

Conceptual Design of Methyl Chloride Production Processes: A Review

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Abstract

The worldwide demand for methyl chloride is continuously increasing because of its industrial applications and the rapid development of the electronics and automotive sectors. Various chemical intermediates and end products from methyl chloride are demanding the increased production of this chemical product. Chlorination of methane and the hydrochlorination of methanol are the industrially existing processes. The stringent environmental regulations and the competition in the market demand the search for alternative processes or process modifications to improve the efficiency of the existing process plants. To meet these requirements continuous research is going on to improve the process efficiencies in terms of yield and environmental concerns. In this research, industrially existing processes and the recent production trends information is provided systematically. To fill the gap between the chemists and the process engineers conceptual design information is provided for both the industrially existing processes and the recent production trends. For simplicity, production processes are divided into catalytic and non-catalytic processes. A total of 11 conceptual process designs are identified from the systematic review and for all the processes conceptual designs are provided. Detailed discussions on recent developments on methyl chloride production processes, advantages, and the process challenges of various technologies are also presented.

Keywords

conceptual design, methyl chloride, methane chlorination, hydrochlorination

1 Introduction

Methyl chloride is an important industrial precursor for specialty chemical industries across the globe. Methyl chloride or chloromethane has a variety of industrial applications; it is used in the production of resins, elastomers, silicone fluids [1–4], and herbicides [5]. Silicone industry is one of the major methyl chloride demanding industries due to its applications in the automotive [6, 7], medical [8], personal care [9, 10], refrigerant [11], polymer industry [12] and in transportation sectors. So, the market for these chloromethanes has been increasing day to day in developing countries [13]. Market trends for methyl chloride show that 13% is used for methylcellulose, 11% for water treatment, 5% for fabric softener, 3% for silicones, 2% for plastic stabilizer, 9% for various uses such as butyl elastomers and organomodified clays, and the remaining 56% is used for the production of agricultural chemicals [14]. The production of these specialty chemicals directly improves the countries' GDP growth [15]. The global production of

methyl chloride is 1.4 Mt per year. Japan raised the capacity to 209 ktonnes in less than a decade. It has been estimated that the production will be about 6.7 billion USD in the year 2027 [16]. It shows the increasing trend of the global market. Considering the worldwide market for methyl chloride derivatives, this review discusses various process engineering developments undergone since the commercialization of methyl chloride. This review article puts efforts to fill the gap for chemists and process engineers for further investigations. The key highlights of this article are as follows:

1. The chemical process technologies are divided into non-catalytic and catalytic processes and discussed with conceptual designs.
2. The reaction mechanism for the commercial catalysts is studied.
3. The advantages and disadvantages have been discussed for each method and the plausible future outlook is given.

4. An inference is provided for the eventual shift in the choice of raw material from methane to methanol that pertained for its advantages.
5. Also, effluents from other chemical industries without any pretreatment are always preferable as raw materials as it reduces the cost of the overall process. This review discusses such a type of process information of both catalytic and non-catalytic pathways.
6. The areas for further improvement of both catalytic and non-catalytic pathways, using interdisciplinary technology solutions. To the best of our knowledge, there is no single article discussing a chronological evolution of process technologies for the production of methyl chloride. The processes discussed in this work are useful for scientists and engineers to understand the technologies involved in methyl chloride production so that they can take the right decisions in the design of new processes or to improve efficiencies of the existing processes.

2 Production paths

Methyl chloride is produced by two methods. First is methane chlorination where the methane reacts with chlorine at high temperature and pressure to form methyl chloride. During the First World War, a German company named Hoechst had first commercialized the synthesis of methane with chlorine at high temperatures and pressure. The second prominent method is the hydrochlorination reaction between methanol and hydrogen chloride [2, 17–21]. In Table 1 [22–32] from industrially existing process pathways to the recent trends, information is provided.

3 Non-catalytic processes

Methane chlorination and methanol hydrochlorination are the two main industrially commercialized processes for the synthesis of methyl chloride. The hydrochlorination of methanol is having the advantage of using methanol that is easy for transportation and storage or direct hooking up the manufacturing plant with suitable petrochemical facilities. Several reports prove that methanol is the best raw material for the generation of methyl chloride than methane [22]. This advantage is encouraging the eventual shift in the selection of raw material.

3.1 Hoechst process

Methyl chloride is industrially synthesized by thermal, catalytic, chemical, and photochemical methods [22, 33, 34]. Thermal chlorination is one of the most probed techniques theoretically and scientifically. In 1858, for the first time, methyl chloride was produced by reacting methane (marsh gas) with chlorine by M. Berthelot. The reaction process is given by Eq. (1).



The reaction is initiated by homolytic cleavage of chlorine bond above 300 °C. This chlorine radical reacts with methane to form methyl chloride [35–37].

