1995 Coal Liquefaction and Gas Conversion Contractors Review Conference

Methyl Chloride Via Oxyhydrochlorination of Methane: A Building Block for Chemicals and Fuels from Natural Gas

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Contract : DE-AC22-91PC-91030 (DoE)
5091-222-2300 (GRI)

Period of performance : October 1, 1991 to September 30, 1995.

Objectives :

The objectives of this program are to (a) develop a process for converting natural gas to methyl chloride *via* an oxyhydrochlorination route using highly selective, stable catalysts in a fixed-bed, (b) design a reactor capable of removing the large amount of heat generated in the process so as to control the reaction, (c) develop a recovery system capable of removing the methyl chloride from the product stream and (d) determine the economics and commercial viability of the process.

Approach :

The general approach has been as follows: (a) design and build a laboratory scale reactor, (b) define and synthesize suitable OHC catalysts for evaluation, (c) select first generation OHC catalyst for Process Development Unit (PDU) trials, (d) design, construct and startup PDU, (e) evaluate packed bed reactor design, (f) optimize process, in particular, product recovery operations, (g) determine economics of process, (h) complete preliminary engineering design for Phase II and (i) make scale-up decision and formulate business plan for Phase II.

Background :

Methyl chloride (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 (Figure 1). In 1992, CH_3Cl consumption in the US was reported to be around 850 million lbs. for these applications[1], although the actual consumption was probably higher than this. Currently, CH_3Cl is derived from methanol, however, the demand for methanol in the US is currently higher than the available domestic supply. As a result, methanol prices have exhibited a high degree of variance recently. Oxyhydrochlorination (OHC) technology utilizes domestic natural gas as a feedstock and thereby provides a reliable, low cost source of CH_3Cl that is independent of methanol. 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 natural gas, oxygen and hydrogen chloride (HCl) in the presence of a specialized catalyst to produce primarily CH_3Cl and some methylene chloride (CH_2Cl_2). These chlorohydrocarbons may then be fed to a fixed bed reactor where they are oligomerized to liquid hydrocarbon fuels (Figure 2)[2]. Data from the Department of Energy's Pittsburgh Energy Technology Center (PETC) show that a mixture of CH_3Cl and CH_2Cl_2 can be converted over ZSM-5 zeolite without undue carbon deposition[3]. 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 the MTG or the FT process.

Methyl chloride usage

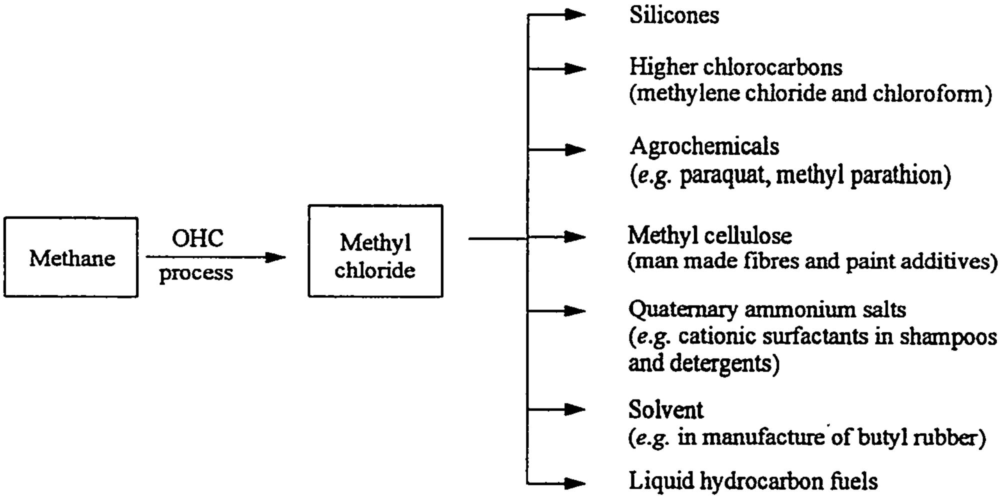


Figure 1.

