Methyl Chloride Via Oxyhydrochlorination of Methane

Quarterly Technical Progress Report No.9
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Contractor

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Contract Objective

The purpose of this contract is to develop a process for converting light alkane gases to methyl chloride via oxyhydrochlorination using highly selective, stable catalysts in fixed-bed reactors designed to remove the large amount of heat generated, so as to control the reaction temperature. Further, the objective is to obtain the engineering data base necessary for developing a commercially feasible process and to evaluate the economics of the process.

Task 1.0 Catalyst Definition and Separation Unit Operation Development

Task 2.0 Process Development Unit (PDU) Design Engineering

Task 3.0 PDU Construction and Procurement

Task 4.0 PDU Start-Up

Task 5.0 Evaluation of Packed Bed Technology

Task 6.0 Separation Optimization

Task 7.0 Process Optimization

Task 8.0 Economic Evaluation

Task 9.0 Preliminary Engineering Design Phase II

Task 10.0 Scale-Up Decision and Business Plan to Phase II

Summary of Technical Progress

The key technical progress this quarter was the great deal of progress in equipment design, instrument selection and data sheet preparation for the PDU. This work is outlined under the Task 2.0 and 3.0 sections below.

Catalyst definition this quarter provided limited progress due to the attempt to start up a new screening reactor than ran at higher pressures. The use of high pressure without the availability of a HCl removal unit operation resulted in many experimental problems. This will be solved by the use of the separation unit operation lab equipment as a catalyst screening reactor in the future.

Work continued on the development of the separation system. Results showed that at a given pressure and L/G, as the amount of methyl chloride in the feed gas increases, the removal efficiency also increases. Variation of column parameters showed that the 'absorber' acts not only as an absorber, but also as a direct contact condenser. This will provide significant benefit to the PDU.

Technical Results

Task 1. Catalyst Definition and Separation Unit Operation Development.

Catalyst Definition -

The primary focus of this quarter's catalyst definition work involved debugging the changes made to the second catalyst screening reactor. The first reactor is presently occupied running a program of experiments to help define the separation unit operation requiring a rigid, predetermined set of reaction conditions with a known catalyst. However, when the second screening reactor was assembled, problems arose. Like the separation unit reactor, the second reactor also was to have the ability to operate at pressures up to 40 psig. However, without the separation unit downstream of the reactor, gases that would have normally been condensed or absorbed, especially HCl, remained in the gas phase. The presence of HCl in the product stream as it exits the pressure valve causes great problems. Chief among these is plugging of the system, preventing the reactor effluent from leaving the system. An HCl condenser was installed in the system between the reactor and pressure valve. However, as shown in the catalyst screening data sets this quarter, reactor plugging continues to be a problem.

Data Set 1 using previously tested catalyst 538DII as a standard for the system was the first experiment run after the installation of the HCl condenser. The effects of system plugging are shown in this data set. Gaps are exhibited in the conversion and selectivity data on pages 2, 3, and 4. Pages 5 and 6 show the effects plugging has on reactor temperature and pressure. Although these results are difficult to interpret, it is encouraging to note that catalyst 538DII apparently approaches our goals of 20% conversion and 80% selectivity at an oven set point of 320°C and 30 psig. Previously, conversion of this magnitude would require temperatures approaching an oven set of 340°C at ambient pressure. This reduction in reaction temperature under pressure could prove advantageous by helping to prevent catalyst deactivation at higher temperatures.

Data Set 2, another attempt to use catalyst 538DII to get a baseline reactivity in the new reactor under pressure, also had data sampling problems. However, one important observation must be noted. After the first data point was taken at 315°C, the temperature was reduced to 305°C. This was due to the fact that at 315°C, CH₄ conversion was 25% and CH₃Cl selectivity only 50%. This low selectivity was due to the production of CO_x, 49%. Interestingly, adjusting the oven set point to 305°C did not curb this reaction. After cutting off the reactant gas feed and gaining control of the system before restarting, CH₄ conversions of between 5 and 7% were seen between 285 and 300°C. Further investigation is forthcoming to determine what factors caused such a great increase in catalyst activity.

