) as Run 10011-1 or Run 9710-19. The CO treatment was the same, 400 cc/min, 270°C, 3 psig, 24 hours. The catalyst bed showed an exotherm of 24°C (to 294°C) and an ascarite trap weight gain of 11.6 grams (for CO_2). The H_2 treatment was doubled in duration with higher flow rate and under both low and high pressures, i.e., 24 hours of 1000 cc/min. at 270°C, 3 psig and 24 hours of 2000 cc/min. at 270°C and 300 psig. No weight gain on the drierite trap (for H_2O) was observed. A feed gas of 45/45/10 composition was introduced. At reaction conditions of 220°C, 300 psig, the conversion was about 9%. The temperature was raised to 270°C and 300 psig; the conversion increased to 37% and selectivity for C_5^+ products was 29%. The temperature and pressure were then lowered to 251°C and 100 psig. The conversion decreased to 15%, but the C_5^+ selectivity increased to 35.5%.

The conversion, selectivity data and simulated distillation are reported in Table 15A and 15B and plotted in Figures 33 to 36. Comparing this run (with 45/45/10 feed) to Run 9710-19 (60/30/10 feed), the selectivity in this run for CH_4 and C_5^+ fraction seems not to be significantly affected by the reaction temperature. No definite trend can be observed on the boiling point distribution of the liquid hydrocarbon collection.

TABLE 15A RESULT OF SYN GAS OPERATION

RUN NO. 10011-2
CATALYST UCC-201 #9939-56 80 CC 49.55GM (50.00 G AFTER THE RUN, +0.45GM)
FEED H2:CO:ARGON OF 45/45/10 @ 400 CC/MIN OR 300 GHSV

RUN & SAMPLE NO.	10011-2-1	10011-2-2	10011-2-3	10011-2-4	10011-2-5
FEED H2:CO:AR	60:30:10	45:45:10	45:45:10	44:46:10	45:45:10
HRS ON STREAM	1.75	19.3	27.0	43.5	51.3
PRESSURE,PSIG	300	301	300	299	297
TEMP. C	220	219	272	268	268
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	1.75	17.5	7.75	16.5	7.75
EFFLNT GAS LITER	40.8	464.4	162.6	341.0	169.2
GM AQUEOUS LAYER	0.0	0.0	8.17	11.12	5.4
GM OIL	0.0	0.0	0.31	0.84	0.42
MATERIAL BALANCE					
GM ATOM CARBON %	93.29	119.91	101.25E	98.28	102.97
GM ATOM HYDROGEN %	95.41	118.24	104.76E	100.90	102.40
GM ATOM OXYGEN %	92.65	120.13	110.92E	103.36	109.12
RATIO CHX/(H2O+CO2)	1.0779	0.9631	0.6812E	0.7988	0.9653
RATIO X IN CHX	3.0036	2.6120	2.6520E	2.6554	2.6418
USAGE H2/CO PRODT	1.7020	1.5886	1.0664E	1.0186	1.0074
K EFFLT SHIFT REACTN	0.9649	0.3500	0.8925E	1.2296	1.1936
CONVERSION %					
ON CO	12.36	6.07	35.00E	35.10	33.72
ON H2	10.00	9.92	40.99E	38.64	37.18
ON CO+H2	10.46	8.62	39.04E	37.45	36.02
PRDT SELECTIVITY,WT %					
CH4	34.60	19.07	GC	20.07	19.12
C2 HC'S	18.10	13.23	MAL-	14.75	15.30
C3H8	12.61	7.64	FUNC-	9.94	10.03
C3H6=	5.98	10.01	TION	8.84	9.18
C4H10	8.30	6.35	-	5.67	5.66
C4H8=	5.85	11.02	-	10.52	10.57
C5H12	7.34	7.90	-	6.06	5.82
C5H10=	0.00	0.82	-	0.75	0.80
C6H14	4.14	5.94	-	4.70	4.27
C6H12= & CYCLO'S	0.00	1.10	-	1.09	1.04
C7+ IN GAS	3.08	16.50	-	13.01	13.12
LIQ HC'S	0.00	0.00	-	3.51	3.82E
TOTAL	100	100	100	100	100
SUBGROUPING					
C1 -C4	85.44	67.74	71.45E	70.89	71.13
C5 -420F	14.56	32.26	26.90E	27.15	26.28
420-700F	0.00	0.00	1.37E	1.85	2.49
700-END PT	0.00	0.00	0.27E	0.12	0.10
C5 -END PT	14.56	32.26	28.55E	29.11	28.87

ISO/NORMAL MOLE RATIO					
C4	0.2394	.2610	-	.2225	.1958
C5	0.6321	.7867	-	.6464	.5167
C6	1.0000	1.2389	-	1.0395	.8753
C4=	-	-	-	.0276	.2154
PARAFFIN/OLEFIN M RATIO					
C3	2.0110	0.7285	-	1.0725	1.0424
C4	1.3689	0.5562	-	0.5202	0.5175
C5	-	9.3488	-	7.8361	7.0387
LIQUID COLLECTION					
PHYS. APPEARANCE			OIL	OIL	OIL
DENSITY					
N, REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	---	---	---	332	---
16	---	---	---	360	---
50	---	---	---	435	---
84	---	---	---	537	---
90	---	---	---	598	---
RANGE(16-84 %)	---	---	---	177	---
WT % @420 F				44.0	
WT % @700 F				96.7	