Gas to liquid fuels process

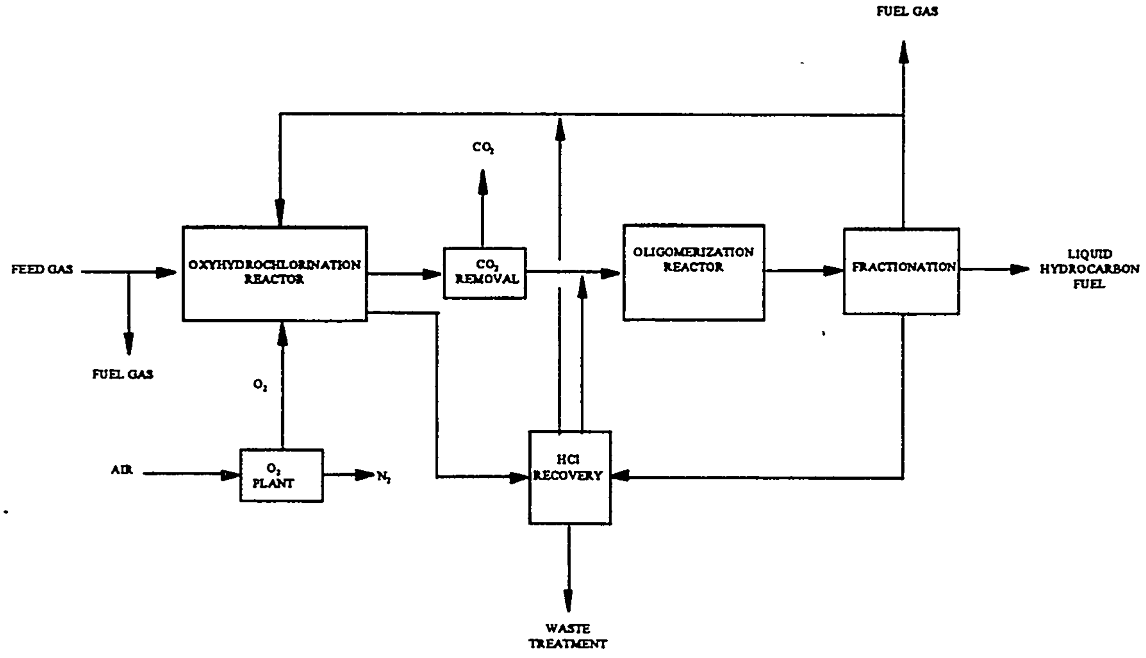


Figure 2.

The activation energy of the primary OHC reaction is 121 $kJmol^{-1}$ (Figure 3) and the overall reaction is highly exothermic with an enthalpy of reaction equal to 157 $kJmol^{-1}$. Secondary chlorination reactions to produce CH_2Cl_2, chloroform ($HCCl_3$) and carbon tetrachloride (CCl_4) also occur with similar activation energies. An additional complication is that methane and chlorinated product can undergo combustion reactions to give carbon monoxide (CO) and carbon dioxide (CO_2). Although the activation energies for these combustion reactions are somewhat higher than for chlorination, the enthalpies of reaction for combustion are significantly higher. Thus, once initiated, the combustion process is difficult to control. Selectivity is a function of temperature, and to minimize undesirable side reactions and maximize CH_3Cl formation, adequate heat transfer and excellent temperature control of the process are essential. Careful selection of the catalyst can also assist in optimizing selectivity.

Oxyhydrochlorination Chemistry

Primary Reaction	ΔE(kJ/Mol)	ΔH(kJ/Mol)
$CH_4 + HCl + 1/2\ O_2 \Longrightarrow CH_3Cl + H_2O$	121	-157
Subsequent Chlorination Reactions		
$CH_3Cl + HCl + 1/2\ O_2 \Longrightarrow CH_2Cl_2 + H_2O$	126	-153
$CH_2Cl_2 + HCl + 1/2\ O_2 \Longrightarrow CHCl_3 + H_2O$	126	-149
$CH_3Cl + HCl + 1/2\ O_2 \Longrightarrow CCl_4 + H_2O$		-142
Combustion Reactions		
$CH_4 + 3/2\ O_2 \Longrightarrow CO + 2\ H_2O$	225	-500
$CH_4 + 2\ O_2 \Longrightarrow CO_2 + 2\ H_2O$	240	-781
$CH_3Cl + O_2 \Longrightarrow CO + H_2O + HCl$	187	-343
$CH_3Cl + 3/2\ O_2 \Longrightarrow CO_2 + H_2O + HCl$	197	-624

Figure 3.

Accomplishments:

The OHC process can be considered as five individual processing steps, *i.e.* (1) natural gas purification and feed, (2) reaction, (3) reactor effluent recovery, (4) HCl recovery, and (5) CH_3Cl purification. The developmental effort associated with this project has been focused primarily on the reaction and reactor effluent recovery since the remaining steps are well understood and routinely operated within Dow Corning.

The construction of a Process Development Unit (PDU) was deemed necessary since adequate heat removal and high gas velocities were not achievable in a smaller lab reactor. Catalyst development studies, however, have continued on a lab scale (see below).

The PDU was built in an existing tower consisting of three 20'x20' floors at Dow Corning's Carrollton, Kentucky manufacturing site. Capital expenditure for the PDU totaled $3.2 million. The PDU utilizes a PC-based Camile data acquisition and process control system comprised of approximately 149 I/O points with intrinsically safe wiring. A schematic of the PDU is shown in Figure 4.

