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TECHNICAL PROGRESS REPORT

DE-AC22-81PC40077

Seventh Quarterly Report

September - November 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

The SSC candidate testing program is centered on the evaluation of new UCC molecular sieves and modified forms of known zeolites, using propylene feed. In this study, we are monitoring the catalytic activity in the conversion of propylene. The product selectivity to liquid hydrocarbons, and the ratio of olefins to saturates is also established. The observed catalytic performance is then used to grade SSC candidates for application in Task 2 catalyst formulation.

We reported in the last quarter on the outstanding performance of UCC-104 with propylene feed. This catalyst had high activity, and it converted the propylene with near quantitative yield to C_5^+ liquid hydrocarbon product. Significantly, the liquid product boiled mainly in the gasoline range. The conversion of the propylene feed to propane, a usually prominent, undesirable reaction with all strong acid zeolites, was nearly absent. Thus, we clearly established that UCC-104 is an outstanding SSC catalyst candidate for Task 2 service.

In order to complete the test of relevant reference materials in the conversion of propylene, we have prepared, and began the evaluation of, several known zeolites in appropriately activated or modified form. Catalyst preparations were based on three new UCC molecular sieves. One was tested this quarter and two will be tested next quarter. In addition, modified forms of zeolites omega and L were also prepared representing varying degrees of acidity. The catalyst synthesis work for Tasks 1 and 2 is reported in Appendix A.

FIA analyses of product molecule types (paraffin, olefin, aromatic) were not reported in the last quarterly report because of analytical problems encountered with the products. We have now found that the cause of the problem is fluorescence of the products from the Berty reactors (see Appendix B). A substitute for the FIA technique is being sought, thus far without success.

Test results for six Berty reactor tests and one microreactor test, all with propylene in the feed, are reported in Appendix C.

Test Results

The LZ-105-6, a medium pore molecular sieve, similar in structure to ZSM-5, is the most active catalyst we have tested so far for the conversion of propylene. At optimal conditions, it converted 90% of the feed versus 63% found with UCC-104. However, the test carried out in the Berty reactor showed that this catalyst has inferior selectivity to C_5^+ (89%) relative to UCC-104 (96%). The lower C_5^+ yield with LZ-105 follows from the increased conversion of the propylene to saturated C_3-C_4 hydrocarbons.

The large pore molecular sieves tested this quarter all deactivated more rapidly than the medium pore materials. Among these catalysts, the multivalent-cation-exchanged Y zeolites deactivated very rapidly. UCC-103, a lower acidity modification of UCC-101, had slightly improved catalyst life and selectivity to C_5^+ products without significant loss of activity compared to UCC-101. In contrast to the medium pore molecular sieves, the large pore molecular sieves tested in this quarter had the advantage of (at least initially) producing some of their liquid products in the diesel range.

TASK 2

Task 2 catalysts consist of the shape selective component (SSC) and the syngas active metal component (MC). In the last quarter we ran a test to firmly establish the performance of an industrial standard catalyst for reference purposes. In addition, the evaluation of the efficiency of various mixing techniques between SSC and MC was sought in terms of syngas conversion activity and selectivity. This information is necessary to the successful formulation of Task 2 catalysts using best SSC catalyst candidates.

Catalysts were synthesized using three different techniques: physical mixtures of the metal component (MC) and the shape selective (SSC) molecular sieve, precipitation of MC from solution onto SSC and occlusion of MC into SSC by calcination after loading the SSC with gaseous metal carbonyls. The iron-containing catalysts were usually promoted with potassium. Work has started on cobalt-based catalysts, most of which will be promoted with thoria.

Surface analysis has indicated a probable cause for the low activity of one Task 2 catalyst tested last quarter: interaction of the iron (MC) with the alumina binder used in formulating the catalyst pellets. Details are in Appendix A.

Test Results

An extensive test is reported using a commercial, state of-the-art, promoted iron catalyst. The catalyst was very active even at 250°C. It produced mostly olefinic hydrocarbons. The selectivity to C_5^+ products was excellent, over 80 wt.% under favorable reaction conditions. The catalyst produced more C_{20}^+ hydrocarbons than would be expected by the Schultz-Flory carbon distribution rule. As a result, the C_5^+ product collected was mostly solid, reflecting the high boiling range and the high n-paraffin content of the hydrocarbons produced. As the reactor temperature was increased, the product selectivity tended more towards lighter products and more methane. It was not until the reaction temperature was increased to 340°C, with almost 40 wt.% of the product being methane, that the liquid hydrocarbons produced were such that the pour point was below room temperature, i.e., the condensed product was all liquid instead of partly solid.

A Task 2 catalyst was prepared by the physical mixture of the reference Fischer-Tropsch catalyst used above and the large pore UCC-101. This catalyst, in contrast to the reference catalyst, did not produce the excess C_{20}^+ products. Here, the hydrocarbons were isomerized and the pour points of all condensed samples were below room temperature. Conditions were adjusted to obtain excellent selectivity to gasoline, 50 wt.%, and total motor fuel, 70 wt.%. The high selectivity was achieved with this catalyst, however, at a relatively low activity level. Importantly, the product distribution of two runs showed signs of a carbon number cut off (shape selective effect). Thus, this experiment demonstrated the efficiency of UCC-101 as SSC component in that it isomerized the hydrocarbons formed on the MC resulting in substantial improvement of the motor fuel products, and it also seemed to show a cut-off at the end of the motor fuel boiling range (C_{20}). Both of these properties are essential for an efficient catalyst applied for the direct conversion of syngas.

Two additional molecular-sieve-containing, unpromoted iron catalysts had excellent selectivity to gasoline, 50 wt.%, and produced little material that boiled above that range.

TASK 3

In work carried out in California under the direction of Professor G. A. Somorjai (U.C. Berkeley), catalysts were synthesized of rhodium, rhodium compounds and thoria. Data are presented in Appendix D on reaction rates and product distributions in their micro-reactor, used in the flow mode. Rhodium metal is shown to be an effective methanation catalyst.

V. CHANGES

Mod A007 was executed, increasing obligation to the fully funded level of $2,384,850.

VI. FUTURE WORK

Effort in the next quarter will be concentrated very strongly on Task 2 testing, using both bays for such tests. The work will have three foci: evaluating new molecular sieves, testing different metal-loading techniques, initiating tests with cobalt as the metal component in the catalyst.

R. C. Eschenbach

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Appendix A: Catalyst Synthesis

P. K. Coughlin
F. P. Gortsema

Task 1 catalyst syntheses this quarter have proceeded along two distinct lines. The first was to complete a series of modifications of well known zeolites. These materials have been used to define the important parameters in Task 1 testing. The results also establish standards against which the new molecular sieves will be compared. Many of these materials have been tested already. Others will be included later in the project if more comparison data are thought to be needed. The sodium-exchanged omega zeolite (synthesized last quarter) was used as a starting material for a partially acid form of the zeolite. An acidity series was also synthesized using potassium L zeolite. The previously known zeolite catalysts synthesized this quarter also included a ZSM-5 and LZ-Y82.

The second type of Task 1 catalyst synthesized this quarter used new molecular sieves. $AlPO_4$-11 which was synthesized last quarter was chemically modified to try to introduce catalytic activity into the otherwise inactive molecular sieve. This material will be tested for Task 1 catalytic activity next quarter. Two other new molecular sieves, UCC-107 and UCC-108, were introduced into the program this quarter. One of them, UCC-107, was tested and the results of the testing are reported in Appendix C. The UCC-108 will be tested and the results reported next quarter.

The synthesis of Task 2 catalysts has proceeded along a number of lines. Most of this work has centered around the investigation of the effects of various modes of metal loading to determine the advantages of each method and determine which is optimal. Previously, most of the catalysts had used precipitation of the iron onto the molecular sieve. A new batch of iron precipitated on UCC-101 was prepared. This time it was potassium-promoted by the impregnation of potassium carbonate solution to give ∿1% K_2O. This catalyst was tested at the end of this quarter and the results will be reported next quarter.

Another mode of metal loading strongly pursued this quarter is a simple physical mixture of the metal component and the molecular sieve which is then pressed into a tablet with no binder. Some potassium-promoted reference iron catalyst, from the same lot that was tested last quarter in Run 10011-6, was ground into powder, physically mixed with UCC-101 powder, and pressed into tablets. A similar catalyst was prepared from a precipitated iron powder source. The $Fe_2O_3 \cdot XH_2O$ was synthesized by the fast addition of aqueous ammonia to a boiling solution of the nitrate. The washed and dried precipitate was impregnated with 1% K_2O from K_2CO_3 solution and dried again. The iron powder was ground slightly, intimately mixed with UCC-101 powder, pressed into pellets and air calcined at 250°C. The results of testing these last two catalysts are reported in Appendix C. This second iron component was also physically mixed with UCC-104 and formed into a catalyst using the same procedure as before. This catalyst was tested this quarter but the results of the testing will be reported next quarter. A reference catalyst of this type will be synthesized (and tested next quarter): the same metal component will be mixed with 1μ particle size α alumina and formed as before. This material should have the properties of the last two catalysts except for the catalytic activity of the molecular sieves.

The other method of metal incorporation which has been pursued is occlusion. This method uses volatile metal compounds which are adsorbed into the molecular sieve and then decomposed inside the molecular sieve. So far the metal carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$ and $Mn_2(CO)_{10}$ have been used as the volatile metal compounds.

One of these catalysts, 10% (4Mn:1Fe) in UCC-103, was tested for Fischer-Tropsch synthesis activity. The results of that test, reported last quarter, showed the extruded product to be almost completely inactive. It had been suggested last quarter that the metal component may have been damaged during the extrusion process. The basis for this suggestion was that the metal-loaded molecular sieve powder was tested in Professor Somorjai's lab and found to be an active catalyst, while the alumina bonded extrudate made from that powder was completely inactive. TEM/XPS analysis showed differences in the metal components before and after the alumina bonding. The 480°C calcination used to set the alumina binder was not the cause for the change in the metal components. The surface of the metal-loaded powder had a manganese to iron ratio of 7.0. When this powder was calcined in air, the manganese to iron (Mn:Fe) ratio dropped slightly to 6.2. This was caused by a slight loss of manganese from the surface. The Mn:Fe ratio on the surface of the calcined extrudate was very low, 3.7. The pulverized pellet had a Mn:Fe ratio of 2.0. When the metal components were indexed to an element in the molecular sieve, it is seen that the manganese concentration was the same as in the calcined powder. The surface iron concentration was 2 to 3 times higher than that on the calcined powder. The alumina bonding process removed iron from the inside of the molecular sieve and brought it to the exterior of the molecular sieve particle.

Not only had the concentration of the iron changed, so had its chemical state. This change was shown by analysis of the binding energies of the XPS photoelectrons which are reflections of the chemical environments in the systems. The binding energies of the manganese photoelectrons changed very little from the powder to the calcined extrudate. While this indicated that the chemical environment of the manganese changed little, it did not reveal the oxidation state of the iron. The binding energy of the $Mn2p^3/_2$ photoelectron does not correlate well with the oxidation state of the manganese between Mn^{2+}-Mn^{4+}. The energy separation (splitting) of the two Mn3s photoelectrons does correlate well with oxidation state. While this splitting was observed in samples synthesized by precipitation of a manganese salt, it was not observed in any of the samples dervied from manganese carbonyl. The normal causes for this kind of behavior (lack of two observable Mn3s lines) were ruled out: possible CO ligands by the IR spectrum, metallic state by the high $Mn2p^3/_2$ photoelectron binding energy. The cause of this lack of two Mn3s photoelectron binding energies and the exact Mn oxidation state are still unknown.

The $Fe2p^3/_2$ photoelectron binding energy correlates much better with changes from Fe^{2+} to Fe^{3+}. The calcined powder had an $Fe2p^3/_2$ binding energy of 711.4 e.v. This value is fairly typical of Fe^{3+} compounds. The $Fe2p^3/_2$ binding energy of the extrudate was 712.4 e.v. This value was outside the range normally seen for Fe^{3+} and indicated a significant change in the iron's chemical state. This high binding energy may be due to interaction with the alumina support.

From this surface analysis, it is evident that the alumina bonding process had little effect on the manganese but a large effect on both the concentration and the chemical state of the iron. The bonding process seems to have brought the iron out of the molecular sieve and possibly out onto the binder. The lack of activity of this extruded catalyst is tentatively attributed to these changes in the iron. While these results do not rule out the use of metal carbonyls as a source of metallic components, they do suggest that such materials should not be alumina-bonded.

Synthesis of Task 2 catalysts has also proceeded along another line. All previous Task 2 catalysts were based on iron as the metal component. Catalysts have now been prepared using cobalt as the metal component. The modified porefilling technique used an aqueous/acetone solution of the nitrate to deliver the cobalt to the alumina-bonded extrudate. The excess liquid was removed on a rotary evaporator. The molecular sieves used so far in this type of catalyst were silicalite and UCC-101. A silica-alumina extrudate was also used to act as a reference for this type of catalyst. In the future the cobalt catalysts will be promoted with thoria.

The catalyst synthesis is still in an exploratory phase, investigating several avenues. The results reported in this quarter and next quarter should start to show which options are most viable so that synthesis can be concentrated on those materials and methods which gave the best results in the exploratory phase.

A description of the catalysts tested and/or reported this quarter is given in Table 1.

TABLE 1

CATALYSTS TESTED AND OR REPORTED THIS QUARTER

TASK 1

NaY-62 10% H-Y62 40% H-Y62	These are a series of large pore zeolites with a three-dimensional pore structure, which were first cation exchanged 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.
Ca-Y62 and RE-Y62	The sodium cation exchanged form of Y was subsequently cation exchanged with a polyvalent ion.
LZ-Y82	The steam-stabilized acid form of Y zeolite.
LZ-105-6	A Union Carbide medium pore molecular sieve with a pore structure similar to ZSM-5 and SiO_2/Al_2O_3 ratio of about 35.
ZSM-5	A medium pore molecular sieve synthesized at Tarrytown based on procedures described by Mobil Oil, with SiO_2/Al_2O_3 ratios of 35 and 85.
UCC-103	The acid extracted form of UCC-101.
UCC-106	A new large pore molecular sieve having moderate acidity.
UCC-107	A new Union Carbide proprietary molecular sieve.

TASK 2

ference Fe	An unsupported potassium-promoted iron catalyst.
-Y52	20% iron as $Fe_2O_3 \cdot XH_2O$ precipitated on sodium LZ-Y52.
C-201	A catalyst with ~40% iron as $Fe_2O_3 \cdot XH_2O$ precipitated from a nitrate slurry with UCC-101.
ppt-UCC-101+K	Similar to UCC-201 but the metal loaded molecular sieve was impregnated with K_2CO_3.
M.-Ref. Fe-UCC-101	The potassium promoted reference iron catalyst ground up, physically mixed with UCC-101 powder and pressed into tablets.
M.-Fe-UCC-101	Similar to the previous catalyst except the source of iron was potassium promoted precipitated $Fe_2O_3 \cdot XH_2O$.
M.-Fe-UCC-104	Same as the previous catalyst except the molecular sieve used was UCC-104.

APPENDIX B - DEVELOPMENT OF ANALYTICAL PROCEDURES

J.M. Basile

A reliable analytical method for quantitatively determining hydrocarbon group-types in LHF samples is still pending.

As reported last quarter, result discrepancies of duplicate samples submitted for analysis made the FIA method suspect. To determine whether this was an "in house" analytical problem, twelve LHF samples (6 pairs of duplicates) were sent to E.W. Saybolt Testing Company for FIA analyses. The reproducibility and "probable " accuracy of Saybolt's results were just as suspect as results obtained by our analytical laboratory. Although reasons for these discrepancies cannot be fully explained, we have found that most of our LHF samples have a natural fluorescence under U.V. light. This may be contributing to, or masking the color bands of the FIA test.

Liquid chromatography as an alternate to FIA analysis has not materialized. Perkin-Elmer has advised us, after many attempts, that present column technology is not suitable to the wide boiling range of our samples. At present, the best that can be done is separation into two fractions - a combination saturates plus olefins fraction and an aromatics fraction.

APPENDIX C

CATALYST TESTING

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

CONTENTS

INTRODUCTION

Both Berty reactors were in operation for this quarter. Each of the bays is equally capable of either Task 1 or Task 2 operation. During the quarter, Bay 2 was used exclusively for Task 1 operation. The Task 1 tests performed in Bay 2 this quarter used the standard test conditions which were defined from the previous quarters tests. A 1:1:2, H_2:C_3H_6:H_2O, molar ratio feed was introduced into the reactor at 0.5 WHSV. Temperature was the only process condition altered during the testing.

Bay 1 was used exclusively for Task 2 operation. Six such tests were conducted this quarter. Some of these tests were quite extensive. The effects of many different process condition changes were studied. These effects were investigated in the early tests to better define the appropriate conditions for the standard task 2 tests. These standard conditions along with standard activation conditions were defined for iron based catalysts. Use of a different metal component is likely to necessitate at least slight changes in these standard conditions.

INTRODUCTION TO TASK 1 TESTING

The results from seven Task 1 tests are reported this quarter. One micro-reactor test from last quarter, three Berty reactor runs begun last quarter, 9972-8 to -10, and three Berty reactor runs from this quarter, 9972-13 to -15, are all presented in this report. In addition four other tests were conducted in the Berty reactor this quarter but their results will be discussed in the next report because not all the analytical data are available yet.

A standard catalyst test has been developed. The propylene is introduced at 0.5 WHSV in a 1:1:2 $H_2:C_3H_6:H_2O$ molar ratio feed. The reactor is maintained at 150 psig. At least two reaction temperatures, 280°C and 340°C, are used. Temperatures of 250°C and 370°C are also frequently included depending upon the activity of the catalyst. Generally the catalyst is tested for two days at each temperature. The time before the next temperature increase is shortened if the catalyst has low activity or rapid deactivation.

The calculations used are the same as described previously. Analysis of the liquid samples has remained a problem as described in the analytical section. The liquid samples fluoresce so strongly that FIA analysis is meaningless. For the present the density and refractive index are used to estimate the percentage of aromatics. The densities and refractive indices of paraffins and olefins with the same carbon number are similar. An aromatic with the same boiling point has a very different density and refractive index. First the simulated distillation is used to obtain an average boiling point of the liquid. An average density and refractive index is calculated from the normal paraffin and olefin with that boiling point. The density and refractive index of the methylated aromatic with the same boiling point is also found. Two equations are set up assuming that the densities and refractive indices are additive. Each one is solved separately for the percentage of aromatics. These two percentages are often close in value; when this is so, the fraction of aromatics is considered to be measured accurately. When the numbers differ, the percentage based on refractive index follows other trends in the samples better than on the one based on density. In these cases the number based on refractive index is used; it is not considered as reliable as when the two numbers almost coincide.

Run 9972-8: UCC-103

UCC-103 is the product of acid extraction of UCC-101. The acid extraction was intended to give UCC-103 even milder acidity than UCC-101. The results of this run are probably best compared to those of 9972-4, which was reported last quarter. The differences in these two runs should show the effect of the acid extraction. There is only a slight difference in the reaction conditions between these two runs. Run 9972-4 had a 1:1:3 H_2:C_3H_6:H_2O mole ratio feed. Run 9972-8 had a 1:1:2 feed. The effect of this difference in water levels should be minor. The direction of the change can be seen for the results of earlier runs with feed ratio of 1:1:0. Some of the comparisons of these early runs with Run 9972-4 were discussed last quarter and will not be repeated here.

The detailed results of the testing are reported in Table 1. Plots of the conversion and product selectivity versus time on stream are presented in Figures 1 and 2. Simulated distillation plots for samples 1,2,3 are given in Figures 3 to 5. This catalyst was tested at the standard conditions previously described. The time at each temperature was shorter than the usual two days because of the low activity of the catalyst. There were no gas chromatographic analyses for samples 3 and 5. Therefore sample 4 is the only completely independent analysis of the activity of the catalyst at 340°C.

The catalytic activity of UCC-103 was very low, as expected. The level of conversion was similar to that seen with UCC-101. Deactivation of the catalyst was observed in spite of the short duration of this test. The deactivation rate for UCC-103 may be slightly less than that of UCC-101 but with samples 3 and 5 being estimates, this is not certain.

The product selectivity was very different from that of UCC-101. While neither catalyst showed significant cracking to C_1 or C_2 products, UCC-103 produced even less than UCC-101. The largest difference in the selectivity was in the C_3 and C_4 saturates formation. Selectivity to butane was up slightly but propane was down drastically. The selectivity to combined C_3 and C_4 saturates was less than half of what it was with the UCC-101 catalyst. These saturates, in particular propane, are formed by hydride transfer to the corresponding olefin. The hydride transfer activity was much lower in UCC-103 than it had been in UCC-101. This lowering of the propane production was the major reason for the increase in C_5^+ yield with UCC-103 the C_5^+ yield increased 35% at 280°C and 50% at 340°C relative to UCC-101. Very little of the C_5^+ product was actually condensed. Most of it was analysed in the gas phase; much of that in the backflush peak in the G.C. which probably contained C_6 to C_{12} hydrocarbons. It appeared from the conversion and product selectivity data that the production of each hydrocarbon remained fairly constant throughout the test with only slight differences between samples taken at 280°C and those at 340°C. The simulated distillation of the condensed liquid products revealed that this was not the case. Sample 1 had a broad smooth distillation curve with no distinguishable amounts of C_9 or C_{12} hydrocarbons. The other samples did show large amounts of C_9 and C_{12} hydrocarbons in the distillation. These samples also showed a significantly narrower boiling range and much lighter product. The refractive index of the condensed product of sample #2 suggested the product contained 30% aromatics. Since these condensed liquid samples were at most 7% of the total hydrocarbons and 10% of the C_5^+ product, the differences between the samples were not quite as large as the analysis of the condensed products may have suggested.

The UCC-101 and UCC-103 were similar in their catalytic activity. There were however, major differences in their product selectivity. UCC-103 produced less light saturates because of reduced hydride transfer activity. The lower light saturates production led to a high selectivity to C_5^+ with UCC-103.