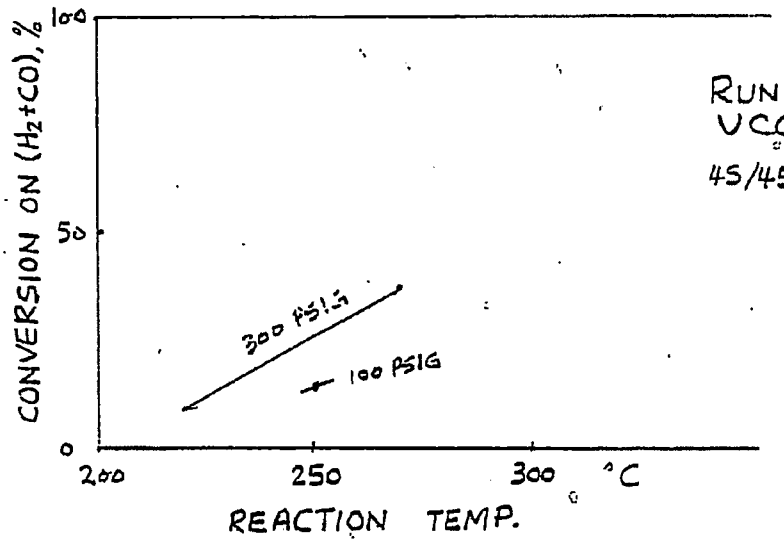
TABLE 15B RESULT OF SYN GAS OPERATION

RUN NO. 10011-2
CATALYST UCC-201 #9939-56 80 CC 49.55GM (50.00 G AFTER THE RUN, 0.45 GM)
FEED H2:CO:ARGON OF 45/45/10 @ 400 CC/MIN OR 300 GHSV

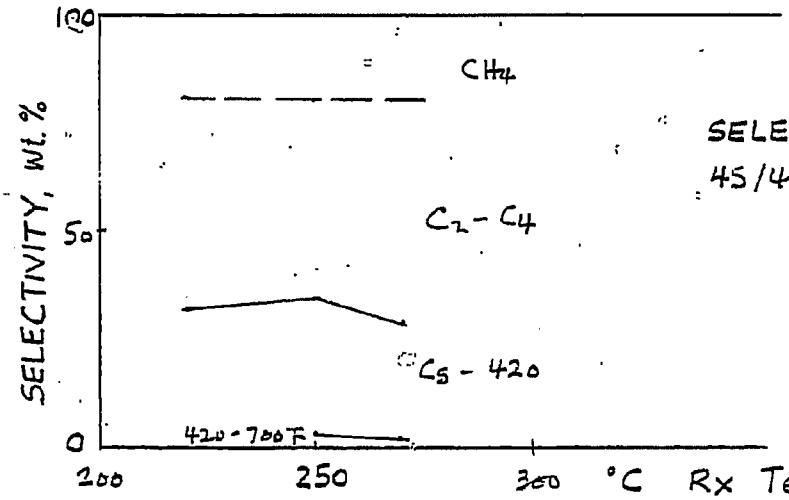
RUN & SAMPLE NO.	10011-2-6
FEED H2:CO:AR	45:45:10
HRS ON STREAM	67.2
PRESSURE,PSIG	100
TEMP. C	251
FEED CC/MIN	400
HOURS FEEDING	15.92
EFFLNT GAS LITER	425.70
GM AQUEOUS LAYER	2.52
GM OIL	0.41
MATERIAL BALANCE	
GM ATOM CARBON %	74.03
GM ATOM HYDROGEN %	92.48
GM ATOM OXYGEN %	76.48
RATIO CHX/(H2O+CO2)	0.7338
RATIO X IN CHX	2.5719
USAGE H2/CO PRODT	1.3489
K EFFLT SHIFT REACTN	0.5941
CONVERSION %	
ON CO	13.20
ON H2	16.04
ON CO+H2	15.23
PRDT SELECTIVITY,WT %	
CH4	19.11
C2 HC'S	14.17
C3H8	6.36
C3H6=	8.95
C4H10	4.20
C4H8=	11.68
C5H12	4.82
C5H10=	1.35
C6H14	3.64
C6H12= & CYCLO'S	1.81
C7+ IN GAS	18.44
LIQ HC'S	5.42E
TOTAL	100
SUBGROUPING	
C1 -C4	64.47
C5 -420F	33.09
420-700F	4.06
700-END PT	0.37
C5 -END PT	35.53

ISO/NORMAL MOLE RATIO	
C4	0.1223
C5	0.2255
C6	0.4444
C4=	0.2490
PARAFFIN/OLEFIN M RATIO	
C3	0.6783
C4	0.3474
C5	3.4699
LIQ HC COLLECTION	
PHYS. APPEARANCE	CLEAR OIL
DENSITY	
N, REFRACTIVE INDEX	
SIMULATED DISTILLATION	
10 WT % @ DEG F	401
16	410
50	503
84	641
90	676
RANGE(16-84 %)	231
WT % @420 F	18.30
WT % @700 F	93.20