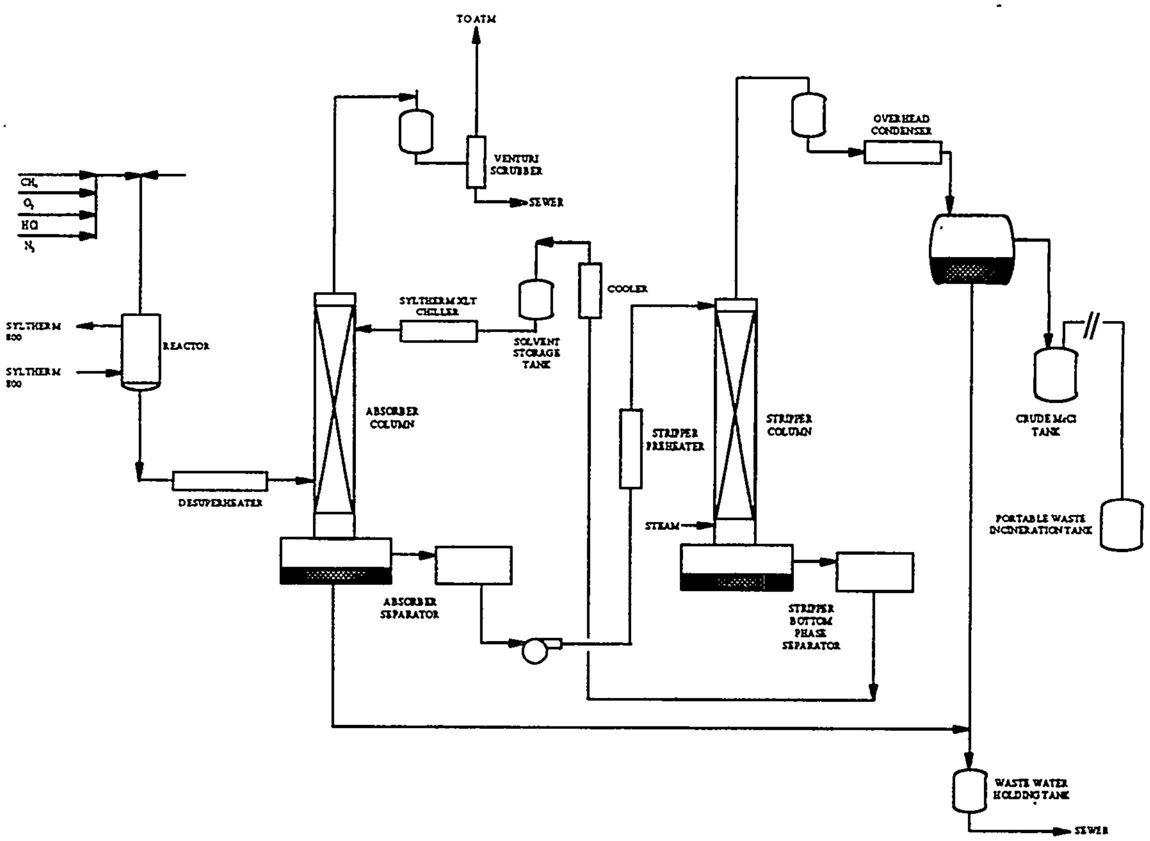


Figure 4.

PDU dimensions

Details of the key process units are summarized in Table 1 below.

Table 1.

Unit	Size/specification	Principal materials of construction
Reactor	Shell and tube design, 19 tubes 0.5"x72"	Hastelloy C
Desuperheater	Shell and tube design, 4 tubes 0.5"x60"	Hastelloy C
Absorber column	4"x120", 3/4" ceramic Intalox packing	Glass-lined
Syltherm® 800 heat exchanger	70 kW heater/ 95,750 BTU/h cooler	Carbon steel
Syltherm® XLT chiller	6 ton chiller	Carbon steel/ Hastelloy C
Stripper column	4"x120", 3/4" ceramic Intalox packing	Glass-lined
Phase separators	Various dimensions	Glass-lined

Reactor Design

In the reactor, methane (CH_4) reacts with HCl and O_2 over a supported metal catalyst at between 280°C and 350°C and 1-50 psig to form CH_3Cl. By-products from the reaction include CH_2Cl_2, H_2O, various combustion products and, to a lesser extent, $CHCl_3$ and CCl_4. A large heat transfer area per volume of catalyst bed is necessary to relieve the exotherms exhibited by the OHC process. Heat transfer coefficients and Aspen™ calculations suggest that a shell and tube reactor design, with catalyst in the tube and Syltherm® 800 heat exchange fluid on the shell side, would be adequate. A reactor containing 19 tubes (0.5" diameter, 72"' long) was constructed with enough heat transfer area to tolerate a heat duty of up to 95,750 Btu/h. The reactor is constructed from Hastelloy C since this material has served well in the lab reactor. The selectivity of the reaction is maximized by (a) limiting the CH_4 conversion to <25%, (b) maintaining high gas velocities which minimize heat and mass transfer limitations and (c) maintaining excess CH_4 in the feed. Excess CH_4 in the reactor feed is also important for maximizing HCl efficiency/conversion. High HCl conversion not only eliminates the need for HCl recovery but also minimizes corrosion problems elsewhere in the PDU.

Reactor Effluent Recovery

Product recovery is difficult given the low conversion of CH_4 and several technologies were initially considered. Membrane separation was discounted on the basis of cost (mainly associated with corrosion resistant compressors) and the lack of a readily available membrane capable of the separation. Pressure swing absorption operating at a high pressure differential would also require expensive compressors and was, therefore, rejected. Absorption and Steam Stripping (AST) appeared to be the best economic approach for product recovery. The advantage of AST over other processes is that it can be operated without high pressure. Reactor effluent is scrubbed in an absorber column with a refrigerated, non-volatile oil in a packed tower where direct contact condensing and gas absorption occurs. The desired recovery is achieved through careful selection of packing height, temperature and L/G ratio. The column operates adiabatically. Absorber bottoms are allowed to separate and the organic phase is fed to the top of the stripper column. Product condensables are removed from the oil with high pressure steam. Regenerated oil exits the stripper, is refrigerated and returned to the absorber column. Stripper overheads, steam, and chlorocarbons are condensed and routed to a second phase separator. The crude chlorocarbons are collected for analysis in the PDU but in a commercial process these would be sent to a distillation column where pure CH_3Cl would be collected overhead while crude methylene chloride would be accumulated in the bottoms. Recovery of >98% CH_3Cl is possible using this absorber/stripper technology.

At the start of this project, AST had not been demonstrated before and an oil with suitable properties had not been identified. Ideally the oil would be non-volatile, acid resistant, possess a high affinity for CH_3Cl, have low viscosity at low temperatures and be thermally stable. It is important that the oil selected has a high affinity for CH_3Cl as this is influential in the determination of L/G, which in turn, has a dramatic impact on the capital cost of the process. Several oils were evaluated before Multitherm™ fluid was selected. Multitherm™ is a hydrogenated dimer of iso-decene (average molecular weight = 272), with a vapor pressure of < 1mm Hg at 21°C. CH_3Cl solubility was found to be approximately 13% by wt. at 0°C and 15 psig. No degradation of the oil was observed after repeated exposure to HCl at elevated temperature.