TABLE 1 RESULT OF PROPYLENE OPERATION

RUN NO. 9972-8
CATALYST UCC LO3 #9939-46 76 CC 35.00GM (34.72GM AFTER THE RUN, -0.28GM)
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 34.30CC/HR H2 150 CCMN, 9.0 L/HR H2O 15 CC/HR
ACTUAL FLOW: 34.4 CCHR EFFLUENT 15.23 L/HR AQ LAYR 14 CC/HR

RUN & SAMPLE NO.	9972-08-1	9972-08-2	9972-08-3	9972-08-4	9972-08-5
C3H6 WHSV	0.5	0.5	0.5	0.5	0.5
HRS ON STREAM	6.8	23.0	30.6	48.9	54.7
PRESSURE,PSIG	150	143	144	150	140
TEMP. C	283	281	341	338	338
FEED C3H6 CC	211.43	570.74	249.82	646.25	203.25
HOURS FEEDING	6.8	16.1	7.6	18.3	6.0
EFFLNT GAS LITER	98.6	243.6	112.8	292.5	95.4
GM AQUEOUS LAYER	97.22	224.51	104.17	254.83	82.36
GM LIQ HYDROCARBON	0.78	1.46	2.93	1.66	0.54
WT FR. LIQ HC/FEED	.0072	.0050	.0230	.0050	.0052
MATERIAL BALANCE WT %	101.43	89.64	91.47E	88.51	93.73E
C3H6 CONVERSION %	10.56	7.66	13.21E	11.45	11.44E
PRDT SELECTIVITY WT %			NO GC		NO GC
CH4	0.04	0.07	0.09E	0.11	0.11E
C2 HC'S	0.05	0.06	0.13E	0.15	0.17E
C3H8	13.04	15.53	16.67E	19.63	19.63E
C4H10	5.29	3.39	3.68E	4.33	4.33E
C4H8=	7.66	7.89	6.75E	7.95	7.95E
C5H12	1.51	0.53	0.45E	0.53	0.53E
C5H10=	0.15	0.16	0.15E	0.18	0.18E
C6H14	12.51	9.50	7.14E	8.41	8.41E
C6H12= & CYCLO'S	15.09	22.07	24.51E	28.87	28.87E
C7+ IN GAS	37.74	33.49	21.13E	24.88	24.88E
LIQ HC'S	6.91	7.31	19.30E	4.96	4.95E
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	26.09	26.94	27.31E	32.17	32.17E
C5 -420 F	68.24	71.23	65.25E	66.24	65.60E
420-700 F	4.08	1.83	7.18E	1.49	2.08E
700-END PT	1.59	0.00	0.25E	0.09	0.15E
C5 -END PT	73.91	73.06	72.69E	67.83	67.83E

ISO/NORMAL MOLE RATIO					
C4	0.4781	0.2797	-	0.1035	-
C5	7.5735		-	1.0928	-
C6	13.9593	7.6118	-	3.7230	-
C4=	0.5747	0.5287	-	0.5354	-
PARAFFIN/OLEFIN M RATIO					
C2	0.6765	0.4074	-	0.8205	
C3	0.0149	0.0124	-	0.0245	
C4	0.6668	0.4149	-	0.5253	-
C5	10.0517	3.1957	-	2.8194	-
LTQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	TRACE OIL
DENSITY		0.802			
N,REFRACTIVE INDEX		1.4537			
SIMULATED DISTILLATION					
10 WT % @ DEG F.	356	273	283	263	NOT
16	410	281	302	277	
50	597	374	396	378	ENO-
84	732	450	492	491	
90	765	478	532	544	UGH
RANGE(16-84%)	322	169	190	214	
WT % @420 F	18.0	75.0	61.5	68.0	
WT % @700 F	77.0	100	98.7	98.1	

RUN NO. 9972–08

Figure 1

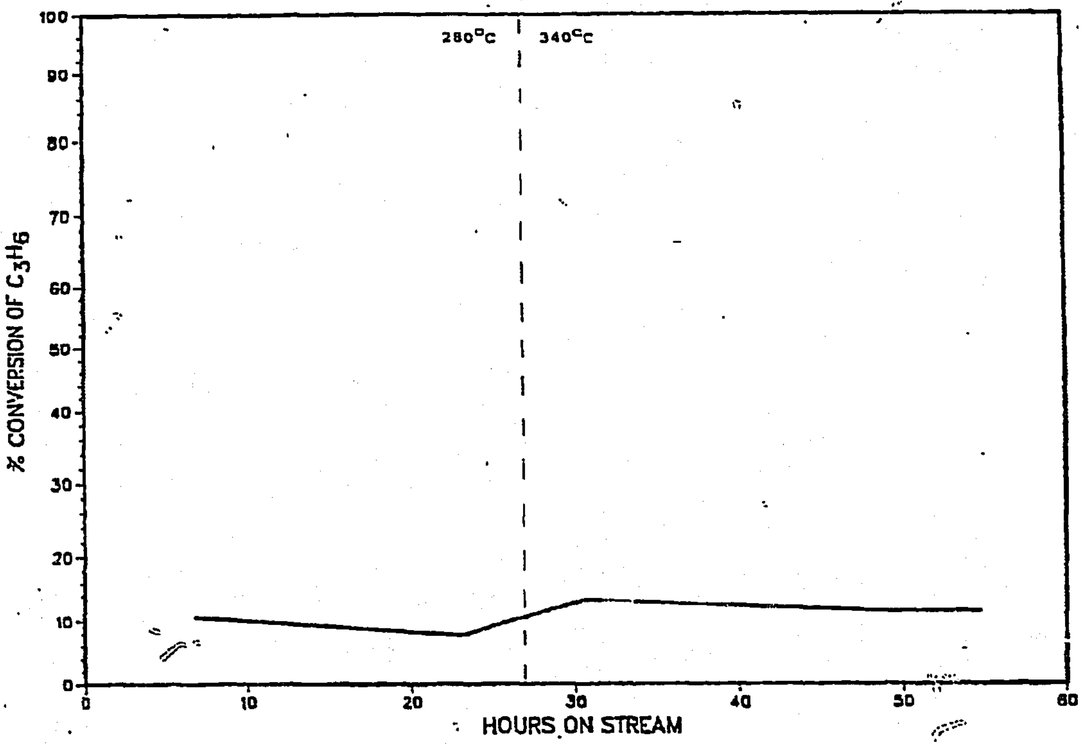


Figure 2

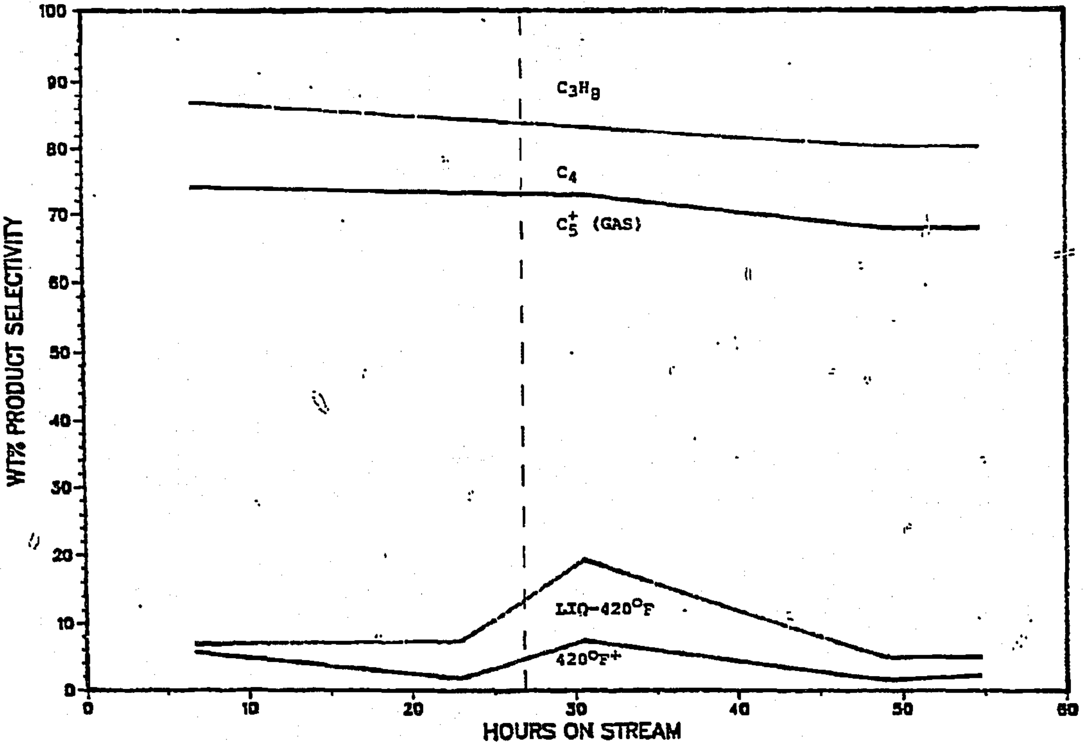
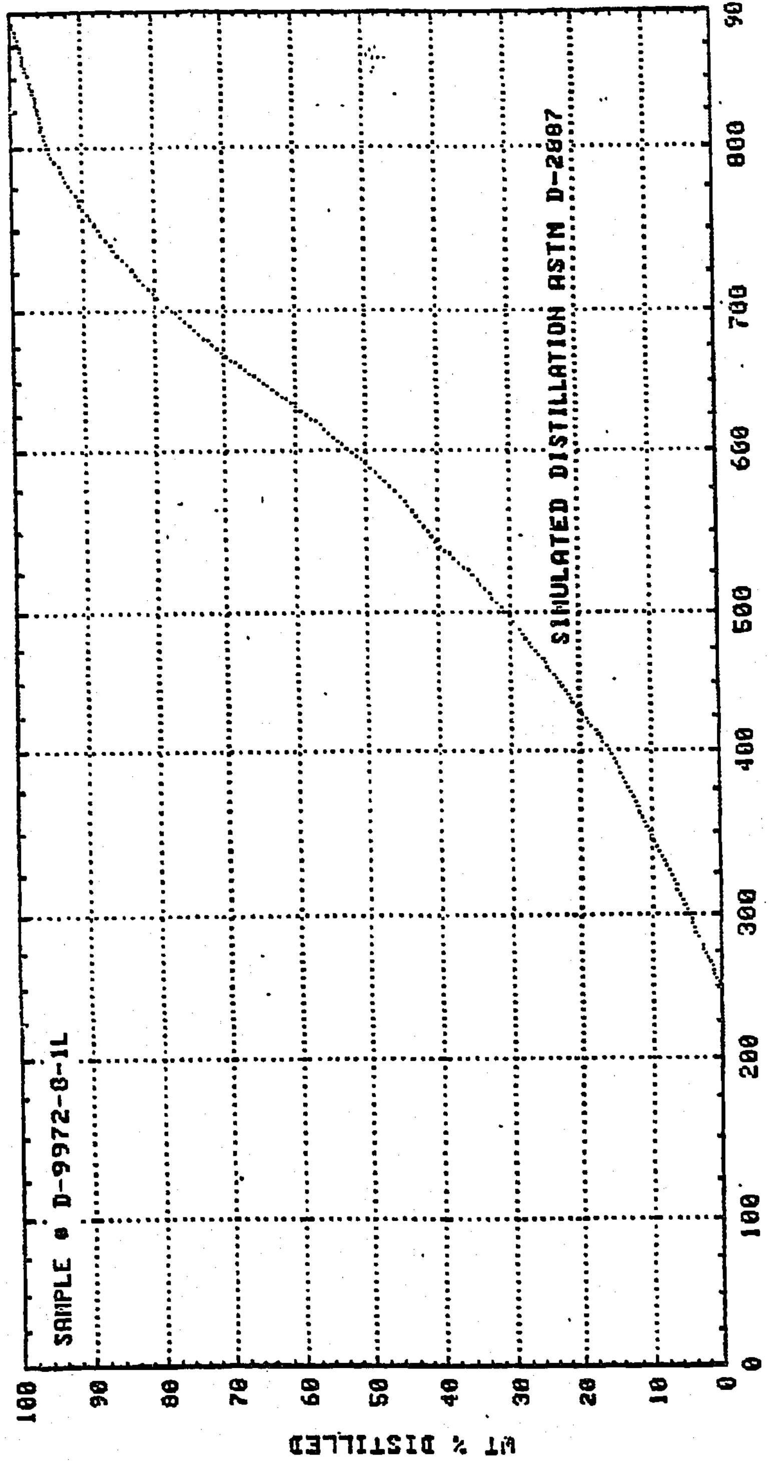


Figure 3



SAMPLE # D-9972-8-1L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
0
10
20
30
40
50
60
70
80
90
100
BOILING POINT (F)
0
100
200
300
400
500
600
700
800
900

Figure 4

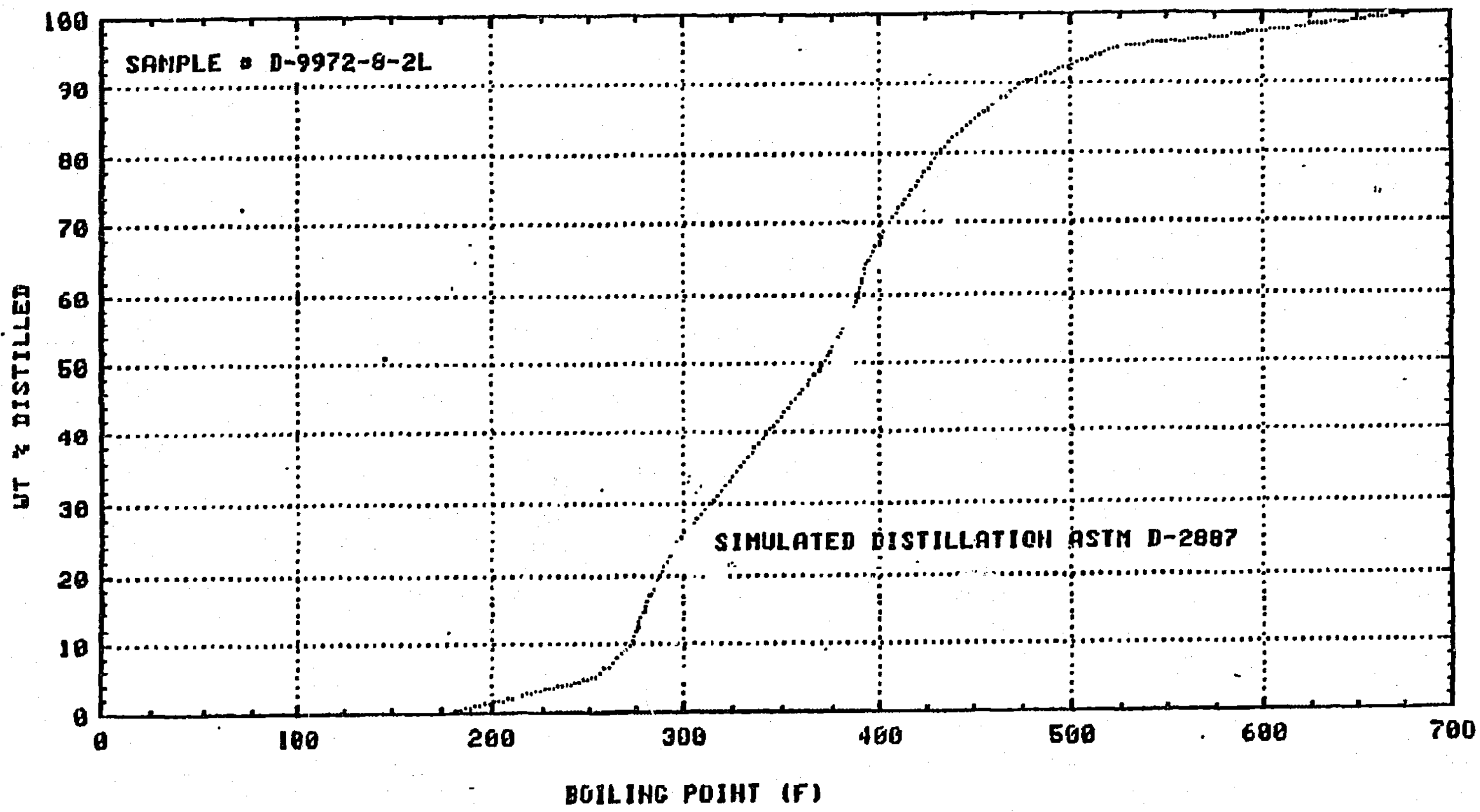
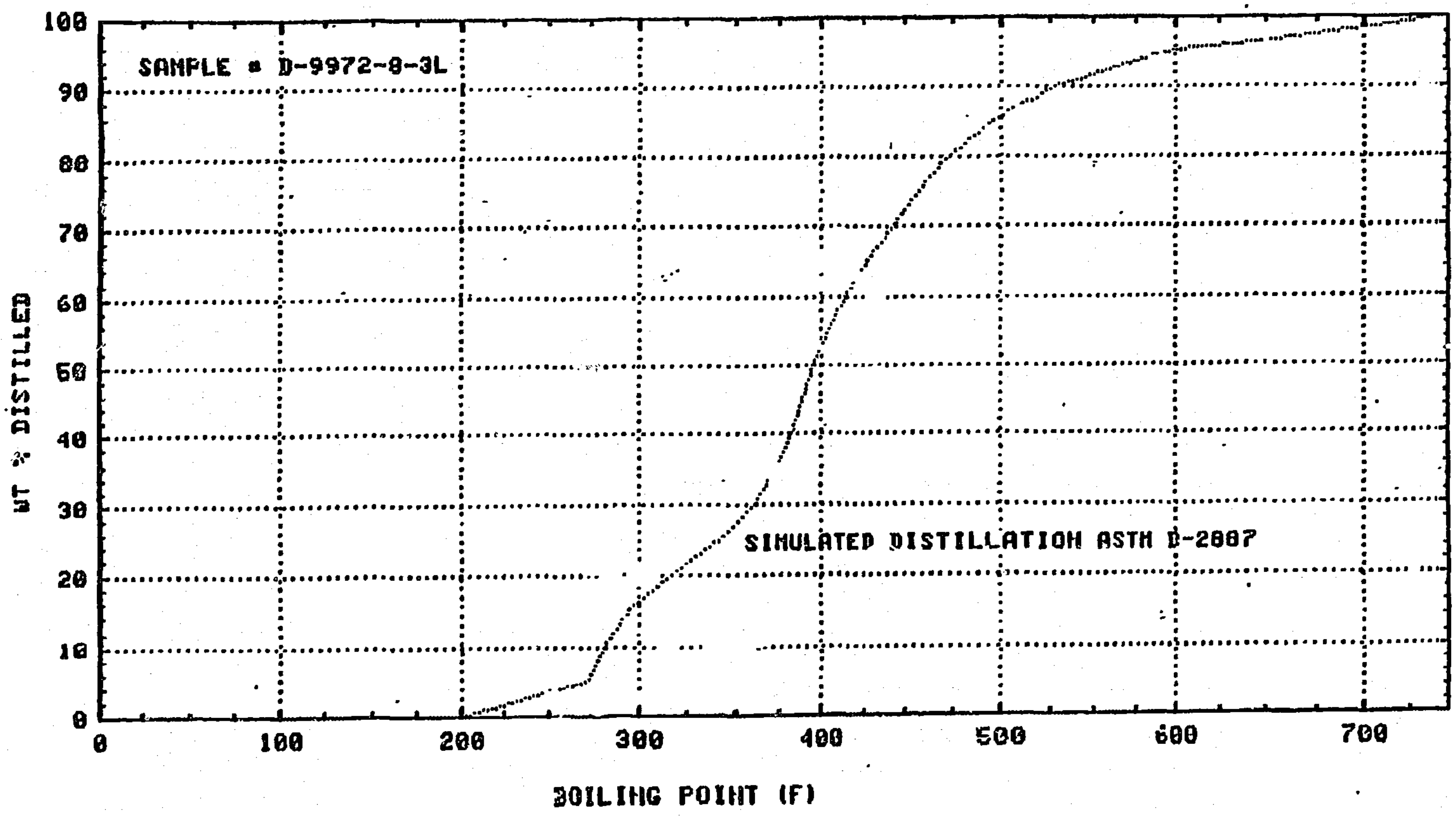

SAMPLE # D-9972-8-2L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
0
10
20
30
40
50
60
70
80
90
100
BOILING POINT (F)
0
100
200
300
400
500
600
700

Figure 5


SAMPLE = D-9972-8-3L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
100
90
80
70
60
50
40
30
20
10
0
BOILING POINT (F)
0
100
200
300
400
500
600
700

Run 9972-9: UCC-106

UCC-106 is a new, large pore molecular sieve of moderate acidity. In this respect, it should be similar to UCC-101 and UCC-103. Therefore, comparisons to those catalysts have been made in our study. The catalyst was tested for 1 day at 280°C. The temperature was then raised to 330°C overnight and to 340°C in the morning. It was tested at 340°C for 1 day before the test was terminated. The detailed results of the test are presented in Tables 2A and 2B. The conversion and product selectivity are plotted versus time on stream in Fugures 6 and 7. The simulated distillation of samples 1, 9 and 4 are presented in Figures 8 and 9. The experimental data was of high quality except for sample 2 which had a material balance of only 85%. Since the results of that sample are in line with those of adjacent samples, the calculated numbers are probably right.

With UCC-106 the initial conversion of 17% was much higher than that of UCC-101 or UCC-103 but the deactivation rate was also higher. The product selectivity seemed to be intermediate between those of UCC-101 and UCC-103. The propane formation was lower than that observed with UCC-101. This lower propane formation was also reflected in the higher C_5^+ yield with UCC-106. In contrast UCC-101 and UCC-103, the C_5^+ yield with UCC-106 did not decrease upon raising the reactor temperature to 340°C. The refractive index of sample 1 suggests that it contained 15% aromatics. The simulated distillation curve for sample 1 revealed large amounts of C_9 and some C_{12} hydrocarbons. However, the products dropped off rapidly beyond C_{12}, indicating molecular sieve effect. Sample 4 had a much smoother distillation curve. The liquid also contained much heavier hydrocarbons.

Because of the low activity and rapid deactivation, UCC-106 is not considered to be an efficient catalyst for propylene oligomerization.

The UCC-106 has some catalytic properties similar to UCC-101. The conversion and deactivation data suggests that UCC-106 is more acidic than UCC-101. The product selectivity data suggests that UCC-106 is intermediate in properties between UCC-101 and UCC-103.

TABLE 2A RESULT OF PROPYLENE OPERATION

RUN NO. 9972-9 (LZ 20)
CATALYST UCC- LO6 #9939-35 56 CC 35.0 GM(35.77GM AFTER THE RUN, +0.77GM)
FEED H_2:C_3H_6:H_2O @1:1:2 MOLE RATIO,0.5 C_3H_6 WHSV,CONTINOUS OVERNITE
C_3H_6 MW- 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C_3H_6 34.33CC/HR H_2 150 CCMN, 9.0 L/HR H_2O 15. CC/HR
ACTUAL FLOW: 34.83 CCHR EFFLUENT 16.43 L/HR AQ LAYR 13.9 CC/HR

RUN & SAMPLE NO.	9972-09-1	9972-09-2	9972-09-3	9972-09-4	9972 09-5
C_3H_6 WHSV	0.5	0.5	0.5	0.5	0.5
HRS ON STREAM	5.6	21.7	27.4	45.9	53.2
PRESSURE,PSIG	164	141	143	143	147
TEMP. C	282	283	282	329	342
FEED C_3H_6 CC	201.99	558.78	201.36	655.06	251.07
HOURS FEEDING	5.6	16.3	5.75	18.5	7.33
EFFLNT GAS LITER	84.6	263.5	96.4	303.4	117.8
GM AQUEOUS LAYER	72.7	227.56	79.53	257.46	101.41
GM LIQ HYDROCARBON	2.68	0.25	0.70	1.24	1.19
WT FR. LIQ HC/FEED	.0260	.0009	.0068	.0037	.0093
MATERIAL BALANCE WT %	90.36	85.70	100.20	89.11	92.55
C_3H_6 CONVERSION %	17.23	7.37	6.20	8.59	11.41
PRDT SELECTIVITY WT %					
CH_4	0.07	0.05	0.21	0.14	0.17
C2 HC'S	0.13	0.14	0.14	0.23	0.26
C_3H_8	20.52	32.65	26.88	26.37	23.29
C_4H_{10}	4.51	7.42	8.88	6.42	5.52
C_4H_8=	6.48	10.53	11.73	8.42	11.78
C_5H_{12}	1.60	0.62	1.21	0.38	2.81
C_5H_{10}=	0.14	0.13	0.14	0.19	1.12
C_6H_{14}	9.80	5.71	4.42	4.67	5.62
C_6H_{12}= & CYCLO'S	13.21	21.82	19.24	28.75	24.75
C7+ IN GAS	26.39	19.55	15.99	19.61	15.81
LIQ HC'S	17.15	1.38	11.16	4.82	8.89
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	31.71	50.80	47.84	41.59	41.01
C5 -420 F	64.40	48.89	49.62	55.76	54.10
420-700 F	3.77	0.30E	2.46E	2.47	4.55E
700-END PT	0.12	0.01E	0.08E	0.18	0.34E
C5 -END PT	68.29	49.20	52.16	58.41	58.99

```
ISO/NORMAL MOLE RATIO
  C4                   0.5793     0.0538     0.0527     0.0610     0.0634
  C5                  21.1778     4.9583    16.6667     2.0857     1.6364
  C6                  16.7875     5.7500     4.5479     2.5316     3.1073
  C4=                  0.3896     0.3768     0.3337     0.4550     0.3566

PARAFFIN/OLEFIN M RATIO
  C2                   0.1444     0.6800     0.7273     0.7423     0.3175
  C3                   0.0415     0.0253     0.0173     0.0241     0.0291
  C4                   0.6723     0.6806     0.7310     0.7367     0.4525
  C5                  10.9670     4.7667     8.2812     1.9286     2.4442

LTO HC COLLECTION
  PHYS. APPEARANCE       OIL
  DENSITY              0.769
  N.REFRACTIVE INDEX   1.4353
  SIMULATED DISTILLATION
    10 WT % @ DEG F.     267                            326
    16                   275                            363
    50                   344                            429
    84                   451                            555
    90                   490                            610

    RANGE(16-84%)        176                            192

    WT % @420 F         77.3                           45.0
    WT % @700 F         99.3                           96.2
```

TABLE 2B RESULT OF PROPYLENE OPERATION

RUN NO. 9972-9 (LZ-20)
CATALYST UCC 106 #9939-35 56 CC 35.0 GM (35.77GM AFTER THE RUN, +0.77GM)
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 34.33CC/HR H2 150 CCMN, 9.0 L/HR H2O 15. CC/HR
ACTUAL FLOW: 34.83 CCHR EFFLUENT 16.43 L/HR AQ LAYR 13.9 CC/HR