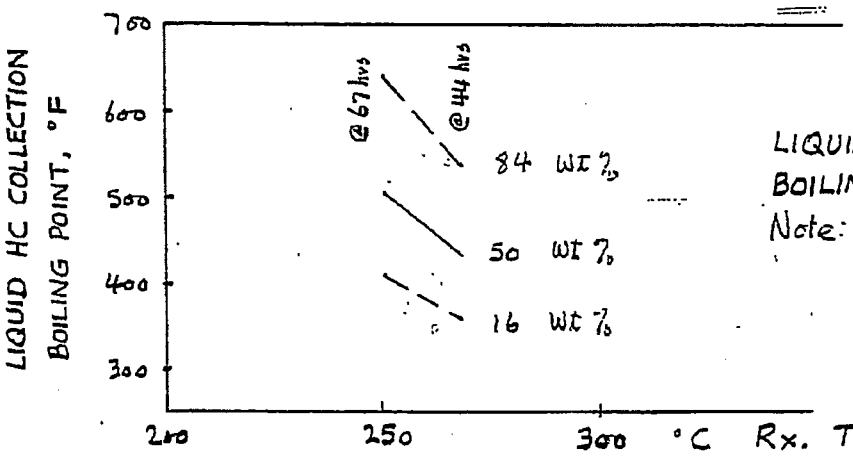
FIGURE 33



RUN 10011-2
VCC-201
45/45/10 H_2/CO/Ar Syngas



SELECTIVITY WITH
45/45/10 (H_2/CO/Ar) Syngas



LIQUID PRODUCT COLLECTION
BOILING RANGE
Note: - In reverse chronological order

FIG. 34

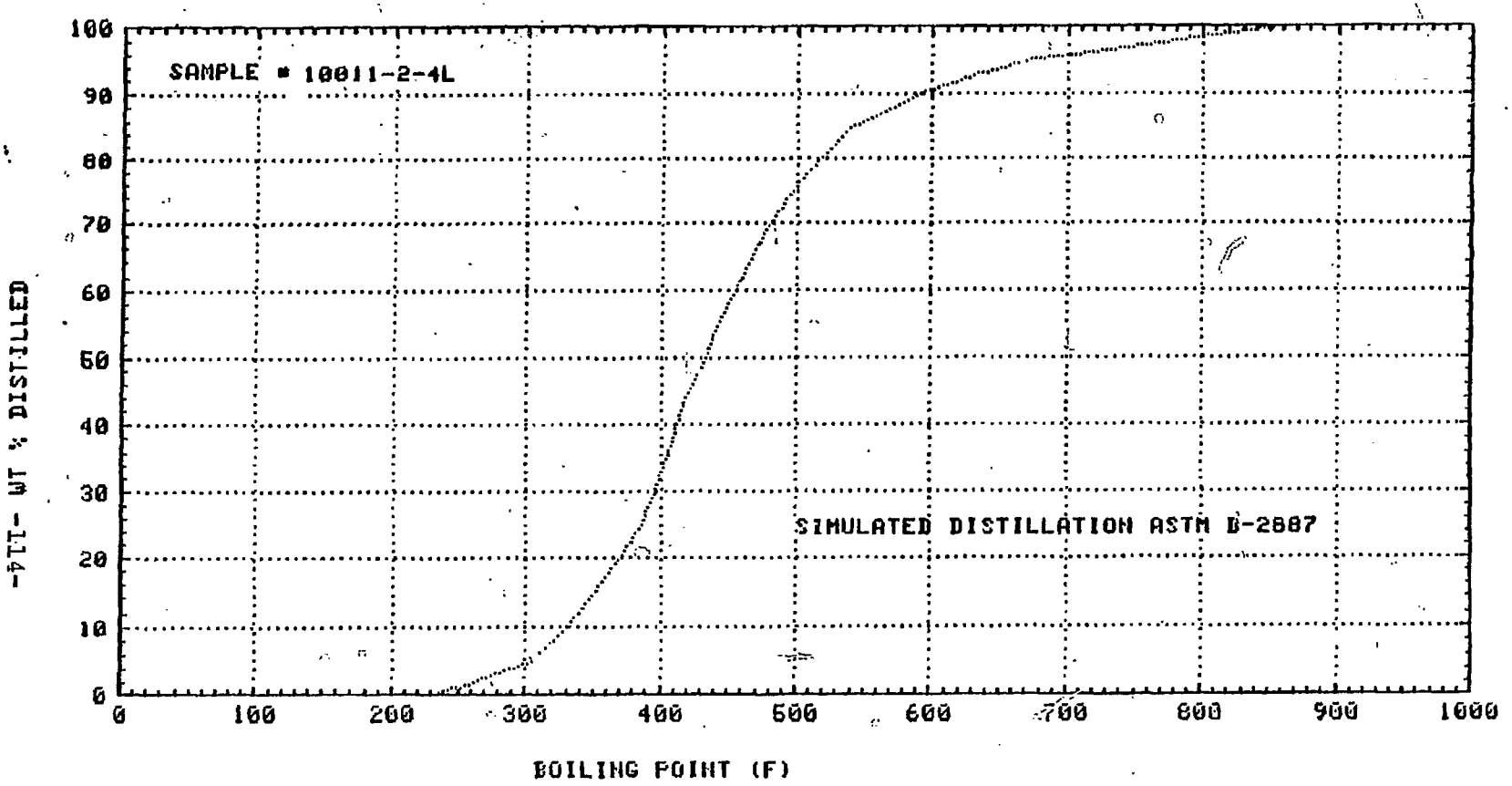

SAMPLE # 10011-2-4L
SIMULATED DISTILLATION ASTM D-2887
-114- WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG. 35