The reaction scheme is shown from Eq. (2) to Eq. (5)

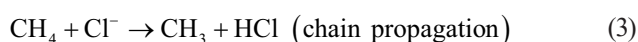
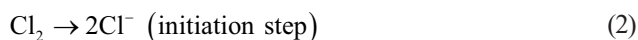
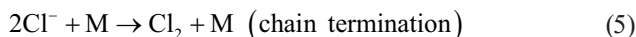
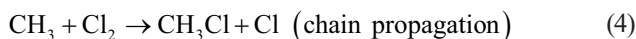


Table 1 Methyl chloride production processes literature table

Year	Name of the Process/Patent	Raw Materials	Reference
1923	Hoechst process	CH ₄ /Cl ₂	[22]
1976	Liquid phase hydrochlorination	CH ₃ OH/HCl	[23]
1999	Liquid phase reaction between methanol and hydrogen chloride in a two - stage reactor process and a single stage reactor process	CH ₃ OH/HCl	[24]
2000	Split stream route	CH ₃ OH/HCl	[25]
catalyst			
1955	From chlorinated paraffin hydrocarbon	Sulphur monochloride	CH ₄ /Cl ₂ [26]
1958	Catalytic hydrochlorination using the zinc chloride catalyst	Zinc chloride	CH ₃ OH/HCl [27]
1970	Chloromethane route	Zinc chloride	CH ₄ /HCl [28]
1984	Hydrochlorination of methanol using the aluminium oxide catalyst	Aluminium oxide	CH ₃ OH/HCl [29]
1990	Hydrochlorination using split methanol feed	Zinc chloride	CH ₃ OH/HCl [30]
1998	Preparation and separation of methyl chloride and dimethyl ether as methanol as extractant	γ-Al ₂ O ₃	CH ₃ OH/HCl [31]
2010	Hydrochlorination of contaminated Si compounds	Zinc chloride, iron chloride, bismuthoxychloride, or amines or quarternary ammonia or phosphonium compounds	CH ₃ OH/HCl [32]



where $\text{M} = \text{O}_2$ or impurities.

The reaction is second-order. It has been reported that the trace presence of oxygen will deprive the synthesis efficiency [38]. The reactor can be operated between the temperatures of 350 °C to 550 °C for maximum conversion.

Methane chlorination is one of the oldest techniques first commercialized by the German company Hoechst in the year 1923. This technique is retained its design with minor improvements. Fig. 1 schematically demonstrates the conceptual design. Initially, the recycled methyl chloride, methane gas (i.e., unreacted during the process) is mixed with the fresh methane and chlorine gas. This mixture is sent into the loop reactor that is coated with nickel or high alloy steel to resist the corrosive by-products formed. The reactor is maintained at a uniform temperature by using a coaxial tube and valve system. The reaction is maintained without loss of heat or mass transfer. The required temperature is maintained by the proper ratio of chlorine to the mixture of methane and methyl chloride gas mixtures [39]. Further, the reacted gases are quenched and purged through a series of absorption units to remove the major byproduct i.e., HCl and water in the form of 31% HCl, is removed in the C-1 absorption unit and 20% HCl is removed in the subsequent absorption unit, finally, the trace acids and chlorine gas are neutralized by adding sodium hydroxide (NaOH). In the first distillation column unreacted methane gas and some percentage of methyl chloride were sent for recycling stream, in the second and the third distillation columns dichloromethane and tetrachloromethane are separated respectively. The conversion values for products CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 are 39.98%, 9.068%, 0.4123% and $4.066 \times 10^{-4}\%$ respectively.

3.2 Liquid phase hydrochlorination

The synthesis of methyl chloride using the hydrochlorination route is described by [23]. This process is

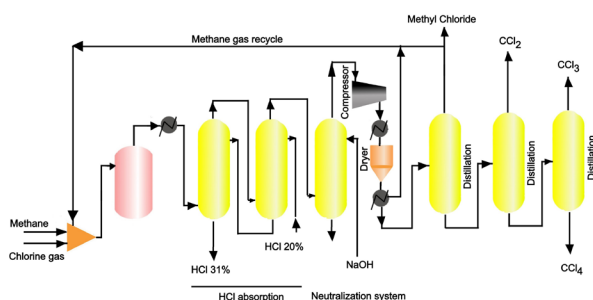


Fig. 1 Schematic process flow diagram for Hoechst process [22]

a non-catalytic hydrochlorination process. Reaction stoichiometry follows the reactions in Eq. (6) and Eq. (7).

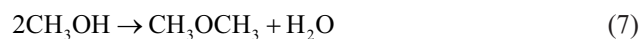
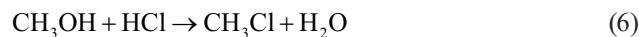


Fig. 2 schematically demonstrates this process.

The primary objective of this process is to improve the efficiency of the liquid phase hydrochlorination reaction by suppressing the formation of the by-product dimethyl ether. It can be achieved by maintaining the reaction temperature above 90 °C and the pressure greater than the atmospheric pressure. The process contains a reactor, two distillation columns, and two absorbers.

Higher reaction rates can be achieved by maintaining the feed composition above the azeotropic composition. The methyl chloride product is collected from the absorption column top streams. Absorption column bottoms are sent to the first distillation column. Vapors from the top of the first distillation column contain, hydrogen chloride and water is recycled back to the reactor. The bottom stream of the first distillation column containing hydrogen chloride and methanol azeotrope is pumped to the second distillation column. Pressure swing distillation is used to maintain the azeotropic composition.

3.3 Liquid phase reaction between methanol and hydrogen chloride in a two-stage reactor process and a single-stage reactor process

The synthesis of methyl chloride using the hydrochlorination route is described by [24]. In Fig. 3, the process is schematically demonstrated.