RUN & SAMPLE NO.	9972-09-6	9972-09-7
C3H6 WHSV	0.5	0.5
HRS ON STREAM	70.7	77.1
PRESSURE,PSIG	148	145
TEMP. C	337	338
FEED C3H6 CC	616.67	200.10
HOURS FEEDING	17.4	6.3
EFFLNT GAS LITER	290.1	100.9
GM AQUEOUS LAYER	244.89	88.56
GM LIQ HYDROCARBON	0.0	0.0
WT FR. LIQ HC/FEED	.0000	.0000
MATERIAL BALANCE WT %	92.50	96.96
C3H6 CONVERSION %	6.26	6.93
PRDT SELECTIVITY WT %		
CH4	0.14	0.19
C2 HC'S	0.24	0.23
C3H8	26.91	26.55
C4H10	5.39	7.40
C4H8=	8.75	9.85
C5H12	0.30	0.31
C5H10=	0.17	0.16
C6H14	4.86	4.85
C6H12= & CYCLO'S	33.01	32.34
C7+ IN GAS	20.23	18.11
LIQ HC'S	0.00	0.00
TOTAL	100.00	100.00
SUBGROUPING		
C1 -C4	41.42	44.23
C5 -420 F	58.58	55.77
420-700 F	0.00	0.00
700-END PT	0.00	0.00
C5 -END PT	58.58	55.77

```
ISO/NORMAL MOLE RATIO
  C4                    0.0589      0.0418
  C5                    2.7059      1.8000
  C6                    2.1801      2.2332
  C4+                   0.4663      0.4328

PARAFFIN/OLEFIN M RATIO
  C2                    0.6000      0.7179
  C3                    0.0174      0.0192
  C4                    0.5948      0.7251
  C5                    1.6579      1.8421

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 NO. 9972-09

Figure 6

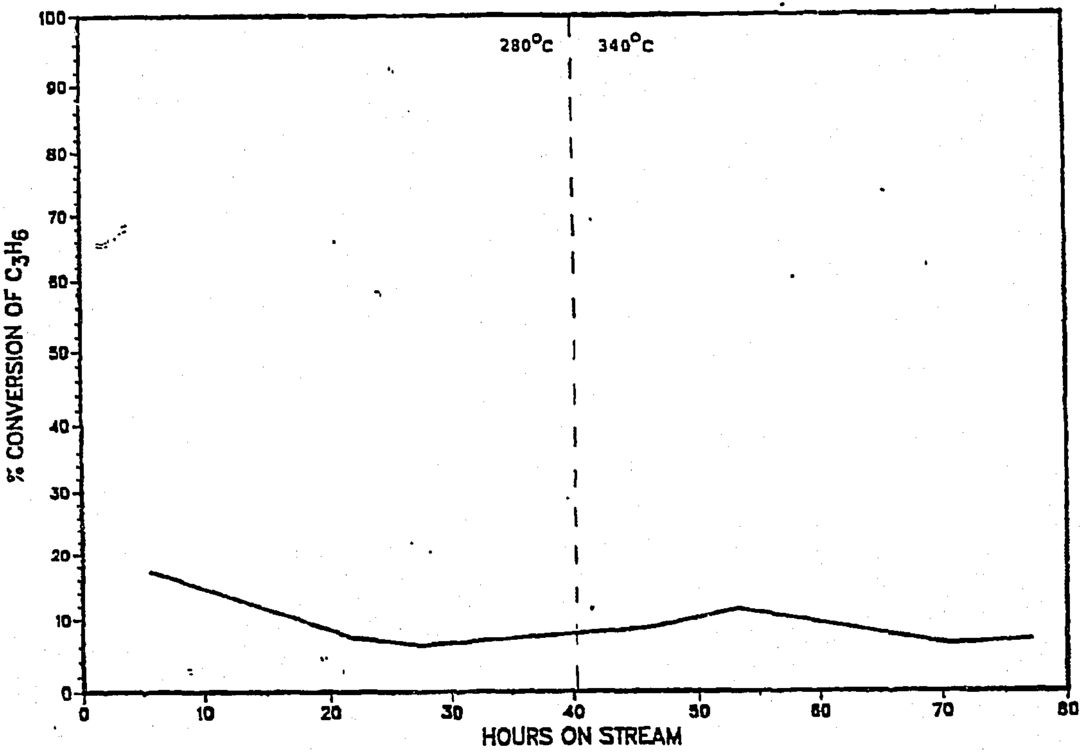


Figure 7

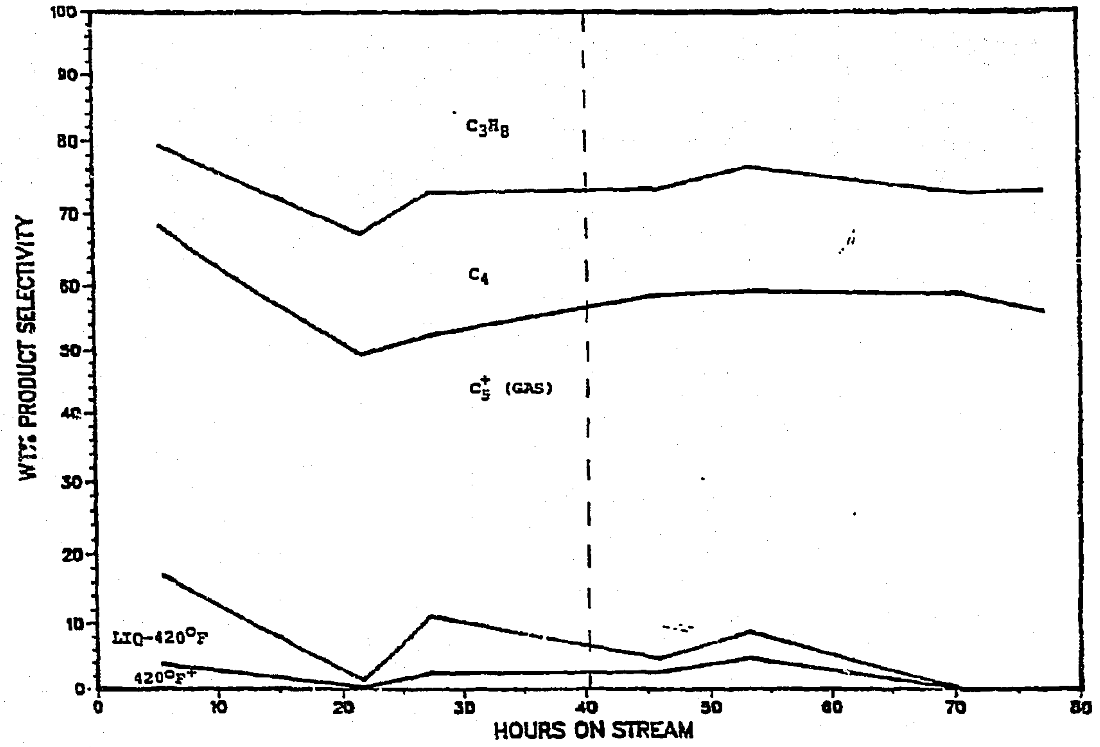


Figure 8

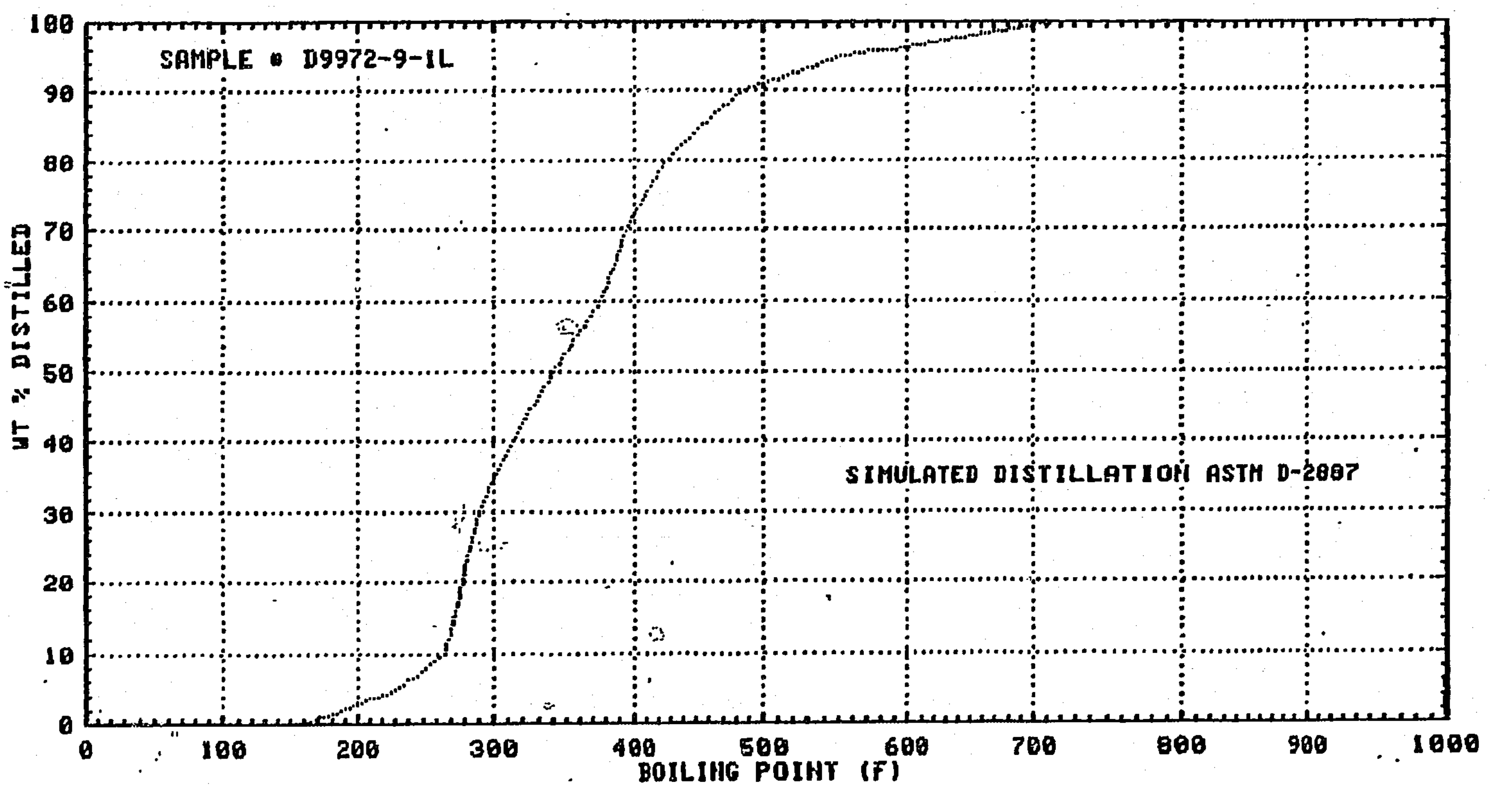
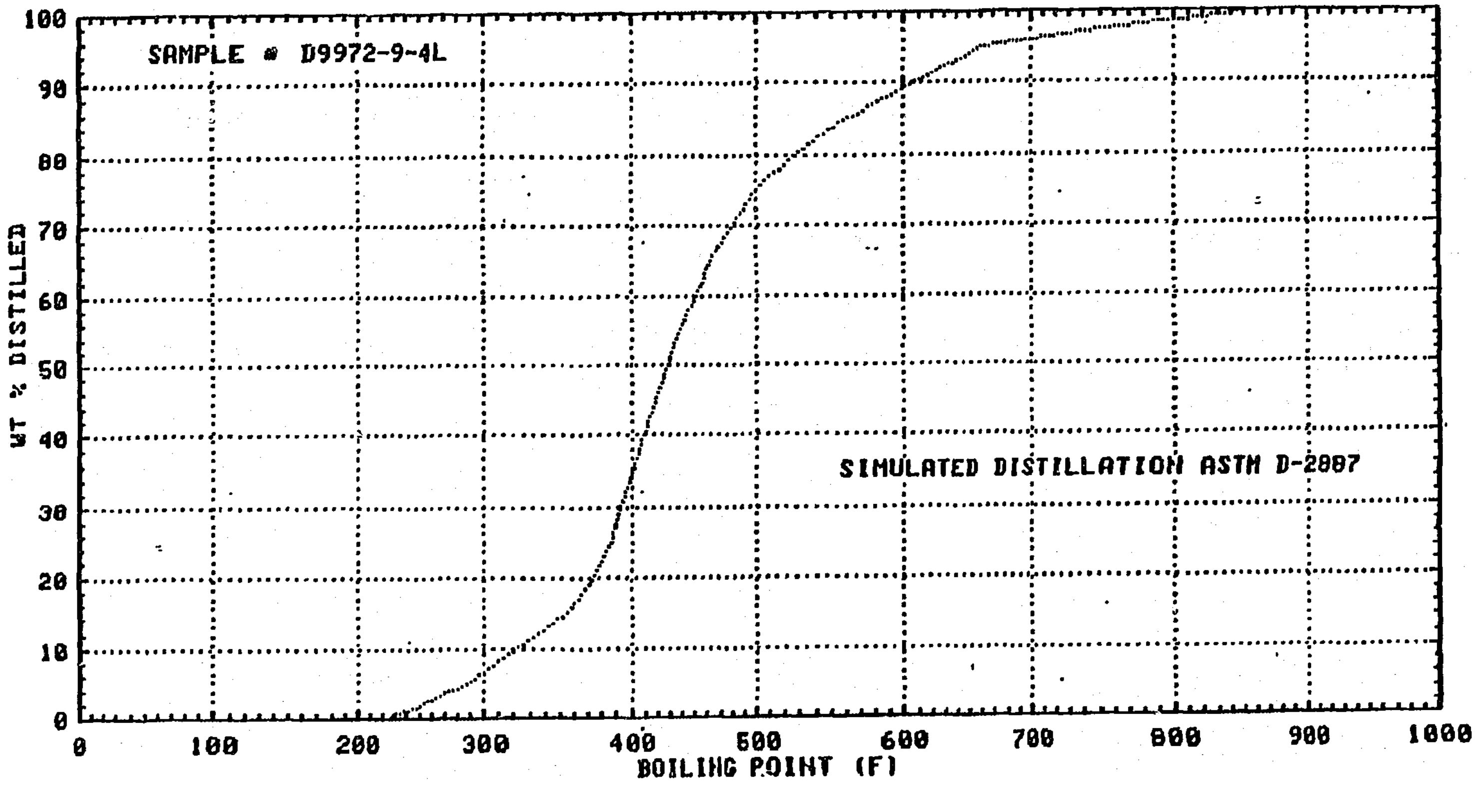

SAMPLE # D9972-9-1L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
0
10
20
30
40
50
60
70
80
90
100
BOILING POINT (F)
0
100
200
300
400
500
600
700
800
900
1000

Figure 9


SAMPLE # D9972-9-4L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
0
10
20
30
40
50
60
70
80
90
100
BOILING POINT (F)
0
100
200
300
400
500
600
700
800
900
1000

Run 9972-10: CaY-62

The catalyst was prepared by calcium exchange of sodium exchanged Y zeolite. Y zeolite is a large pore molecular sieve with a three dimensional pore structure. The acid forms of this zeolite were tested in a micro-reactor. Rare earth exchanged Y zeolite was tested in Run 9972-15. The results from both of these catalysts will be discussed later in this report. The subject catalyst, CaY62, was tested for 31 hours at 280°C. The temperature was then raised to 357°C overnight and adjusted to 340°C in the morning. The test was terminated after 30 hours at 340°C. The material balance, conversion and product selectivity data are presented in Tables 3A and 3B. Plots of the conversion and pr duct selectivity are given in Figures 10 and 11. The simulated distillations of the condensed products from Samples 1 and 2 are shown in Figures 12 and 13. Samples 2 and 6 are suspect because of low material balances. The elimination of those samples does not affect the evaluation of the catalyst.

The propylene conversion was quite low, similar to UCC-101. The rate of deactivation was even worse. Raising the temperature resulted in lower conversions because of rapid deactivation. The product selectivity to C_5^+ was poor due to the formation of large amounts of propane, up to 45% at 340°C. The C_5^+ yield decreased with the increased propane formation. The distillation of the condensed products from Samples 1 and 2 indicated that much of those materials boiled above the gasoline range. Unfortunately, this was an insignificant portion of the total hydrocarbon product.

The low activity and rapid deactivation with this catalyst make it of no further interest for LHF production. The generally bad performance of this catalyst is ascribed to its strong-acid nature.

TABLE 3A. RESULT OF PROPYLENE OPERATION

RUN NO. 9972-10
CATALYST CA-Y-62 #9939 37 55 CC 35.00GM(32.59GM AFTER THE RUN, -2.41GM)
FEED H2:C3H6:H2O @1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINOUS OVERNITE
C3H6 MW= 42.0813 DENSITY= 0.5104L GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 150 CC/MN, 9.0 L/HR H2O 15 CC/HR
ACTUAL FLOW: 34.4 CCHR EFFLUENT 15.3 L/HR AQ LAYR 13.9CC/HR

RUN & SAMPLE NO.	9972-10-1	9972-10-2	9972-10-3	9972-10 4	9972-10-5
C3H6 WHSV	0.5	0.5	0.5	0.5	0.5
HRS ON STREAM	7.42	23.7	30.7	48.0	53.6
PRESSURE,PSIG	145	146	146	140	145
TEMP. C	280	280	279	357	340
FEED C3H6 CC	245.41	569.48	237.23	608.93	184.37
HOURS FEEDING	7.417	16.333	7.00	17.25	5.5
EFFLNT GAS LITER	113.4	253.4	110.50	281.10	88.1
GM AQUEOUS LAYER	100.31	228.11	97.81	239.49	76.0
GM LIQ HYDROCARBON	1.58	0.94	0.00	0.00	0.0
WT FR. LIQ HC/FEED	.0134	.0032	.0000	.0000	.0000
MATERIAL BALANCE WT %	94.31	84.85	97.56	93.22	100.42
C3H6 CONVERSION %	10.47	9.14	5.99	2.45	2.38
PRDT SELECTIVITY WT %					
CH4	0.04	0.04	0.12	0.74	0.21
C2 HC'S	0.16	0.14	0.05	0.61	0.29
C3H8	20.32	25.71	30.44	37.97	34.21
C4H10	2.40	8.22	7.57	1.65	15.80
C4H8=	7.33	11.56	13.43	13.89	13.35
C5H12	1.79	1.74	3.85	0.33	2.18
C5H10=	0.18	0.22	1.58	0.00	1.07
C6H14	11.16	8.37	8.63	1.48	5.13
C6H12= & CYCLO'S	16.66	17.71	12.52	24.42	15.52
C7+ IN GAS	26.10	22.12	21.82	18.92	12.24
LIQ HC'S	13.86	4.16	0.00	0.00	0.00
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	30.25	45.68	51.60	54.86	63.85
C5 -420 F	64.69	52.14	48.40	45.14	36.15
420-700 F	4.85	2.02	0.00	0.00	0.00
700-END PT	0.21	0.17	0.00	0.00	0.00
C5 -END PT	69.75	54.32	48.40	45.14	36.15

ISO/NORMAL MOLE RATIO					
C4	3.2118	0.2095	0.4038	0.0732	0.0116
C5	29.6667	51.4000	25.4194	1.3333	1.6667
C6	16.0000	11.5238	9.2533	8.6364	32.0000
C4-	0.4181	0.3406	0.3934	0.0339	0.1338
PARAFFIN/OLEFIN M RATIO					
C2	0.3119	0.6923	0.5294	0.1176	1.1429
C3	0.0229	0.0251	0.0189	0.0093	0.0081
C4	0.3163	0.6867	0.5438	0.1148	1.1428
C5	9.9077	7.8209	2.3671	-	1.9785
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	TRACE OIL		
DENSITY	.	.			
N, REFRACTIVE INDEX	.	.			
SIMULATED DISTILLATION					
10 WT % @ DEG F.	281	333	---	---	---
16	298	364	---	---	---
50	393	425	---	--	---
84	491	538	---	---	---
90	535	606	---	---	---
RANGE(16-84%)	193	174	---	---	--
WT % @420 F	63.5	47.5	---	--	---
WT % @700 F	98.5	96.0	---	---	--

```
     TABLE 3B    RESULT OF PROPYLENE OPERATION

RUN NO.   9972-10
CATALYST CAY.62  #9939-37 55 CC 35.00GM (32.59GM AFTER THE RUN, -2.41GM)
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 150 CC/MN, 9.0 L/HR  H2O      15 CC/HR
ACTUAL FLOW:        34.43 CCHR  EFFLUENT      15.3 L/HR  AQ LAYR 13.9 CC/HR

RUN & SAMPLE NO.     9972-10-6 9972 10-7
                     ========= =========
C3H6  WHSV                0.5       0.5
HRS ON STREAM            71.6      77.6
PRESSURE.PSIG             144       146
TEMP.  C                  340       340

FEED C3H6 CC           618.56    207.66
HOURS FEEDING           18.08       6.0
EFFLNT GAS LITER       239.2       97.4
GM AQUEOUS LAYER       249.68     84.48
GM LIQ HYDROCARBON       0.00      0.00
WT FR. LIQ HC/FEED     .0000     .0000

MATERIAL BALANCE WT %   79.99     94.53
C3H6 CONVERSION %        1.78      2.15
PRDT SELECTIVITY WT %
  CH4                    0.38      0.15
  C2 HC'S                0.30      0.36
  C3H8                  45.31     39.99
  C4H10                  3.75     10.13
  C4H8=                  5.10      6.68
  C5H12                  0.00      3.10
  C5H10=                 0.00      0.51
  C6H14                  3.30      1.44
  C6H12= & CYCLO'S      30.32     29.10
  C7+ IN GAS            11.56      8.53
  LIQ HC'S               0.00      0.00

  TOTAL                100.00    100.00
  SUBGROUPING
    C1 -C4              54.83     57.31
    C5 -420 F           45.17     42.69
    420-700 F            0.00      0.00
    700-END PT           0.00      0.00
    C5 -END PT          45.17     42.69
```

```
ISO/NORMAL MOLE RATIO
  C4                      0.0493     0.0856
  C5                        -        0.5000
  C6                      0.7700     3.9444
  C4-                     0.2190     0.4550

PARAFFIN/OLEFIN M RATIO
  C2                      0.7143     1.2759
  C3                      0.0080     0.0086
  C4                      0.7095     1.4629
  C5                        -        5.8462