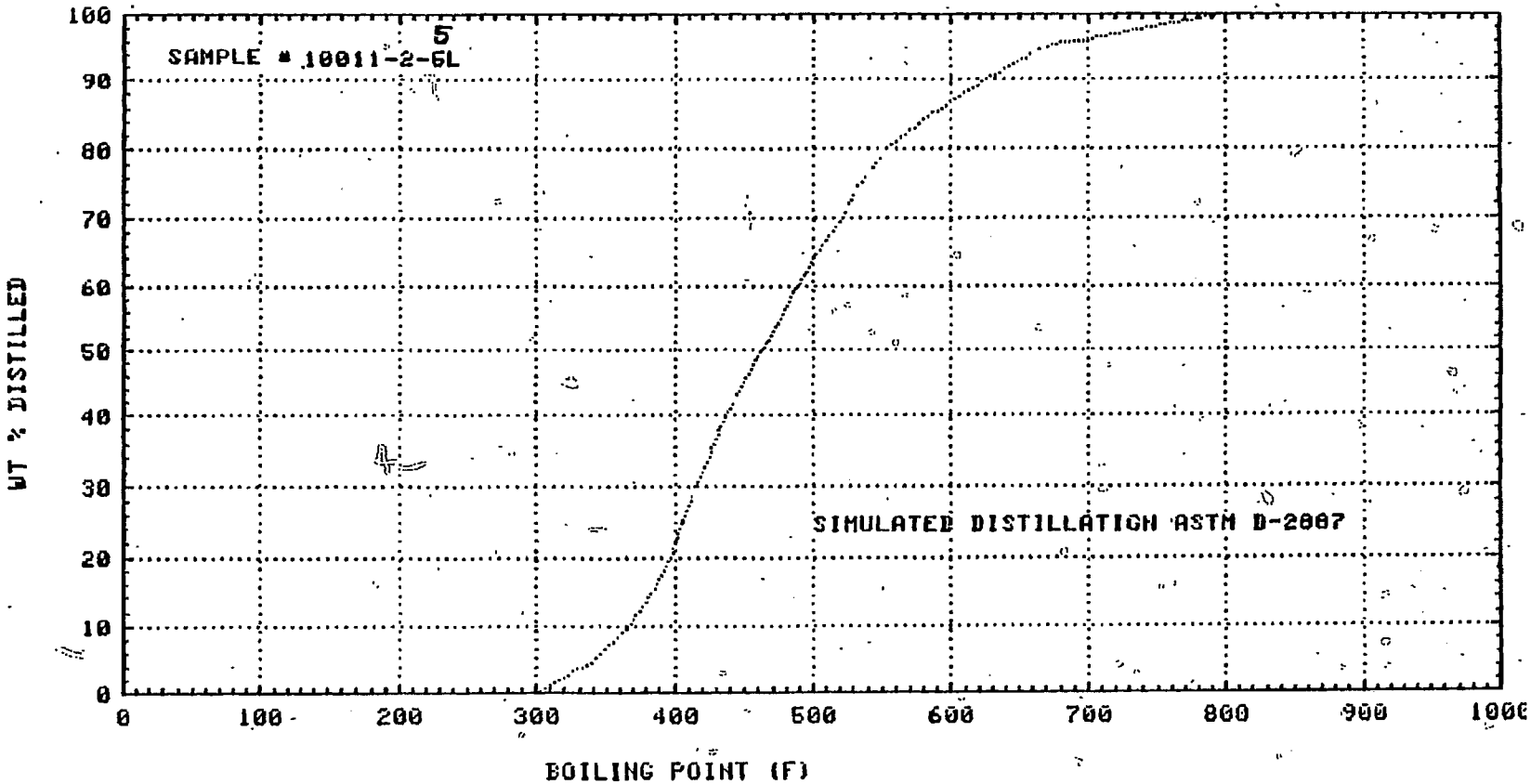
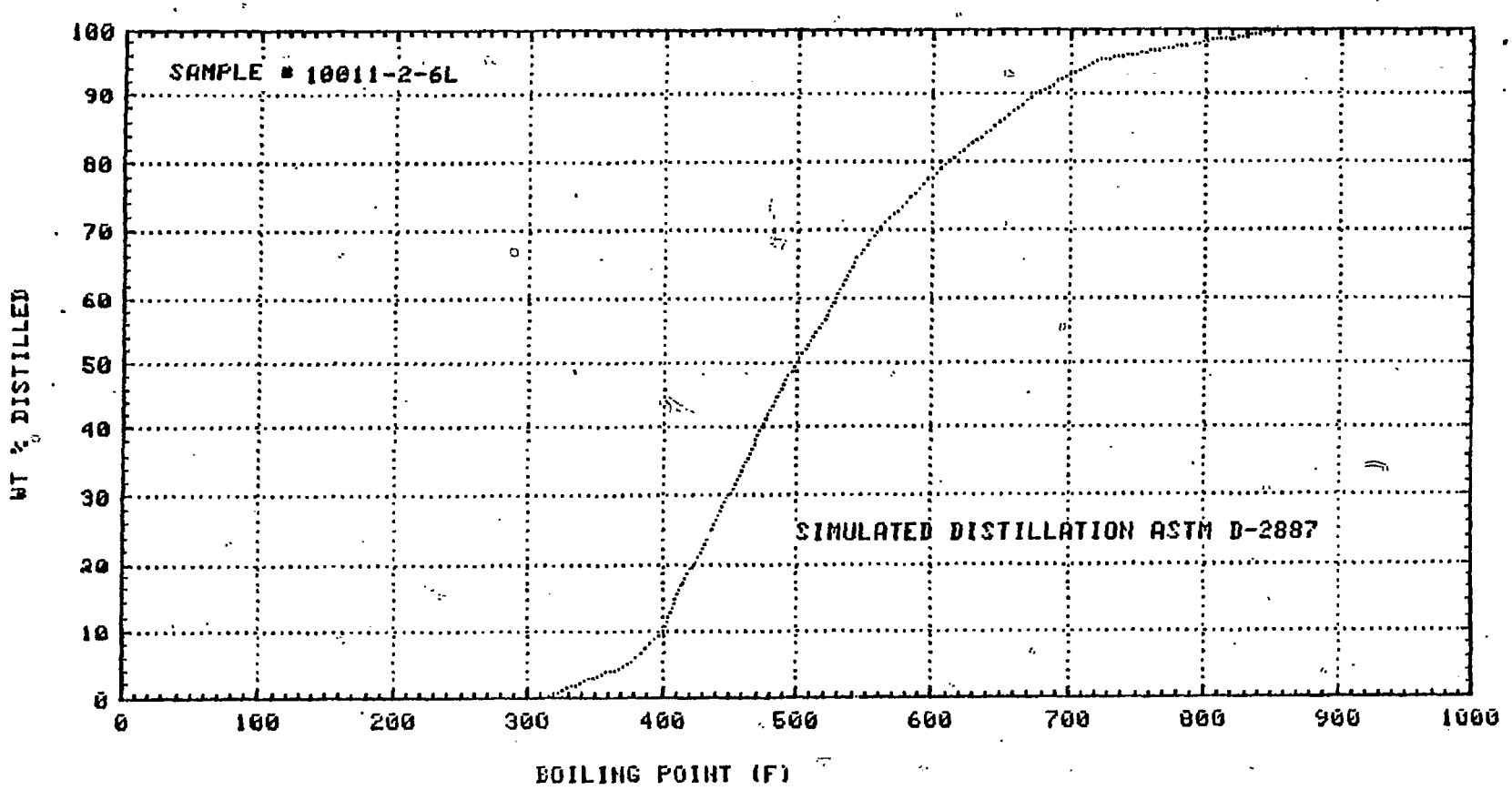

SAMPLE # 10011-2-6L
5
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIG 36


SAMPLE # 10011-2-6L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Run 10011-4 on UCC-201 (Fe-UCC-101) Catalyst

In the previous four runs on Fe-UCC-101 catalyst, (Runs 9710-18, -19, 10011-1, -2), the catalyst was activated by a procedure which calls for a carburization step first (generally at 270-300°C with pure CO gas), followed by a hydrogenation step at the same temperature. The catalyst was then generally brought on stream with 60/30/10 syngas at slightly lower temperature. We shall call this procedure A. In this run, Run 10011-4, the catalyst was activated by a different procedure which calls for a hydrogenation step first (at 400-450°C), and then a carburization step at 250°C with 45/45/10 H_2/CO/Argon syngas. We shall call this procedure B.