A study was completed to determine CH_3Cl removal efficiency as a function of CH_3Cl loading on the absorption column. Different ratios of methyl chloride to nitrogen were fed to the column while keeping the total volumetric flow rate constant. Solvent flow rates and system pressure were varied while column temperature was kept constant at 0°C. Table 2 lists % CH_3Cl in the feed, the ratio of liquid to gas mass flow rate (L/G), pressure and associated CH_3Cl removal efficiencies.

Table 2.

% CH_3Cl in feed	L/G	Pressure (psig)	% CH_3Cl 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

(Total volumetric flowrate of CH_3Cl and N_2 = 165 ml/min. STP)

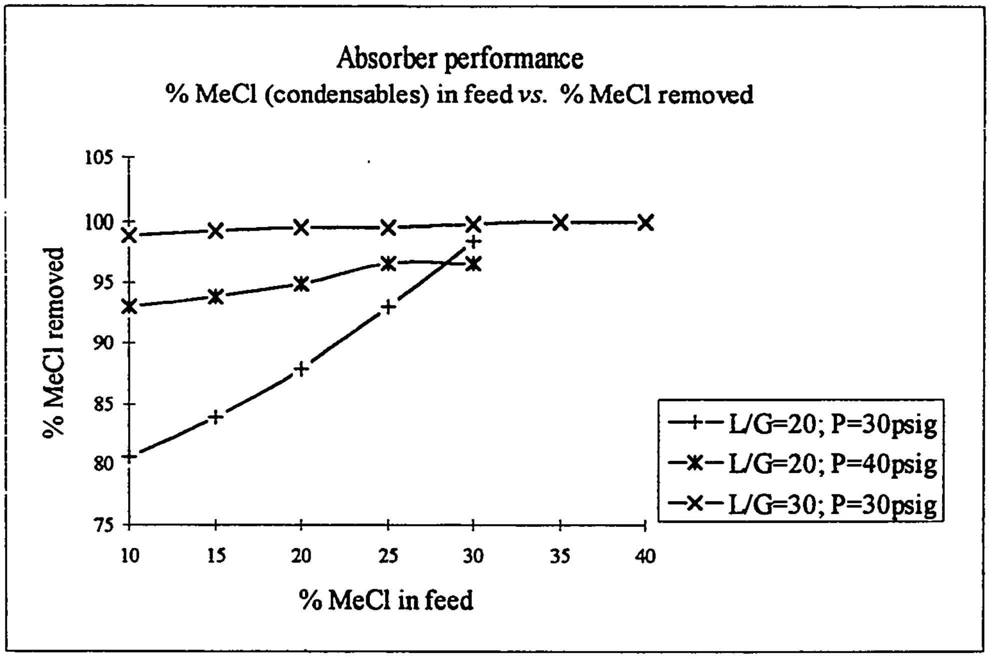


Figure 5.

The data show that, at a given pressure and L/G, more CH_3Cl will be removed by the absorber column as the percentage of CH_3Cl in the feed is increased. An increase in pressure and L/G also facilitates CH_3Cl recovery. Under the conditions used, CH_3Cl condenses and, in effect, the absorber operates both as an absorber and as a direct contact condenser.

Problems were initially encountered when the PDU absorber column was operated at temperatures below 0°C due to water, which is carried over from the solvent storage tank, freezing and blocking the column. Reliable flow is possible, however, with a column temperature of between 5°C and 10°C and CH_3Cl recovery trials were completed to evaluate absorber and stripper performance prior to introducing reactants into the unit.

Pressure Effects

Typically, as pressure is increased, the selectivity of the OHC reaction increases for a given methane conversion. For example, Figure 6 shows a typical set of data for a Cu/La/Li catalyst on an alumina support. The reaction was conducted at 0, 30 and 40 psig and CH_4 conversion was kept constant at approximately 15%. The percentage of CH_3Cl in the product stream increases from 72% to 85% over this pressure range. In order to keep methane conversion constant, the temperature was reduced from 340°C to 310°C as the pressure was increased from 0 psig to 40 psig.