Catalyst 540, a remake of catalyst 539 (Cu-La-Li on Al₂O₃), is examined in Data Set 3. Again, plugging and control system problems aborted the run, but it appears that catalyst 540 exhibited adequate conversion of CH₄.

Data Set 4 also represents measurements taken using catalyst 540. Plugging problems were avoided, and catalyst 540 showed an adequate CH₄ conversion of 13% at 315°C. However, an attempt to reach 20% conversion went astray when the oven set point was changed to 320°C. CH₄ conversion jumped to 29%, while CH₃Cl selectivity decreased to 49% due to 31% CO_x being produced. Page 5 of Data Set 4 shows that upon attempting to raise the reaction temperature 5°C, the activation barrier to forming oxygenates was exceeded. The formation of oxygenates, more exothermic than oxyhydrochlorination, caused the larger than expected temperature increase that was observed.

Plugging problems again show themselves in Data Set 5. However, the data that was taken using catalyst 540 again shows conversions and selectivities approaching our 20%/80% goals.

Separation unit operation studies should conclude at the beginning of next quarter. It is planned at that time to discontinue catalyst screening experiments in the new reactor. The separation unit has obviously shown its efficacy at removing HCl and other gases from the reactor effluent. Hopefully, with the screening reactions being done using the separation unit to condense and absorb HCl, plugging problems can be avoided allowing more and better catalyst screening data to be collected next quarter.

The necessity of a non-aqueous impregnation will be investigated in addition to La promoter studies. Methods of avoiding, lowering, or substituting for La will be investigated due to the prohibitive cost of this lanthanide.

Subtask 1.6 -Evaluation of Separation Technology-

Development of methyl chloride absorption/stripping technology continued this quarter. Work efforts have concentrated on increasing methyl chloride loading and finding flooding limits on the absorption column.

A series of runs were set up to determine the methyl chloride removal efficiency as a function of the methyl chloride loading of the absorption column (EXP. 11202-12,-14,-15,-16). Different ratios of methyl chloride to nitrogen were fed to the absorption column keeping the total volumetric flowrate constant. Multitherm

solvent flow rates and system pressure were varied to see their effect. The temperature of the column was kept constant at 0°C.

Table 1 lists the run conditions of % methyl chloride in the feed, liquid mass flowrate to gas mass flowrate (L/G), system pressure and associated methyl chloride removals. Figure 1 is a graphical representation of the data and depicts % methyl chloride removed vs. % methyl chloride in the gas feed.

Figure 1 shows that at a given pressure and L/G, as the amount of methyl chloride in the feed gas increases, more methyl chloride will be removed by the absorption column. Also, increasing the pressure and L/G facilitates the removal of methyl chloride. Methyl chloride's vapor pressure is 23 psig at 0°C. At the conditions the column was run, 0°C and a minimum pressure of 30 psig, methyl chloride will condense. So in effect, the "absorber" acts not only as an absorber but also as a direct contact condenser.

Another experiment was set up to find flooding limits of the absorber column (Lab Book #11202, pgs 52-55).

A 24"L x 5/8"ID teflon tube packed with glass helices served as the column. A cooling jacket was not installed so gas and liquid dynamics could be seen. A Multitherm flowrate was set and nitrogen flow rates increased to increase the theoretical percent of flooding of the column.

At a solvent flowrate of 3.5 ml/min and the nitrogen flowrate as high as 600 ml/min, **NO** liquid holdup was seen. The liquid flowrate were then doubled to 7.1 ml/min. Again with the vapor flowrate as high as 600 ml/min, **NO** liquid holdup was seen. Flooding did not occur until the Multitherm flowrate was tripled to 10.7 ml/min and the nitrogen flowrate reached 400 ml/min. During actual methyl chloride absorption runs, Multitherm flow rates are 3-4 ml/min and gas flow rates range from 150-200 ml/min, definitely not near the flooding regime.

Task 2.0 PDU Design Engineering and Task 3.0 PDU Construction and Procurement

Work this quarter involved detail design of the PDU. Status updates are given below for each discipline.