More specifically, the catalyst, having been calcined in air at 500°C, was treated with H_2 at 1500 cc/min. (1125 GHSV), 300 psig, for 7 hours at 340°C and 49 hours at 450°C. The catalyst was cooled to 250°C under H_2 (total weight gain in the drierite trap was 8.5 gm) and then treated with 45/45/10 syngas at 400 cc/min (300 GHSV), 100 psig, for 48 hours at 250°C. During this 48 hours, the syngas conversion was 7-11% (refer to samples 1 to 4, table 16A) No liquid product, aqueous or oil, was observed during that time, and it was felt that the catalyst needed another activation, a shortened version of procedure A. The catalyst was treated for 5 hours with CO at 400 cc/min, 3 psig, 270°C, followed by 16 hours with H_2 at 1500 cc/min., 100 psig and 270°C. The 45/45/10 syngas feed was brought on stream again at 400 cc/min., 100 psig, and 273°C The conversion was 17% (sample 6). The temperature was raised to 302°C and the conversion increased to 35%. The conversions and the selectivities are plotted in Figure 37. The catalyst performance in this run was poor. Throughout the whole run, not enough oil product was made for collection.

TABLE 16A RESULT OF SYN GAS OPERATION

RUN NO. 10011-4
CATALYST UCC-201 #9939-73 80 CC 51.24GM (47.10 G AFTER THE RUN, -4.14GM)
FEED H2:CO:ARGON OF 45/45/10 @ 400 CC/MIN OR 300 GHSV

RUN & SAMPLE NO.	10011-4-1	10011-4-2	10011-4-3	10011-4-4	10011-4-5
FEED H2:CO:AR	45:45:10	45:45:10	45:45:10	45:45:10	45:45:10
HRS ON STREAM	5.7	21.5	28.4	46.7	53.6
PRESSURE,PSIG	102	99	100	98	99
TEMP. C	252	252	251	251	273
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	5.75	15.83	6.92	18.33	6.92
EFFLNT GAS LITER	163.4	432.4	189.1	499.6	176.3
GM AQUEOUS LAYER	0.0	0.0	0.0	0.0	0.0
GM OIL	0.0	0.0	0.0	0.0	0.0
MATERIAL BALANCE					
GM ATOM CARBON %	112.38	108.86	107.82	109.64	101.54
GM ATOM HYDROGEN %	111.95	108.85	110.01	109.16	101.52
GM ATOM OXYGEN %	114.66	110.22	108.94	108.52	102.80
RATIO CHX/(H2O+CO2)	0.6126	0.7611	0.8025	1.1920	0.7611
RATIO X IN CHX	2.8932	2.8342	2.8285	2.5908	2.8342
USAGE H2/CO PRODT	1.6348	1.6897	1.7221	1.7201	1.6897
K EFFLT SHIFT REACTN	0.2611	0.2678	0.2647	0.3021	0.2678
CONVERSION %					
ON CO	4.33	5.12	5.32	7.63	5.12
ON H2	8.77	9.70	9.85	12.31	9.70
ON CO+H2	7.29	8.17	8.36	10.74	8.17
PRDT SELECTIVITY,WT %					
CH4	22.55	21.53	22.07	15.67	21.53
C2 HC'S	24.17	22.58	21.25	14.90	22.58
C3H8	19.31	17.05	16.79	13.14	17.05
C3H6=	3.31	4.74	4.55	27.21	4.74
C4H10	10.02	8.33	8.16	6.21	8.33
C4H8=	2.76	3.89	4.42	3.51	3.89
C5H12	8.18	8.01	7.68	5.84	8.01
C5H10=	0.00	0.00	0.00	0.00	0.00
C6H14	5.10	6.13	6.63	5.34	6.13
C6H12= & CYCLO'S	0.00	0.00	0.26	0.44	0.00
C7+ IN GAS	4.61	7.73	8.17	7.73	7.73
LIQ HC'S	0.00	0.00	0.00	0.00	0.00
TOTAL	100	100	100	100	100
SUBGROUPING					
C1 -C4	82.12	78.12	77.25	80.64	78.12
C5 -420F	17.88	21.88	22.75	19.36	21.88
420-700F	0.00	0.00	0.00	0.00	0.00
700-END PT	0.00	0.00	0.00	0.00	0.00
C5 -END PT	17.88	21.88	22.75	19.36	21.88

ISO/NORMAL MOLE RATIO					
C4	0.4636	0.2951	0.2696	0.2322	0.2951
C5	3.4035	2.2211	1.7909	1.2264	2.2211
C6	---	4.9394	4.6923	3.0448	4.9393
C4=	---	---	---	---	---
PARAFFIN/OLEFIN MOLE RATIO					
C3	5.5747	3.4355	3.5192	0.4607	3.4355
C4	3.5046	2.0681	1.7841	1.7106	2.0681
C5	---	---	---	---	---
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	---	---	---	---	---
16	---	---	---	---	---
50	---	---	---	---	---
84	---	---	---	---	---
90	---	---	---	---	---
RANGE(16-84 %)	---	---	---	---	---