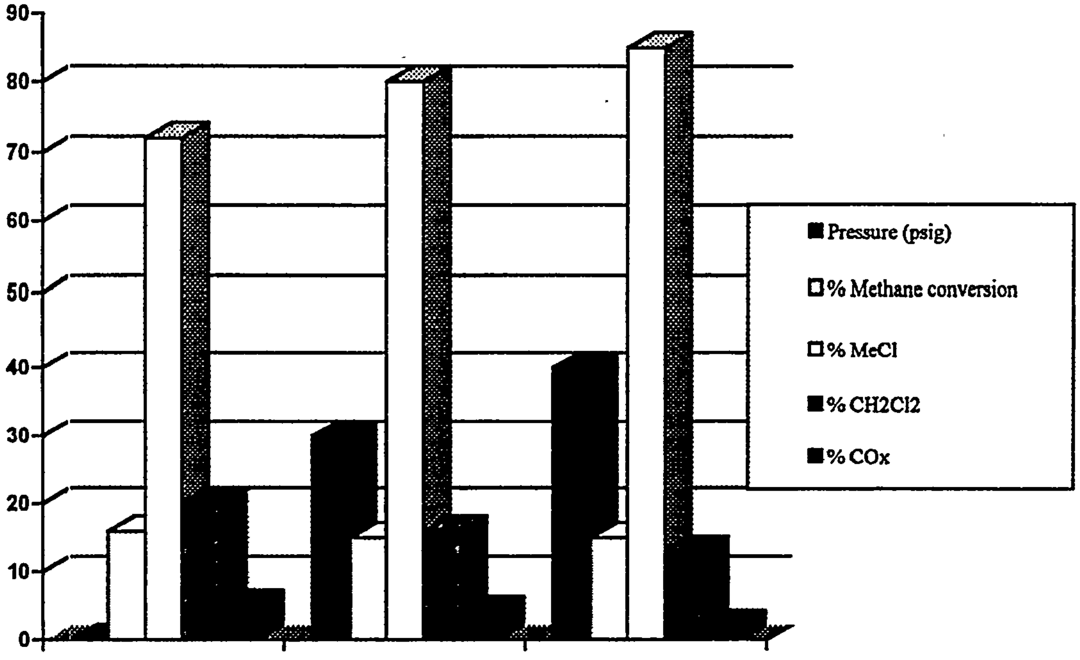


Figure 6.

Temperature Effects

Typically, OHC catalysts display the same pattern of decreased selectivity with increased methane conversion and/or increased temperature. Figure 7 shows a typical set of data for a Cu/La/Li catalyst on an alumina support. As the temperature is increased from 315°C to 340°C, methane conversion increases from 11% to 23%. HCl conversion similarly increases from 34% to 83%. The percentage of CH_3Cl in the product stream, however, decreases from 77% to 57% over this temperature range whereas the amounts of methylene chloride and combustion products increase.

Figures 6 and 7 demonstrate the impact that pressure and temperature have on the OHC reaction. Much of the work that will be performed on the PDU will be aimed at optimizing these process conditions for maximum CH_3Cl production.

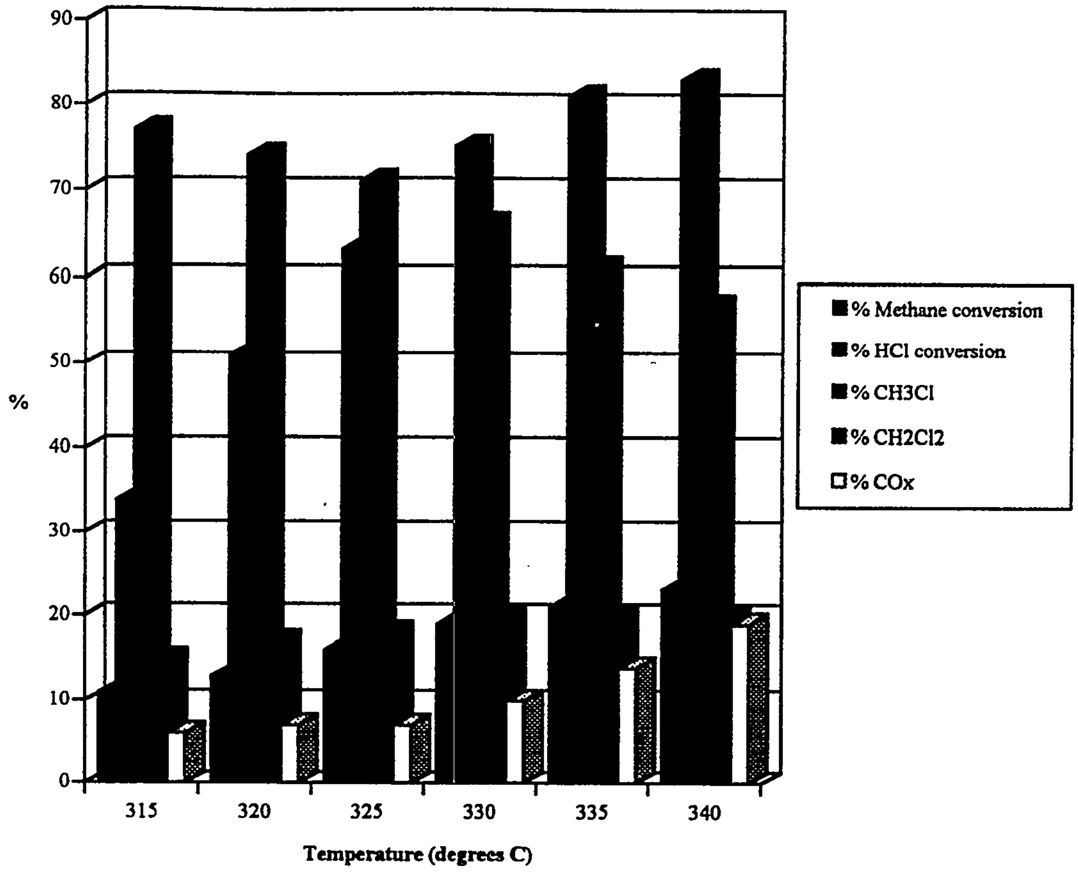


Figure 7.

Catalyst Development

Work in this area has focused upon optimization of metal-support-promoter combinations to enhance selectivity and catalyst activity. Traditionally, catalysts used for OHC chemistry usually contain copper, although iron and cobalt have been reported as being useful[4]. The copper is generally deposited on an oxide support such as silica or alumina. Potassium chloride or lanthanum chloride may be used as promoters in the system. The precursor materials used for the metal deposition, the impregnation technique, and catalyst preparation all have a major impact on the resulting catalyst. Many experiments have been conducted within Dow Corning to explore the effect that metal type, metal loading, temperature, feed ratio, *etc.* have upon catalyst performance. The results obtained have provided much information concerning catalyst performance although studies have been limited in that reactions are mass transfer limited (sufficient gas velocities are not generated in the lab to overcome this) and the reactor is not operating isothermally (insufficient heat transfer capabilities). Future studies on the PDU, which does not suffer these problems, will allow better evaluation of new and existing OHC catalysts.