PROCESS ENGINEERING

The project scope was reduced by \$211 M and a supplemental capital authorization was approved by the board of directors in December bringing the total authorized funds for the project to \$2.5 MM. P&ID's were updated to show the project deletions and were reviewed by the safety audit team (SAT). This meeting was the first review by the SAT for the project.

Our application for a material safety data sheet (MSDS) for our chlorocarbon product stream, which will be disposed of by off-site incineration, was approved by corporate personnel. A portable waste incineration cylinder design was identified that qualified as an approved transportation vessel by the Department of Transportation.

We continued to work with a vendor to determine the scope of our on-line FTIR process analyzer and sampling system. This work was essentially complete and purchasing negotiations were in progress by the end of the quarter.

Several maintainability reviews were held with mechanical, instrumentation, and electrical maintenance personnel. The unit design was reviewed to determine if the process could be maintained easily and safely.

A great deal of time was spent supporting equipment design, instrument selection, and data sheet preparation activities. Also, a lot of work was done reviewing the detail engineering output.

CIVIL

A new concrete surface was added to the first level of the process tower to repair damage from demolition work. All concrete equipment pads inside of the process tower were poured in December.

Structure steel design was completed this quarter. The scope of this work essentially involved only steel required to support the equipment since the process tower already exists. In order to speed up the work, we tried to create a partnering arrangement with our mechanical contractor. However, this arrangement didn't hold together during target price negotiations. It was eventually awarded to a low bidder and the steel was ordered in December.

Around half of the steel had arrived on-site for painting at the end of the quarter. The steel erection firm selected had estimated a shorter work duration time than what we had estimated. This should allow the structural steel installation activity to be completed on time with respects to the July start-up date schedule. This will help us to recover some of the lost time experienced due to delays that occurred with the equipment design work.

Other work that occurred this quarter included having the process tower wrapped in plastic and a steam heater installed to facilitate steel erection work which was scheduled to begin in January.

MECHANICAL

Equipment design work was started and continued throughout the entire quarter and is expected to be wrapped up in January. This activity involved much more work than initially estimated and during the peak of the activity all three of the plant engineering group's mechanical engineers were working full time on it in order to meet the schedule. This work took about a month longer than anticipated. Furthermore, equipment data sheet work, a supporting activity, lasted two months taking over twice as long as anticipated.

Approximately 83% of the equipment was on order by the end of the quarter. In order to meet the schedule, purchase orders (P.O.) were sent out with equipment support details specified (instead of leaving this to the vendor) in order to release the structural steel package for construction. Furthermore, we allowed vendors to order materials when the purchase order was issued which should shorten delivery times. Usually, materials are not ordered until approval drawings are returned approved by the buyer (this takes around two to three weeks after the P.O.). By providing detailed specifications up-front we should be able to improve delivery times.

Equipment layout work continued and was 99% complete by the end of the quarter. This activity involved several iterations as each of several interferences were discovered and resolved. The final layout has been reviewed by the SAT.

Piping specifications were compiled and tubing specifications were completed.

Preliminary piping isometrics were completed and reviewed by the SAT. These drawings showed the basic routing of the piping. However, no dimensions were shown. These drawings will be used to prepare the fabrication isometrics. It was decided by the team not to produce piping plans and elevations drawings since it was felt that the payback was not worth the effort required to make these drawings. The fabrication piping isometrics will be used instead to check for interferences and, to facilitate this, they will show several lines per drawing (grouped around each piece of equipment) versus the usual one or two lines per drawing. These drawings were started at the end of the quarter.

The existing safety shower and eye-wash stations were reworked. This involved replacing the stations and the associated piping, insulation, and instrumentation.

ELECTRICAL

Very little work was done in this area this quarter with the exception of updating some existing drawings and supporting equipment design activities.

INSTRUMENTATION

Instrumentation design was started with the bulk of the work involving data sheet preparation and instrument selection. A purchase order was placed for the Camile® process control computer.

In order to save time and money, it was decided to partner with Ready Electric for this portion of the project. This has allowed us to tailor our construction packages to the contractors need. For example, Ready will not require loop diagrams (estimated to be a 100 hour preparation activity) but instead will require only a termination schedule prepared in the form of a spread sheet (estimated to be a 50 hour activity).

Junction box and marshaling panel design work began this quarter. Also, a majority of the termination schedule work was completed.