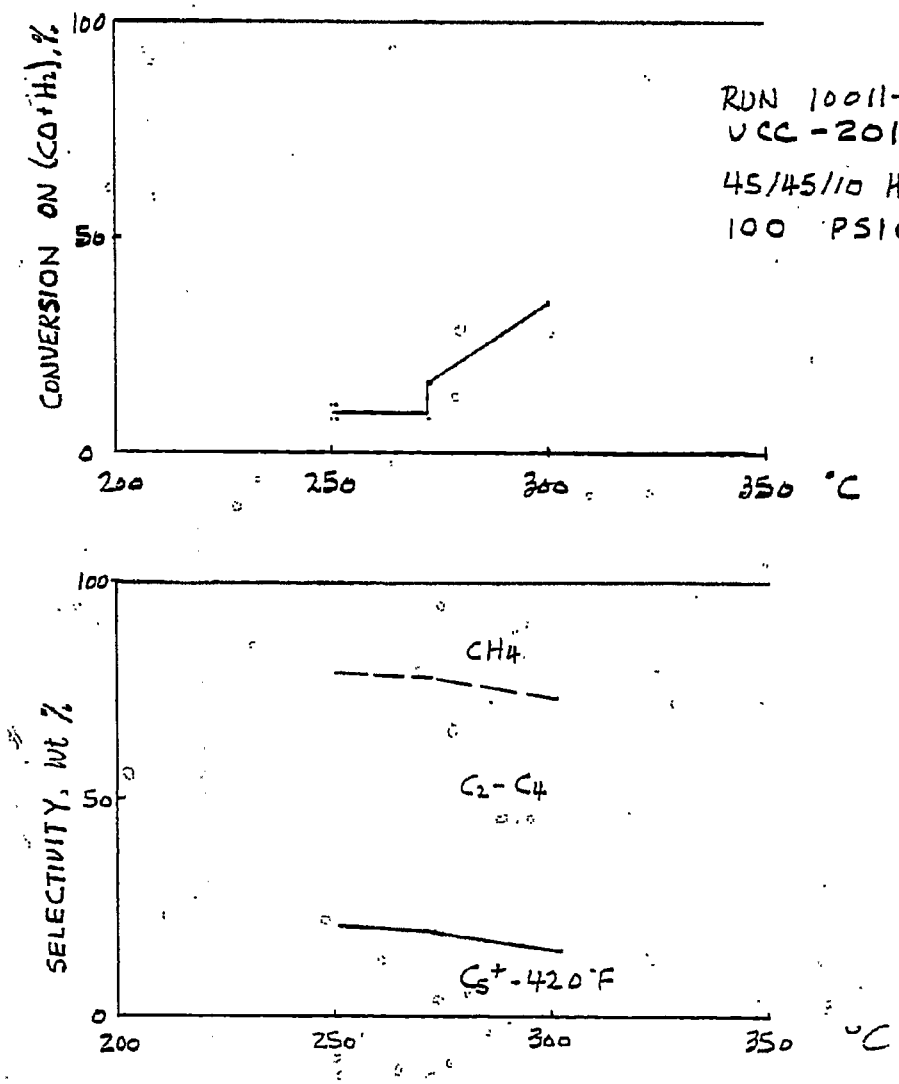
TABLE 16B RESULT OF SYN GAS OPERATION

RUN NO. 10011-4
CATALYST UCC-201 #9939-73 80 CC 51.24GM (47.10 G AFTER THE RUN, -4.14GM)
FEED H2:CO:ARGON OF 45/45/10 @ 400 CC/MIN OR 300 GHSV

RUN & SAMPLE NO.	10011-4-6	10011-4-7	10011-4-8	10011-4-9	10011-4-10
FEED H2:CO:AR	45:45:10	45:45:10	45:45:10	45:45:10	45:45:10
HRS ON STREAM	71.4	78.4	97.2	101.8	122.7
PRESSURE,PSIG	98	101	104	105	103
TEMP. C	273	303	304	299	300
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	17.83	7.0	18.75	4.67	20.83
EFFLNT GAS LITER	455.9	156.0	416.4	103.7	475.1
GM AQUEOUS LAYER	3.57	0.0	7.05	0.0	7.45
GM OIL	0.0	0.0	0.0	0.0	0.0
MATERIAL BALANCE					
GM ATOM CARBON %	106.66	108.94	104.56	111.04	113.22
GM ATOM HYDROGEN %	107.76	105.76	107.23	106.95	114.29
GM ATOM OXYGEN %	108.25	109.62	110.09	110.25	116.39
RATIO CHX/(H2O+CO2)	0.8559	0.9700	0.7945	1.0398	0.8775
RATIO X IN CHX	2.8360	2.9613	2.9796	2.9354	2.9232
USAGE H2/CO PRODT	1.3364	0.8734	0.9227	0.9286	0.9683
K EFFLT SHIFT REACTN	0.6782	5.4364	2.5123	4.4506	2.3358
CONVERSION %					
ON CO	13.21	37.88	38.60	33.27	36.01
ON H2	18.46	34.36	37.11	31.74	35.89
ON CO+H2	16.72	35.55	37.60	32.26	35.93
PRDT SELECTIVITY,WT %					
CH4	22.24	26.52	28.08	26.17	26.31
C2 HC'S	22.37	26.22	26.20	24.45	23.43
C3H8	18.29	22.83	21.82	19.73	19.44
C3H6=	4.93	2.95	3.41	3.85	4.34
C4H10	8.42	2.42	2.50	7.93	7.98
C4H8=	4.34	2.35	2.67	3.00	3.51
C5H12	7.40	7.45	6.60	6.20	6.07
C5H10=	0.24	0.11	0.08	0.09	0.18
C6H14	4.81	4.06	3.81	3.67	3.58
C6H12= & CYCLO'S	0.09	0.29	0.22	0.15	0.35
C7+ IN GAS	6.86	4.79	4.61	4.75	4.81
LIQ HC'S	0.00	0.00	0.00	0.00	0.00
TOTAL	100	100	100	100	100
SUBGROUPING					
C1 -C4	80.59	83.29	84.68	85.13	85.01
C5 -420F	19.41	16.71	15.32	14.87	14.99
420-700F	0.00	0.00	0.00	0.00	0.00
700-END PT	0.00	0.00	0.00	0.00	0.00
C5 -END PT	19.41	16.71	15.32	14.87	14.99