The mechanism originally suggested by Deacon for oxychlorination involves the following steps :

$$\begin{aligned}
&2CuCl_2\,(s) &&\rightleftharpoons\; Cu_2Cl_2\,(s) + Cl_2\,(g)\\
&Cu_2Cl_2\,(s) + 1/2\,O_2\,(g) &&\rightleftharpoons\; CuO.CuCl_2\,(s)\\
&CuO.CuCl_2\,(s) + 2HCl\,(g) &&\rightleftharpoons\; 2CuCl_2\,(s) + H_2O\,(g)
\end{aligned}$$

Scheme 1.

Work by Allen[5] and Ruthven[6] has substantiated this mechanism through various kinetic studies. Kenney[7] reports first order kinetics for O_2 and zero or negative order kinetics for Cl_2 and suggests the following redox mechanism:

$$\begin{array}{lllllllll}
2Cu^{2+} & + & 2Cl^{-} & \rightleftharpoons & 2Cu^{+} & + & Cl_2 & & \text{(fast)} \\
2Cu^{+} & + & 1/2\ O_2 & \rightleftharpoons & 2Cu^{2+} & + & O^{2-} & & \text{(slow)} \\
O^{2-} & + & 2HCl & \rightleftharpoons & H_2O & + & 2Cl^{-} & & \text{(fast)}
\end{array}$$

Scheme 2.

In the above reaction scheme, the thermal dissociation of $CuCl_2$ is in equilibrium and the oxidation of CuCl to $CuCl_2$ is rate determining. Figure 8 shows a simple OHC catalyst system formed by impregnation of silica with 2% by wt. $Cu(CH_3CN)_4{}^{+}PF_6{}^{-}$. At 340°C, the overall activity for this catalyst is low, with methane conversion less than 5%, using a CH_4:O_2:HCl reaction stoichiometry of 4:1:1.3. This is well below the desired CH_4 conversion of 20%.

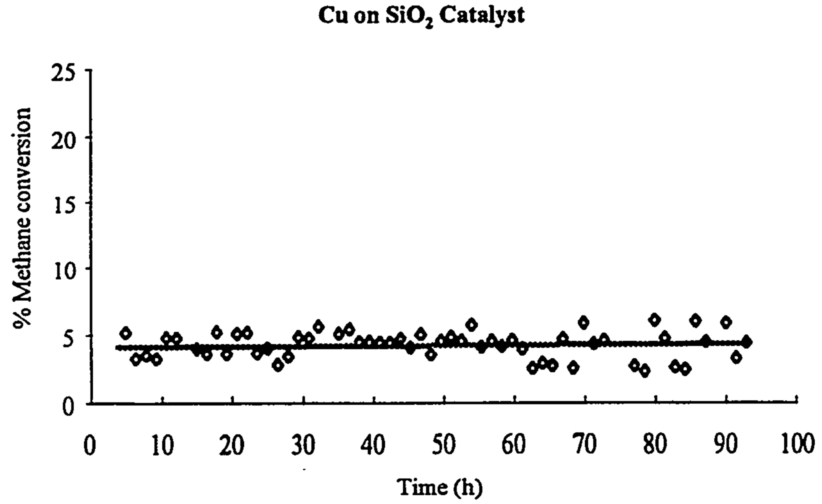


Figure 8.

By adding lanthanum chloride as a promoter, catalyst activity can be dramatically increased from below 5% to approximately 20% CH_4 conversion (Figure 9). Unfortunately, over a 200 h. period catalyst activity declines to less than half of the original activity. The conditions employed were identical to those used in Figure 8. The enhanced reactivity is thought to be due to the acceleration of the rate-controlling oxidation of the Cu^{+} species in the mechanism described above. The addition of $LaCl_3$ raises the pre-exponential factor in the rate constant without affecting the activation energy. It is also possible that the lanthanum competes effectively with copper for available chloride, thereby releasing more copper for oxychlorination.

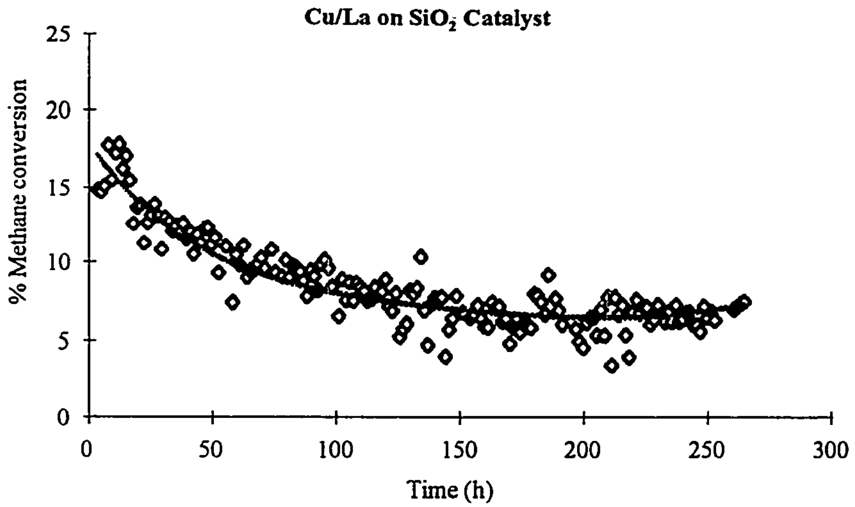
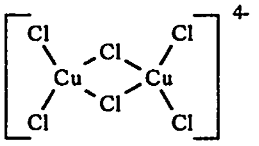


Figure 9.

