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Methyl Chloride Via Oxyhydrochlorination of Methane

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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

Abstract

Continuous progress is being made toward the contract objectives in our attempt to produce "Methyl Chloride via Oxyhydrochlorination of Methane." Specifically, gains have been achieved in Task 1.0 Catalyst Development and Separation Unit Operation Development and Task 5.0 Evaluation of Packed Bed Technology. Task 4.0 PDU Startup has been completed.

A recent patent by Asahi Glass Company (JP 06340560) claims significant improvement in the OHC process through the use of a zirconia-alumina support compared to the prior art of silica or alumina supports. A zirconia-alumina support has been synthesized and impregnated with Cu/La/Li. This catalyst will be screened to test the claims of the competing patent. A new catalyst evaluation system is being sought to expand the capabilities of the OHC catalyst research. A ROTOBERTY reactor will allow proper evaluation of catalysts through measurement of intrinsic kinetics. It will also allow the present tube reactor to be converted for use in catalyst lifetime studies.

The PDU brought chemical feeds on and produced methyl chloride completing Task 4.0 PDU Startup. In order to accomplish this, however, the stripper column had to be replaced with new PFA-lined materials. With this new equipment in place, the PDU ran at 30 psig between 285°C and 325°C forming a product stream containing as much as 3% methyl chloride. This analysis was performed by GC due to clouding of the FTIR windows almost immediately upon the introduction of chemical feeds to the unit. These are the initial stages of Task 5.0 Evaluation of Packed Bed Technology.

Introduction

Methyl chloride (MeCl or CH_3Cl) is an important feedstock for the silicone industry. It is also used as an intermediate in the manufacture of other chlorocarbons, agrochemicals, methyl cellulose, quaternary ammonium salts, and as a solvent in the production of butyl rubber. MeCl consumption in the US was reported to be around 850 million lbs. in 1992 for these applications, although the actual consumption was probably much higher because of unreported, captive capacity. Currently, MeCl is derived from methanol. However, the demand for methanol in the U.S. is higher than the available domestic supply. As a result, methanol prices have recently exhibited a high degree of variance. Oxyhydrochlorination (OHC) technology utilizes domestic natural gas as a feedstock and thereby provides a reliable, low cost source of MeCl that is independent of the methanol market. Considerable savings are believed to be achievable via the application of this technology.

OHC is a key step in a potential gas-to-liquid fuels process. Currently, two approaches exist for converting natural gas to liquid hydrocarbon fuels, namely the Methanol-To-Gasoline (MTG) and the Fischer-Tropsch (FT) routes. Both of these processes begin with the production of synthesis gas from methane which is a high temperature, endothermic, and costly operation. The OHC process reacts methane, oxygen, and hydrogen chloride (HCl) in the presence of a special catalyst under controlled conditions to produce primarily MeCl and a byproduct, methylene chloride

(CH₂Cl₂). These chlorohydrocarbons may then be fed to a fixed bed reactor where they are oligomerized to produce liquid hydrocarbon fuels. Data from the Department of Energy's Pittsburgh Energy Technology Center (PETC) show that a mixture of MeCl and CH₂Cl₂ can be converted over ZSM-5 zeolite without undue carbon deposition. Unconverted methane and other light hydrocarbons may be recycled and the HCl recovered, thus improving the economics of the process. Despite the need for special materials of construction, OHC appears to be an attractive alternative to either MTG or the FT process.

Methyl chloride is a key raw material for the production of silicones. Currently, methanol and HCl are converted to MeCl which, in turn, reacts with silicon to produce dimethyldichlorosilane, (CH₃)₂SiCl₂, as the major product. Silicones are produced by hydrolysis of (CH₃)₂SiCl₂ which liberates HCl for recycle as shown in the equations below:

The overall reaction can be described by the equation below. However, the reaction sequence must go through CH₃Cl and the chlorosilane to manufacture silicones with the general formula: [(CH₃)₂SiO]_x.

The world's \$5.5 billion silicone market relies on the Direct Process to produce nearly all of its basic intermediates. U.S. producers supply almost 50% of the global market which has a healthy growth rate of 7-8% that is expected to continue into the future. Improved processes for manufacturing MeCl will enhance our domestic competitiveness in global markets. Dow Corning Corporation started working under contracts with DoE and GRI for the development of OHC in 1991.

Technical Strategy

The initial development of oxyhydrochlorination technology was accomplished in the laboratory. Years of studies developed a workable catalyst system including the choices of active OHC catalysis metal, activity promoter metal, stability promoter metal, and catalyst support. The absorber/stripper product recovery system was also initially developed in the laboratory. The absorbing oil was chemically and thermally tested for reactivity and decomposition. MeCl absorbance trials were then conducted both in batch and continuous modes.

Although an acceptable catalyst system has been developed, further laboratory studies continue. Dow Corning's Quality Policy states: Dow Corning will provide products and services that meet or exceed the expectation of our customers through our total commitment to continuous

improvement in everything we do. The OHC catalyst system is continuously being examined and improved upon in an attempt to optimize the OHC system as a whole. A new avenue of research has begun. A designed experiment to optimize the support surface area and catalyst metal loadings is partially complete. Competitor patent claims of improved OHC catalyst supports are currently being investigated.

Final testing of developed catalysts is being accomplished on a larger scale in the PDU. More realistic conditions, including a shell and tube heat exchanging reactor, will more accurately test both the catalyst's activity and lifetime. The process as a whole is being piloted on this scale, including the product recovery system. Methane, oxygen, and HCl are being used to produce MeCl which is recovered as product. Data from the PDU is to be used both in an economic evaluation and for scale-up of the system to the next larger size demonstration unit. The PDU has finished Task 4 Startup and has just begun Task 5 Evaluation of Packed Bed Technology.