The main reaction in the first reactor (liquid phase hydrochlorination) to produce methyl chloride is given by Eq. (6) and the secondary reaction is given by Eq. (7). The selectivity of reaction in Eq. (6) is 99.2% and the reaction in Eq. (7) has to be suppressed. The hydrochlorination reaction is conducted in a two-stage reactor at a pressure of 1 bar and a temperature of 90 °C to 130 °C in the first

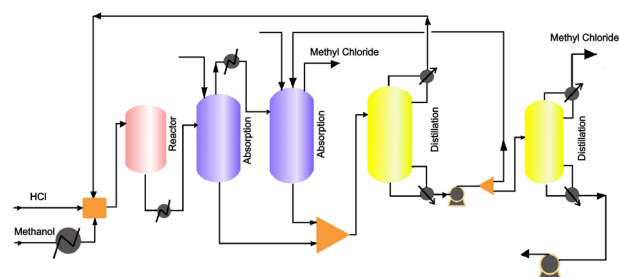


Fig. 2 Schematic diagram for the liquid phase hydrochlorination of methanol [23]

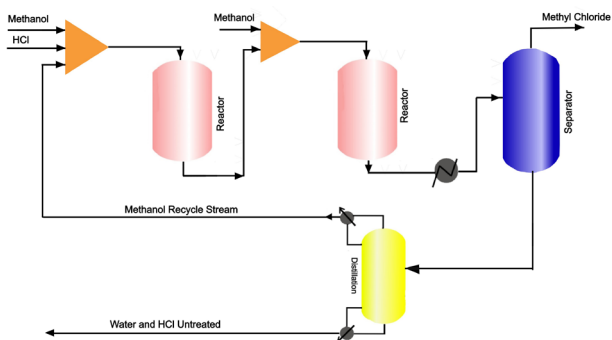


Fig. 3 Liquid phase reaction between methanol and hydrogen chloride in a two-stage reactor [24]

stage and a pressure of 1 bar and temperature of 100 °C to 150 °C in the second stage. In the first stage reactor, hydrogen chloride is supplied in excess to suppress the formation of by-product dimethyl ether. In the second stage reactor, excess methanol is supplied to maintain the concentration of hydrogen chloride below the azeotropic composition. This increases the conversion of hydrogen chloride with methanol to form methyl chloride. This procedure reduces the formation of the by-product dimethyl ether.

To suppress the dimethyl ether formation, for the first stage reactor, the feed ratio of methanol to hydrogen chloride is from 0.8 to 0.95. For the second stage reactor, the feed ratio is from 1.05 to 1.3. Reaction time for the overall process is 2 to 8 hours. The product mixture from the first stage reactor containing methyl chloride, water, and unreacted reactants are transferred to the second stage reactor. In the second stage reactor, sufficient heat is supplied to promote the hydrochlorination reaction and to selectively boil off water by-products. The gaseous product mixture from the second stage reactor is cooled by using a condenser. After cooling the product mixture methyl chloride gas and the aqueous methanol solution containing unreacted hydrogen chloride are separated. The unreacted methanol and the water containing the hydrogen chloride are separated in a distillation column. The pure methanol obtained from the top of the distillation column is recycled back to the first stage reactor for further reaction. Methanol feed to the first stage reactor is adjusted relative to the amount of hydrogen chloride discharged from the distillation column bottom. Since no catalyst is used in this process, the equipment for adding the catalyst and controlling the concentration of the catalyst is not required. The reactants containing the impurities can also be used as reactants. This is the major advantage of this process. Methyl chloride obtained from this process can be used as the industrial grade.

Fig. 4 schematically describes the modified form of the process shown in Fig. 3. In this process, two reactors are replaced by a single reactor. The volume of the single reactor is equal to the summation of two reactor volumes. The remaining unit operations are all same. The reactor is maintained at 120 °C. The total conversion obtained is 87.7%. It is low compared to the two-stage reactor conversion of 98.2%. But the total and operating costs of this process are low compared to the multistage reactor or two-stage reactor processes. Using these multistage and single-stage reactor processes industrial standard methyl chloride can be prepared.

3.4 Split stream route

The production of methyl chloride using the catalytic liquid phase a hydrochlorination reaction is described [25] and the schematic diagram is shown in Fig. 5. In this reaction, methanol reacts with hydrogen chloride in the catalytic liquid medium to produce methyl chloride. The reaction stoichiometry is similar to Eq. (6) and Eq. (7). The selectivity of the first reaction is 95%. The reaction is

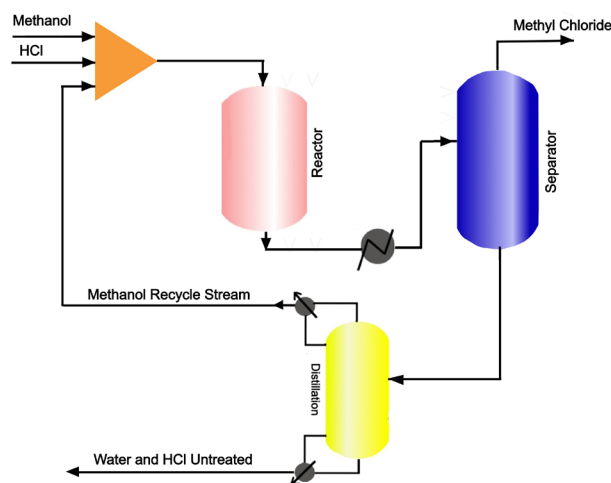


Fig. 4 Liquid phase reaction between methanol and hydrogen chloride in a stage reactor process [24]