ISO/NORMAL MOLE RATIO					
C4	0.2096	2.1429	1.4897	0.2044	0.1939
C5	1.3643	1.7747	1.6799	1.5772	1.2295
C6	2.9560	4.1635	3.9867	3.6960	3.1136
C4=	0.0205	0.0267	0.0254	0.0271	25.5854
PARAFFIN/OLEFIN M RATIO					
C3	3.5444	7.3902	6.1101	4.8941	4.2735
C4	1.8738	0.9945	0.9009	2.5568	2.1973
C5	30.0909	66.5926	81.5263	63.7273	32.6000
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N, REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	---	---	---	---	---
16	---	---	---	---	---
50	---	---	---	---	---
84	---	---	---	---	---
90	---	---	---	---	---
RANGE(16-84 %)	---	---	---	---	---

FIGURE 37


CONVERSION ON (CO+H2), %
100
50
0
200
250
300
350 °C
RUN 10011-4,
VCC-201
45/45/10 H2/CO/Ar Syngas
100 PSIG
SELECTIVITY, wt %
100
50
0
CH4
C2-C4
C5+-420°F
200
250
300
350 °C
REACTION TEMP. °C

Run 10011-5 on UCC-201 (Fe-UCC-101) Catalyst

The activation procedure used in this run was almost identical to the previous run (Run 10011-4). The catalyst, having been calcined in air at 250°C, was activated by treating first with H_2 at 2000 cc/min (1500 GHSV), 3 psig (low pressure this time) for 7 hours at 300°C, and 33 hours at 400°C, cooled under H_2 to 250°C (Drierite trap wt. gains 7.2 gm.) and then treated with 45/45/10 syngas, 400 cc/min, 100 psig, 48 hours at 250°C and 24 hours at 280°C. The conversion at 250°C was low, only 7% (Sample 2, Table 17). The catalyst was subjected to another procedure A activation of CO at 400 cc/min. 3 psig, 280°C, 6 hours, followed by H_2 at 2000 cc/min. 3 psig, 280°C, 18 hours, with a drierite trap weight gain (H_2O) of 1.7 gm. and ascarite trap weight gain (CO_2) of 0.1 gm. No discernable exotherm was observed. The 45/45/10 syngas was brought on stream again at 400 cc/min, 105 psig, 279°C for 26 hours. The conversion was still quite poor, only 12% at 279°C (sample 3, Table 17).

TABLE 17 RESULT OF SYN GAS OPERATION

RUN NO. 10011-5
CATALYST UCC-201 #9938-88 80 CC 47.5 GM (42.74 G AFTER THE RUN, -4.76GM)
FEED H2:CO:ARGON OF 45/45/10 @ 400 CC/MIN OR 300 GHSV

RUN & SAMPLE NO.	10011-5-1	10011-5-2	10011-5-3
FEED H2:CO:AR	45:45:10	45:45:10	45:45:10
HRS ON STREAM	25.7	44.7	93.1
PRESSURE,PSIG	97	94	105
TEMP. C	249	249	279
FEED CC/MIN	400	400	400
HOURS FEEDING	25.75	19.0	25.667
EFFLNT GAS LITER	625.6	463.0	602.4
GM AQUEOUS LAYER	0.0	6.0	0.00
GM OIL	0.0	0.0	0.0
MATERIAL BALANCE			
GM ATOM CARBON %	102.21	100.06	95.03
GM ATOM HYDROGEN %	102.51	105.11	95.76
GM ATOM OXYGEN %	104.86	106.13	95.46
RATIO CHX/(H2O+CO2)	0.3795	0.2293	0.9357
RATIO X IN CHX	2.9423	2.8491	2.9208
USAGE H2/CO PRODT	1.9370	1.9806	1.3862
K EFFLT SHIFT REACTN	0.0786	0.0369	0.7258
CONVERSION %			
ON CO	1.90	2.09	9.59
ON H2	6.17	9.67	13.50
ON CO+H2	4.75	7.23	12.21
PRDT SELECTIVITY,WT %			
CH4	28.59	27.32	30.33
C2 HC'S	22.72	17.38	21.54
C3H8	13.93	13.31	12.56
C3H6=	4.90	6.06	7.30
C4H10	6.96	6.97	5.64
C4H8=	4.03	5.17	5.42
C5H12	7.22	6.53	6.16
C5H10=	0.00	6.35	0.21
C6H14	6.27	5.14	4.72
C6H12= & CYCLO'S	0.00	0.00	0.00
C7+ IN GAS	5.38	5.78	6.13
LIQ HC'S	0.00	0.00	0.00
TOTAL	100	100	100
SUBGROUPING			
C1 -C4	81.13	76.21	82.78
C5 -420F	18.87	23.79	17.22
420-700F	0.00	0.00	0.00
700-END PT	0.00	0.00	0.00
C5 -END PT	18.87	23.79	17.22

ISO/NORMAL MOLE RATIO			
C4	0.4433	0.3964	0.3373
C5	6.3125	4.5714	2.6852
C6	---	---	4.5435
C4=	---	---	---
PARAFFIN/OLEFIN M RATIO			
C3	2.7132	2.0968	1.6403
C4	1.6667	1.3025	1.0044
C5	---	1.0000	28.4286
LIQ HC COLLECTION			
PHYS. APPEARANCE			
DENSITY			
N, REFRACTIVE INDEX			
SIMULATED DISTILLATION			
10 WT % @ DEG F	---	---	---
16	---	---	---
50	---	---	---
84	---	---	---
90	---	---	---
RANGE(16-84 %)	---	---	---