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 NO. 9972—10

Figure 10

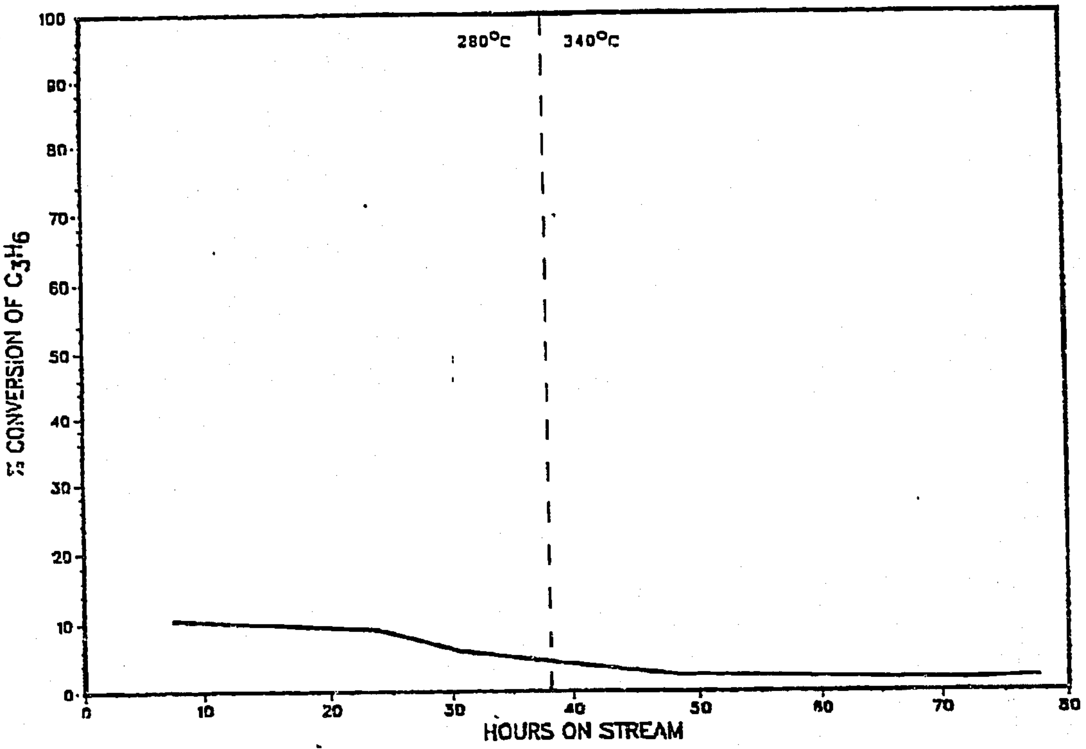


Figure 11

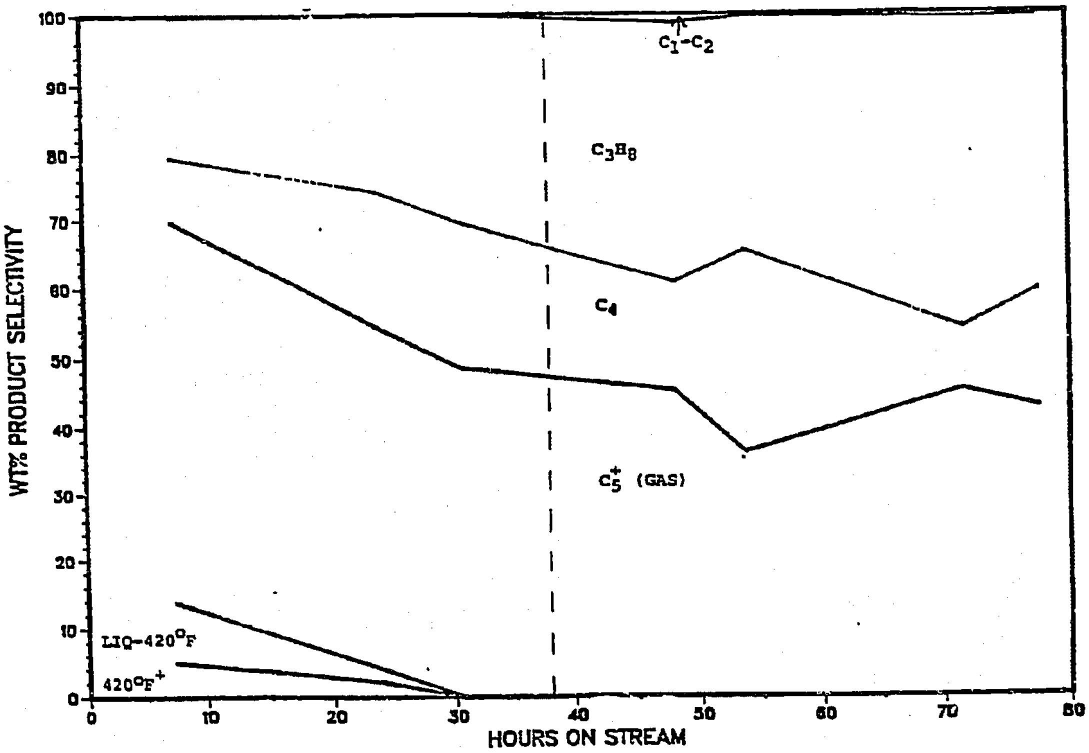


Figure 12

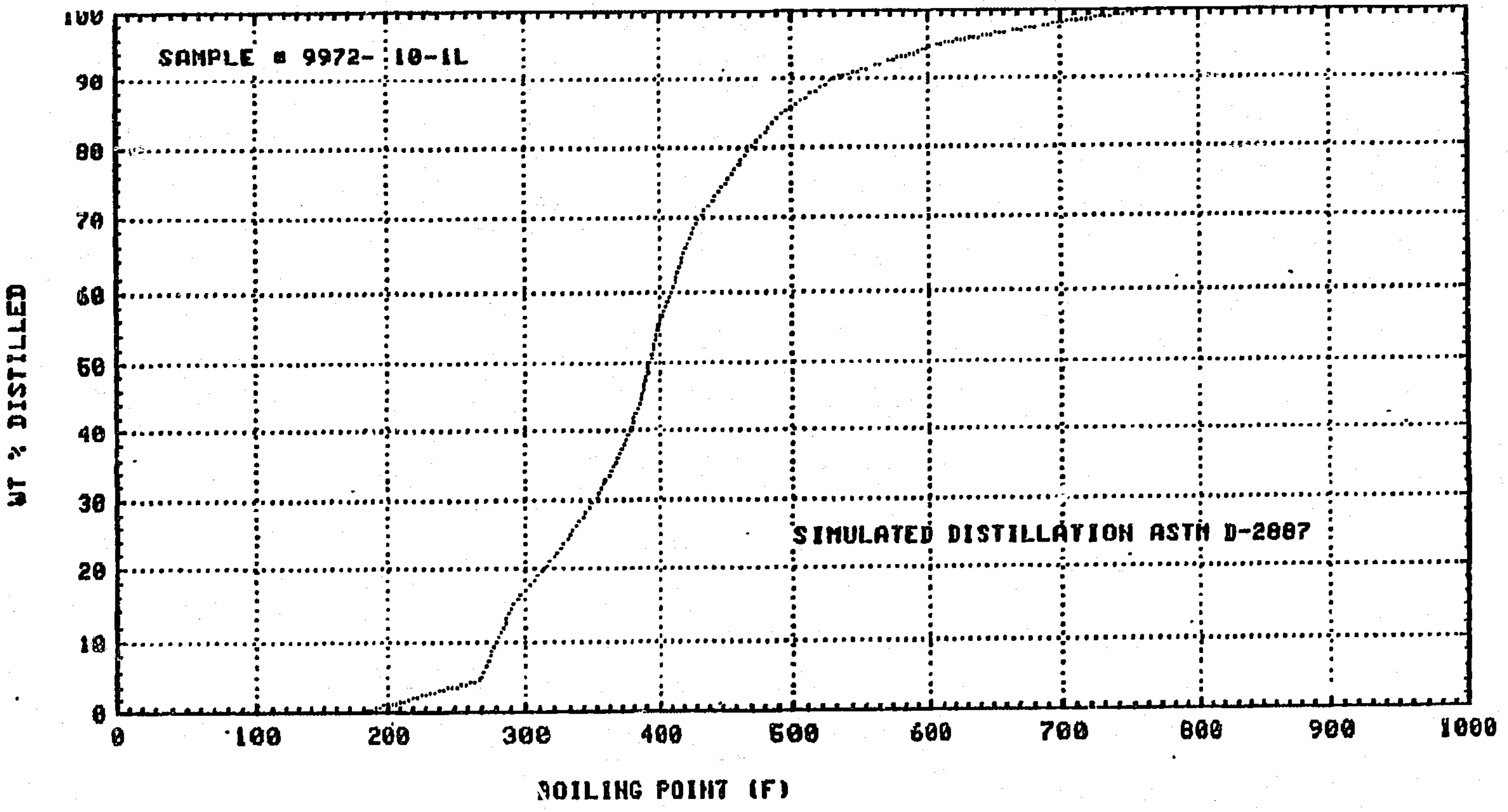
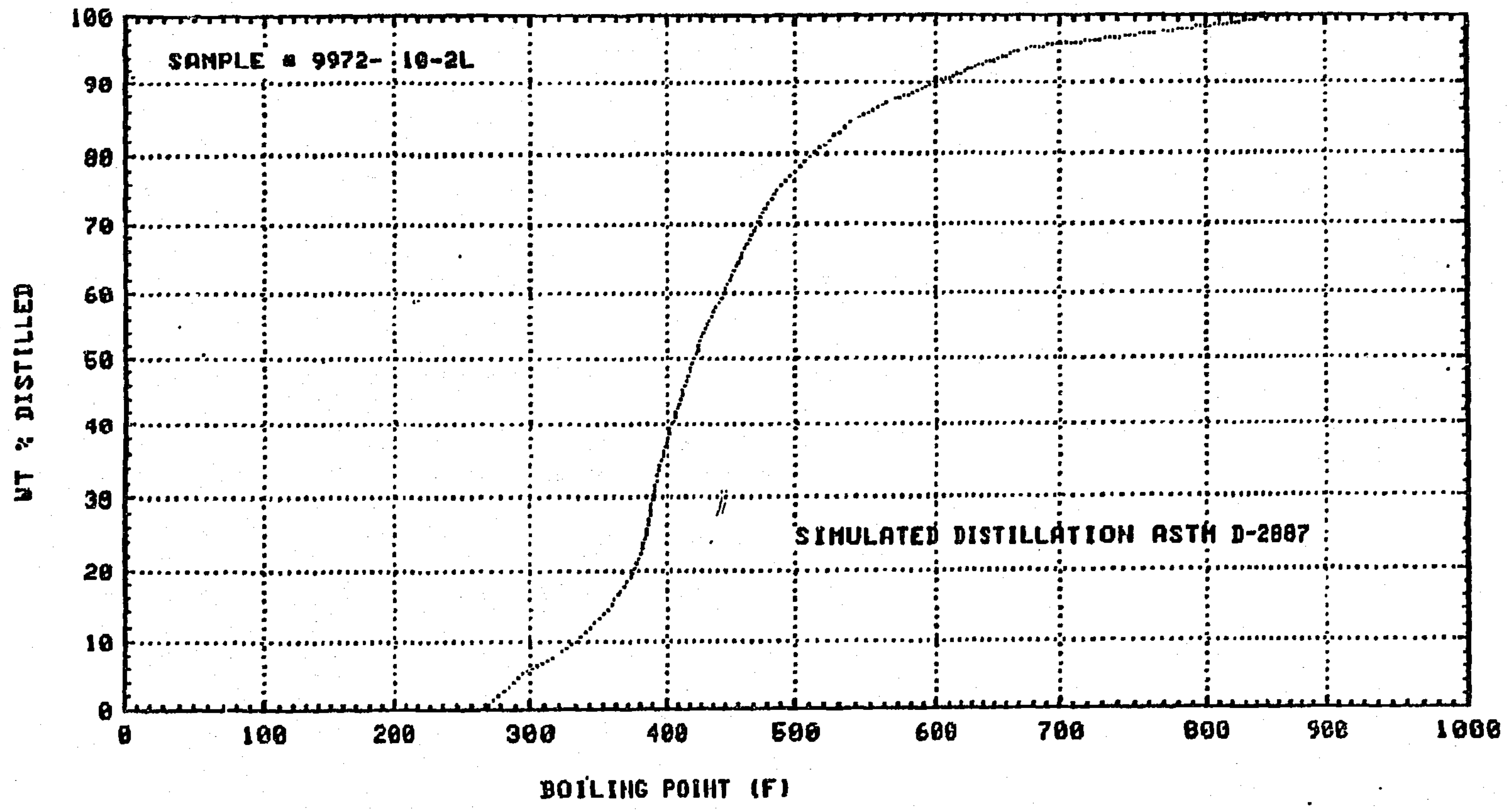

SAMPLE # 9972- 10-1L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
0
10
20
30
40
50
60
70
80
90
100
BOILING POINT (F)
0
100
200
300
400
500
600
700
800
900
1000

Figure 13


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

RUN 9972-13: LZ-105-6

LZ-105-6 is a medium pore molecular sieve with a structure similar to that of ZSM-5 with a SiO_2/Al_2O_3 ratio of 35. This zeolite has been tested extensively in this program for both methanol and propylene conversions. The purpose of the present test was to extend the knowledge of this catalyst into the range of process conditions which have become the standard test. LZ-105 was tested last quarter under the same temperature and pressure conditions but without water in the feed in run 9972-1. Tests of ZSM-5 of two different SiO_2/Al_2O_3 ratios will be reported next quarter. Extensive comparisons among these materials will be delayed until the next report when all the data will be available.

The material balances, conversions and product selectivity for the samples taken during this Run are presented in Tables 4A to 4D. The conversion and product selectivity data is plotted versus time on stream in Figures 14 and 15. Simulated distillation plots of samples representative of the process conditions studies are presented in Figures 16 to 21. The catalyst was tested for three days at 280°C and 150 psig, with a 1:1:2 $H_2:C_3H_6:H_2O$ molar ratio feed. The temperature was then raised to 340°C after 2 more days, then to 370°C where it was kept until the run was terminated 2 days later. Except for Sample #2, all the material balances show the experimental data to be of high quality.

The initial conversion at 280°C was quite high. Almost 97% of the propylene was converted. This was very similar to the initial conversion in 9972-1, 96%. This catalyst showed slow deactivation with the conversion dropping to 90% at 48 hours on stream. In 9972-1 after 40 hours on feed, the conversation at 280°C was only 84%. Even though 9972-1 was run to retard deactivation , the catalyst was deactivating faster than it did in the run with water in the feed. During this run when the temperature was raised to 340°C, much of the catalyst's activity returned but the catalyst still deactivated at the same rate. The temperature increase to 370°C again did not significantly alter the deactivation rate. During run 9972-1 the conversion rates at 340°C and 370°C were 95% and 97% respectively. These higher conversions were probably due to lower catalyst deactivation which resulted from the shorter sampling times between temperature changes. That is, they were measured after fewer hours on steam. In run 9972-2 at 410°C with water added to the feed, this same lot of LZ-105-6 was found not to deactivate. The stabilizing influence of the added water had only a partial effect at 280 to 370°C but had a large effect at 410°C.

In the prior test at 410°C the product selectivity also showed only minor changes over the course of the test. This test showed much greater changes. Most changes occurred at 280°C and the changes decreased as the temperature was increased. In no catalyst tested thus far was the production of C_1 and C_2 hydrocarbons from C_3H_6 feed significant. The selectivity to butenes was constantly increasing throughout the run to a point where their concentration in the effluent was close to that of propylene. The selectivity to propane and particularly butane were both very high initially but dropped quickly. They increased again with temperature change. As the temperature increased the rate of change of the selectivity to these two components decreased. These two paraffins are the products of hydride transfer to the corresponding olefin. A change in these concentrations is related to changes in the rate of hydride-transfer. These changes in propane and butane concentrations in the gas phase are reflected in changes in the concentration of aromatics in the liquid.

The high selectivity to C_5^+ resulted from the low quantities of propane and butane produced. The fraction of C_5^+ decreased as these two products plus butene increased. In this run, the C_5^+ was as high as 89% of the total hydrocarbons at 280°C, decreasing to 69% at 370°C. A similar change in selectivity was seen in run 9972-1. At 280°C 91% of the hydrocarbons were in the C_5^+ range, while at 370%C only 63% of them were. This decrease coincided with an increase in light saturates production. The differences in the composition among these liquid samples is obvious from the refractive indices. The initial sample in this run contained 50% aromatics. The corresponding sample in 9972-1 contained less than 20% aromatics. The final sample from this run taken at 280°C was less than 20% aromatic while the corresponding sample from 9972-1 was still 15% aromatics. At 280°C, water added to the feed increased the percentage of aromatics in the condensed product but it did not stop the deactivation of this aromatization activity. At 340°C the first sample was again about half aromatics but dropped to 30% by the last sample. At 370°C the first sample was 40% aromatics but the aromatics were still above 30% by the last sample. From 9972-1 there is data only from initial samples. At 340°C the sample was half aromatics; at 370°C the condensed liquid was 70% aromatics. The water in the feed was better at reducing deactivation at 340°C than at 280°C. At 370°C the water almost completely stopped deactivation of aromatization. The price paid for this slower deactivation was lower activity.

These trends in aromatic concentrations calculated from refractive indices were verified by the simulated distillations. The distillation of Sample 1 revealed the presence of xylenes and C_9 aromatics in the liquid. Sample 5 had a much smother distillation curve and did not show signs of xylenes in the sample. Sample 6 again contained xylenes and trimethylbenzenes. Sample 10 still had observable amounts of xylenes but no detectable C_9 aromatics. This sample also probably contained toluene. Sample 12 contained both xylenes and C_9 aromatics. The last sample still contained these aromatics but also had appreciable quantities of toluene. This liquid product contained mostly secondary products of the propylene oligomerization reaction. The distillations did not contain the large amounts of C_6, C_9 and C_{12} olefins that were easily observable in previous samples.

LZ-105 is an excellent catalyst for propylene oligomerization even at 280°C. The catalyst has high activity and good selectivity to liquid products. At these lower temperatures, the catalytic activity, particularly the aromatization activity, deactivates in spite of the presence of water in the feed. While the selectivity to C_5^+ products was not quite as good as that of UCC-104, reported last quarter, the activity was higher.

TABLE 4A RESULT OF PROPYLENE OPERATION

RUN NO. 9972-13
CATALYST LZ-105-6 #9939-01 67CC 35.06GM (37.10GM AFTER THE RUN,+2.04GM)
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,10.1 L/HR H2O 15 CC/HR
ACTUAL FLOW: 28.45 CCHR EFFLUENT 13.8 L/HR AQ LAYR 10.5 CC/HR

RUN & SAMPLE NO.	9972-13-1	9972-13-2	9972-13-3	9972-13-4	9972-13-5
C3H6 WHSV	0.42	0.42	0.42	0.42	0.42
HRS ON STREAM	5.03	23.9	30.9	48.0	55.0
PRESSURE,PSIG	161	157	154	155	156
TEMP. C	280	280	280	280	280
FEED C3H6 CC	138.44	534.87	176.19	492.08	193.81
HOURS FEEDING	5.033	18.90	7.00	17.10	7.00
EFFLNT GAS LITER	65.35	235.75	88.90	222.30	88.50
GM AQUEOUS LAYER	49.01	197.72	73.99	180.05	71.50
GM LIQ HYDROCARBON	24.89	138.89	48.98	133.18	55.29
WT FR. LIQ HC/FEED	.3522	.5087	.5447	.5303	.5589
MATERIAL BALANCE WT %	88.72	81.58	93.30	91.23	98.42
C3H6 CONVERSION %	96.66	94.11	92.61	90.29	90.41
PRDT SELECTIVITY WT %					
CH4	0.02	0.01	0.02	0.01	0.01
C2 HC'S	0.12	0.10	0.11	0.07	0.07
C3H8	9.78	2.67	2.66	2.03	1.78
C4H10	16.20	4.07	3.99	2.50	2.36
C4H8=	2.24	4.57	5.68	6.27	6.36
C5H12	12.14	3.93	3.79	2.83	2.49
C5H10=	0.07	0.16	0.24	0.23	0.22
C6H14	7.68	6.40	6.39	7.24	6.90
C6H12= & CYCLO'S	0.77	1.68	1.97	1.79	2.55
C7+ IN GAS	7.79	9.28	9.80	11.75	12.17
LIQ HC'S	43.19	67.12	65.35	65.29	65.07
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	28.36	11.42	12.46	10.88	10.59
C5 -420 F	67.80	82.60	78.52	83.44	80.56
420-700 F	3.84	5.97	9.02	5.68	8.85
700-END PT	0.00	0.00	0.00	0.00	0.00
C5 -END PT	71.64	88.58	87.54	89.12	89.41

ISO/NORMAL MOLE RATIO					
C4	1.7003	2.4154	2.3051	2.6302	2.3587
C5	2.0616	2.1181	1.9322	2.0860	2.0297
C6	6.0933	10.5051	9.5125	12.1574	12.8041
C4=	0.4936	0.4681	0.4411	0.4371	0.4152
PARAFFIN/OLEFIN M RATIO					
C2	1.1074	0.2107	0.3782	.	.
C3	2.7274	0.4059	0.3180	0.1794	0.1598
C4	6.9926	0.8609	0.6771	0.3849	0.3585
C5	174.2464	23.5243	15.0714	11.9156	10.7620
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	0.792	0.759	0.747	0.745	0.749
N.REFRACTIVE INDEX	1.4540	1.4323	1.4296	1.4266	1.4257
SIMULATED DISTILLATION					
10 WT % @ DEG F.	180	172	182	173	173
16	204	200	209	202	207
50	294	292	307	292	304
84	389	391	409	391	409
90	411	414	444	413	443
RANGE(16-84%)	185	191	200	189	202
WT % @420 F	91.1	91.2	86.2	91.3	86.4
WT % @700 F	100	100	100	100	100

TABLE 4B RESULT OF PROPYLENE OPERATION

RUN NO. 9972-13
CATALYST LZ 105-6 #9939-01 67CC 35.06GM (37.10GM AFTER THE RUN, +2.04GM)
FEED H_2:C_3H_6:H_2O @ 1:1:2 MOLE RATIO, 0.5 C_3H_6 WHSV, CONTINOUS OVERNITE
C_3H_6 MW- 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C_3H_6 34.3 CC/HR H_2 168 CCMN, 10.1 L/HR H_2O 15 CC/HR
ACTUAL FLOW: 28.45 CCHR EFFLUENT 13.8 L/HR AQ LAYR 10.5 CC/HR

RUN & SAMPLE NO.	9972-13-6	9972-13-7	9972-13-8	9972-13-9	9972-13-10
C_3H_6 WHSV	0.42	0.42	0.42	0.42	0.42
HRS ON STREAM	71.5	78.7	95.4	102.7	119.1
PRESSURE, PSIG	157	149	150	152	158
TEMP. C	340	339	338	338	338
FEED C_3H_6 CC	481.38	195.52	484.53	190.67	485.79
HOURS FEEDING	16.50	7.25	16.75	7.25	16.40
EFFLNT GAS LITER	231.10	102.00	234.40	100.40	230.60
GM AQUEOUS LAYER	173.41	77.41	175.42	75.78	171.51
GM LIQ HYDROCARBON	88.99	38.19	93.39	38.59	95.19
WT FR. LIQ HC/FEED	.3622	.3963	.3776	.3965	.3839
MATERIAL BALANCE WT %	92.38	103.08	95.76	102.38	91.11
C_3H_6 CONVERSION %	93.75	92.49	91.23	90.80	89.38
PRDT SELECTIVITY WT %					
CH_4	0.06	0.05	0.04	0.04	0.04
C2 HC'S	0.42	0.42	0.39	0.41	0.40
C_3H_8	7.25	6.05	5.02	4.69	4.22
C_4H_{10}	13.72	12.07	9.98	9.20	7.60
C_4H_8=	5.91	7.27	8.52	8.92	9.58
C_5H_{12}	10.50	10.05	8.75	8.09	6.73
C_5H_{10}=	0.17	0.42	0.38	0.39	0.30
C_6H_{14}	7.76	8.63	8.94	8.99	9.00
C_6H_{12}= & CYCLO'S	1.19	1.51	1.60	1.74	1.77
C7+ IN GAS	10.68	12.22	12.64	13.58	12.62
LIQ HC'S	42.35	41.30	43.75	43.94	47.75
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	27.37	25.86	23.95	23.26	21.83
C5 -420 F	68.61	70.50	72.42	72.35	74.41
420-700 F	4.02	3.64	3.63	4.39	3.76
700-END PT	0.00	0.00	0.00	0.00	0.00
C5 -END PT	72.63	74.14	76.05	76.74	78.17

ISO/NORMAL MOLE RATIO					
C4	2.5130	2.3893	2.4320	2.4708	2.6692
C5	3.0550	2.4097	2.4092	2.3612	2.6237
C6	8.1918	7.8099	8.6750	8.8595	10.0478
C4=	0.4577	0.4327	0.4345	0.4343	0.4544
PARAFFIN/OLEFIN M RATIO					
C2	0.5772	0.3732	0.3282	0.3597	0.3044
C3	1.0466	0.7199	0.5009	0.4444	0.3399
C4	2.2397	1.6013	1.1308	0.9955	0.7659
C5	60.2097	23.5307	22.2957	20.2755	21.7099
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	0.770	0.785	0.775	0.738	0.746
N,REFRACTIVE INDEX	1.4494	1.4451	1.4398	1.4396	1.4349
SIMULATED DISTILLATION					
10 WT % @ DEG F.	166	168	162	166	162
16	200	200	196	198	194
50	295	298	294	289	285
84	390	387	384	384	379
90	416	411	408	410	406
RANGE(16-84%)	190	187	188	186	185
WT % @420 F	90.5	91.2	91.7	91.5	92.13
WT % @700 F	100	100	100	100	100

TABLE 4C RESULT OF PROPYLENE OPERATION

RUN NO. 9972-13
CATALYST LZ-105-6 #9939-01 67CC 35.06GM (37.10GM AFTER THE RUN, 2.04GM)
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, 10.1 L/HR H2O 15 CC/HR
ACTUAL FLOW: ~28.45 CCHR EFFLUENT 13.8 L/HR AQ LAYR 10.5 CC/HR

RUN & SAMPLE NO.	9972-13-11	972-13-12	972-13-13	972-13-14	9972-13-15
C3H6 WHSV	0.42	0.42	0.42	0.42	0.42
HRS ON STREAM	126.8	143.1	150.7	166.9	172.7
PRESSURE, PSIG	154	150	157	153	148
TEMP. C	338	370	370	370	370
FEED C3H6 CC	210.8	484.53	213.43	473.83	156.69
HOURS FEEDING	7.7	16.3	7.58	16.25	5.75
EFFLNT GAS LITER	106.9	238.9	110.6	237.0	83.5
GM AQUEOUS LAYER	80.74	169.10	78.81	168.16	59.56
GM LIQ HYDROCARBON	41.30	80.04	37.28	75.14	26.25
WT FR. LIQ HC/FEED	.3838	.3236	.3539	.3107	.3282
MATERIAL BALANCE WT %	96.71	100.42	106.26	95.88	109.56
C3H6 CONVERSION %	89.22	88.41	87.83	85.46	84.55
PRDT SELECTIVITY WT %					
CH4	0.04	0.13	0.12	0.12	0.12
C2 HC'S	0.38	0.78	0.76	0.80	0.86
C3H8	3.95	7.46	6.55	6.10	5.82
C4H10	7.41	12.14	10.63	9.56	9.02
C4H8	9.99	10.82	11.07	13.26	13.82
C5H12	6.44	9.06	8.13	7.04	6.73
C5H10=	0.30	0.51	0.47	0.38	0.41
C6H14	9.02	8.53	8.68	8.86	9.33
C6H12= & CYCLO'S	1.89	1.79	1.93	1.93	2.18
C7+ IN GAS,	14.82	11.92	14.02	13.59	15.07
LIQ HC'S	45.76	36.85	37.64	38.35	36.66
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	21.77	31.34	29.12	29.85	29.63
C5 -420 F	74.62	65.96	68.20	67.68	68.09
420-700 F	3.62	2.70	2.68	2.47	2.28
700-END PT	0.00	0.00	0.00	0.00	0.00
C5 -END PT	78.23	68.66	70.88	70.15	70.37

ISO/NORMAL MOLE RATIO					
C4	2.5057	2.2601	2.2867	2.2908	2.3034
C5	2.5651	2.2856	2.2850	2.4551	2.4084
C6	10.1939	8.7282	9.0431	10.7955	10.7362
C4=	0.4403	0.4291	0.4341	0.4414	0.4416
PARAFFIN/OLEFIN M RATIO					
C2	0.2506	0.5230	0.4913	0.4576	0.4499
C3	0.3129	0.5474	0.4560	0.3445	0.3060
C4	0.7166	1.0827	0.9277	0.6961	0.6300
C5	20.7721	17.2261	16.7365	18.0000	16.0911
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	0.762	0.740	0.759	0.771	0.770
N, REFRACTIVE INDEX	1.4337	1.4458	1.4434	1.4411	1.4381
SIMULATED DISTILLATION					
10 WT % @ DEG F.	164	164	164	162	163
16	196	197	196	194	194
50	288	290	289	286	285
84	381	376	375	372	371
90	407	403	402	398	397
RANGE(16-84%)	185	179	179	178	177
WT % @420 F	92.1	92.67	92.89	93.55	93.78
WT % @700 F	100	100	100	100	100