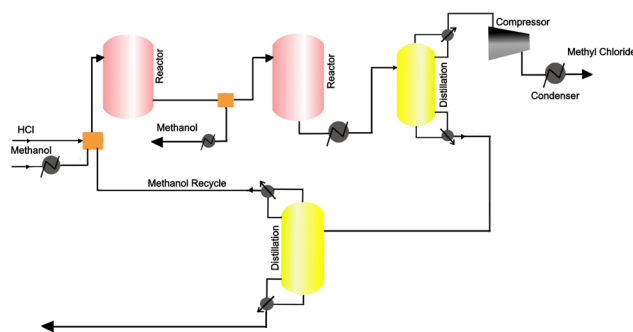


Fig. 5 Methanol split stream route [25]

performed in a staged reactor. The reactor may be a plug flow reactor, bubble column reactor, or a continuous stirred tank reactor. The specialty of this process is reactant methanol stream is split into two portions to contact with the hydrogen chloride. The first portion of the methanol stream containing 60 to 95% of methanol is preheated to 90 °C and introduced to the first stage reactor. The reactor temperature is maintained at 115 °C to 170 °C. The second split of methanol containing 40% to 5% is introduced at the second reactor at a temperature of 100 °C to 160 °C. This split stream mechanism provides stoichiometrically excess portion methanol relative to the hydrogen chloride and increases the formation of more methyl chloride product. It reduces the formation of dimethyl ether by-products. The gaseous product mixture from the second stage reactor is cooled using a condenser and the product methyl chloride is separated using a distillation column. The product stream is compressed and cooled. The bottom stream containing the unreacted methanol is separated in the second distillation column and it is recycled back to the first stage reactor for further reaction.

4 Catalytic processes

4.1 Chlorination of paraffin hydrocarbons

In this process, the synthesis of methyl chloride using the chlorination of paraffin hydrocarbons is described [26] and is shown in Fig. 6 schematically. Paraffin hydrocarbons used are methane, ethane, propane, and butane. In this reaction, paraffin hydrocarbons react with chlorine in the presence of the catalyst to produce a methyl chloride product. The reaction present in the production of methyl chloride is given by Eq. (1) and it is the direct chlorination of methane.

The catalyst used is Sulphur monochloride diluted with an organic liquid. The organic liquid is a highly chlorinated hydrocarbon (e.g., carbon tetrachloride). Operating conditions for the reaction are low temperature and pressure. Temperature is less than 100 °C preferably it is 20 °C. Chlorine and chlorinated hydrocarbon are passed

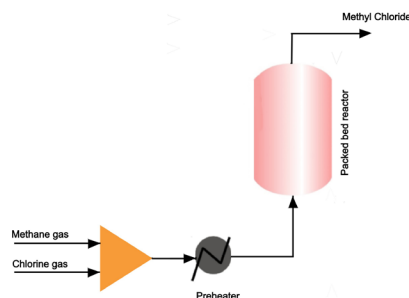
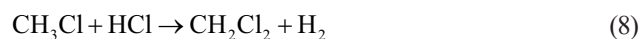


Fig. 6 Chlorinated paraffin hydrocarbon route [26]

counter-currently through a tubular reactor. Cooling tubes or cooling jacket is provided to control the reaction temperature at 20 °C. To control the chlorination reaction, the reaction zone in the reactor is shielded from actinic light; otherwise, the chlorination reaction will become uncontrollable and becomes explosive. Methane and chlorine are introduced in 2.2:1 portions into the base of the vertical tubular reactor packed with glass beads and containing sulphur monochloride catalyst. The product stream contains methyl chloride, unconverted methane, and traces of methyl chloride. The conversion of methane to methyl chloride is 80%. Conversion can be improved by increasing the time of contact or by increasing the ratio of methane to chlorine. The best temperature for the production of CH_3Cl is between 65 °C to 75 °C.

4.2 Catalytic hydrochlorination using the zinc chloride catalyst

The production of methyl chloride from the reaction between dilute aqueous hydrogen chloride and methanol is described [27] and is depicted in Fig. 7. In this reaction, both methanol and hydrogen chloride is in the liquid phase. Methanol in the presence of zinc chloride catalyst reacts with dilute aqueous hydrogen chloride. By-products are also formed and the reactions are given in Eq. (6) and in Eqs. (8)–(10). The selectivity of Eq. (6) is 90% to 95%.



The feed mixture containing the aqueous solution of hydrogen chloride, methanol, and the necessary quantities of methyl chloride is introduced into the first reactor. In the first two reactors, aqueous zinc chloride solution is maintained at a concentration of 65% to 75% by weight and temperature of 120 °C to 140 °C. The pressure of the reactor is greater than 21 to 345 kPa. Hydrogen chloride and methanol are converted into vapors in the

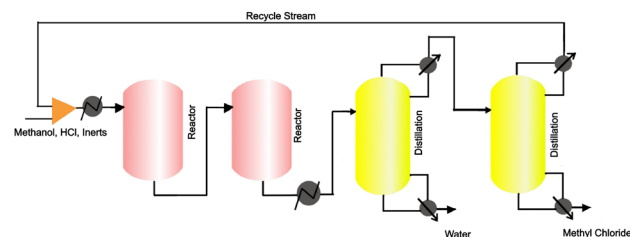


Fig. 7 Catalytic hydrochlorination using the zinc chloride catalyst [27]

first reactor and then the reaction progresses. The product mixture from the first reactor contains methyl chloride, water, unconverted methanol, and hydrogen chloride. This product mixture from the first reactor is introduced into the second reactor containing the aqueous zinc chloride solution at different points to enhance the adequate dispersion of the feed. In the second reactor (having the same catalyst concentration), the unconverted hydrogen chloride and methanol react and give more methyl chloride. The product mixture from the second reactor is condensed to separate the unconverted hydrogen chloride, water, and product methyl chloride. Unconverted methanol and unconverted hydrogen chloride are recycled back to the first reactor. The entrained zinc chloride solution is refilled to maintain the reaction. In the first reactor conversion is 65% and in the second reactor, it is 95%.