Existing control room equipment was removed and the work was charged to plant expenses. The control room layout for our process was also determined.

BUDGET

In spite of the additional time required during equipment design, actual engineering hours were still predicted to be at approximately 98% of what has been planned. Significant cost adders to the project this quarter were: 1) \$40 M (estimated total adder for whole project) for SMI charge-out rate that was incorrectly estimated, and 2) \$65 M (estimated total adder for whole project) for state taxes on equipment

and materials. Taxes were not included in the initial estimate, however, it was discovered that we will be required to pay them since this unit will not add to the overall production capacity of the plant.

SCHEDULE

A procurement schedule and a preliminary construction schedule were prepared and integrated with the design schedule. This overall schedule will be used to predict the start-up date when more equipment delivery times are known and the construction plan is "fleshed-out". The schedule has proved to be a useful tool for predicting the critical path of the project and has helped the team direct resources to minimize deviations from the schedule. A rough guess at this point would put start-up at around the beginning of August, 1994.

List of Figures

Table 1- Methyl Chloride Lab Absorber Performance

Figure 1- Methyl Chloride Lab Absorber Performance

Data Appendices

Data Appendix A- Experimental Data Sets

Data Appendix B- Catalyst Synthesis Information

Table 1

% MeCl in Feed	L/G	Pressure (psig)	% MeCl Removed
10	20	30	80.6
15	20	30	83.9
20	20	30	87.9
25	20	30	93.1
30	20	30	98.5
10	20	40	93.0
15	20	40	93.8
20	20	40	94.9
25	20	40	96.6
30	20	40	96.7
10	30	30	98.9
15	30	30	99.3
20	30	30	99.5
25	30	30	99.6
30	30	30	99.8
35	30	30	99.9
40	30	30	99.9

Note: All data from Experiments 11202-12, -14, -15, -16. Total volumetric flowrate of MeCl and N₂ = 165 ml/min STP.
Absorber Column temperature = 0 °C.

Figure 1 : Lab Absorber Performance
% MeCl (Condensibles) in Feed vs. % MeCl Removal

Data Appendix A
Experimental Data Sets

0077189 HOOD #6 RAMPING EXPERIMENT DEFINITION
 0077189
 0077189
 0077189 OPERATOR NAME: B. CRUM DATE: 21-OCT-83
 0077189 LOG BOOK #: 11046 PAGE #: 48
 0077189 RUN #: 11046021 CATALYST #: 538DII
 0077189 CATALYST NAME: Cu/Li/La ON SILICA
 0077189 COMMENTS: TRYING TO SHAKE DOWN HOOD AFTER ADDING CONDENSER
 0077189
 0077189
 0077189 MASS OF CATALYST (g): 0.81
 0077189 REACTOR INSIDE DIAM (CM): 0.46
 0077189 CATALYST BED HEIGHT (CM): 10.2

0077047
 0077047 TEMPERATURE RAMPING EXPERIMENT FOR HOOD #6
 0077047
 0077047 INITIAL FINAL ABSOLUTE
 0077047 TEMP TEMP RAMP RATE
 0077047 (DEG C) (DEG C) (DEG C / MIN)
 0077047
 0077047 BOTTOM: 320 320 3 SPACE VELOCITY 9.0 CM/SEC
 0077047 MIDDLE: 320 320 3 RUN TIME 220 HRS
 0077047 TOP : 320 320 3

(INITIAL TEMPERATURE CAN BE GREATER THAN FINAL TEMPERATURE)

0077047 CH4 FLOW RATE (CC/MIN): 80 O2 FLOW RATE (CC/MIN): 13.3
 0077047 HCl FLOW RATE (CC/MIN): 17.3 AUX FLOW RATE (CC/MIN): 0
 0077047