Run 10011-3 on UCC-202 (Mn-Fe-UCC-103) Catalyst

This is a manganese-iron loaded UCC-103 catalyst. The catalyst was activated by a modified procedure A, with 45/45/10 H_2/CO/Argon syngas as the carburizing gas at 400 cc/min, 100 psig, 250°C for 20 hours, and later again at 265°C for 18 hours, followed by H_2 treatment of 1000 cc/min 3 psig, 270°C for 7 hours, and 2000 cc/min., 300 psig, 270°C for 21 hours (both low and high pressure). The 45/45/10 syngas feed was then brought on stream at 400 cc/min. 300 psig and 220°C. The conversion was very low, only 3% (samples 1 and 2, table 18). The conversion was still very low at 4% for a higher temperature of 252°C (sample 3). Despite the uncertainties with regard to the best activation procedure, the very poor performance of this catalyst is attributed to the catalyst itself and the way it was prepared. The metal component of the catalyst was added through the decomposition of manganese and iron carbonyls adsorbed onto the catalyst; catalyst activity may have been damaged during the alumina bonding to form extrudate.

TABLE 18 RESULT OF SYN GAS OPERATION

RUN NO. 10011-3
CATALYST UCC-202 #9673-11D 80CC 38.91GM (39.05 G AFTER THE RUN, +0.14GM)
FEED H2:CO:ARGON OF 45/45/10 @ 400 CC/MIN OR 300 GHSV

RUN & SAMPLE NO.	10011-3-1	10011-3-2	10011-3-3
FEED H2:CO:AR	45:45:10	45:45:10	45:45:10
HRS ON STREAM	1.5	19.0	26.3
PRESSURE,PSIG	299	302	302
TEMP. C	221	221	252
FEED CC/MIN	400	400	400
HOURS FEEDING	1.5	17.5	7.25
EFFLNT GAS LITER	42.0	499.3	208.1
GM AQUEOUS LAYER	0.0	0.0	0.0
GM OIL	0.0	0.0	0.0
MATERIAL BALANCE			
GM ATOM CARBON %	101.77	110.05	109.98
GM ATOM HYDROGEN %	112.66	114.77	110.66
GM ATOM OXYGEN %	106.09	114.21	113.98
RATIO CHX/(H2O+CO2)	0.0618?	0.1188?	0.1833?
RATIO X IN CHX=	3.3971	2.6351	2.9055
USAGE H2/CO PRODT	2.0007	1.9711	1.9007
K EFFLT SHIFT REACTN	0.0154	0.0185	0.0494
CONVERSION %			
ON CO	0.34	0.59	1.03
ON H2	4.46	4.68	5.39
ON CO+H2	3.18	3.35	3.94
PRDT SELECTIVITY,WT %			
CH4	66.85	31.40	39.44
C2 HC'S	17.71	50.66	16.99
C3H8	0.00	1.96	4.43
C3H6=	7.55	8.99	13.38
C4H10	0.00	0.00	9.14
C4H8=	0.00	0.00	0.00
C5H12	0.00	0.00	0.00
C5H10=	0.00	0.00	0.00
C6H14	4.69	0.00	1.89
C6H12= & CYCLO'S	0.00	0.00	0.00
C7+ IN GAS	3.20	6.99	14.72
LIQ HC'S	0.00	0.00	0.00
TOTAL	100	100	100
SUBGROUPING			
C1 -C4	92.11	93.01	83.39
C5 -420F	7.89	6.99	16.61
420-700F	0.00	0.00	0.00
700-END PT	0.00	0.00	0.00
C5 -END PT	7.89	6.99	16.61

ISO/NORMAL MOLE RATIO			
C4	---	---	---
C5	---	---	---
C6	---	---	---
C4=	---	---	---
PARAFFIN/OLEFIN M RATIO			
C3	---	0.2083	0.3161
C4	---	---	---
C5	---	---	---
LIQ HC COLLECTION			
PHYS. APPEARANCE			
DENSITY			
N, REFRACTIVE INDEX			
SIMULATED DISTILLATION			
10 WT % @ DEG F	---	---	---
16	---	---	---
50	---	---	---
84	---	---	---
90	---	---	---
RANGE(16-84 %)	---	---	---
WT % @420 F			
WT % @700 F			

SUMMARY OF THE SYNGAS OPERATION

The results from the syngas operation reported this quarter were poor, worse than expected. Since none of the catalysts whose results were reported here had been promoted, there was little expectation for good selectivity to heavy hydrocarbons. We did have reason to expect the conversions to have better than they were. All the reasons for the poor results are not clear at this time. Generally, the activation procedures used, while possibly not being optimal, should have been quite adequate. Analysis of the feed streams failed to show that the feed could have contaminated the catalysts. It is suspected that one batch of catalyst, used for most of the tests reported above, may have been damaged in some way.

Starting with run 10011-6, conducted this quarter (the results of which will be reported next quarter) the catalysts have shown higher conversions and apparently good selectivity to desired products in Task 2 tests.

G. A. Somorjai

APPENDIX D: SURFACE STUDIES

We have completed construction of the new low pressure-high pressure apparatus to be used for catalyst surface studies. Preliminary studies of CO hydrogenation were carried out in this apparatus. On a previously built chamber, CO hydrogenation reactions at 3-6 atm pressure have been carried out using rhenium metal surfaces. While the clean metal is a mediocre methanation catalyst, the addition of potassium to the surface increases the yield of C_2 and C_3 hydrocarbons (ethane and propane) and suppresses the methane yield.

Samples of catalysts prepared by the oxidative decomposition of iron and manganese carbonyls inside the molecular sieve, UCC-103, were provided by P.K. Coughlin. Auger electron spectroscopy showed little metal on the surface. In comparison to simple metal, metal oxide, and metal alkali oxide systems, the molecular sieve supported catalyst showed high yields and good selectivity towards olefins at 3 atm of total pressure and 275°C.

We have recently constructed a Mn evaporation source and are currently examining changes in activity and selectivity which occur on Fe foil promoted with Mn monolayers. In the following few months we will also examine the Fe/Mn system with O and K additives combining the high pressure results with ultra-high vacuum analysis.

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