To improve the yield of methyl chloride, the reaction product is continued without separating it into its components. Other chloromethanes formed in the reaction (Carbon tetrachloride, chloroform) are inert towards the chlorination because of this, they are allowed to pass along with the methyl chloride and hydrogen chloride for subsequent reaction to obtain additional quantities of methyl chloride product. Reaction products from the second reactor are fractionated and the product methyl chloride is obtained in gas form from the top of the distillation column. This process gives the efficient conversion of aqueous solutions of hydrogen chloride with minimum by-products.

4.3 Catalytic chloromethane route using the zinc chloride catalyst

Synthesis of methyl chloride using the chlorination route is schematically shown in Fig. 8 [28]. Organic gases like methane react with chlorine and give methyl chloride. The reaction stoichiometry is the same as the reaction in Eq. (1). Conversion reported is 90%. The reactor is adiabatic, diabatic, or isothermal based on the requirements of the process. The optimum reaction temperature range is from 350 °C to 500 °C, preferably it is in the range of 400 °C to 450 °C. The feed ratio of chlorine gas to organic

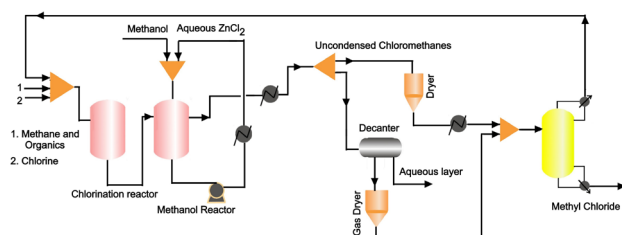


Fig. 8 Catalytic chloromethane route using the zinc chloride catalyst [28]

material varies from 0.15 to 4 moles of chlorine gas per mole of organic material. The reaction pressure is maintained at atmospheric pressure.

The first reactor is the chlorination reactor and the second reactor is the methanol reactor. The products from the chlorination reactor are passed to the methanol reactor. The gaseous effluents from the chlorination reactor containing the higher chlorides are sent to the methanol reactor. Since the reactants are in the gas phase, a packed bed reactor is used for the methanol reactor.

The zinc chloride catalytic solution is placed in the packing or the solution passed through the reactor in a counter-current fashion, to disperse the catalyst in the effluent gases. The catalytic solution enters the upper portion of the reactor. Methanol makeup in liquid form is mixed with the zinc chloride solution is introduced into the top of the methanol reactor. The gas stream from the chlorination reactor, methanol makeup, and zinc chloride catalyst all flow towards the bottom of the methanol reactor counter-currently. Zinc chloride catalyst is dispersed using the packing among the reactant gases. The preferable temperature in the packed bed reactor is 135 °C and the pressure is 1 bar. Maintaining low pressures avoids the additional high-pressure equipment capital investments. Zinc chloride concentration is 52 to 80 weight percent in the reactors.

The catalyst is withdrawn through the bottom of the methanol reactor, it is cooled, and it is recycled back to the reactor. The product gases from the methanol reactor contain methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. This gas mixture is collected from the top of the packed bed reactor, sent to the condenser and then next to the decanter. In the decanter, the organic and aqueous layers are separated. The organic layer containing methylene chloride, chloroform, and carbon tetrachloride are sent to the drier. For drying K_2CO_3 is used as a drying agent. K_2CO_3 removes the water present in the organic liquid. Organic liquids are sent to the distillation column for the separation and recovery of chloromethanes. The uncondensed chloromethanes are sent to the gas dryer to remove the water present in the gases. The gases from the gas dryer are further condensed using a condenser to convert the organic gases into liquids. Uncondensed gases containing large portions of methyl chloride are recycled back to the chlorination reactor for further reaction with incoming chlorine gas. The organic liquid condensed in the condenser is merged with the stream existing from the organic liquid dryer and sent to the distillation column for separation. Methyl chloride product is collected at the bottom stream of the distillation column.

4.4 Hydrochlorination of methanol using the aluminium oxide catalyst

In this process, the synthesis of methyl chloride using the hydrochlorination route is described and is shown in Fig. 9 [29]. This process describes the catalytic gas phase hydrochlorination reaction for the production of methyl chloride. The catalyst used is aluminum oxide catalyst. The reaction stoichiometry is given by Eq. (6). Here all the reactants are in the gas-phase. Methanol and chlorine are preheated and introduced into the reactor. The reaction is carried out in a packed bed reactor containing a bundle of tubes. These tubes are cooled from a cooling jacket, arranged outside of the reactor. The temperature maintained in the reactor is from 250 °C to 500 °C. Reactor pressure maintained in between 100 to 1100 kPa.