Time	A18CO	A18CO2	A18COX	A18M1	A18M2	A18M3	A18M4	ID6	MBC6	Q6CH4C	Q6HCLC	Q6O2C	Q1812
83114	0	0	0	0	0	0	0	0	1	164	21	0	31
88279	0	0	0	0	0	0	0	0	1	200		0	42
93433	0	0	0	0	0	0	0	0	1	167	21	0	43
98598	0	3	3	74	20	3	0	0	1	154	17	97	30
103750	0	2	2	77	19	2	0	0	1	157	18	99	30
108915	0	3	3	77	20	0	0	0	1	164	19	101	41
114079	0	3	3	78	19	0	0	0	1	167	18	0	29
119237	0	8	8	92	0	0	0	0	1	159	7	0	337
124404	0	25	25	75	0	0	0	0	1	180	3	98	100
129557	0	0	0	0	0	0	0	0	1	196		0	101
134715	0	0	0	0	0	0	0	0	1	197		0	101
139867	0	0	0	0	0	0	0	0	1	196		0	0
145034	0	0	0	0	0	0	0	0	1	197		0	101
150200	0	0	0	0	0	0	0	0	1	196		0	102
155342	0	0	0	0	0	0	0	0	1	196		0	0
160466	0	0	0	0	0	0	0	0	1	196		0	102
165608	0	0	0	0	0	0	0	0	1	171	15	0	23
611602	0	0	0	89	11	0	0	0	1	163	17	88	17
616517	0	2	2	86	12	0	0	0	1	165	14	71	5
621669	0	2	2	84	14	0	0	0	1	168	13	69	5
626838	0	2	2	86	13	0	0	0	1	162	15	77	9
631996	0	2	2	86	12	0	0	0	1	163	12	63	2
637156	0	2	2	84	15	0	0	0	1	163	14	71	5
642318	0	2	2	83	15	0	0	0	1	163	15	79	9
647477	0	2	2	85	13	0	0	0	1	176	25	0	321
652643	0	0	0	0	0	0	0	0	1	169	9	0	100
657794	0	0	0	0	0	0	0	0	1	188		0	101
662962	0	0	0	0	0	0	0	0	1	196		0	101
668124	0	0	0	0	0	0	0	0	1	196		0	101
673284	0	0	0	0	0	0	0	0	1	196		0	101
678443	0	0	0	0	0	0	0	0	1	181		0	95
683596	0	2	2	82	15	0	0	0	1	170	16	81	11
688754	0	2	2	84	14	0	0	0	1	164	17	87	12
693917	0	2	2	84	13	0	0	0	1	172	17	88	10
699078	0	2	2	83	15	0	0	0	1	171	17	86	8
704235	0	2	2	84	14	0	0	0	1	171	20	102	14
709394	0	3	3	81	16	0	0	0	1	167	19	101	14
714550	0	2	2	84	14	0	0	0	1	165	0	0	0
719718	0	2	2	83	15	0	0	0	1	171	17	91	9
724871	0	2	2	83	15	0	0	0	1	166	16	85	100
730035	0	2	2	84	13	0	0	0	1	174	20	0	100
735205	0	6	6	94	0	0	0	0	1	200		7198	100
740365	0	0	0	0	0	0	0	0	1	182	2	0	101
745524	0	0	0	0	0	0	0	0	1	197		0	101
750682	0	0	0	0	0	0	0	0	1	198		0	102
755842	0	0	0	0	0	0	0	0	1	197		0	101
760984	0	0	0	0	0	0	0	0	1	199		0	101

RUN NEVER CAME TO A STEADY STATE BETWEEN PLUGS. DATA SHOULD BE USED WITH CARE

RUN 11046020

CATALYST 538DII

RUN 11046020

CATALYST 538DII

—■— SELECTIVITY TO M1

RUN 111046020 CATALYST 538DII

RUN 11046020

CATALYST 538DII

RUN 11046020

CATALYST 538DII

RUN 11046025

CATALYST 538DII

—■— CONVERSION OF CH₄

RUN 11046025
CATALYST 538DII

RUN 11046025
CATALYST 538DII

RUN 11046025

CATALYST 538DII

RUN 11046025

CATALYST 538DII

0008507 ===== OHC/JSS
 0008507 HOOD #6 RAMPING EXPERIMENT DEFINITION
 0008507 =====
 0008507 OPERATOR NAME: B. CRUM DATE: 06-DEC-83
 0008507 LOG BOOK #: 11048 PAGE #: 60
 0008507 RUN #: 11048026 CATALYST #: 540
 0008507 CATALYST NAME: Cu/LiLa ON ALUMINA
 0008507 COMMENTS: 30 PSIG 310 TO 315 @ 1/MIN
 0008507