Figure 10 shows the impact of adding a lithium promoter to the copper catalyst using the same conditions as described above. In this case, catalyst activity is increased to around 10% CH_4 conversion. Again, over a 200 h. period, catalyst activity decreases to half the original value. Non-dissociated CuCl or Cu_2Cl_2 are both volatile and not readily oxidized. The formation of these species can account for low reactivity and poor catalyst stability. Villadsen[8] has reported that upon addition of KCl to copper chloride-based OHC catalysts, cuprous complexes with the following structure are formed :



These species are readily oxidized to the oxygen-bridged analogue, which in turn, reacts with HCl to form $(Cu_2Cl_6)^{2-}$ and/or $(CuCl_4)^{2-}$ complexes. These complexes may be reduced to Cu^+ with concomitant evolution of chlorine, thus bringing greater reactivity to the system. Figure 10 suggests that similar behavior is observed with LiCl. Catalyst stability, however, is still clearly an issue in this case.

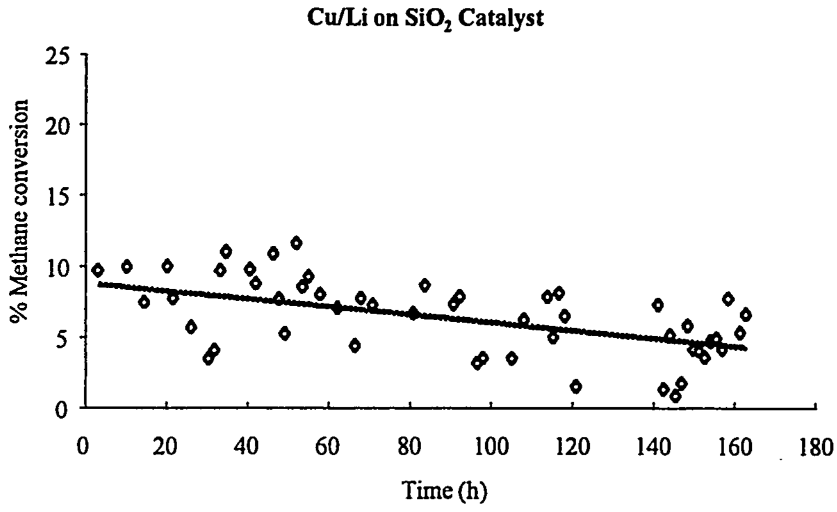


Figure 10.

The best results are obtained when all three metals, *i.e.* Cu, La and Li are present (Figure 11). Such a catalyst shows almost 20% CH_4 conversion and has greater stability than Cu/La alone (Figure 9). $LaCl_3$ is expensive and to reduce the overall cost of the catalyst, a mixed lanthanide starting material was subsequently used without adversely affecting performance.

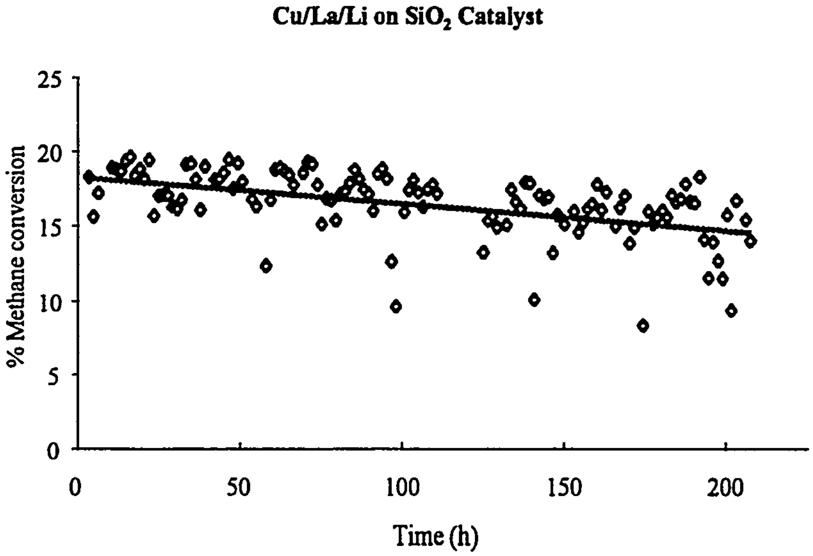


Figure 11.

Support Effects

Results have shown that catalysts made using alumina as the support exhibit greater stability compared to silica analogues (Figures 11 and 12) due to the stronger interaction between copper and alumina[9]. Pre- and post-reaction catalysts were characterized to determine chemical and physical properties. The principle techniques used were BET surface area measurements; thermal gravimetric analysis (TGA) to determine volatility and thermal stability; X-ray photoemission spectroscopy (XPS) to determine the chemical state of the metal loading; Scanning Auger spectroscopy (SAM) to map compositional gradients of the elements on the catalyst surface; Scanning Electron Microscopy (SEM) to determine microscopic morphology of metal crystallites and X-ray diffraction measurements (XRD) to determine the extent of crystallinity. SEM clearly showed a difference between an alumina- and a silica-supported catalyst. Micrographs for the alumina system showed little or no change in metal distribution before and after reaction whereas the silica analogue showed significant crystallite growth on the surface after reaction. At OHC reaction temperatures, the catalyst is not held strongly to the silica surface and migration of the metal through the bed takes place, resulting in reduced catalyst life. The catalyst illustrated in Figure 14 represents the best performance achieved to date and is the catalyst that will be used in extended PDU trials.