RUN NO. 9972-13

Figure 14

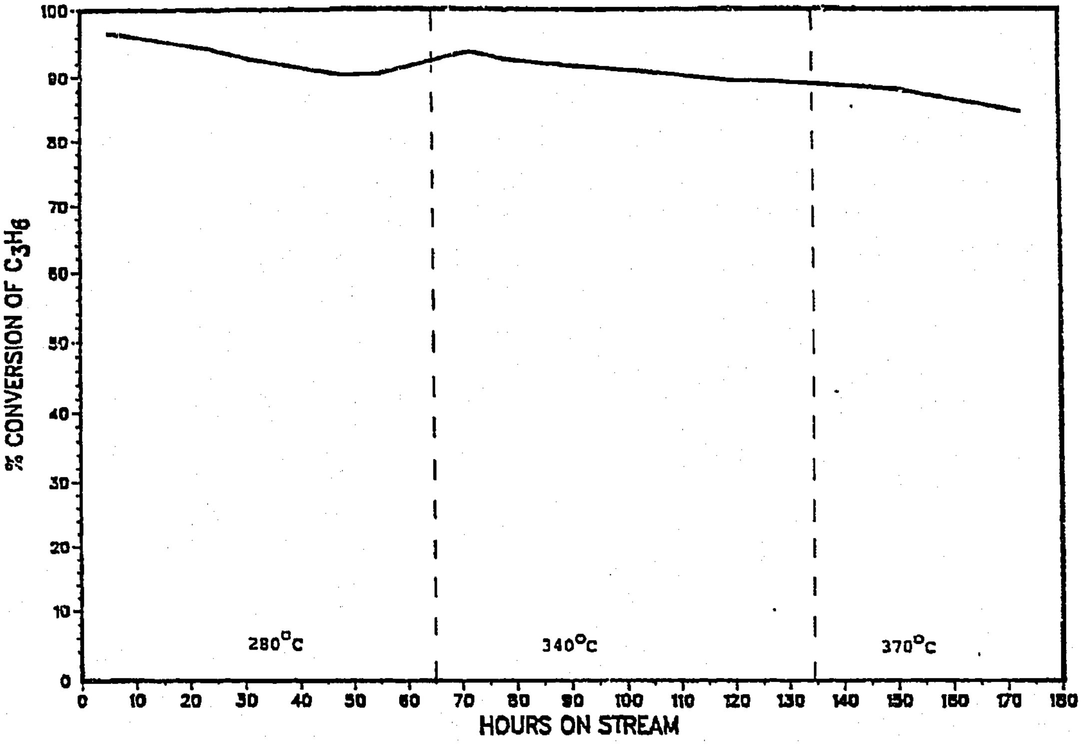


Figure 15

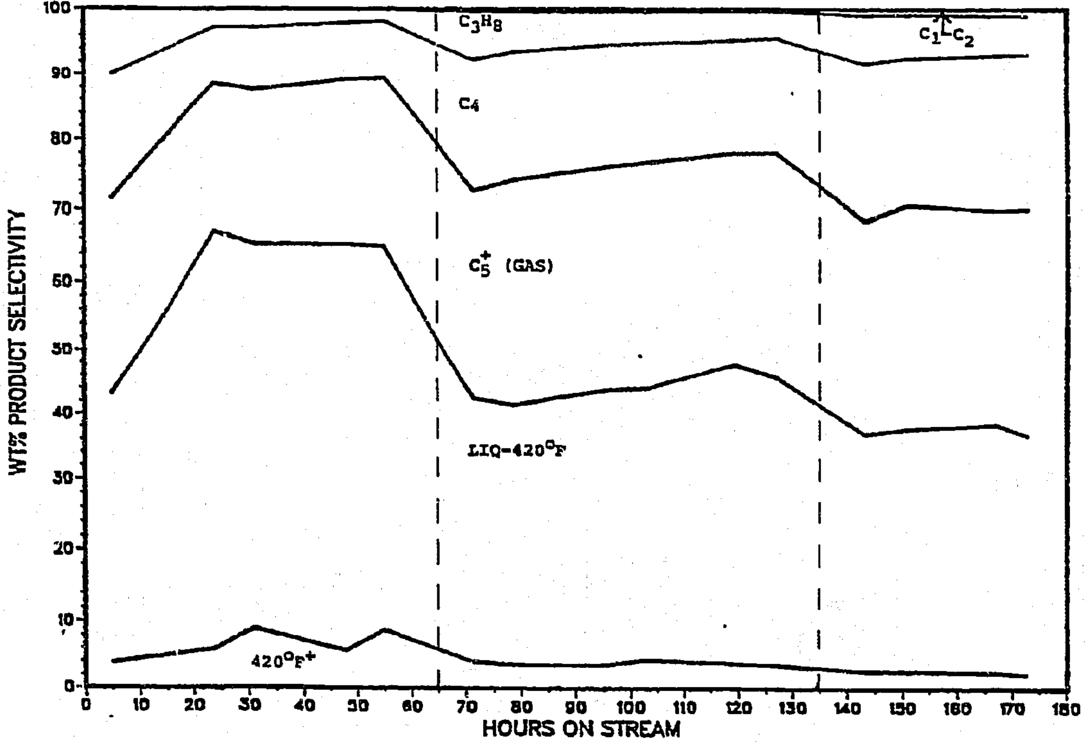


Figure 16

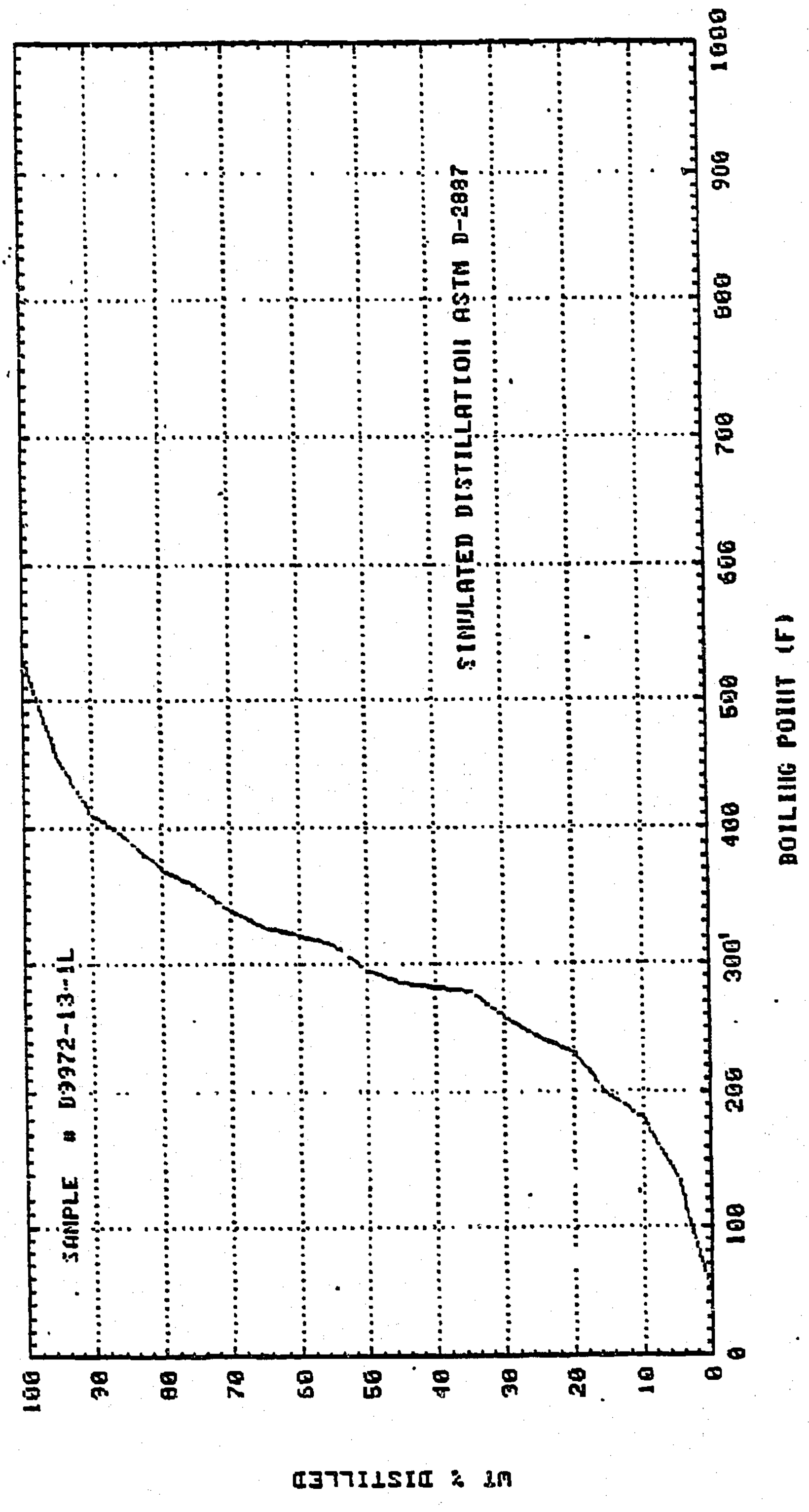

SAMPLE # D9972-13-1L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
0
10
20
30
40
50
60
70
80
90
100
BOILING POINT (F)
0
100
200
300
400
500
600
700
800
900
1000

Figure 17

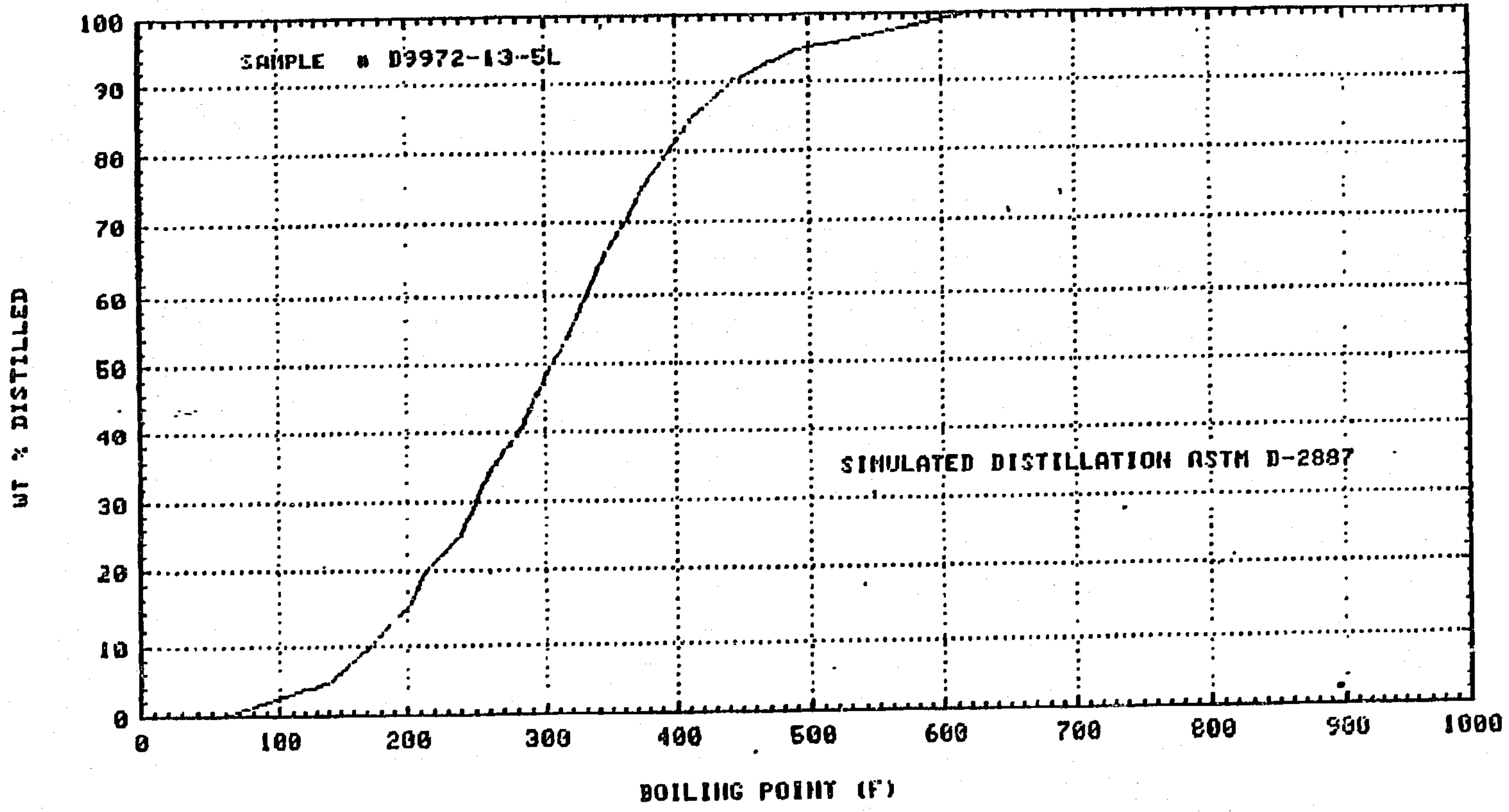

SAMPLE # D9972-13-5L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
0
10
20
30
40
50
60
70
80
90
100
BOILING POINT (F)
0
100
200
300
400
500
600
700
800
900
1000

Figure 13

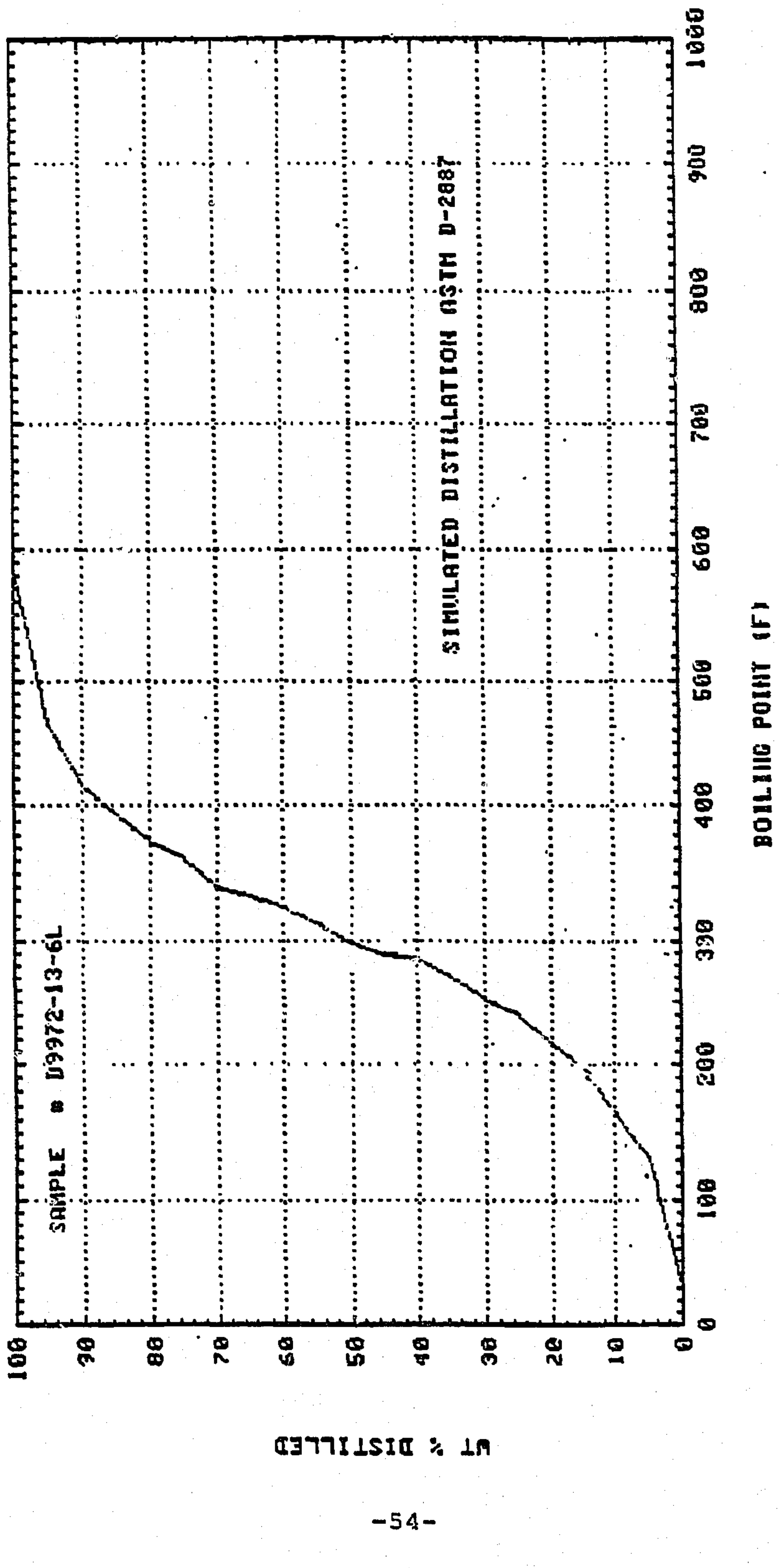

SAMPLE = D9972-13-6L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Figure 19

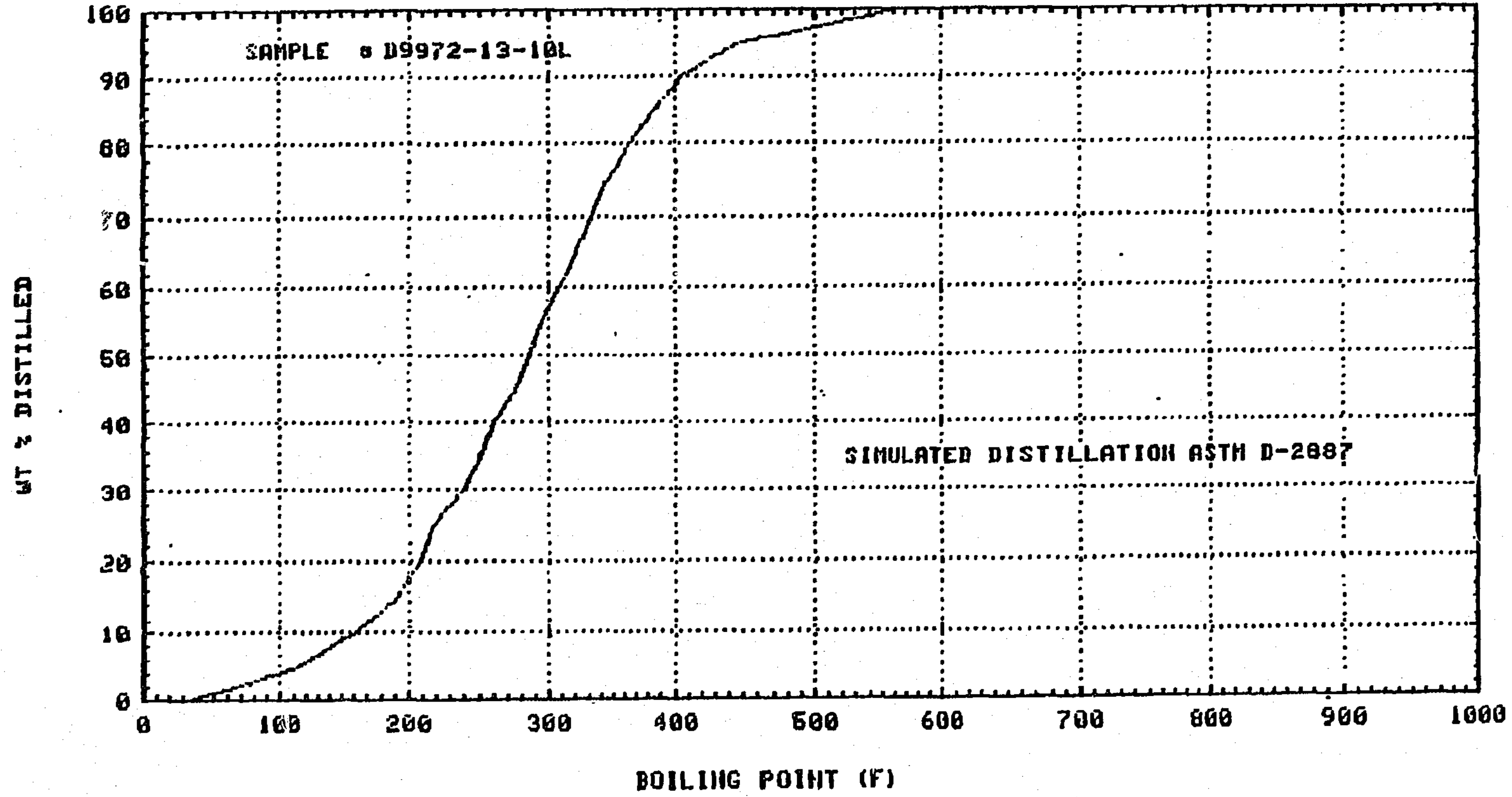

SAMPLE # D9972-13-10L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
0
10
20
30
40
50
60
70
80
90
100
BOILING POINT (F)
0
100
200
300
400
500
600
700
800
900
1000

Figure 20

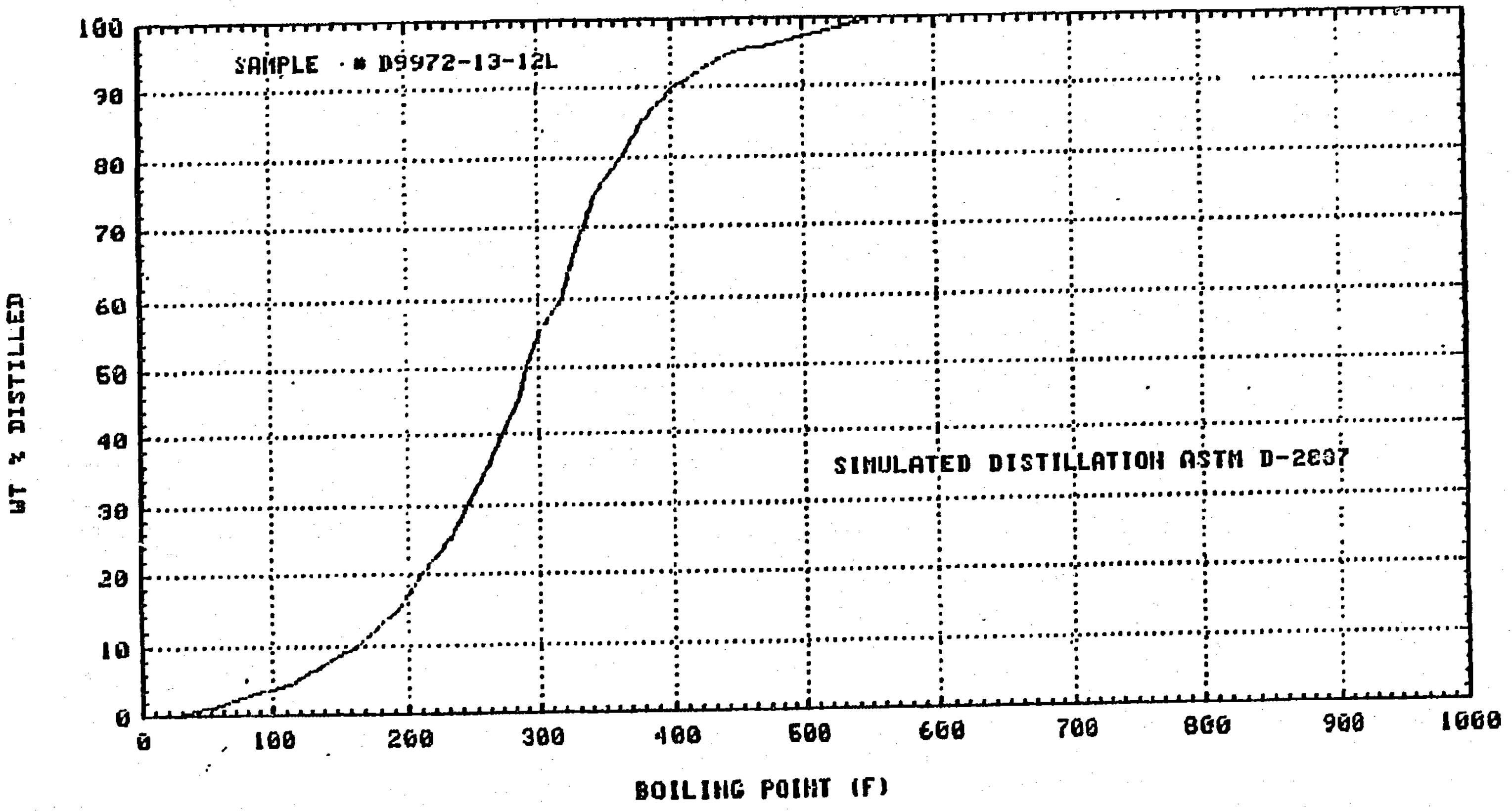
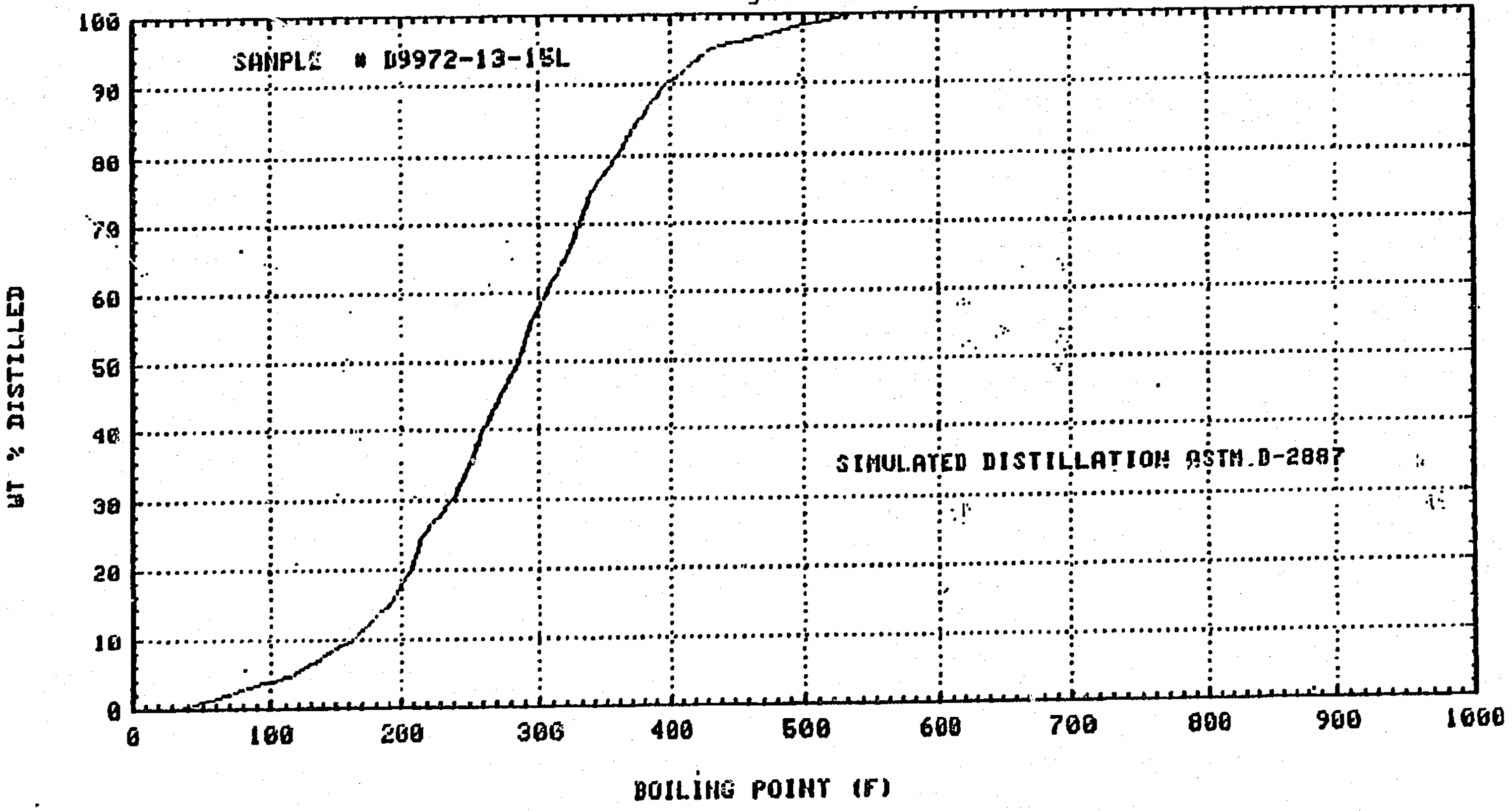

SAMPLE · # D9972-13-12L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Figure 21


SAMPLE # D9972-13-15L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
800
900
1000
BOILING POINT (F)

Run 9972-14: UCC-107

UCC-107 is a new Union Carbide proprietary large pore molecular sieve. It was tested for 4 days at 280°C. The temperature was then increased to 340°C for 1 day and 370°C for 1 day, after which the test was terminated. The detailed data analysis is presented in Tables 5A to 5C. The conversion and product selectivities are also presented in Figures 22 and 23. The simulated distillation of the condensed product from Samples 1 and 2 are plotted in Figures 24 and 25. All the material balances are satisfactory except for Sample 5. Since the calculated numbers are not out of line with the other samples, the results are probably reliable.