0008507 MASS OF CATALYST (g): 3.52
 0008507 REACTOR INSIDE DIAM (CM): 0.46
 0008507 CATALYST BED HEIGHT (CM): 19.7

0008313 =====
 0008313 TEMPERATURE RAMPING EXPERIMENT FOR HOOD #6
 0008313 =====
 0008313 INITIAL FINAL ABSOLUTE
 0008313 TEMP TEMP RAMP RATE
 0008313 (DEG C) (DEG C) (DEG C / MIN)
 0008313 =====
 0008313 BOTTOM: 310 315 1
 0008313 MIDDLE: 310 315 1
 0008313 TOP : 310 315 1

0008313 (INITIAL TEMPERATURE CAN BE GREATER THAN FINAL TEMPERATURE)

0008313 CH4 FLOW RATE (CC/MIN): 100 O2 FLOW RATE (CC/MIN): 22.8
 0008313 HCl FLOW RATE (CC/MIN): 29.8 AUX FLOW RATE (CC/MIN): 0

Time	AI6CO	AI6CO2	AI6COX	AI6M1	AI6M2	AI6M3	AI6M4	ID6	MBC6	Q6CH4C	Q6HCLC	Q6O2C	TQ612
15877		0			0	0	0	0	1	39	15	0	17 315
21155	3	2	4	80	14	1	0	0	1	53	14	52	15 315
26315	3	1	4	84	12	0	0	0	1	42	13	49	13 315
31459	0	3	3	77	18	2	0	0	1	123	82	4101	93 315
36618	0	0	0	100	0	0	0	0	1	11	9	0	-267 315
41766	0	22	22	78	0	0	0	0	1	0	0	0	0 209
46932	0	0	0	0	0	0	0	0	1	0	0	0	0 140
52067	0	0	0	0	0	0	0	0	1	0	0	0	0 98
57245	0	0	0	0	0	0	0	0	2	0	0	0	0 74
85775	3	1	4	84	12	0	0	0	1	40	14	50	16 315
90996	2	1	4	81	12	4	0	0	1	71	11	44	12 315
96155	4	1	6	80	14	0	0	0	1	62	17	61	24 315
101315	3	1	4	80	16	0	0	0	1	42	13	50	11 315

This run down several times due to plugging problems as well as Camile problems. This data should be examined closely before it is used to draw conclusions.

RUN 11046026
CATALYST 540

RUN 11046026

CATALYST 540

—■— SELECTIVITY TO M1

RUN 11046026

CATALYST 540

RUN 11046026

CATALYST 540

RUN 11046026

CATALYST 540

00005183 HOOD #6 RAMPING EXPERIMENT DEFINITION
 00005183
 00005183
 00005183 OPERATOR NAME: B. CRUM DATE: 13-DEC-93
 00005183 LOG BOOK #: 11046 PAGE #: 62
 00005183 RUN #: 11046027 CATALYST #: 540
 00005183 CATALYST NAME: Cu/Li/La ON ALUMINA
 00005183 COMMENTS: RAMP TO TEMP @ 1DEG/MIN 315 AND 320 30 PSIG
 00005183
 00005183

00005183 MASS OF CATALYST (g): 3.53
 00005183 REACTOR INSIDE DIAM (CM): 0.46

00005183 CATALYST BED HEIGHT (CM): 19.7

00005071 TEMPERATURE RAMPING EXPERIMENT FOR HOOD #6

00005071

00005071 INITIAL FINAL ABSOLUTE
 00005071 TEMP TEMP RAMP RATE
 00005071 (DEG C) (DEG C) (DEG C / MIN)

00005071

00005071 BOTTOM: 310 315 1 SPACE VELOCITY

00005071 MIDDLE: 310 315 1 RUNTIME 9.0 CM/SEC

00005071 TOP : 310 315 1 24 HRS

00005071
 00005071 (INITIAL TEMPERATURE CAN BE GREATER THAN FINAL TEMPERATURE)