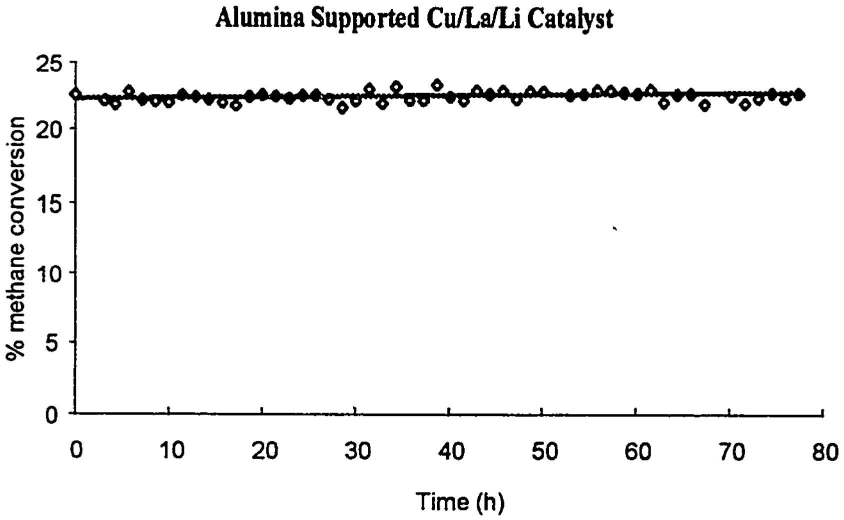


Figure 14.

It should be noted that catalyst support also affects the selectivity of the reaction. As already mentioned, selectivity toward CH_3Cl tends to decrease as CH_4 conversion increases. Figure 13 shows data collected for two catalysts which are identical in all respects except for the nature of the support. For a given conversion, the alumina-supported catalyst shows a higher percentage of oxygenates in the product stream.

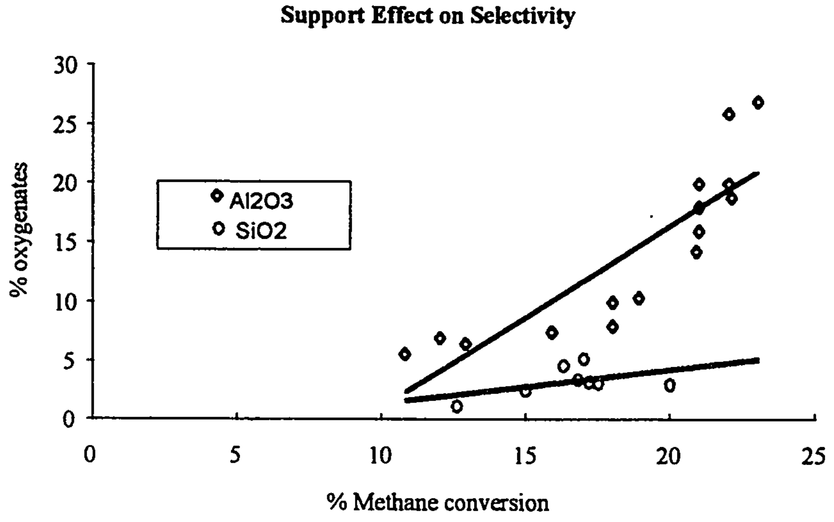


Figure 13.

The data presented above were generated using pure methane as the feed to the OHC reactor. The PDU and the lab reactor are currently using natural gas, which contains up to 4% of higher alkanes, as the feed. In this case, many more by-products are possible and catalyst performance is significantly changed. Studies are in progress to fully understand this system.

Conclusions :

Process Engineering

- OHC technology demonstrated in laboratory has been successfully taken to PDU scale
- Construction of the PDU has been completed
- The system has been successfully operated at pressure
- The Syltherm® 800 and Syltherm® XLT chiller systems have been fully tested
- The Solvent loop and hydraulics have been tested
- Absorber/stripper hydraulics have been evaluated
- CH_3Cl recovery runs have been successfully completed
- The FTIR on-line analyzer has been installed and commissioned
- The best catalyst to date has been identified, manufactured and loaded into the PDU
- The PDU has been successfully started up
- CH_3Cl has been produced and recovered in the PDU

Catalyst Development

- A catalyst containing Cu, La, and Li has been developed which shows good reactivity, selectivity and stability
- Cu is essential for catalysis but La and Li enhance reactivity
- An alumina support gives greater catalyst stability than silica but selectivity is reduced somewhat

The technology described herein is the subject of two patent applications.

Future work :

Much additional work remains to be done to render this technology commercially viable. On the PDU, designed experimentation will be used to optimize process conditions for maximum CH_4 conversion, CH_3Cl selectivity and CH_3Cl recovery. The effects of corrosion will also have to be closely monitored and, where possible, eliminated. Extended reaction runs are planned to determine catalyst lifetime under process conditions. The economics of the process will be determined once mass balances and operating costs are fully understood. Finally, the effects of operating the PDU using natural gas as opposed to pure methane will be examined.

As far as the catalyst is concerned, further studies of promoter and support effects are underway. It is also hoped that through a more detailed and sophisticated characterization of various OHC catalysts that a better understanding of the mechanism can be obtained.

Acknowledgments :

The authors would like to thank Bruce Crum (Catalyst development), Mike Diaz, Jeff Hale, Jay Hein, Scott Kleman, Cory Knutson, and Keith Toole (PDU start-up team).

This project was partially funded by the DoE, GRI and Texas Gas.

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