The conversion was low initially, and it did not change significantly during the test. The catalyst showed fast deactivation with the conversion dropping by a factor of 3 in the first two days on stream. Increasing the temperature to 340°C partially restored activity but it dropped quickly. The temperature increase to 370°C again restored activity but only for a short period of time.

It seems to be common for fast deactivating catalysts with ultimate low activity that propane is a major product of propylene. The selectivity to propane was fairly constant over the test and did not seem to be a function of temperature or deactivation. Butenes were also major products. The selectivity to butenes was also independent of temperature or time. The selectivity to C_5^+ products varied only from 69% at the beginning of the run to 61% at the end. The distribution of hydrocarbons among the C_5^+ product was not as constant as the previous numbers may have indicated. The amount of condensed product dropped from 12% to 0% in 1 day. The simulated distillation curves had signs of C_6's and C_{12}'s present but the condensed product was only a small percentage of the total product.

The UCC-107 is a poor catalyst for propylene oligomerization. It deactivated too quickly. It seemed to deactivate by a different mechanism than previous catalysts since the propane and butenes selectivities were fairly constant over the entire run.

TABLE 5A RESULT OF PROPYLENE OPERATION

RUN NO. 9972-14
CATALYST UCC-107 #10042-21 56CC 35.00GM (33.83GM AFTER THE RUN, -1.17GM)
FEED H_2:C_3H_6:H_2O @ 1:1:2 MOLE RATIO,0.5 C_3H_6 WHSV,CONTINOUS OVERNITE
C_3H_6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C_3H_6 34.3 CC/HR H_2 170 CCMN,10.2 L/HR H_2O 15 CC/HR
ACTUAL FLOW: 35.15 CCHR EFFLUENT 20.4 L/HR AQ LAYR 13.9 CC/HR

RUN & SAMPLE NO.	9972-14-1	9972-14-2	9972-14-3	9972-14-4	9972-14-5
C_3H_6 WHSV	0.5	0.5	0.5	0.5	0.5
HRS ON STREAM	6.3	25.9	30.3	49.3	52.7
PRESSURE,PSIG	157	150	149	147	149
TEMP. C	280	279	280	279	280
FEED C_3H_6 CC	208.28	690.3	144.73	682.13	113.27
HOURS FEEDING	6.33	19.6	4.4	19.0	3.3
EFFLNT GAS LITER	116.9	395.3	88.5	391.5	67.6
GM AQUEOUS LAYER	82.48	269.11	60.56	260.74	46.07
GM LIQ HYDROCARBON	1.59	1.17	0.00	0.00	0.00
WT FR. LIQ HC/FEED	.0173	.0033	.0000	.0000	.0000
MATERIAL BALANCE WT %	95.27	91.29	100.60	92.23	80.15
C_3H_6 CONVERSION %	13.18	5.95	4.53	3.34	4.14
PRDT SELECTIVITY WT %					
CH_4	0.00	0.00	0.00	0.00	0.00
C2 HC'S	0.00	0.00	0.00	0.00	0.00
C_3H_8	21.49	24.28	29.93	33.18	26.58
C_4H_{10}	3.33	2.67	2.00	0.54	3.00
C_4H_8=	5.88	9.01	3.53	2.73	7.75
C_5H_{12}	1.50	1.67	0.58	0.00	0.13
C_5H_{10}=	0.13	0.08	0.16	0.00	0.15
C_6H_{14}	9.35	6.07	7.12	6.34	5.44
C_6H_{12}= & CYCLO'S	7.04	12.21	15.35	17.69	15.50
C7+ IN GAS	39.08	37.90	41.33	39.53	41.45
LIQ HC'S	12.20	6.10	0.00	0.00	0.00
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	30.70	35.97	35.45	36.45	37.33
C5 -420 F	65.15	60.56	64.55	63.55	62.67
420-700 F	3.78	3.10	0.00	0.00	0.00
700-END PT	0.37	0.38	0.00	0.00	0.00
C5 -END PT	69.30	64.03	64.55	63.55	62.67

ISO/NORMAL MOLE RATIO					
C4	1.3338	0.3317	0.6330	-	0.1901
C5	8.5424	4.8085	5.5455	-	-
C6	13.0000	5.1481	4.7734	3.5138	3.6404
C4=	0.4014	0.4007	0.6234	0.6923	0.4336
PARAFFIN/OLEFIN M RATIO					
C2	-	-	-	-	-
C3	0.0316	0.0149	0.0138	0.0111	0.0111
C4	0.5465	0.2862	0.5453	0.1908	0.3739
C5	11.0392	19.5000	3.6000	.	0.8571
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY	.	.			
N, REFRACTIVE INDEX	.	.			
SIMULATED DISTILLATION					
10 WT % @ DEG F.	277	341	---	---	---
16	288	368	---	---	---
50	387	439	---	---	--
84	491	568	---	---	---
90	550	642	---	---	---
RANGE (16-84%)	203	200	---	---	---
WT % @420 F	66.0	43.0	--	---	---
WT % @700 F	97.0	91.8	---	---	---

TABLE 5B RESULT OF PROPYLENE OPERATION

RUN NO. 9972-14
CATALYST UCC-107 #10042-21 55CC 35.00GM (33.83GM AFTER THE RUN, -1.17GM)
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 170 CCMN,10.2 L/HR H2O 15 CC/HR
ACTUAL FLOW: 35.15 CCHR EFFLUENT 20.4 L/HR AQ LAYR 13.9 CC/HR

RUN & SAMPLE NO.	9972-14-6	9972-14-7	9972 14-8	9972-14-9	9972-14-10
C3H6 WHSV	0.5	0.5	0.5	0.5	0.5
HRS ON STREAM	73.8	77.25	97.8	103.8	123.8
PRESSURE,PSIG	147	149	147	150	152
TEMP. C	280	280	279	339	337
FEED C3H6 CC	754.48	115.78	721.76	205.52	713.58
HOURS FEEDING	21.2	3.4	20.6	6.0	20.0
EFFLNT GAS LITER	435.0	71.3	424.8	123.3	411.9
GM AQUEOUS LAYER	291.46	48.09	282.76	82.85	275.77
GM LIQ HYDROCARBON	0.00	0.00	0.00	0.15	0.6
WT FR. LIQ HC/FEED	.0000	.0000	.0000	.0015	.0016
MATERIAL BALANCE WT %	93.22	88.35	93.51	100.99	92.42
C3H6 CONVERSION %	2.67	3.19	3.02	8.70	4.98
PRDT SELECTIVITY WT %					
CH4	0.00	0.00	0.00	0.2	0.28
C2 HC'S	0.00	0.00	0.00	0.21	0.00
C3H8	38.46	32.04	33.15	29.02	28.13
C4H10	0.48	3.85	3.01	1.33	1.46
C4H8=	2.35	6.85	7.37	5.97	4.75
C5H12	0.00	0.20	0.24	0.72	0.39
C5H10=	0.00	0.00	0.00	0.22	0.25
C6H14	5.67	5.10	4.88	7.25	6.49
C6H12= & CYCLO'S	0.00	16.93	17.75	15.25	19.48
C7+ IN GAS	53.03	35.02	33.61	38.07	35.21
LIQ HC'S	0.00	0.00	0.00	1.66	3.57
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	41.30	42.75	43.52	36.82	34.61
C5 -420 F	58.70	57.25	56.48	62.43	63.79
420-700 F	0.00	0.00	0.00	0.68	1.57
700-END PT	0.00	0.00	0.00	0.08	0.03
C5 -END PT	58.70	57.25	56.48	63.18	65.39

ISO/NORMAL MOLE RATIO					
C4	-	0.1254	0.1567	1.2363	0.4068
C5	.		.	1.3553	1.0769
C6	3.2892	2.6477	2.3564	4.1263	2.4791
C4=	0.7533	0.4940	0.4587	0.5796	0.6238
PARAFFIN/OLEFIN M RATIO					
C2	-	-	-	-	-
C3	0.0103	0.0103	0.0100	0.0258	0.0143
C4	0.1982	0.5423	0.3939	0.2144	0.2964
C5	-	-	-	3.1404	1.5000
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	---	---	---	---	---

```
     TABLE 5C    RESULT OF PROPYLENE OPERATION

RUN NO.   9972-14
CATALYST UCC-107 #10042-21 56CC 35.00GM (33.83GM AFTER THE RUN,-1.17GM)
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 170 CCMN,10.2 L/HR  H2O      15 CC/HR
ACTUAL FLOW:       35.15 CCHR  EFFLUENT     20.4 L/HR  AQ LAYR 13.9 CC/HR

RUN & SAMPLE NO.    9972-14-11 9972-14-12
                    ========== ==========
C3H6  WHSV               0.5       0.5
HRS ON STREAM          127.5     145.0
PRESSURE,PSIG            153       149
TEMP.  C                 370       371

FEED C3H6 CC          116.41    629.89
HOURS FEEDING            3.7      17.5
EFFLNT GAS LITER        74.1     358.5
GM AQUEOUS LAYER       50.28    240.66
GM LIQ HYDROCARBON      0.00      0.00
WT FR. LIQ HC/FEED     .0000     .0000

MATERIAL BALANCE WT % 108.41     90.66
C3H6 CONVERSION %       8.05      5.68
PRDT SELECTIVITY WT %
  CH4                   0.75      0.56
  C2 HC'S               0.92      0.52
  C3H8                 33.56     29.89
  C4H10                 1.45      1.98
  C4H8=                 6.81      6.37
  C5H12                 0.70      0.38
  C5H10=                0.28      0.12
  C6H14                 7.56     21.72
  C6H12= & CYCLO'S     16.81     15.79
  C7+ IN GAS           31.37     22.67
  LIQ HC'S              0.00      0.00

  TOTAL               100.00    100.00
  SURGROUPING
    C1 -C4             43.28     39.32
    C5 -420 F          56.72     60.68
    420-700 F           0.00      0.00
    700-END PT          0.00      0.00
    C5 -END PT         56.72     60.68
```

```
  ISO/NORMAL MOLE RATIO
    C4                   0.8378    0.2025
    C5                   1.0385    0.5000
    C6                   2.9103    0.1749
    C4-                  0.5503    0.4490

  PARAFFIN/OLEFIN M RATIO
    C2                   0.6774      -
    C3                   0.0284    0.0175
    C4                   0.2050    0.3004
    C5                   2.4091    3.1579

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 NO. 9972–14

Figure 22

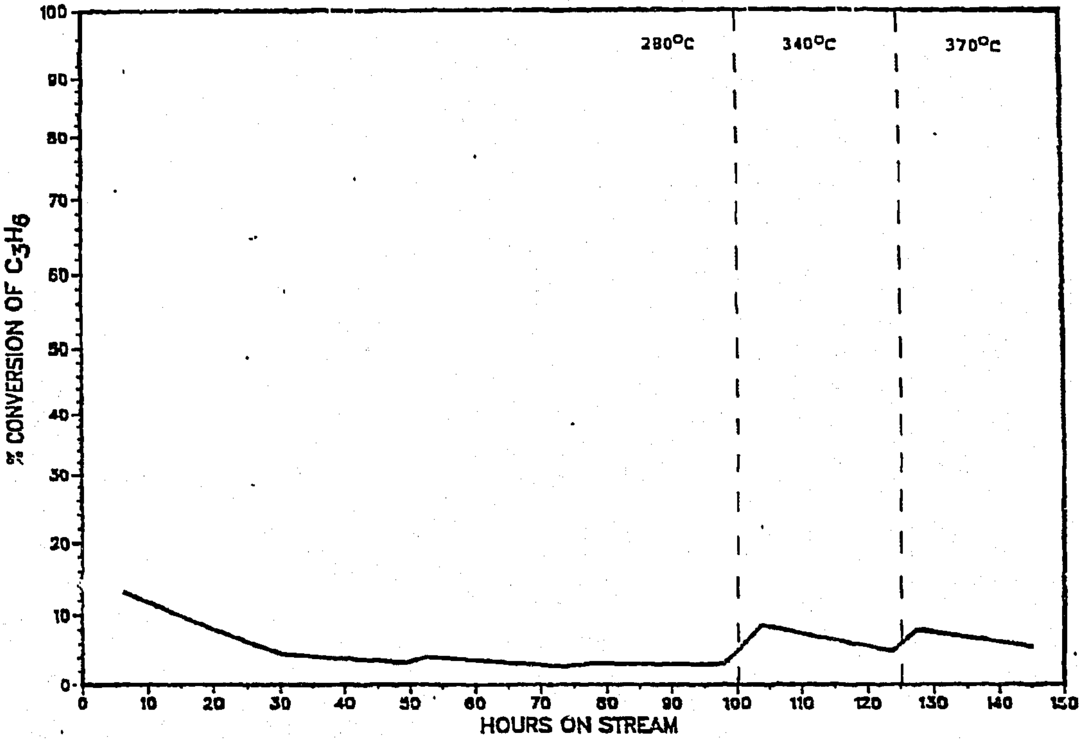


Figure 23

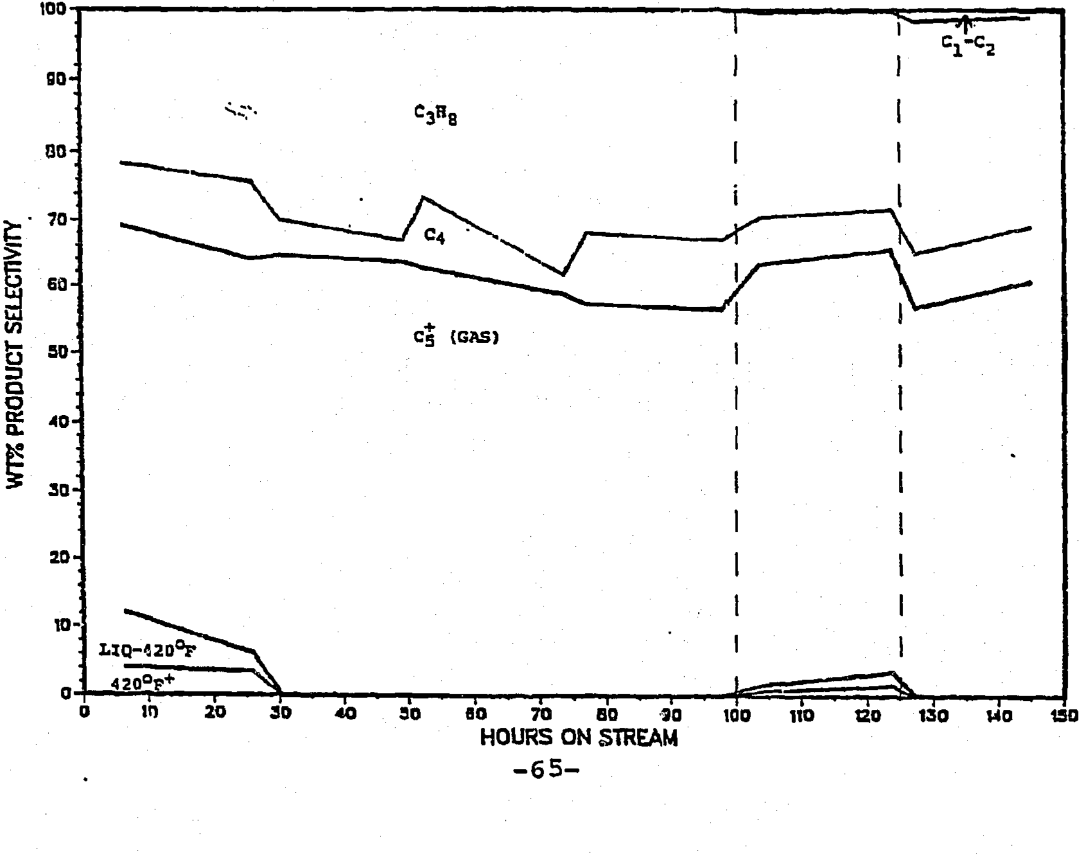


Figure 24

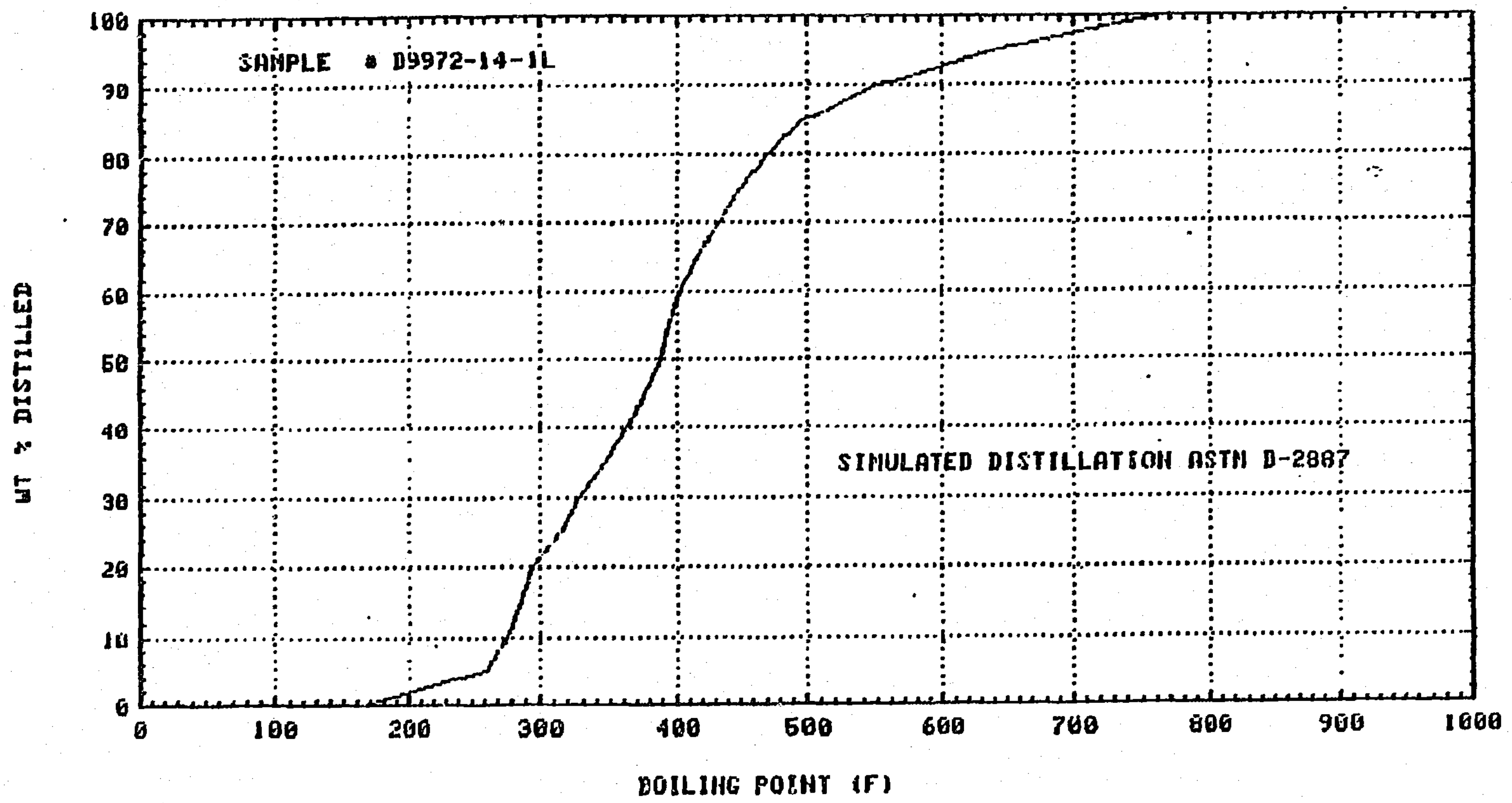
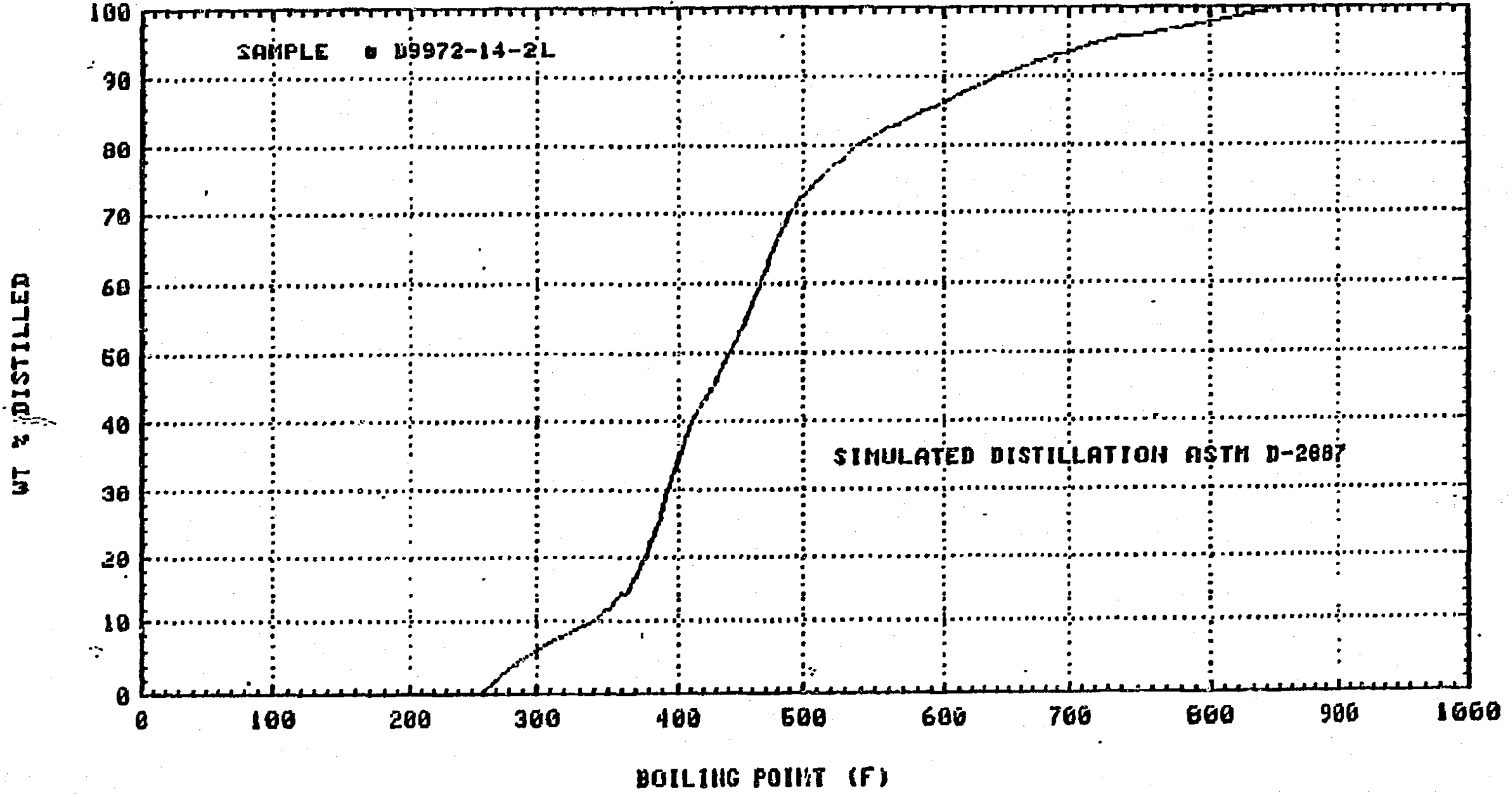

SAMPLE # D9972-14-1L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
BOILING POINT (F)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Figure 25


SAMPLE # D9972-14-2L
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
800
900
1000
BOILING POINT (F)

Run 9972-15: REY-62

Sodium Y-62 was cation exchanged with rare earth to produce this catalyst. The tri-valent rare earth should introduce acidity into the molecular sieve. The catalyst was tested at 280°C, 340°C and 370°C. The results are reported in Tables 6A and 6B. The conversion and product selectivity are shown in Figures 26 and 27. Simulated distillation curves of two samples are presented in Figures 28 and 29. The catalyst performance was poor, displaying low activity and rapid deactivation. Propane was a major product which increased with deactivation at 280°C. This selectivity to propane decreased with increasing temperature. The selectivity to butenes increased with increased temperature. The distillation curve of Sample 1 had some unusual features. 70% of the material (3%-73%) distilled in a 200°F range. The next 25% distilled in a 600°F range. The other sample, #8, was more normal. It showed a narrow distribution and had only a small high temperature trail.

The ReY-62 catalyst performed even worse than the CaY-62 catalyst. The catalyst showed similar initial conversion but deactivated much more rapidly. The ReY-62 has higher acidity than the CaY-62 and this higher acidity was probably the cause of the faster deactivation rate.

TABLE 6A RESULT OF PROPYLENE OPERATION

RUN NO. 9972-15
CATALYST RE-Y62 #9939-97 63 CC 35.00GM (40.87GM AFTER THE RUN,+5.87GM)
FEED H_2:C_3H_6:H_2O @1:1:2 MOLE RATIO,0.5 C_3H_6 WHSV,CONTINOUS OVERNITE
C_3H_6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C_3H_6 34.3 CC/HR H_2 170 CCMN,10.2L/HR H_2O 15 CC/HR
ACTUAL FLOW: 35.3 CC/HR EFFLUENT 20.0L/HR AQ LAYR 13.7CC/H

RUN & SAMPLE NO.	9972-15-1	9972-15-2	9972-15-3	9972 15 4	9972-15-5
C_3H_6 WHSV	0.5	0.5	0.5	0.5	0.5
HRS ON STREAM	7.3	25.4	32.7	50.9	54.3
PRESSURE,PSIG	158	152	149	151	151
TEMP. C	280	280	280	279	279
FEED C_3H_6 CC	230.31	644.99	251.70	663.87	113.27
HOURS FEEDING	7.25	18.083	7.25	18.167	3.417
EFFLNT GAS LITER	120.8	367.8	147.8	373.8	70.0
GM AQUEOUS LAYER	95.76	250.05	100.02	250.08	47.36
GM LIQ HYDROCARBON	1.40	0.00	0.00	0.00	0.00
WT FR. LIQ HC/FEED	.0119	.0000	.0000	.0000	.0000
MATERIAL BALANCE WT %	89.21	93.08	94.42	91.76	NORMALIZED
C_3H_6 CONVERSION %	10.46	2.13	1.65	1.31	0.99
PRDT SELECTIVITY WT %					
CH_4	0.00	0.00	0.37	0.00	0.00
C2 HC'S	0.46	0.00	0.00	0.00	0.00
C_3H_8	27.55	55.66	64.09	71.11	70.11
C_4H_{10}	3.10	4.54	2.52	1.93	0.96
C_4H_8-	4.97	8.16	4.05	2.20	2.04
C_5H_{12}	2.34	1.35	1.36	0.32	0.00
C_5H_{10}=	0.25	0.00	0.00	0.00	0.00
C_6H_{14}	8.80	4.76	3.97	2.61	0.85
C_6H_{12}= & CYCLO'S	3.95	4.99	5.10	0.00	0.00
C7+ IN GAS	35.62	20.54	18.54	21.83	26.04
LIQ HC'S	12.97	0.00	0.00	0.00	0.00
TOTAL	100.00	100.00	100.00	100.00	100.00
SUBGROUPING					
C1 -C4	36.08	68.35	71.03	75.24	73.11
C5 -420 F	58.60	31.65	28.97	24.76	26.89
420-700 F	3.75	0.00	0.00	0.00	0.00
700-END PT	1.57	0.00	0.00	0.00	0.00
C5 -END PT	63.92	31.65	28.97	24.76	26.89