4.5 Hydrochlorination using split methanol feed

The schematic process flow diagram for this process is shown in Fig. 10. This process contains two hydrochlorination reactors in series followed by a quench tower, caustic tower, and drying tower [30]. Quench tower, caustic tower, and drying towers are scrubbers and their function is the purification of methyl chloride vapors. Methyl chloride is produced by the catalytic hydrochlorination of methanol in the liquid phase. The main catalyst used in this process is 68% zinc chloride [40]. In this reaction, a small quantity of dimethyl ether by-product is produced as given

by Eq. (7). The formation of dimethyl ether is reduced by conducting the reaction in a series or in a parallel arrangement of reactors. Usually, two reactors in series are used.

Anhydrous hydrogen chloride and methanol vapor mixed stream is introduced into the bottom of the first chlorination reactor. Methanol stream is introduced as a split stream into the first and second reactors. The overall molar feed ratio range between methanol and hydrogen chloride is 0.65 to 1.15 with excess HCl are used for Eq. (6). The reaction pressure is maintained from 100 kPa to 500 kPa and the reaction temperature is maintained from 100 °C to 200 °C. In the reaction medium, hydrogen chloride is maintained in bubbling form and methanol as a gaseous mixture. The percent of methanol introduced to the first reactor is 40 to 80% and the remaining quantity is introduced into the second reactor.

After the reaction, methyl chloride is collected from the top of the first reactor. This stream contains methyl chloride along with unconverted HCl. Additional methanol or split methanol combines with the unreacted HCl in the second reactor and gives more methyl chloride product. The reaction mixture in vapor phase removed from the top of the second reactor is purified in a quench tower and in caustic scrubber consecutively. The temperature of the top stream containing the crude methyl chloride vapor from the second reactor is 150 °C and this temperature is reduced by using a condenser to 50–60 °C. This cooled stream is introduced into the water scrubber. Here, the aqueous scrubbing liquid circulated through the quench tower is cooled to a temperature of 20 to 35 °C by passing through a heat exchanger. A considerable portion of the hydrogen chloride present in the stream is diluted in water and this diluted HCl is removed as weak an acid and is sent for further treatment. Good operation of the quench tower can be obtained, if the entering water stream temperature is maintained between 10 to 20 °C and the leaving water temperature below 40 °C. After scrubbing in the water scrubber to remove the hydrogen chloride, the vapor stream is directed to the caustic scrubber to remove the remaining hydrogen chloride.

The vapor stream from the caustic scrubber is sent to the drying tower. Here, the solution is scrubbed with the concentrated sulfuric acid solution. At the bottom of the tower fresh treating acid is introduced and the spent acid is withdrawn. The acid removes the dimethyl chloride from the vapor stream. Finally, the purified methyl chloride from the drying tower top stream is compressed and

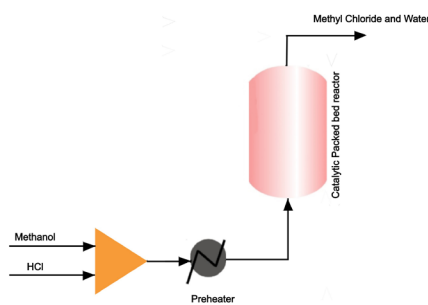


Fig. 9 Hydrochlorination route using aluminum oxide catalyst [29]

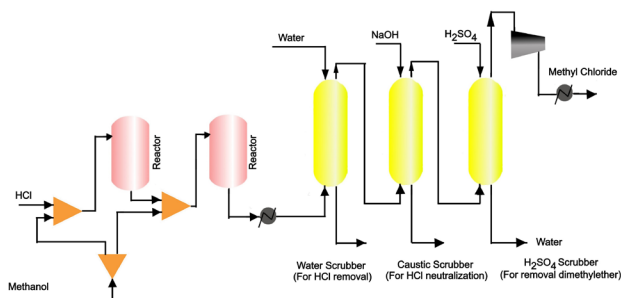


Fig. 10 Schematic process flow diagram for catalytic hydrochlorination of methanol [30]

cooled for storage purposes. The product stream contains water, unreacted methanol, hydrochloric acid, dimethyl ether, and methyl chloride. Dimethyl ether is removed by scrubbing with sulfuric acid in a drying tower (H_2SO_4 scrubber). Then the pure methyl chloride vapor from the drying tower is first compressed, condensed, and collected in the storage tank. Using sulfuric acid to remove dimethyl ether increases the process cost and also creates disposal problems.

4.6 Preparation and separation of methyl chloride and dimethyl ether as methanol as extractant

In this process, methyl chloride and dimethyl ether are produced and separated using extractive distillation. Methanol is used as an extractant [31]. The schematic process flow diagram is shown in Fig. 11. The product mixture is prepared by a catalytic reaction between methanol and hydrogen chloride. The catalyst used is aluminum oxide. The reaction stoichiometry is given in Eq. (6) and in Eq. (7). The mixture is then distilled to remove water and is subsequently subjected to an extractive distillation with methanol as extractant, with chloromethane resulting as a top product. In another distillation step, the remaining dimethyl ether is separated from the methanol.

Methanol and HCl in vapor form are introduced into a two-stage esterification reactor. The esterification reactor is designed as a two-stage tubular reactor. In the first stage, methanol, and excess HCl were added. Methanol and excess HCl flows through the first stage in which the catalyst is charged. Here the reaction takes place between the methanol and excess HCl. The product mixture flows to the second stage of the reactor.