Experimental

Catalyst development is occurring on a laboratory scale. A CAMILE control system runs the system from reactant gas feeds to on-line GC analysis. Methane, oxygen, and HCl are fed through mass flow controllers to the reactor which is heated to approximately 300-320°C by a three zone furnace. The reactor, constructed of 1/4" Hastelloy C276 tubing, is a downfeed system containing approximately 12" of catalyst supported on 4" of inert packing. Catalyst compositions and syntheses are covered in detail in Appendix A. The product line exiting the reactor is heat traced to an on-line GC where continuous process monitoring takes place. The product then proceeds to a column where chlorocarbons, water, and HCl are absorbed to prevent corrosion of the valve that maintains the system pressure at 30 psig.

Final testing of the catalyst and process occurs in the PDU. This unit has been described in detail elsewhere, so only a brief overview follows. The PDU is similar to the laboratory unit, but has many improvements. The reactor contains 19 tubes in a shell and tube arrangement that allows control over the very exothermic OHC reactions. Product stream composition will be monitored using on-line FTIR allowing a quick analysis of the product stream as well as measurement of HCl, which is not possible with a GC. The PDU also regenerates its absorber oil by stripping out the chlorocarbons so that the oil can be recirculated and used continuously.

Results and Discussion

Task 1: Catalyst Development and Separation Unit Operation Development

An Asahi Glass Company patent (JP 03640560) claims to get 53% conversion of methyl chloride to form methylene chloride at 73% selectivity. This technology is closely related to our OHC technology, so their novel support is being investigated. A zirconia-alumina support has been synthesized according to the Asahi patent's directions. The support was then ground and sieved to 12x25 mesh and impregnated with Cu/La/Li as shown in Appendix A - Catalyst Compositions and Syntheses. This catalyst will be tested to verify the Asahi patent's claims.

A ROTOBERTY reactor is being sought for OHC catalyst development research. The new reactor will allow better evaluation of catalysts through the measurement of intrinsic kinetics. Obviously, knowing the kinetics of the OHC reaction can only help in the development of the process. Getting the new reactor would also free up the existing tube reactor for catalyst lifetime studies. The addition of a new ROTOBERTY reactor should help significantly in the completion of Task 1.

Task 4: PDU Startup

Due to chemical etching of glass-lined equipment, a new PFA-lined stripper column was installed. This new material's chemical resistance seems to be sufficient, and no problems have been detected to date. A nitrogen booster pump was also installed to increase the flexibility of gas flow ranges at which the PDU could be run.

Chemical feeds were again brought on-line, and the system appears to be running smoothly with one exception. The FTIR windows again clouded over as soon as chemicals were introduced to the system. Inspection of the windows showed corrosion, although the cause is unknown at this time. This is now a top priority for allowing the PDU to run as smoothly as possible. Even with the FTIR problems, Task 4.0 PDU Startup is now complete.

Task 5: Evaluation of Packed Bed Technology

With PDU startup complete, evaluation of the packed bed technology commenced. The reactor was run at 30 psig between 285°C and 325°C. Product analysis by FTIR was not possible due to corrosion of the FTIR windows causing a drastic decrease in throughput. Instead, bag samples had to be taken and analyzed by GC. This analysis showed a maximum content of 3% methyl chloride in the product stream. The results, although not up to expectations or maintained for an extended time, indicated that the system could operate and produce methyl chloride.

Conclusions

The PDU was successfully started up and produced methyl chloride. Retrofitting the stripper seems to have solved the materials of construction problems encountered in the past. A nitrogen booster pump has been installed to give greater flexibility in running the PDU at various gas flows. Intense effort is being put into solving the corrosion of the FTIR windows. Evaluation of the packed bed technology is upcoming and will demonstrate the strengths and/or weaknesses of OHC technology.

The second half of the catalyst metal loading designed experiment remains. In the meantime, an OHC catalyst supported on zirconia-alumina is being investigated due to recent patent claims. Also, a ROTOBERTY reactor is being sought to improve OHC catalyst evaluation through the measurement of intrinsic kinetics.

Appendix A - Catalyst Compositions and Syntheses

Zirconia-Alumina Cogel Synthesis

Two solutions containing 250 g $\text{Al}(\text{NO}_3)_3 \cdot x\text{YH}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{YH}_2\text{O}$, respectively, in 750 g of deionized water were prepared. The Al salt was very soluble in water, but the Zr salt required a number of hours before dissolving. The solutions were combined in a 2 L addition funnel connected to a 5 L 3-neck flask containing 2 L of deionized water and fitted with a Teflon paddle and air motor stirrer.

The pH of the water was adjusted to 8 by ammonium hydroxide addition. The salt mixture was added over one hour with rapid stirring. The pH inadvertently decreased to neutral during that time period. Ammonium hydroxide was added to readjust the pH, and the solution immediately gelled. The mixture was stirred for 6 hours and allowed to sit for two days.

The gel was filtered using a Buchner funnel and washed twice with equal volumes of deionized water. It was then oven dried at 110°C for 24 hours (168 g collected) and pyrolyzed at 505°C for 20 hours (116 g collected, 97% yield). This yielded a solid corresponding to an idealized Al_2O_3 - ZrO_2 composition of 18.6%-61.9% compared to the 21% Al_2O_3 cited in Asahi's patent. The support was then ground and sieved to 12x25 mesh.

Catalyst 579 Synthesis

1.40g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, 5.21g $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, and 0.84g LiCl were dissolved in 50 ml of distilled water. To this solution was added 10g of zirconia-alumina cogel (12x25 mesh). This mixture was allowed to sit for two days. The solution was then placed under flowing nitrogen overnight to dry.