Methyl Chloride Via Oxyhydrochlorination of Methane

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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

Significant progress was made in catalyst and PDU development this quarter. The key points of these developments are:

- 1) Initial discussions have taken place with a catalyst supplier, United Catalysts, Inc. UCI came up with some good catalyst development suggestions and has agreed to produce a batch of catalyst for the PDU.
- 2) Previous plans for supply of methane for the PDU have fallen through. New options, including getting gas from Carrollton Utilities, are being evaluated.
- 3) PDU equipment installation is completed, and piping is 40% complete. The electrical work is close to being finished, and the instrumentation is underway.
- 4) The PDU budget forecast is now 2.59MM, 104% of the CAR.

Technical Results

Task 1.0 Catalyst Definition and Separation Unit Operation Development.

Catalyst Definition

A very enlightening meeting was held with United Catalysts, Inc. (UCI) of Louisville, Kentucky. We discussed our catalyst system and together we came up with some intriguing suggestions:

- 1) With the high total metal loadings that we are using in the OHC catalysts, it might be advantageous to use alumina as a binder in a compounded extrudate.
- 2) Try to lower catalyst cost by lowering La level to minimum required to get acceptable catalyst activity.
- 3) Try making catalyst less expensive by substituting mixed lanthanide chlorides for lanthanum chloride in the catalyst synthesis.
- 4) Look into La recovery from spent catalysts.

UCI has also agreed to provide a large batch of catalyst for the PDU. Various catalyst preps will be tested and screened before ordering the PDU catalyst batch.

Micromeritics, located in Norcross, Georgia, examined catalysts 539 and 540 by N_2O chemisorption to measure Cu metal surface area. Catalysts 539 and 540 are both Cu/La/Li

on Al_2O_3 and differ only in the Cu loading level. 539 is 0.894 wt.%, and 540 is 0.451 wt.%. The measured surface areas were $0.55 \text{ m}^2/\text{g}$ for 539 and $0.42 \text{ m}^2/\text{g}$ for 540. These measurements seem plausible. 539, with double the Cu loading of 540, is measured as having a higher Cu surface area, but not twice as high as the percent loading might indicate. This is because as more and more Cu is put on the surface of the catalyst, the chance is more likely that the next Cu added will stack on top of Cu instead of on the alumina. Dispersion, as calculated by percent of Cu loading shown to chemisorb N_2O , shows 539 at 12% and 540 at 18%. Whether the measurements are exactly correct or not, the trends seem reasonable. Samples of our most important catalysts are currently being gathered to be shipped to Micromeritics for metal surface area measurements.

A secrecy agreement has been arranged with Calscat of Erie, Pennsylvania. They will be used as an alternate competitive catalyst supplier.

Catalyst definition lab screening experiments ran into two difficult problems this quarter. The first was periodic CAMILE data downloading failures. This problem was eventually solved, but did cost us two sets of lab data. The second, more serious, problem was plugging of the OHC lab setup. Plugging was a continuous problem throughout the quarter and ruined many catalyst screening runs. This certainly shows the extreme importance of the correct materials of construction for the PDU and the necessity to have good, complete heat tracing downstream of the reactor to prevent condensation of HCl and H_2O and thereby prevent corrosion.

A very interesting catalyst was synthesized this quarter. The alumina supported analogue of catalyst 513 was made. This used Li_2CuCl_4 in THF to impregnate the alumina. Catalyst 513, Li_2CuCl_4 on silica, is the only catalyst to date not containing La to show significant methane conversion. However, catalyst 513 exhibited stability problems that will hopefully be addressed by using an alumina support which should have a stronger interaction with the Cu.

Task 2.0 PDU Design Engineering

ENGINEERING

Actual engineering hours versus plan were @ 112% (excluded a charge out rate increase for SMI process engineering hours) as of 6/23/94. This overage was due primarily to changes being processed through the system and also due to higher than expected construction support.

PROCESS ENGINEERING

Previous plans for the supply of PDU methane were changed this quarter. Originally, Jim Allison of Texas Gas and B. Naasz (Dow Corning) had worked a deal where Texas Gas would give Dow Corning (DC) methane from a compressor station located in Jeffersontown, KY. New government regulations made this very difficult and expensive for Texas Gas. Allison suggested a solution to this problem. DC could get the gas from a Carrollton Utilities tie-in provided that the site has enough room for a tube trailer truck. DC would have to supply a compressor because the pipeline pressure is only 475-600 PSIG. We met with Carrollton Utility personnel and checked out the site. Some minor landscaping (remove a grassy area and gravel it) may have to be done for better accessibility. It was planned to contact PCI, the tube trailer company, to see if they could accommodate this. Carrollton Utilities said that they would be happy to supply mercaptan-free methane to DC for the PDU at minimal cost.

