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QUARTERLY TECHNICAL REPORT- Final

CONTRACT TITLE AND NUMBER:

Methyl Chloride Via Oxyhydrochlorination of Methane

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CONTRACTOR NAME: Dow Corning Corp.
US HWY 42
Carrollton, KY 41008

CONTRACT PERIOD: 10-1-91 - 9-30-94

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 either fixed-bed or fluid bed reactors designed to remove the large amount of heat generated, so as to control the reaction necessary for developing a commercially feasible process and to evaluate the economics of the process.

The progress made toward fulfilling this objective is outlined in this report. This quarters' technical progress comprised of work done in several process development areas. This work was targeted at Task 1.0 Catalyst Definition and Task 2 Miniplant Design Engineering.

Work directed to catalyst development began with the study of the role of copper in the oxyhydrochlorination of methane. . This work had begun prior to the contract. Several new catalysts were synthesized and evaluated in our continued effort to evaluate the sensitivity of the catalyst to the type of Cu used as an active site. Several synthetic strategies were evaluated. Our work to date can be summarized as consisting of three separate areas. These are catalyst preparation using single metal systems, bimetallic catalyst synthesis from clusters as precursors, evaluation of these catalyst via our micro packed bed screening reactors, and characterization of these catalysts via elemental analysis and selected dispersion studies. These approaches are outlined below.

Our catalyst synthesis strategy began with an attempt to definitively establish the role of Cu(I) vs Cu(II) metal sites on the selectivity of the OHC reaction. Our new abilities to anaerobically prepare catalysts were used. Two CuCl catalysts were made from an acetonitrile impregnation with all water and OH⁻ groups being stringently excluded. Final metal loadings were similar. No differentiation between the catalysts' selectivity was noted.

In an attempt to modify the environment of the Cu sites on the catalyst chemically, work has begun to support hetero-bimetallic compounds of traditional silica supports. Cu was modified to provide a Cu-Al bimetallic site via the preparation of a {Al(OH)₆Cu₆(Et₂NCH₂CH₂O)₆} {ClO₄}₃ cluster. A

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systematic evaluation of site modification will be pursued. Catalytic screening results for our first attempt are not yet complete.

Dispersion studies of some of our standard catalysts have been completed. These results will aid in development of potentially patentable catalysts. Control of the total number of active sites will be a key factor in providing an optimal catalyst.

Intrinsic rate studies of the primary and secondary reaction steps in the laboratory were initiated. This information will provide the basis for a total rate model that will be useful in catalyst development and reactor design. The determination of the intrinsic rates along with the associated mass transfer models will provide valuable overlap between our catalyst development and an engineering oriented analysis of the screening results. Our first goal with this work is to show in this very active system that mass transfer to the surface of the catalyst is not the rate determining step in the reaction.

In addition to our traditional catalyst evaluations several other approaches were pursued to help provide the engineering data base necessary to begin the detail engineering design of the miniplant unit planned in the contract. Evaluation of a novel reactant feed system are underway. This potentially patentable design will allow for much simpler unit operation design.

Task 2 miniplant design effort was also initiated prior to contract. The strategy for miniplant design is to keep the economics of a large scale process in mind at this level rather than to optimize the process on a small scale that will not allow for commercialization. Several key issues have been identified that will play a key role in the definition of the miniplant. They are: HCl recovery development, reactor design, economic modelling, and determination of separation processes. The status of this pre-design work is described here.

Several strategies for HCl recovery were evaluated. The results point to three key conclusions. These studies show several strategies are possible and several important and possible patentable factors will be important in designing the HCl recovery systems.

The reactor design strategies have focused upon interacting with the catalyst development work to make sure that the rate information necessary for accurate design is being determined. This effort is nearly finished.

Without a doubt the key to an large scale process being economically viable and fundamentally operational is the separation of the condensible products efficiently from the large non-condensable stream in which they present. Several alternative strategies for this separation were evaluated conceptually and via ASPEN simulations.

A traditional condensation system would absolutely be unacceptable. Any indirect contact methods for condensing the products did not appear promising. Given that, the first alternative studied was that of the use of a solvent to quench/absorb the reactor effluent stream. ASPEN simulations show the absorbing the reactor effluent gases using di-n-butyl ether can give very high product recovery. However, the capital and

operational costs associated with this system are astronomical. As such the solvent absorption separation scheme under evaluation for reactor effluent separation was deemed to be impractical. Work continues to evaluate other methods to accomplish this separation. Currently we are studying a combined PSA/ indirect cooling operation that appears to have promise.

SUMMARY:

The contract effort is off to a good start. The catalyst development and micro-packed bed screening studies are well underway. Development on these two issues will continue as scheduled during next quarter. The associated engineering support for pre-design on the miniplant is currently struggling with the unit operations problem associated with separation of products from unreacted methane in the reaction product stream. This issue remains the critical step in defining the process.

Brian Naasz
Project Manager

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