The second stage is also charged with the catalyst. In the second stage 20% excess methanol is charged to react with the HCl. The resulting mixture contains dimethyl ether, chloromethane, water, and methanol leaving the reactor is condensed and pumped to the first distillation column. The liquid stream pumped is vaporized before it enters into the first distillation column. From the first distillation column bottoms, water is withdrawn. First distillation

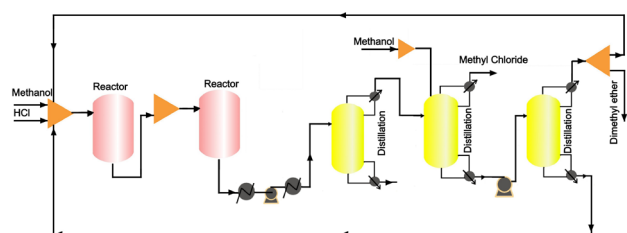


Fig. 11 Schematic process flow diagram for methyl chloride production by catalytic hydrochlorination and extractive distillation [31]

column tops contain the mixture of methanol, dimethyl ether, and chloromethane. The distillate stream from the first column is the feed to the extractive distillation column. The extractive distillation column operates under pressures between 100 and 2500 kPa. For the extractive distillation methanol is used as an extractant and it is introduced through the top of the extractive distillation column. From the top of the extractive distillation column, chloromethane product is collected. From the bottom stream, the mixture of dimethyl ether and methanol is obtained. This bottom stream is introduced to the second distillation column. Methanol is collected at the bottom stream of the second distillation column. Part of the methanol withdrawn is recycled to the reactor and the remaining portion of the methanol is introduced as the extractant to the extractive distillation column. Dimethyl ether is withdrawn from the top of the second distillation column.

4.7 Hydrochlorination of contaminated Si compounds

This process is based on the production of methyl chloride from the contaminated hydrogen chloride with the Si compounds [32]. The silicon (Si) compounds used are methoxymethylsilanes, methylchlorosilanes, hydrolysis and condensation products. Si compounds present in the product mixture are removed by condensation, and by washing out with methanol. The schematic diagram is shown in Fig. 12.

Hydrogen chloride contaminated with the Si compounds and methanol is fed to the reactor. The reactor is maintained at the desired temperature. Depending on the impurities present in the hydrogen chloride the selection of the catalyst varies. Frequently used catalysts for liquid-phase processes are metal chlorides having Lewis acid properties like iron chloride, zinc chloride, quaternary ammonium or phosphonium compounds bismuth oxychloride, or amines. Initially, the catalyst mixed with water is placed in the reactor.

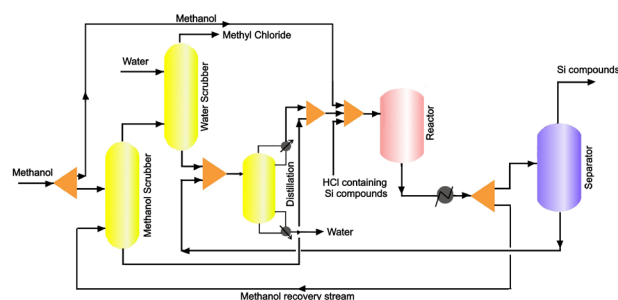


Fig. 12 Schematic process flow diagram for methyl chloride production using the hydrochlorination reaction between the methanol and hydrogen chloride containing Si compounds [32]

The products from the reactor containing chloromethane, water, Si compounds, unreacted methanol, and unreacted hydrogen chloride are passed to the condenser, and are diverted to the separation column. Separation column bottoms containing the water and methanol are feed to the distillation column for methanol recovery. The methyl chloride from the condenser is diverted to the methanol scrubber. In the scrubber, fresh methanol removes the Si compounds. The methanol from the scrubber, the feed methanol containing the Si compounds, and the methanol

recovered at the distillation column are recycled to the reactor. The chloromethane from the methanol scrubber is sent to the water scrubber. At scrubber, methanol present with the methyl chloride is washed out and the pure methyl chloride is collected. The stream containing the methanol from the water scrubber is sent to the distillation column, where methanol is separated and it is used as feed to the reactor.

In Table 2, the advantages and the process challenges for methyl chloride production are provided.

Table 2 Advantages and process challenges involved in methyl chloride production processes