Engineering support continued for the vendor detailed design of our FTIR analyzer. A personal computer for the FTIR was procured and sent to the vendor for configuration.

Programming for our data acquisition and control system (CAMILE) was done this quarter. However, this effort was slowed somewhat due to engineering support requirements being higher than expected (due to the concentrated, fast-track nature of the job). One of the startup team members were brought on-board to work as a "back-up" programmer and to become familiar with the system and programming (however, this person later left the project for another job opportunity in August). Dow Chemical and Dow Corning were able to come to an agreement on statements in the licensing agreement for the CAMILE. Hopefully, this can be used as a "blanket agreement" for all transactions between both companies.

Chilworth Technologies, Inc. (CTI) agreed to do some flammability testing of an OHC reactant mixture. Their work was to involve a review of published literature relating to the flammability of methane with effects of temperature, pressure, and inerts; determination of UFL and LFL of a mixture of methane, oxygen, and a-HCl at 400°C and 75 PSIG; and a Process Hazards Assessment (PHA). The PHA was to identify process and materials hazards, design concepts for the reactor systems, and basic safety and loss prevention techniques. CTI was given a package to familiarize them to OHC. This

package contained basic OHC chemistry, PFD's and P&ID's of reactor system, pertinent information on the PDU design, and MSDS's.

By the end of the quarter, CTI had completed their literature review on the flammability of methane. The original aim of the report was to find data on the subject of flammability of mixtures of methane, a-HCl, and oxygen/air. However, no relevant data was found. The search was extended to find flammability data of mixtures of methane in atmospheres of oxygen/air at varying temperatures, pressures and concentrations of inerts. The report provided a good introduction to understanding flammability limits of mixtures much like OHC reactor mixtures. Flammability testing of methane, oxygen, and a-HCl was completed. A complete report was being awaited at the end of the quarter.

Finally, a HAZOP was held this quarter to discuss some design issues.

Task 3.0 PDU Construction and Procurement

MECHANICAL ENGINEERING

The majority of this work was completed by March. However, a great deal of construction support was required throughout the quarter. This included procurement of miscellaneous items and tracking the delivery of equipment. Some estimating work was done this quarter to help negotiate the target price for the mechanical package. Support was also provided to the instrument engineer for instrumentation design. Time was also spent this quarter developing and implementing the following scope changes:

- 1) Addition of a tempered water system (a Safety Audit Team requirement to prevent the formation of methyl chloride hydrates on the stripper condenser tube wall surfaces).
- 2) Addition of a suction strainer (pump 125).
- 3) Addition of a suction strainer (pump 123).
- 4) Addition of a tempered Syltherm 800 cooler for the desuperheater service.
- 5) Some electric heat trace changes.
- 6) Drum unloading pump modifications.
- 7) Level and DP transmitter flange connections.
- 8) Increased methane transfer line size to span pipe pole supports due to physical layout.
- 9) Tubing modifications to the FTIR (a detailed design activity that was realized as specified by the vendor).
- 10) Flow meter and sample valves added to sample waste water from the chlorocarbon/water phase separator. This was a request by the waste water treatment unit.

Also, \$6 M were spent to install a gravel road to bring the methane tube trailers closer to the process. The road was required because the trailers needed to be > 75 ft from the hydrogen storage tank per NFPA requirements. A Concrete pad to store our waste cylinders on was also added for \$3 M in the 90 day hazardous waste storage area. Finally, \$8 M were allocated for upgrades to an existing analyzer shed that we are going to use to house our FTIR. This was a change to the scope since the initial idea was not to use a shed, but it was learned that the internal electronics needed climate control. This would not have been difficult to achieve, however, for winter maintenance it was decided that it would be better to house the analyzer in a shed.

INSTRUMENTATION ENGINEERING

Instrumentation procurement and instrument data sheet preparation work was completed this quarter. This work was the main engineering activity this quarter. However, it was significantly delayed due to a lack of engineering resources. An additional designer was

brought on board with the project this quarter to help finish off the work. During the procurement, it was discovered that the delivery dates of several instruments were going to be much longer than initially expected. This had a significant impact on the construction schedule and made work in the field difficult.

CONSTRUCTION

Construction completion was expected to be around the end of the first quarter. At the beginning of the quarter, equipment installation activities were happening. Carbon steel pipe installation work was done, also. All of the carbon steel process pipe had been fabricated, delivered to the site and painted. At the end of the quarter, equipment installation was completed and the piping was 40% complete. Overall, the electrical work was close to being finished, and the instrumentation work was underway. Total mechanical construction hours were at 61% of the target amount while actual costs were at only 56% of the target. Unfortunately, though, work continued to be slowed due primarily to delayed instrument deliveries and also, to a smaller extent, due to changes (made earlier) being constructed.