00005071 CH4 FLOW RATE (CC/MIN): 100 O2 FLOW RATE (CC/MIN): 22.8
 00005071 HCl FLOW RATE (CC/MIN): 29.6 AUX FLOW RATE (CC/MIN): 0

00005071
 00005071 TIME TO MAINTAIN FINAL TEMPERATURES (HOURS): 12

Time	AI6CO	AI6CO2	AI6COX	AI6M1	AI6M2	AI6M3	AI6M4	ID6	MBC6	Q6CH4C	Q6HCLC	Q6O2C	TQI612
12029	2	2	4	85	11	0	0	1	46	13	46	8	315
17192	3	1	4	81	15	0	0	1	45	13	51	8	315
22350	2	1	4	84	12	0	0	1	45	13	48	6	315
27569	2	1	4	84	12	0	0	1	44	13	47	8	315
32731	2	1	4	84	12	0	0	1	44	13	47	7	315
37890	2	1	3	83	13	0	0	1	45	13	48	6	315
43033													
48209	3	1	4	85	12	0	0	1	44	13	47	7	315
53372	2	1	3	80	17	0	0	2	51	13	49	8	316
59250	5	2	7	78	16	0	0	2	46	17	62	23	320
64469	15	8	24	54	18	3	0	2	55	29	102	99	320
69692	17	19	36	45	17	2	0	2	38	29	84	99	320
74908	16	18	34	49	16	2	0	2	55	30	88	99	320
AVERAGES AI6CO	AI6CO2	AI6COX	AI6M1	AI6M2	AI6M3	AI6M4	ID6	MBC6	Q6CH4C	Q6HCLC	Q6O2C	TQI612	
AVG 315	2	1	4	83	13	0	0	1	46	13	48	7	315
STD	0	0	0	2	2	0	0	0	2	0	1	1	
AVG 320	16	15	31	49	17	2	0	2	49	29	90	99	320
STD	1	5	5	4	1	1	0	0	8	0	8	0	

RUN 11046027

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00005015 HOOD #6 RAMPING EXPERIMENT DEFINITION
 00005015 =====
 00005015 OPERATOR NAME: B. CRUM DATE: 14-DEC-93
 00005015 LOG BOOK #: 11046 PAGE #: 64
 00005015 RUN #: 11046028 CATALYST #: 540
 00005015 CATALYST NAME: Cu/Li/La ON ALUMINA
 00005015 COMMENTS: ATTEMPT TO BRING UP SLOW
 00005015 RUN SHUT OFF BETWEEN HOUR 27 AND 42 DUE TO PLUGGING PROBLEMS

00005015 MASS OF CATALYST (g): 3.25 SPACE VELOCITY 9.0 CM/SEC
 00005015 REACTOR INSIDE DIAM (CM): 0.46 RUN TIME 52 HRS
 00005015 CATALYST BED HEIGHT (CM): 19.7

00004904 OHC/JSS
 00004904 =====
 00004904 TEMPERATURE RAMPING EXPERIMENT FOR HOOD #6
 00004904 =====
 00004904 INITIAL FINAL ABSOLUTE
 00004904 TEMP TEMP RAMP RATE
 00004904 (DEG C) (DEG C) (DEG C / MIN)
 00004904 =====
 00004904 BOTTOM: 310 314 .5
 00004904 MIDDLE: 310 314 .5
 00004904 TOP : 310 314 .5

00004904 (INITIAL TEMPERATURE CAN BE GREATER THAN FINAL TEMPERATURE)

00004904 CH4 FLOW RATE (CC/MIN): 100 O2 FLOW RATE (CC/MIN): 22.8
 00004904 HCl FLOW RATE (CC/MIN): 29.6 AUX FLOW RATE (CC/MIN): 0