Process	Advantages	Process challenges
Hoechst	Low investment cost and if by-products (like dimethyl chloride, trimethyl chloride and tetramethyl chloride) are also desired all can be produced by adjusting the process conditions.	Controlling the heat of reaction adiabatically close to critical temperature is a challenge. If the reaction goes beyond a critical temperature (~550 °C–700 °C) it leads to methyl chloride decomposition.
Liquid phase hydrochlorination of methanol	Reaction efficiency is can be improved by suppressing the formation of by-product dimethyl ether.	Operating all unit operations at different pressures to maintain higher space times
Liquid phase hydrochlorination in a multi-stage and single-stage reactor	The reactants containing the impurities can also be used as reactants and the formation of by-product dimethyl ether can be controlled.	Maintaining the hydrogen chloride concentration below the azeotropic composition.
Split stream route	Splitting the methanol stream eliminates the additional processing steps for hydrogen chloride recovery and recycling which reduces the capital cost for the process and also it reduces the formation of dimethyl ether.	Continuously monitoring the ratio between the methanol and hydrogen chloride is necessary to increase the conversion.
From chlorinated paraffin hydrocarbon	Operating at low temperature and low pressure.	Controlling the chlorination reaction from explosions
Catalytic hydrochlorination using the zinc chloride catalyst	Gives the efficient conversion of aqueous solutions of hydrogen chloride with minimum by-products.	Dispersing the product mixture from the first reactor at different locations of the second reactor.
Chloromethane route	The reaction can be performed either in single- stage or in multi-stage reactors based on the requirements of the process and the hydrogen chloride is completely utilized.	Handling the catalyst dispersion in the reactor.
Hydrochlorination of methanol using the aluminium oxide catalyst	The speed of catalyst inactivation and the precipitation of carbon are reduced. This feature demands less reactor volumes.	Decreasing conversions and increasing unreactive methanol along with the formation of the by-product.
Hydrochlorination using split methanol feed	Split arrangement of the feeding methanol reduces the conversion of methanol into dimethyl ether and reduces the utilization of the sulfuric acid in the process. Another advantage of this process is the cost of raw material and the cost involved in the production of the product can be reduced.	The disadvantage of this process is while the split arrangement is processed into the two reactors there is no improvement in conversions of methanol into methyl chloride. It was maintained constant and the overall conversion decreased.
Preparation and separation of methyl chloride and dimethyl ether as methanol as extractant	Two stage reactors used in this process improve the production of methyl chloride.	Continuous monitoring of extractive distillation operation is necessary.
Hydrochlorination of contaminated Si compounds	The products contaminated with the Si compounds can be used as the feed to this process.	Based on the complexity and number of operations, operating the process is challenging.

5 Catalysis

The Gibbs free energy of methylchloride from methane and chlorine is -36 kJ/mol. So it requires high energy for the methane to occur homolytic cleavage further react with chlorine. Whereas methanol chlorination is a slow process at room temperature, also the alcohol reactivity order is $3 > 2 > 1 > \text{methyl}$. Consequently, the reaction of methyl alcohol with Lucas reagent (solution of anhydrous zinc chloride in concentrated hydrochloric acid) does show any form of higher alkyl groups. So, it requires high temperature and pressure or catalytic medium for higher conversion of methyl chloride.

In this method, methyl chloride is produced by the reaction between boiling methanol in the liquid phase and the hydrogen chloride in the gas phase in the presence of zinc chloride catalyst. Alumina catalyst is used for the same reaction at higher temperatures. In this case, both the reactants are in vapor phase. Catalyst plays an important role in enhancing the reaction rate [17, 40]. Catalysts activities with $\gamma\text{-Al}_2\text{O}_3$ [3, 41–45] and with ZnCl_2 modified zeolite catalysts [46, 47] are explained in detail for achieving the higher conversions. Parameters like pH of the reaction medium and catalyst loading are the crucial parameters in deciding the product formation [48]. In the other cases, the role of η -alumina doped with group one metal salts [49] and the interaction of alumina catalyst with hydrogen chloride improved the conversion rates are observed [50]. Hydrochlorination reaction is reported as the economical process for producing methyl chloride [39]. The major drawback of hydrochlorination at higher temperatures (300 °C to 450 °C) is the formation of by-products or higher derivatives of chloromethane, due to uncontrolled reactions [23]. The second method is the direct chlorination of methane with molecular chlorine gas in the presence of an oxyhydrochlorination catalyst [51–54]. In this case, the temperature played a major role in improving the conversion rates [39, 55, 56]. Here, along with the methyl chloride, the other chloromethanes like methylene chloride, chloroform, and carbon tetrachloride are also formed [57–60]. This method is preferable when higher chloromethanes are desired.

For chemical reactor design, kinetics information of reactions is very important [40]. To fill this gap, various kinetic models are proposed and the crucial parameters like frequency factor, activation energy are calculated and tested for their experimental fitness [61–64]. The results of these investigations helped in the design of industrial reactors.

6 Process safety

Methyl chloride is toxic in nature. Storing and handling harmful chemicals like methyl chloride safely at the process plant facilities is important [65, 66]. Since the emissions of methyl chloride are carcinogenic, to protect the environment controlling the emissions is necessary [67]. Hazard modeling software can be used to do consequence analysis by predicting the toxic emissions from the industry [68]. Hazard modeling results can be used for chemical disaster preparedness and mitigation [69].

7 Future outlook

The innovation of new products from methyl chloride keeps on increasing so as the demand for this product. Currently, catalytic hydrochlorination of methanol is a widely accepted process for the commercial production of methyl chloride at a large scale. The usage of catalysts is a costly affair and also inactivation of the catalyst due to carbon deposition is a major concern in the industry. The disposal of spent catalysts is another environmental issue. Non-catalytic processes using single or multistage reactors are the way forward not only to reduce the production cost of methyl chloride but also to produce in an environmentally friendly manner. Scaling up the laboratory scale processes is needed to meet the demands of the worldwide chloromethane market.

8 Conclusions

The rising market for silicone polymers and numerous industrial applications of chloromethane or methyl chloride is demanding knowledge of various methyl chloride manufacturing processes. The existing catalytic processes are offering more yields with the risk of catalyst maintenance. Higher yields of methyl chloride from non-catalytic processes are the future technology with less operating costs and fewer contaminations. In conclusion, the research has to be continued to find new catalysts and processes to replace the existing processes or to improve the efficiency of the existing catalytic and non-catalytic processes for the production of methyl chloride.

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