```
  ISO/NORMAL MOLE RATIO
    C4                  12.4651     0.7906     3.6129     2.2143       -
    C5                  11.5893     2.5652     1.9524     0.0000
    C6                  21.8454     4.3778     4.0667     1.8276
    C4=                  0.3342     0.3077     0.3235     0.3019     0.3939

  PARAFFIN/OLEFIN M RATIO
    C2                   0.1605       -          -          -          -
    C3                   0.0313     0.0119     0.0106     0.0093     0.0069
    C4                   0.6019     0.5369     0.6008     0.8491     0.4545
    C5                   9.2763       -          -          -          -

LIQ HC COLLECTION
  PHYS. APPEARANCE        OIL         -          -          -          -
  DENSITY                  .          .
  N.REFRACTIVE INDEX       .          .
  SIMULATED DISTILLATION
    10 WT % @ DEG F.      286        ---        ---        ---        ---
    16                    308        ---        ---        ---        ---
    50                    395        ---        ---        ---        ---
    84                    589        ---        ---        ---        ---
    90                    861        ---        ---        ---        ---

    RANGE(16-84%)         281        ---        ---        ---        ---

    WT % @420 F          59.0        ---        ---        ---        ---
    WT % @700 F          87.9        ---        ---        ---        ---
```

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TABLE 6B RESULT OF PROPYLENE OPERATION

RUN NO. 9972-15
CATALYST RE-Y62 #9939-97 63 CC 35.00GM(40.87GM AFTER THE RUN,5.87GM)
FEED H2:C3H6:H2O @1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINOUS OVERNITE
C3H6 MW- 42.0813 DENSITY= 0.5104L GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 170 CCMN,10.2 L/HR H2O 15 CC/HR
ACTUAL FLOW: 35.3 CC/HR EFFLUENT 20.0 L/HR AQ LAYR 13.7CC/H

RUN & SAMPLE NO.	9972-15-6	9972-15-7	9972-15-8	9972-15 9
C3H6 WHSV	0.5	0.5	0.5	0.5
HRS ON STREAM	75.1	80.4	98.5	101.9
PRESSURE,PSIG	152	159	155	159
TEMP. C	343	343	373	373
FEED C3H6 CC	748.54	188.78	643.14	112.64
HOURS FEEDING	20.75	5.333	18.167	3.417
EFFLNT GAS LITER	424.1	105.9	364.3	66.7
GM AQUEOUS LAYER	287.16	72.39	249.52	46.7
GM LIQ HYDROCARBON	0.66	0.00	0.92	0.00
WT FR. LIQ HC/FEED	.0017	.0000	.0028	.0000
MATERIAL BALANCE WT %	91.39	93.96	90.97	94.18
C3H6 CONVERSION %	4.23	4.17	7.99	8.01
PRDT SELECTIVITY WT %				
CH4	0.40	0.38	0.52	0.62
C2 HC'S	0.00	0.34	0.50	0.31
C3H8	35.62	35.27	22.46	23.15
C4H10	0.78	0.86	0.78	0.73
C4H8=	5.66	5.69	11.04	11.78
C5H12	0.36	0.48	0.75	0.74
C5H10=	0.44	0.53	0.76	0.85
C6H14	5.76	6.31	7.50	7.86
C6H12- & CYCLO'S	12.88	13.39	11.90	12.79
C7+ IN GAS	33.68	36.74	39.96	41.18
LIQ HC'S	4.43	0.00	3.85	0.00
TOTAL	100.00	100.00	100.00	100.00
SUBGROUPING				
C1 -C4	42.46	42.54	35.29	36.59
C5 -420 F	55.68	57.46	63.05	63.41
420-700 F	1.55	0.00	1.58	0.00
700-END PT	0.31	0.00	0.07	0.00
C5 -END PT	57.54	57.46	64.71	63.41

ISO/NORMAL MOLE RATIO				
C4	0.7273	0.6364	0.9369	1.1236
C5	0.2353	0.8667	0.6019	0.5714
C6	3.0426	3.1467	4.4822	4.3789
C4+	0.3907	0.3926	0.2827	0.2775
PARAFFIN/OLEFIN M RATIO				
C2	-	-	0.5138	-
C3	0.0153	0.0149	0.0189	0.0195
C4	0.1326	0.1463	0.0685	0.0596
C5	0.7925	0.8750	0.9593	0.8462
LIQ HC COLLECTION				
PHYS. APPEARANCE			OIL	
DENSITY	.	.		
N,REFRACTIVE INDEX	.	.		
SAVELATED DISTILLATION				
10 WT % @ DEG F.	---	---	297	---
16	---	---	325	---
50	---	---	408	---
84	---	---	518	---
90	---	---	569	---
RANGE(16-84%)	---	---	193	--
WT % @420 F	---	---	57.0	---
WT % @700 F	---	---	98.1	---

RUN NO. 9972-15

Figure 26

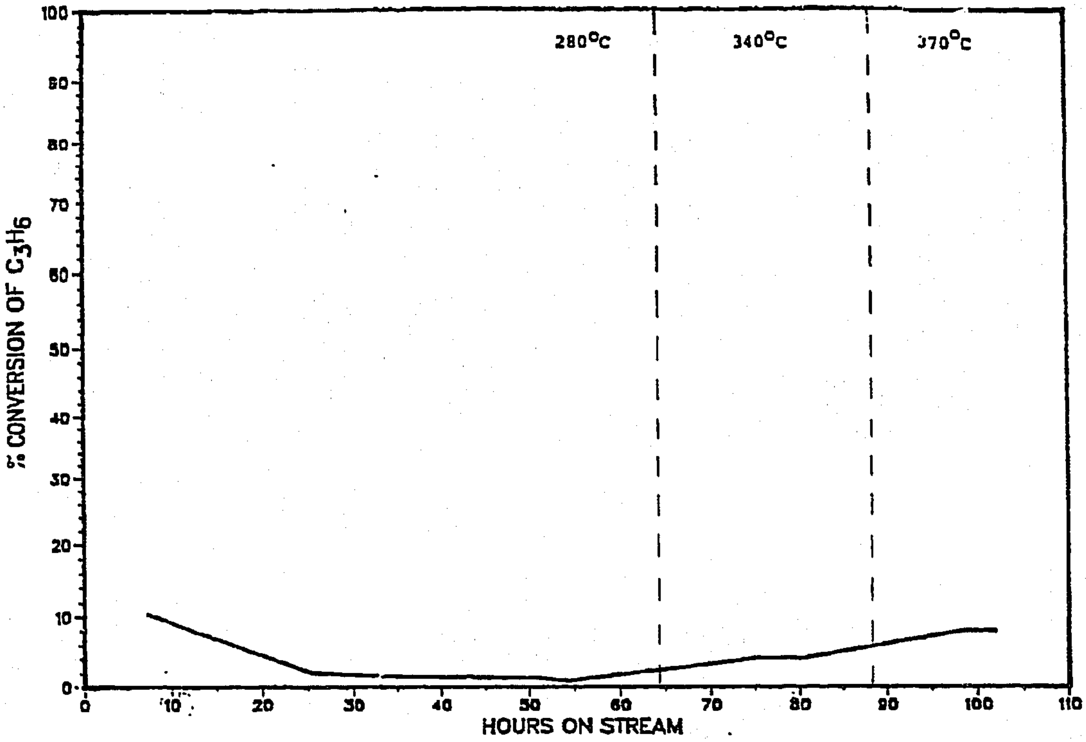


Figure 27

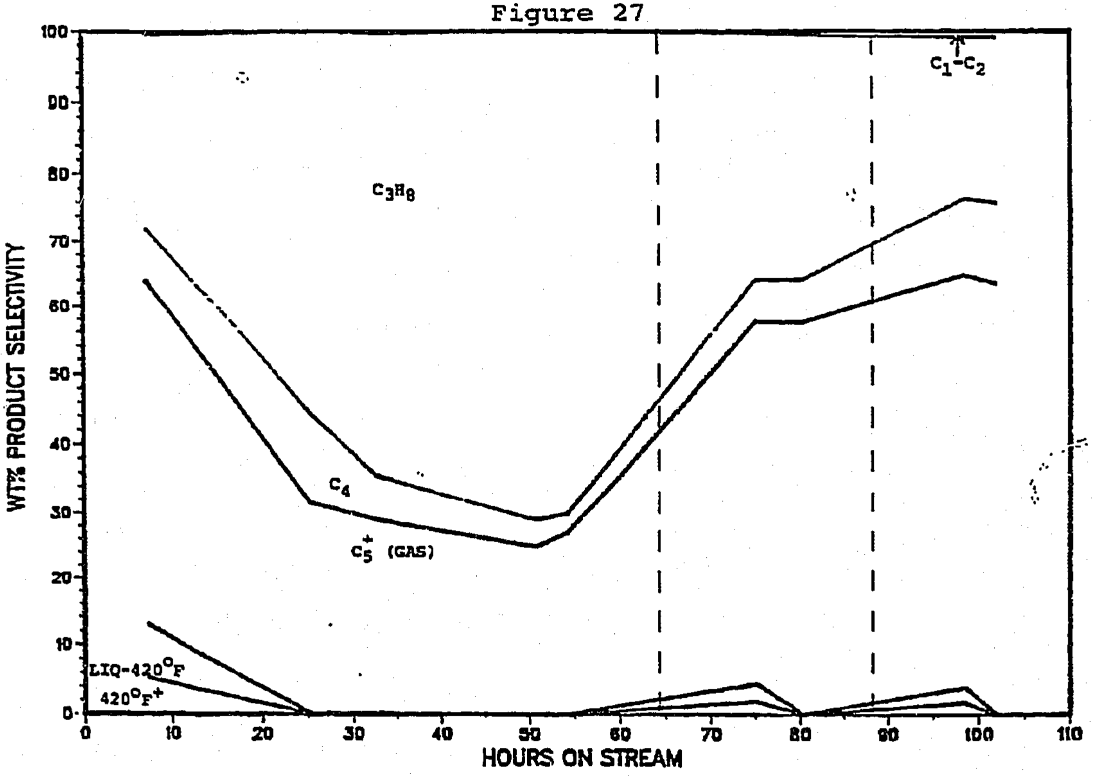


Figure 28

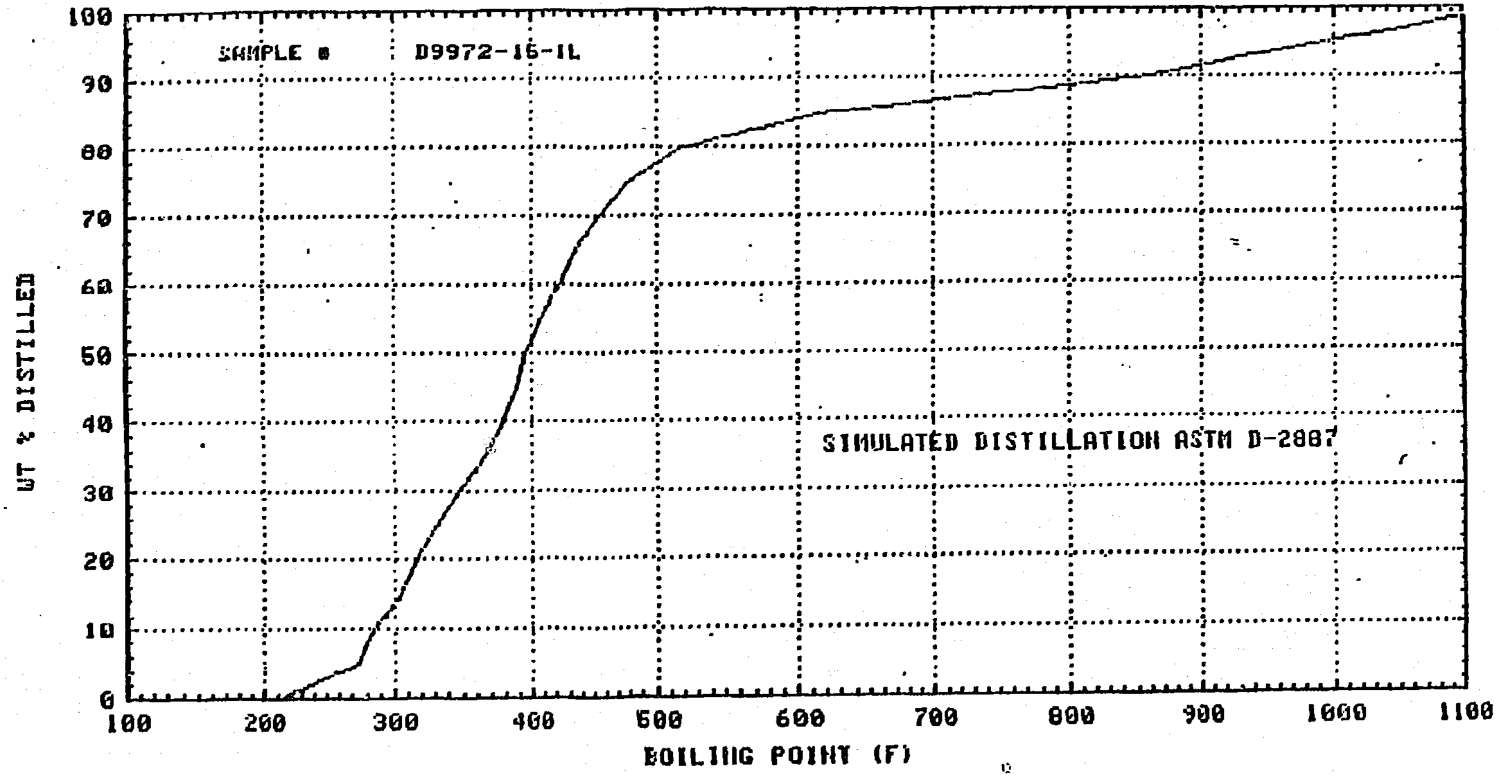
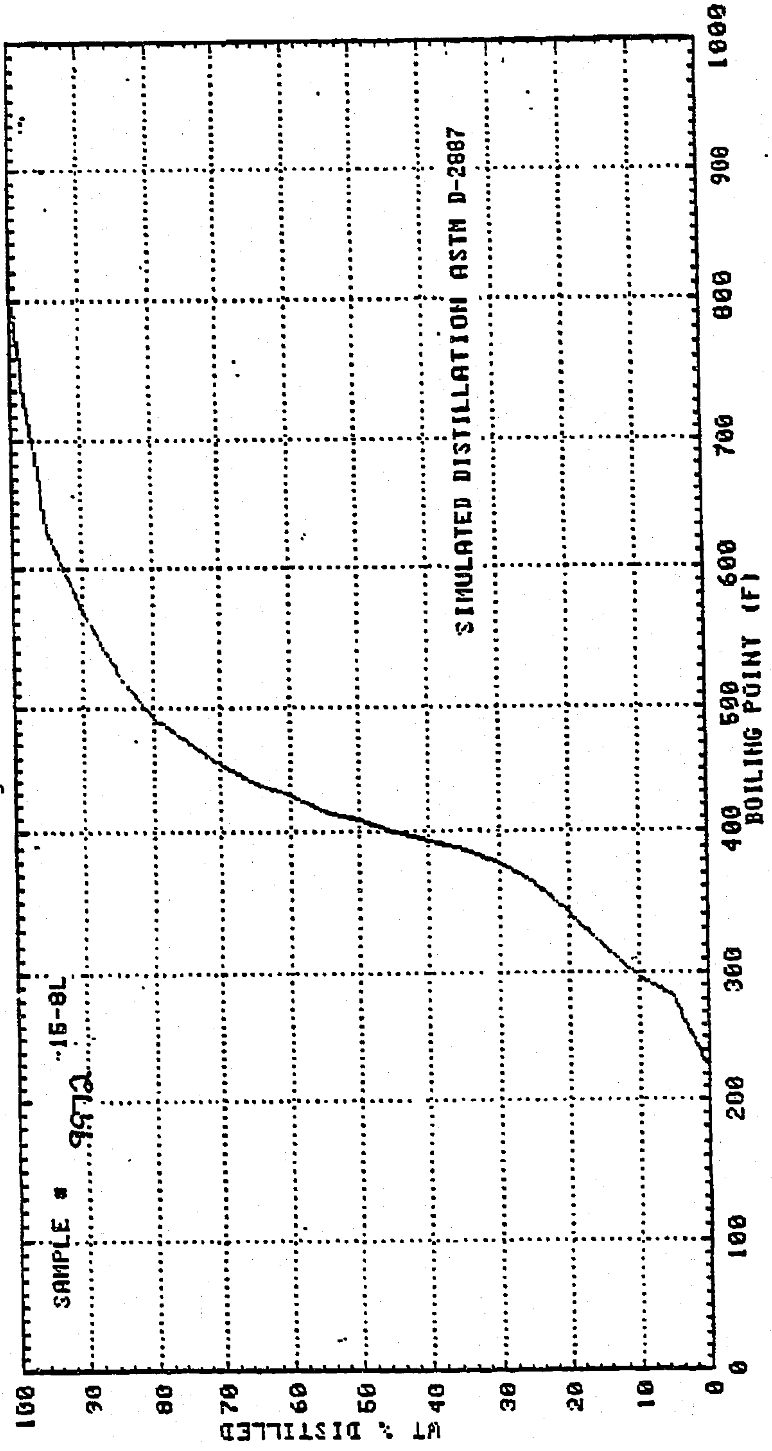

SAMPLE # D9972-16-IL
SIMULATED DISTILLATION ASTM D-2887
WT % DISTILLED
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
600
700
800
900
1000
1100
BOILING POINT (F)

Figure 29


SAMPLE # CL5B -15-8L
SIMULATED DISTILLATION ASTM D-2887
BOILING POINT (F)
WT % DISTILLED
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

Micro-reactor Run LZ-105

An LZ-105 micro-reactor run from last quarter is reported here. The exact conditions used were discussed last quarter. Briefly, a 2:1 $H_2:C_3H_6$ molar ratio was fed during the day and H_2 was fed overnight. The reactor was held at 150 psig, 340°C. The detailed results of the run are presented in Table 7. The catalyst tested was LZ-105-6. It was used to evaluate the differences between the Berty and micro-reactors. The conversion of propylene was almost quantitative in the micro-reactor. (It was 95% in the Berty reactor.) This small difference may reflect material which can bypass the catalyst in the Berty. The selectivity to propane was higher in the micro-reactor. The butane was also higher, suggesting an accompanying highly aromatic liquid product. The amounts of C_5 and C_6 saturates obtained are lower in the micro-reactor. In a Berty reactor, the catalyst would see the recycled product mixture, and therefore never a high propylene concentration. In a plug flow micro-reactor, only the front of the active catalyst bed would see a high propylene concentration. Since large amounts of propane were produced, the aromatic precursors must have been formed before all the propylene was converted. We assume that the aromatics found were formed right at the reaction zone and not from secondary reactions further in the bed. The high propane and butane formation were the cause of the low C_5^+ selectivity, being only 41% in the micro-reactor and 68% in the Berty reactor.

LZ-105 gave slightly different results in the micro-reactor than in the Berty reactor. The conversion was comparable in both cases. The product selectivity was different due to the differences between (continuous stirred tank reactor) plug flow and CSTR reactors.

TABLE 7 PROPYLENE OPERATION IN MICRO-REACTOR

NTBK NO. 10027 MICRO-REACTOR RUN WITH CATALYST WT 7.00 GMS
FEED H2:C3H6 @ 2:1 MOLE RATIO, 1.0 C3H6 WHSV, DAY-TIME FEED ONLY
C3H6 MW= 42.0813 DENSITY= 0.51041 GM/CC (@ 73 F)
TARGET FLOW: C3H6 13.7 CC/HR H2 135 CCMN, 8.1 L/HR
ACTUAL FLOW: 15.3 CC/HR EFFLUENT 12.5 L/HR

RUN NO.	10027-02
CATALYST	LZ-105-6
C3H6 WHSV	1.1
HRS ON STREAM	7.25
PRESSURE,PSIG	150
TEMP. C	340
FEED C3H6 CC	111.14
HOURS FEEDING	7.25
EFFLNT GAS LITER	62.77
GM LIQ HYDROCARBON	11.34
WT FR. LIQ HC/FEED	.1999
MATERIAL BALANCE WT %	82.56
C3H6 CONVERSION %	99.69
PRDT SELECTIVITY WT %	
CH4	0.63
C2 HC'S	1.62
C3H8	30.32
C4H10	23.12
C4H8=	0.57
C5H12	8.96
C5H10=	0.26
C6H14	3.30
C6H12= & CYCLO'S	0.42
C7+ IN GAS	5.45
LIQ HC'S	25.34
TOTAL	100.00
SUB-GROUPING	
C1 -C4	56.27
C5 -420 F	32.33
420-700 F	11.15 E
700-END PT	0.25 E
C5 -END PT	41.40

```
  ISO/NORMAL MOLE RATIO
    C4                      1.2838
    C5                      3.2381
    C6                      7.2715
    C4=                     0.5459

  PARAFFIN/OLEFIN M RATIO
    C2                     37.6116
    C3                     95.7476
    C4                     38.8192
    C5                     33.571

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 TASK 1 TESTING

Based on tests from the previous quarter, standard test conditions were established. This test was flexible enough to allow temperature changes during the run, and comparable enough to allow comparisons between catalysts. Generally, the medium pore molecular sieves tested were excellent catalysts for propylene oligomerization. Several of the other catalysts tested were disappointing, whowing either low activity or very rapid deactivation.

LZ105-6 was already known to be a good catalyst for propylene oligomerization. The test this quarter was only to extend our knowledge of its reactivity to the range of the standard test conditions. This medium pore molecular sieves showed only modest deactivation and good selectivity to liquid products. The percentage of aromatics in the condensed product was low because of the low reaction temperature. At the lowest temperatures, the aromatization process showed greater deactivation than the oligomerization process.