TIME TO MAINTAIN FINAL TEMPERATURES (HOURS): 6																
Time	AI6CO	AI6CO2	AI6COX	AI6M1	AI6M2	AI6M3	AI6M4	ID6	MBC6	Q6CH4C	Q6HCLC	Q6O2C	TQI612			
12142	2	2	4	86	10	0	0	0	1	40	15	53	12	314		
17363	2	1	4	86	10	0	0	0	1	124		226	10	314		
22523	2	1	3	84	12	0	0	0	1	41	14	50	9	314		
27681	2	1	3	85	12	0	0	0	1	42	14	50	9	314		
32841	2	1	3	84	13	0	0	0	2	123		232	10	315		
38097	0	1	1	85	15	0	0	0	2	64	14	54	10	315		
43265	2	1	3	87	9	0	0	0	2	56	14	49	10	315		
48441	2	1	3	83	14	0	0	0	2	40	14	51	10	315		
53604	2	1	3	81	16	0	0	0	2	51	14	55	12	315		
58762	2	1	3	80	17	0	0	0	3	40	14	52	9	315		
64041	2	1	4	82	15	0	0	0	3	62	16	58	15	316		
69203	2	1	3	86	11	0	0	0	3	35	13	49	8	316		
74424	0	1	1	83	13	3	0	0	3		8	0	0	316		
79578										72	16	41	17	316		
84799	3	1	4	85	12	0	0	0	4	182		359	14	317		
90081	3	1	4	83	13	0	0	0	4	57	15	56	16	317		
159740	3	1	5	82	13	0	0	0	1	41	15	54	14	317		
164945	4	2	5	79	13	2	0	0	1	51	15	58	18	317		
170123	3	2	5	81	14	0	0	0	2	54	14	54	12	318		
175747	3	2	5	81	13	1	0	0	2	56	17	65	19	318		
180983	3	2	5	83	12	0	0	0	2	39	15	53	15	318		
AVG 314	AI6CO	AI6CO2	AI6COX	AI6M1	AI6M2	AI6M3	AI6M4	ID6	MBC6	Q6CH4C	Q6HCLC	Q6O2C	TQI612			
STD	0	0	0	1	1	0	0	0	0	36	1	76	1			
AVG 315	2	1	3	83	14	0	0	0	2	62	14	82	10	315		
STD	1	0	1	2	2	0	0	0	0	28	0	67	1			
AVG 316	1	1	3	83	13	1	0	0	3	56	13	37	10	316		
STD	1	0	1	2	1	2	0	0	0	16	3	22	6			
AVG 317	3	1	4	82	13	0	0	0	3	83	15	132	15	317		
STD	0	0	1	2	1	1	0	0	2	58	0	131	2			
AVG 318	3	2	5	82	13	0	0	0	2	49	15	57	15	318		
STD	0	0	0	1	1	0	0	0	0	8	1	5	3			

RUN 11046028

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CAT 540

Data Appendix B

Catalyst Synthesis and Composition Information

CATALYST 538DII

SUPPORT	Silica CS-1040, PQ Corp. Lot #1229-2201
SOURCE	$[\text{Cu}(\text{CH}_3\text{CN})_4]\{\text{PF}_6\}$. 11291 lab-book page 13.
LOADING	Approximately 1% Cu, 18% La and 1% Li.
IMPREGNATION METHOD	Yellow THF solution of copper species left overnight with support for impregnation. After drying with flowing nitrogen, water was added and then removed with flowing nitrogen. Aqueous solution of La and Li salts was then left overnight for impregnation before drying with nitrogen.
PRETREATMENT	2 hours flowing nitrogen at 350 °C.
COLOR	Speckled yellow and gray.

CATALYST 540

SUPPORT	Al ₂ O ₃ , CS331-1, UCI, Lot # 3208-S.
SOURCE	[Cu(CH ₃ CN) ₄]{PF ₆ }. Lab-book 11291 page 46.
LOADING	0.45% Cu, 14.2% La, 0.61% Li, and 0.24% P.
IMPREGNATION METHOD	Al ₂ O ₃ was left overnight to impregnate with a THF solution containing [Cu(CH ₃ CN) ₄]{PF ₆ }. THF was removed with flowing nitrogen before impregnation overnight with aqueous solution of La and Li salts. Solution was then evaporated using flowing nitrogen.
PRETREATMENT	Al ₂ O ₃ was ground and sifted keeping particles between 10 and 24 mesh. These were then heated under dynamic vacuum at 180°C for 4 hours and then 100°C overnight.
COLOR	Yellow-green.