Methyl Chloride Via Oxyhydrochlorination of Methane

Quarterly Technical Progress Report No.9
For the period October 1993-December 1993

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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 CH₂Cl selectivity only 50%. This low selectivity was due to the production of COₓ, 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 CH₂Cl selectivity decreased to 49% due to 31% COₓ 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

<table>
<thead>
<tr>
<th>% MeCl in Feed</th>
<th>L/G</th>
<th>Pressure (psig)</th>
<th>% MeCl Removed</th>
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</table>

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

- L/G=30, P=30
- L/G=20, P=40
- L/G=20, P=30

% MeCl Removal vs. % MeCl in Gas Inlet
Data Appendix A

Experimental Data Sets
RUN NEVER CAME TO A STEADY STATE BETWEEN PLUGS. DATA SHOULD BE USED WITH CARE.
RUN 11046020
CATALYST 538DII

CONVERSION OF CH4
RUN 11046020
CATALYST 538DII

TIME (HRS)

SELECTIVITY TO M1
RUN 11046020
CATALYST 538DII

TIME (HRS)

0 50 100 150 200 250

Rx TEMP

OVEN SET
### Temperature Ramping Experiment for Hood #6

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<th>Initial</th>
<th>Final</th>
<th>Absolute</th>
<th>Temp</th>
<th>Temp</th>
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<th>(Deg C)</th>
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- **Outcome**: dysfunction in the temperature ramping experiment for Hood #6.

---

**Data Set 2 - Page 1**

### CH4 Flow Rate (CC/Min): 100

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<th>Time</th>
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**Outcome**: abnormal flow rates observed in the CH4 and HC1 channels.

---

**Notes**: Further investigation is required to determine the cause of these deviations.
RUN 11046025
CATALYST 538DII

CONVERSION OF CH4
RUN 11046025
CATALYST 538DII

SELECTIVITY TO M1
RUN 11046025
CATALYST 538DII

PSIG vs. TIME (HRS)
## Temperature Ramping Experiment for Hood #6

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**Mass of Catalyst:** 3008507

**Catalyst Name:** CuLilO on Alumina

**Catalyst Bed Height (CM):** 19.7

**Initial Temperature Can Be Greater Than Final Temperature**

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<td>AUX Flow Rate (CC/Min):</td>
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This run was performed several times due to plugging problems as well as Camie problems. This data should be examined closely before it is used to draw conclusions.
RUN 11046026
CATALYST 540

TIME (HRS)

SELECTIVITY TO M1
**HOOD #6 RAMPING EXPERIMENT DEFINITION**

**OPERATOR NAME:** B. CRUM  
**DATE:** 13-DEC-93

**LOG BOOK #:** 11046  
**PAGE #:** 62

**RUN #:** 11046027  
**CATALYST #:** 540

**CATALYST NAME:** Cu/La ON ALUMINA

**COMMENTS:** RAMP TO TEMP @ 1DEG/MIN 315 AND 320 30 PSIG

**MASS OF CATALYST (g):** 3.53

**REACTOR INSIDE DIAM (CM):** 0.46

**CATALYST BED HEIGHT (CM):** 19.7

**INITAL ABSOLUTE TEMP (DEG C):** 310 315 1

**FINAL ABSOLUTE TEMP (DEG C):** 310 315 1

**SPACE VELOCITY CMLSEC:** 9.0

**RUNTIME:** 24 HRS

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

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**AVERAGES A16CO A16CO2 A16COX A18M1 A18M2 A18M3 A18M4 ID6 MBC6 Q8CH4C Q8HCLC Q8Q2C TQ1512**

| Avg 315 | 2     | 1      | 4      | 83    | 13    | 0     | 0     | 1   | 46   | 13    | 46    | 8     | 315    |
| 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
CAT 540

TIME (HRS)

CONVERSION OF CH4
RUN 11046027
CAT 540

SELECTIVITY TO M1

TIME (HRS)
RUN 11046027
CAT 540

![Graph showing selectivity over time for M2, M3, and COX](image)

- **Selectivity to M2**
- **Selectivity to M3**
- **Selectivity to COX**
# Verification of Cu/ZnO on Alumina Catalyst

## Experiment Details

- **Date:** 14-Dec-93
- **Operator:** B. Crum
- **Log Book #:** 11046
- **Page #:** 64
- **Run #:** 11046028
- **Catalyst Name:** Cu/ZnO on Alumina
- **Run Shut Off Between:** Hour 27 and 42 due to plugging problems
- **Mass of Catalyst (g):** 3.25
- **Reactor Inside Diameter (CM):** 0.46
- **Catalyst Bed Height (CM):** 19.7

### Temperature Ramping Experiment for Hood #6

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<th>A13Cox</th>
<th>A13M1</th>
<th>A13M2</th>
<th>A13M3</th>
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### Catalyst Name: Cu/ZnO on Alumina

- **Mass Reactor Inside Diameter (CM):** 0.46
- **Run#:**
- **CH4 Flow Rate (CC/Min):** 100
- **O2 Flow Rate (CC/Min):** 22.8
- **HCl Flow Rate (CC/Min):** 0
- **Aux Flow Rate (CC/Min):** 0

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**Notes:**
- Attempt to bring up slowly
- Data Set 5 - Page 1
RUN 11046028
CAT 540

% SELECTION TO M1

TIME (HRS)
Data Appendix B

Catalyst Synthesis and Composition Information
CATALYST 538DII

SUPPORT: Silica CS-1040, PQ Corp. Lot #1229-2201


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  
Al₂O₃ CS331-1, UCI, Lot # 3208-S.

SOURCE  
[Cu(CH₃CN)₅]{PF₆}. Lab-book 11291 page 46.

LOADING  
0.45% Cu, 14.2% La, 0.61% Li, and 0.24% P.

IMPREGNATION METHOD  
Al₂O₃ was left overnight to impregnate with a THF solution containing [Cu(CH₃CN)₅]{PF₆}. 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  
Al₂O₃ 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.