<u>With its higher activity but slightly inferior selectivity to C_5^+ products, this catalyst, LZ-105, is comparable to UCC-104, which is the best catalyst for this reaction reported thus far.</u>

The multivalent ion, (calcium or rare earth) exchanged Y zeolites were very poor catalysts for propylene oligomerization. They both showed low initial conversion and rapid deactivation. The more acidic REY-62 showed much more rapid deactivation than CaY-62.

The new materials reported this quarter, UCC-103, 106 and 107, were also disappointing catalysts. The UCC-103 (acid extracted UCC-101) was superior to UCC-101. The activity was comparable and deactivation was slightly less. The selectivity to liquid was better because of the lower selectivity to propane. Even with being better than UCC-101, the UCC-103 suffered from low activity and only fair stability. UCC-106 had higher initial conversion than UCC-101 or 103, but deactivated more rapidly. UCC-107 had low initial conversion and very rapid deactivation.

INTRODUCTION TO TASK 2 TESTING

Six syngas tests are reported this quarter, 10011-6 to -9 and 9972-11 and -12. Some of these tests were quite extensive, investigating many different process conditions. Three of the runs, 10011-6, 9972-11 and 9972-12 were begun last quarter but are reported here. Additionally three runs 10011-10 to -12 were begun this quarter but will be reported next quarter. This one month offset between testing and reporting periods is necessary to obtain all the analytical information for the test.

Unlike last quarter, the tests run this quarter were not shakedown runs. The catalysts tested were very active and had good product distributions. The various activation procedures investigated last quarter allowed the adoption of a reliable activation procedure this quarter. The many process conditions examined in the tests early in the quarter also allowed for the establishment of standard initial test conditions.

The standard activation procedure used for iron based catalysts is as follows. The catalyst is heated to 270°C under nitrogen at 50 psig. At temperature CO is introduced slowly into the nitrogen feed. This slow introduction is to control initial exotherms. The CO concentration is increased to 25% of the total feed, 400 cc/min. CO, 1200 cc/min N_2. The CO is fed over the catalyst for 24 hours. The feed is then switched to hydrogen at 2000 cc/min. and this is fed over the catalyst for 18 to 24 hours.

For the standard initial test condition, the reactor is kept at 300 psig and 250°C. 1:1 H_2:CO syngas is fed into the reactor at 400 cc/min. Depending upon the information desired about the catalyst, the test conditions may be altered after an initial period which is usually 4 days. Many tests are terminated directly after this initial period. For those tests that continue, the change in process conditions usually involves changing the temperature or the H_2:CO ratio of the feed.

Most of the calculations involved in the data analysis were discussed last quarter and will not be reiterated here. The new analysis which has been included this quarter is the product distribution presented in a Schultz-Flory format. This will be an important tool for catalyst evaluation from now on. The concentrations of the C_1 to C_5 hydrocarbons are taken from the G.C. analysis. The concentrations of the components in the condensed phase are calculated from simulated distillations. For this calculation it is assumed that the product boiling between the boiling points of normal $C_{n-1}H_{2n}$ and normal C_nH_{2n+2} has the carbon number n. This is a good assumption if the product is not highly aromatic because isoparaffins and olefins usually boil at temperatures lower than that of the normal paraffin but above that of the next lower paraffin. The exceptions to this occur in the lower carbon number products which are mostly analyzed in the gas phase. The liquids produced this quarter fit this low aromatic assumption. By refractive index analysis, described in the introduction to Task 1 testing, the liquids produced this quarter contained less than 5% aromatics.

The difference in aromatics can be accounted for. Aromatics of carbon number n generally boil in the range of C_{n+1} olefins and paraffins. This carbon number product distribution can take aromatics into consideration if the percentage of aromatics is known and the assumption is made that the aromatics are fairly equally distributed amont the carbon numbers. That is the aromatics have the same boiling point distribution as the product as a whole. For highly aromatic products, this has to be true. For low percentages of aromatics, it is unimportant. A problem might occur for very heavy products with 20 to 30% aromatics. The heavier oils may dealkylate giving a lower average molecular weight to the aromatics than the paraffins and olefins.

In our present analysis, the hydrocarbons are not well-defined. The total weight percent of this material is known but the distribution among carbon numbers is unknown. Presently certain gas samples are bubbled into methanol. This methanol is analyzed on a capillary column G.C. to see the distribution of hydrocarbon among the various carbon numbers. Until better correlations can be established to define this distribution, the C_6 to C_{10} products will be ignored in this analysis. The data is plotted in a Schultz-Flory format, $\ln(W_n/_n)$ versus n where W_n is the weight fraction of the product with carbon number n.

Run 10011-6: Reference Iron Catalyst

Run 10011-6 was very extensive with the catalyst being on stream for over 450 hours. The catalyst was potassium-promoted iron oxide containing no shape selective component. This catalyst represents the state-of-the-art of iron catalysts, a standard against which the molecular sieve containing catalysts will be compared. For a sieve containing catalyst to be superior, it should have either a higher selectivity to desired products, gasoline or diesel oil, or it should have superior product characteristics, such as higher octane gasoline, and lower pour point, for the heavier distillate fuels, while maintaining high activity.

The catalyst was kept on stream for a long time to investigate the catalyst's characteristics under many process conditions. These conditions were studied for two purposes. Firstly, the conditions were chosen to maximize the C_5^+ product and then altered in an attempt to convert the solid condensed product to oil. The data was to be used to choose the best conditions to test the molecular sieve containing catalysts. The second reason for testing at so many process conditions was to have a reference material result to compare to that with a molecular sieve containing catalyst at a variety of test conditions.

The material balances, activities, and product selectivities for all the samples in the run are reported in Tables 8A to 8H. A summary of the conversions and product selectivities are represented in Figures 30 and 31. The boiling point distributions of condensed products representative of the various process conditions are shown in Figures 32 to 36. The Schultz-Flory hydrocarbon product distributions of those representative samples are shown in Figures 37 to 41. The first seven samples were taken with the reactor at 100 psig and 250°C. The on-line-blended 1.06:1 H_2:CO syngas was fed at 400 cc/min. After ~70 hours on stream the feed gas was changed to a preblended 1:1 H_2:CO syngas which contained a 10% argon tracer. At ~120 hours on stream, the feed gas was again changed this time to a preblended 60:30:10 H_2:CO:Ar syngas. The higher hydrogen ratio syngas should produce lighter, more hydrogen-rich hydrocarbons and possibly change the solid condensed product to an oil. After ∿175 hours on stream, the temperature was raised to 280°C. It was raised further to 310°C at ∿250 hours on stream. These temperature increases were further attempts to reduce the amounts of heavy products. At ∿315 hours on stream, the reactor pressure was lowered from 100 psig to 30 psig. This lower reactant concentration lowered the probability of chain growth and gave lighter products. At ∿435 hours on stream, the temperature was finally raised to 340°C and the run terminated at 455 hours on stream. This range of process conditions gives a wide spectrum from which to choose conditions which will be optimal for the molecular sieve containing catalysts.

The addition of potassium to an iron catalyst has a number of effects on its catalytic activity. The alkali introduces water gas shift activity into the catalyst. This allows for the efficient use of low H_2 to CO ratio syngas, the kind produced by modern coal gasifiers. With these CO rich compositions less of the hydrogen, the more valuable component of the syngas, is lost to byproduct water formation. The price paid is that more of the CO is diverted to the production of CO_2. From stoichiometry, the molar ratio $CH_x/(H_2O+CO_2)$ must be 1.0. This ratio, reported for every sample, was often less than 1.0 at the early stages of the run. This was probably caused by further reduction of the iron oxide to iron metal producing CO_2 or H_2O but no hydrocarbons. $CH_x/(H_2O+CO_2)$ values far different from 1.0, particularly well into a run suggests that the data is suspect. This catalyst showed good water gas shift activity. With the 1:1 syngas at 250°C approximately 1/2 the CO became CO_2 with little water being produced. The switch to 2:1 syngas obviously lowered the amount of CO_2 produced but kept the water gas shift constant at the same value. With increased temperature, the water gas shift increased while the actual % of the CO becoming CO_2 decreased. This was due to the absolute amounts of CO and H_2 in the effluent. The drop in pressure initially increased the percentage of CO becoming CO_2. During this run, the shift activity showed faster deactivation rates than the F-T synthesis itself.

The addition of potassium to iron Fischer-Tropsch catalysts is also known to increase the amount of oxygenates produced, particularly C_2^+ alcohol. Many of the aqueous layer samples were analyzed for alcohols. Ethanol generally predominated over the other alcohols being up to 5% of the aqueous layer. Methanol, iso and n-propanol were also detected. Some of the later samples, 31, 32 and 34, actually had isopropanol as the predominate alcohol (at 0.2%). The aqueous samples not analyzed for specific alcohols were analyzed for total organic carbon, TOC. The results gave 10-50 mg/ml TOC. This corresponded to less than 1.5% of the carbon in the hydrocarbon product. With approximately half the carbon going to CO_2, the exclusion of alcohols from the product analysis does not significantly affect the product distribution or the material balance.

The conversion of syngas, the combined $CO+H_2$ conversion, showed significant deactivation over the first two days of operation. It dropped from the initial 74% to approximately 45%. After this, the conversion remained relatively constant even though the reaction conditions were altered significantly. Some of this was due to the deactivation being overcome by the more rigorous test conditions employed. The syngas conversion decreased with the introduction of the 2:1 feed at 250°C. This was not due to a deactivation of the catalyst. We envision that the high concentration of hydrogen was not effectively used. The H_2/CO usage ratio clearly showed this. In the 1:1 syngas the usage ratio was approximately 0.6. The reaction was using more CO than hydrogen. The introduction of extra hydrogen to such a system would not be efficient. The usage ratio did increase to ∿0.75 for the 2:1 syngas at 250°C. While the combined conversion of $CO+H_2$ decreased with the introduction of the 2:1 syngas, due to this inefficient usage of the hydrogen, the percent conversion of the CO actually increased. With lower CO_2 production and higher CO conversion, the percent conversion of CO to hydrocarbons was actually 42% higher in sample 14, from 2:1 syngas at 250°C, than in sample 5, from 1:06:1

syngas at 250°C, even though the combined syngas conversion is 7% lower. The Fischer-Tropsch reaction is very sensitive and changes in product distribution and feed usage ratios result from changes in test conditions. This makes careful analysis of all the data necessary to evaluate the effect of any test condition change. Simply looking at combined syngas conversion can imply trends going in the wrong direction. Comparisons of the activities of different catalysts must be made with great care to see what the real differences in the two catalysts are and what losses or gains in activities were the cause of these differences. The increase in combined syngas conversion with increased temperature was not as great as expected. The conversion was $\sim$41% at 250°C and increased to only 59% at 310°C. Rather than this being due to the activation energy for the reaction, the small change is probably a sign of deactivation and changes in the catalyst with the increased temperature.

The changes in the reaction conditions had large effects on the hydrocarbon product distribution. The heaviest hydrocarbons were produced at the lowest reaction temperatures. The selectivity to methane was initially very low, 4%, then increased to 7.0% with the introduction of the 2:1 syngas feed. While this was a 75% increase, the absolute amount of methane was still quite low. The selectivity to methane remained at or below 10% until the pressure was reduced to 30 PSIG at 310°C. With that change, the methane selectivity increased 150% to 27 wt.%. When the temperature was increased to 340°C, the methane selectivity increased another 40% to 37 wt.%.

The light gases, other than methane, showed much less dramatic changes with the various test conditions. The C_3's and C_4's did not increase with the drop in pressure or the temperature increase to 340°C. The paraffin to olefin ratio of the C_3-C_5 hydrocarbons indicated the entire hydrocarbon product was probably highly olefinic. The percentage of paraffins increased with decreased pressure and increased temperature. The iso/normal ratio of the light paraffins, C_4-C_6, was low as expected. This ratio showed no clear trend with changes in test conditions until the pressure was decreased, when it increased. The iso/normal ratio increased further with the temperature increase at the low pressure. Analysis of these light gases has not helped to identify optimal test conditions. The choice must be left to the analysis of the C_5^+ product.

At the start, the C_5^+ yield was 83% at 250°C and decreased steadily to 33% at 340°C. The amount of material which was condensed showed an even more dramatic decrease, changing from 68% of the total hydrocarbons at 250°C to only 13% at 340°C. Since C_5^+ is the desired product, this would seem to give a clear advantage to 250°C with 1:1 syngas feed as the optimal test conditions. The choice is not as simple, however, since the nature of the C_5^+ product also changed with process conditions. Different conditions would be chosen as best depending upon how the product would be further upgraded.

At 250°C, the condensed hydrocarbon product was a solid wax at room temperature. The condensed product from all the conditions tested was solid except for the final condition, 340°C when a liquid condensed product was collected. At 250°C with 1:1 syngas feed, very heavy hydrocarbons were produced. 23% of the hydrocarbons produced boiled in the gasoline range, the hydrocarbons starting with C_5 which boil below 420°F. 29% boiled between the gasoline range and the upper limit of the diesel range, 700°F. 32% of all the hydrocarbons produced (47% of the condensed product) boiled above the diesel range. While this final material, wax, may be a good cracking feed, it has little value in a once-through operation. This maximum selectivity to C_5^+ was not the maximum selectivity to motor fuel range materials.

With so much of the condensed product being wax, it is not surprising that the condensed product from the reaction at 250°C was solid. The condensed product remained solid while the percentage of material boiling above the diesel range decreased from 47% to 20%. The lower pressure which decreased the C_5^+ selectivity from 60% to 40% actually increased the percentage of the condensed 700°F$^+$ product from less than 20% to 23%. The final condensed product which was the first totally liquid sample actually contained a higher percentage of 700°F$^+$ material, 25%, than the previous solid samples. It may seem contradictory that the liquid product was heavier than the solid product but the reason for this can easily be seen in the data. Analysis of the light paraffins showed that the hydrocarbons produced under most conditions were straight chains. These hydrocarbons pack well together and solidify at relatively high temperatures, i.e., they have high pour points. At 340°C, these light paraffins showed more branching. It is reasonable to assume that the heavier hydrocarbons were also highly branched. Branched hydrocarbons have much lower pour points than the corresponding normal hydrocarbons. The reaction conditions at 340°C produced liquid condensed products instead of solids not because it produced a lighter product but because it produced a more isomerized one.

The maximum amount of material in the motor fuel range, C_5 to 700°F, was produced at 280°C with 2:1 syngas at 100 psig. The other conditions at 100 psig were all close producing about 90% as much material in that boiling range.

The plots of the simulated distillations of the condensed samples were all smooth and broad showing no high concentration of individual compounds as had been previously seen in many of the Task 1 tests. The condensed products had little material boiling below 300°F and many of the samples contained material which boiled above 1000°F. This boiling point distribution data was combined with the gas product analysis to give the product distribution for the catalyst. As described in the introduction, C_5-C_{10} are not well characterized at this time and were not included in the graphs.

The reference F.T catalyst was expected to give a Schultz-Flory distribution. A Schultz-Flory distribution is obtained when the probability of chain growth is independent of carbon number. This distribution gives a straight line when plotted as ln(Wn/n) vs. n where Wn is the weight fraction of the product with carbon number n. Sample 10011-6-4 had some scatter in the data but it did follow the expected straight line SF distribution. A straight line through the data gives an α of 0.83. A later sample, 10011-6-9, which was taken under the same reaction conditions did not give a single straight line product distribution. Up to C_{20}, it gave a straight line with an $\alpha = 0.84$. At C_{20} there was a sharp change and α increased to 0.91. This double α product distribution was seen in the rest of the samples taken during this run. Sample 10011-13 which was taken at 250°C but with 2:1 syngas showed similar α's of 0.84 and 0.91 with the change at $\sim C_{20}$. The other samples taken at higher temperatures all had lower α's but there were still two α's with the change occurring at about C_{20}.

A simple explanation of this double α is that the probability of chain growth may actually increase with increased molecular weight. The probability of chain termination should increase with the increased ability of intermediates to desorb from the surface of the catalyst. Because of their low vapor pressure, the heavier hydrocarbons should have trouble desorbing from the catalyst even at the reaction temperature. This increase in α would be gradual and not a sharp break at C_{20}. It would reflect the gradual changes in the hydrocarbon properties with increased carbon number.

There is another explanation which could explain this double α type product distribution. These two α's may indicate there are two distinct active sites each with its own distinct α. The site with the lower α may have dominated the product distribution at carbon numbers below C_{20}, while the other site may have dominated the distribution of the heavier hydrocarbons. If the α's were different enough a fairly sharp break would occur. It is possible that one of the sites corresponded to a potassium-promoted one while the other was unpromoted. The fact that the double α was not seen in the first sample would indicate that the high α site took longer to become activated. The two sites appeared to be deactivating at similar rates. If this is the correct explanation for the two α's it is unlikely that the nature of the sites will be easily defined since only a small percentage of the possible iron sites are actually used.

A double α product distribution (when the second α is higher than the first) has a greater percentage of wax formation than a single α distribution with the same first α. It would be better if the high carbon number α were less than the low carbon number α. This situation would give more product in the desired motor fuel range with less than expected $700^{\circ}F^{+}$ formation. This kind of product distribution cannot be the result of two active sites, but it can be accomplished with shape selective control From the results of this catalyst it would seem that the molecular sieve containing catalysts should be tested at 250°C with a 1:1 syngas feed. These are the most difficult conditions for the molecular sieve containing catalyst to halt the formation of heavy waxes. If the sieve cannot accomplish this, the conditions can be made progressively less stringent until the formation of wax product is stopped.

TABLE 8A RESULT OF SYNGAS OPERATION

RUN NO. 10011 6
CATALYST FE2O3, 1% K2O, #9673-11E, REFERENCE CATALYST, 80CC 86.86 GM
FEED: H2:CO:AR OF 50/50/0, 45/45/10 & 60/30/10 @ 400CC/MN OR 300GHSV

RUN & SAMPLE NO.	10011-6-1	10011-6-2	10011-6-3	10011-6-4	10011-6-5
FEED H2:CO:AR	51:48:0	51:48:0	51:48:0	51:48:0	51:48:0
HRS ON STREAM	5.167	21.9	24.4	28.9	45.6
PRESSURE, PSIG	102	99	101	101	101
TEMP. C	254	253	256	253	253
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	5.167	16.58	2.5	7.0	16.7
EFFLNT GAS LITER	61.4	227.0	35.4	98.6	326.7
GM AQUEOUS LAYER	3.21	10.99	0.943	2.64	4.08
GM OIL & WAX	3.82	19.38	2.650	7.43	20.61
MATERIAL BALANCE					
GM ATOM CARBON %	83.44	89.67	88.13	79.99	98.74
GM ATOM HYDROGEN %	86.38	93.88	89.73	82.78	99.51
GM ATOM OXYGEN %	93.05	100.03	93.97	82.28	106.39
RATIO CHX/(H2O+CO2)	0.8013	0.7882	0.8589	0.9221	0.7762
RATIO X IN CHX	2.1684	2.1585	2.1473	2.1351	2.1388
USAGE H2/CO PRODT	0.6053	0.6089	0.6023	0.6823	0.5762
K EFFLNT SHIFT REACTN	39.22	18.29	16.48	6.63	8.32
CONVERSION %					
ON CO	94.16	87.30	80.34	63.02	55.79
ON H2	55.37	51.30	46.90	40.27	32.33
ON CO+H2	74.24	68.82	63.17	51.34	43.75
PRDT SELECTIVITY, WT %					
CH4	6.22	5.59	5.17	4.44	4.56
C2 HC'S	8.21	7.08	6.57	5.57	5.90
C3H8	1.10	0.90	0.83	0.65	0.66
C3H6=	12.28	9.22	8.38	6.38	6.06
C4H10	1.03	0.81	0.77	0.60	0.61
C4H8=	9.30	6.92	6.41	4.92	4.59
C5H12	2.00	1.55	1.43	1.15	1.08
C5H10=	7.10	5.29	4.92	3.96	0.00
C6H14	2.19	1.63	1.53	1.27	0.11
C6H12= & CYCLO'S	4.18	3.23	3.06	2.56	0.00
C7+ IN GAS	20.32	16.40	16.13	15.03	12.78
LIQ HC'S	26.06	41.39	44.79	53.48	63.65
TOTAL	100	100	100	100	100

SUB-GROUPING					
C1 -C4	38.16	30.52	28.14	22.55	22.38
C5 -420 F	52.40	47.13	46.74	44.45	29.25
420-700 F	8.73	18.38	20.44	26.85	27.62
700-END PT	0.72	3.97	4.68	6.15	20.75
C5 -END PT	61.84	69.48	71.86	77.45	77.62
ISO/NORMAL MOLE RATIO					
C4	.1323	.1364	.1393	.1210	.1455
C5	.1740	.1726	.1695	.1750	.1392
C6	.2321	.1843	.2368	.2019	--
C4-	.0877	.0884	.0913	.0858	.0794
PARAFFIN/OLEFIN M RATIO					
C2	.2586	.2921	.2721	.2707	.2479
C3	.0858	.0927	.0946	.0969	.1047
C4	.1068	.1132	.1154	.1173	.1279
C5	.2736	.2859	.2820	.2811	
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	WAX
DENSITY	0.778	0.789		0.794	
N, REFRACTIVE INDEX	1.4297	1.4336		1.4372	
SIMULATED DISTILLATION					
10 WT % @ DEG F	257	281	LIQ	305	348
16	291	303	UID	342	384
50	385	441	NOT	480	576
84	518	650	COL-	670	822
90	564	697	LECT-	714	884
			ED		
RANGE(16-84 %)	227	347	LUMPED	328	438
			INTO		
WT % @420 F	63.7	46.0	SAMPLE	38.3	24.0
WT % @700 F	97.2	90.4	4	88.5	67.4

TABLE 8B RESULT OF SYNGAS OPERATION

RUN NO. 10011-6
CATALYST FE2O3,1% K2O, #9673-11E,REFERENCE CATALYST, 80 CC 86.86 GM
FEED H2:CO:AR OF 50/50/10,45/45/10 & 60/30/10 @ 400CC/MN OR 300GHSV

RUN & SAMPLE NO.	10011-6-6	10011-6-7	10011-6-8	10011-6-9	10011-6-10
FEED H2:CO:AR	51:48:0	51:48:0	45:45:10	45:45:10	45:45:10
HRS ON STREAM	51.0	71.4	93.9	101.9	118.2
PRESSURE,PSIG	101	99	97	99	94
TEMP. C	253	253	253	253	253
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	5.4	20.4	22.5	8.0	16.3
EFFLNT GAS LITER	103.3	391.6	395.0	139.0	280.5
GM AQUEOUS LAYER	0.3	0.85	0.0	0.0	0.0
GM OIL & WAX	8.47	34.14	32.81	9.63	23.34
MATERIAL BALANCE					
GM ATOM CARBON %	106.51	106.91	94.55	90.03	92.48
GM ATOM HYDROGEN %	106.72	107.22	92.66	89.67	90.96
GM ATOM OXYGEN %	102.83	105.32	93.70	93.31	91.80
RATIO CHX/(H2O+CO2)	1.1192	1.0491	1.0283	0.8914	1.0229
RATIO X IN CHX	2.1193	2.1259	1.9866	2.1388	1.9867
USAGE H2/CO PRODT	0.6675	0.6347	0.5811	0.5649	0.5792
K EFFLNT SHIFT REACTN	12.73	14.43	15.72	15.85	15.78
CONVERSION %					
ON CO	58.12	58.77	61.87	60.43	61.77
ON H2	35.61	34.81	36.42	35.31	36.16
ON CO+H2	46.56	46.47	49.15	47.90	48.97
PRDT SELECTIVITY,WT %					
CH4	3.70	3.94	4.04	4.67	4.15
C2 HC'S	4.26	4.33	4.13	4.63	3.81
C3H8	0.49	0.47	0.41	0.49	0.41
C3H6=	4.59	4.34	3.94	4.66	3.88
C4H10	0.47	0.43	0.39	0.46	0.38
C4H8=	3.42	3.32	3.05	3.51	2.91
C5H12	0.79	0.77	0.72	0.80	0.67
C5H10=	2.66	2.66	2.43	2.88	2.41
C6H14	1.00	0.89	0.66	0.75	0.75
C6H12= & CYCLO'S	1.51	1.62	1.60	1.69	1.45
C7+ IN GAS	14.91	9.63	9.19	10.07	9.08
LIQ HC'S	62.19	67.60	69.43	65.38	69.99
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 -C4	16.93	16.83	15.96	18.42	15.65
C5 -420 F	33.07E	22.87	21.27	22.27	20.30
420-700 F	26.74E	28.53	29.51	28.77	31.57
700-END PT	23.26E	31.77	33.26	30.53	32.48
C5 -END PT	83.07	83.17	84.04	81.58	84.35
ISO/NORMAL MOLE RATIO					
C4	.1667	.1675	.1454	.1503	.1595
C5	.1806	.1978	.1406	.2124	.1947
C6	.3180	.3184	.0519	.0938	.2563
C4=	.0867	.0848	.0836	.0823	.0769
PARAFFIN/OLEFIN M RATIO					
C2	.2462	.2456	.2742	.2643	.2474
C3	.1017	.1037	.0989	.1010	.1018
C4	.1325	.1241	.1245	.1259	.1262
C5	.2901	.2798	.2894	.2714	.2725
LIQ HC COLLECTION					
PHYS. APPEARANCE	WAX	WAX	WAX	WAX	WAX
DENSITY					
N. REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	-	414	422	424	431
16	-	453	463	465	475
50	-	676	684	674	673
84	-	955	965	954	948
90	-	1014	1023	1010	1006
RANGE(16-84 %)		502	502	489	473
WT % @420 F	19.6E	10.8	9.6	9.3	8.5
WT % @700 F	62.6E	53.0	52.1	53.3	53.6