The electrical portion of the job was essentially completed by the end of the quarter with the exception of the heat tracing. Our E&I contractor got set up in the field in May and ran the cable trays. Home run cables were run from the junction boxes to the control room and field cables were run into the process. Some wiring terminations were made and instrument locations were identified in the field. Overall E&I work was delayed this quarter due to delayed instrument deliveries. However, one encouraging note was that the electricians work side by side with the pipe fitters very well.

BUDGET

The cost forecast at the end of the quarter for the project was \$2.59 MM. This new forecast put us @ 104% of the CAR (capital authorization request). The main reasons for being above our CAR were due to: 1) the extremely low estimate for the mechanical work, 2) changes to fix-up the process design, and 3) "hard hitters" to the project (Kentucky State Sales tax, which is not normally required for capital projects, but since our unit does not increase the capacity of the plant, we are not exempt from state sales tax. Also, wrong engineering charge out rate used in the estimate).

A target price for the electrical and instrumentation work was agreed to this quarter with our E&I contractor Ready Electric. E&I material and labor was projected to be at \$121 M which was within 5% of our original estimate.

Engineering, material and labor estimates were made for each of the 42 project scope changes that have been made and they total to \$249 M. These changes involve any changes from the CAR scope. Some changes involve additions that increased the cost of the project, while others involved changes that resulted in cost savings. For example,

using glass lined vessels and columns versus Teflon lined equipment resulted in \$23 M savings compared with the CAR budget. Actual savings as compared with quotations received during engineering, though, were \$42 M. The changes can be segregated into two categories: 1) process related scope changes @ \$124 M, and 2) non-process related changes @ \$125 M (Kentucky State Sales tax @ \$75 M and wrong charge out rate given @ \$50 M). The estimate for the project that was used to prepare the capital authorization request was \$2.44 MM. Revising this to include the scope change costs (note that these costs do not include contingency or other factors, such as, contractor overheads) gave an updated estimate of \$2.68 MM. Comparing the current cost forecast with this updated estimate shows that the project was pretty close to being on-track at 96.5% forecast/revised budget.

In summary, the budget was very tight at the end of this quarter. All changes were being scrutinized as close as possible in order to control the budget. However, the rate at which the forecast was growing indicated that an overrun may be coming.

SCHEDULE

Construction completion was delayed this quarter due primarily to delays in equipment and also instrument deliveries. In particular, our glass lined equipment delivery was delayed significantly as one of the vessels had to be "glassed" five times before it passed a spark test. Not having the vessel installed delayed the installation of the PTFE lined pipe since it was not in place to get final dimensions for pipe fabrication. Glass lined pipe spools for the columns were also delayed. Another delayed delivery involved PFA lined pipe for which the order apparently got lost in the cracks by the vendor during purchasing. These delays were compounded this quarter as our purchasing expeditor moved to a new job leaving a vacancy. At the end of the quarter, purchasing renewed efforts to expedite the orders. To a smaller extent, changes being processed through the construction also served to delay construction completion. In addition, a one week delay was experienced as the contractors were stretched by shutdown work.

On the process side of things, the start of SOP writing had been delayed. Team members worked hard to finish off previous commitments. However, they were not able to become available as early as was hoped.

Task 4.0 PDU Start-up

STARTUP

A startup kick-off meeting was held in April. Planning and pre-startup work was done this quarter. Standard operating procedure writing was started and well underway by the end of the quarter. Our capital project lead mechanical engineer was brought on board joining the startup team to work as a shift engineer during the startup. This brought the team to four shift engineers. It was decided this quarter to use six shift engineers for the startup. Job candidates were selected to be interviewed for PDU (Process Development Unit) Engineer positions. The interviewing began at the end of the quarter.

In addition to safety training this quarter, several vendors gave short training sessions where the equipment was described and startup and operating procedures were reviewed. These classes were very informative and useful.

SAFETY

There were no safety incidents for the project this quarter.

The startup team completed HAZMAT technician training. This qualified them to be responders to hazardous material incidents.

Data Appendix A

Catalyst Synthesis and Composition Information

CATALYST 553

SUPPORT	Alumina CS331-1, United Catalyst, Lot #3208-S
SOURCE	Dilithium copper tetrachloride- lab book 11291 page 65.
LOADING	1.65% Cu, 0.334% Li.
IMPREGNATION METHOD	Copper species in THF transferred via canula to dry alumina. Alumina was impregnated for 16 hours before THF was removed under flowing nitrogen. Catalyst was dried for 16 hours at 330°C under dynamic vacuum.
PRETREATMENT	Alumina dried at 325°C under vacuum for 16 hours.
COLOR	Dark Brown.