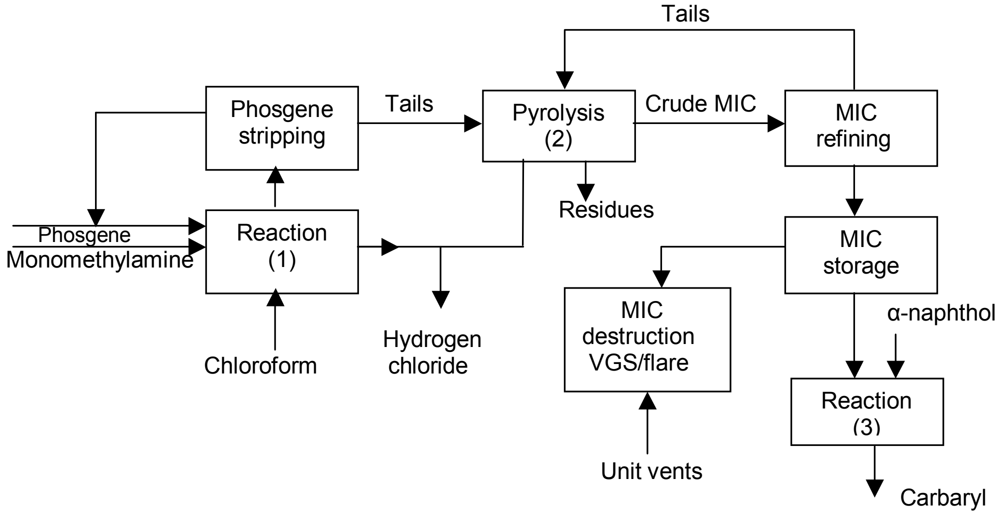
BHOPAL: COULD WE HAVE AVOIDED IT?

Introduction:
Shortly after midnight on December 3, 1984, the worst industrial disaster in the history of mankind took place in the Indian town of Bhopal. The leak of 41 tons of poisonous gas, methyl isocyanate (MIC) from the pesticide plant of Union Carbide have caused deaths of almost 4,000 people and disabled another 3,000. The horrifying events of that night have been extensively described in literature, for instance in “A Killing Wind” by D. Kurzman (McGraw-Hill, 1987) or in “Bhopal – Anatomy of Crisis” by P. Shrivastava (Paul Chapman Publishing, 1992). A brief technical analysis of Bhopal disaster can be found in volume 3 of the book “Loss Prevention in the Process Industries” by F. P. Lees (Butterworth-Heinemann, 1996), available in the DelftChemTech departmental library.

The Bhopal plant opened in 1969. At first, it only formulated carbamate pesticides from concentrates imported from U.S. , but in 1975 the plant was licensed by the Indian government to produce its own carbaryl (trade name"sevin"). Methyl isocyanate (MIC) is a chemical intermediate in the sevin manufacturing process chosen by Union Carbide. For a time, the Bhopal plant depended on MIC imported from Union Carbide's plant in Institute, West Virginia. However, UC added an MIC production unit to the Bhopal plant in 1979. The unit was approved and designed by UC in the United States. The licensed registered capacity of the plant was 5,250 tons in 1983.

In opinion of many experts the tragedy of Bhopal could have been prevented, or at least minimized, by using the principles of Inherently Safer Process Design during the development and design of Union Carbide process. The aim of the present assignment is to analyze the technology used in Bhopal and try to develop a safer alternative, focusing on the reactor design and process intensification issues, as well as other issues related to hazard minimization in the process.

Process description:
The Union Carbide process used in Bhopal produced carbaryl (Sevin), a pesticide, via the so-called methyl isocyanate route, as shown in a simplified scheme below.



The MIC process route of Union Carbide begins with reaction of monomethylamine (MMA) with excess phosgene (used as a lethal gas in World War I and produced in Bhopal on-site from chlorine and carbon monoxide) in the vapour phase to produce methylcarbamoyl chloride (MCC) and hydrogen chloride:

(1) $$\underset{\text{Phosgene}}{COCl_2} + \underset{\substack{\text{Monomethyl-}\\\text{amine}\\\text{(MMA)}}}{CH_3NH_2} \rightarrow \underset{\substack{\text{Methylcarbamoyl}\\\text{chloride}\\\text{(MCC)}}}{CH_3NHCOCl} + \underset{\substack{\text{Hydrogen}\\\text{chloride}}}{HCl} + \text{Heat}$$

Phosgene is preheated to 205^{o}C enters the reactor together with MMA preheated to 240^{0}C. Molar ration between phosgene and MMA is 1.25:1. An excess of phosgene is required to prevent formation of methylamine hydrochloride in a gaseous phase and the excess phosgene has to be separated from the quench solvent. The non-catalytic gas-phase reaction (1) is strongly exothermic, very fast (residence time in the reactor is 1.5 second) and runs at 260^{o}C, at normal pressure. At the reactor outlet methylcarbamoyl chloride (MCC, selectivity 100%) and unreacted phosgene are absorbed and quenched in chloroform (5^{o}C), down to 40^{o}C.

The unreacted phosgene is separated by distillation from the quench liquid and recycled to the reactor. The liquid from the still is fed to the pyrolysis section where MIC is formed. The pyrolysis reaction

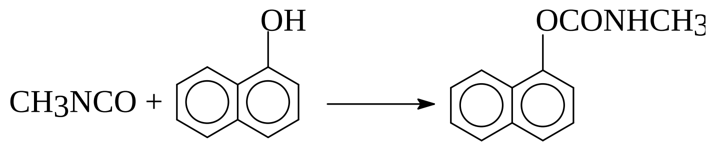
(2) $$\underset{\text{(MCC)}}{CH_3NHCOCl} \xleftrightarrow{\text{Heat}} \underset{\substack{\text{Methyl isocyanate}\\\text{(MIC)}}}{CH_3NCO} + HCl$$

is liquid-phase and reversible. It is endothermic and heat has to be added in order to shift the equilibrium to the MIC-side. The reaction (2) is non-catalytic, however the presence of hydrogen chloride under these conditions catalyzes the side reaction of polymerization of methyl isocyanate and expensive polymerization inhibitors must added to the reaction mixture to avoid this unwanted side reaction. The pyrolysis reaction takes place at temp. 90ºC, pressure 9,5-10 bar, and with residence time of 21 hrs. About 80% of the MMC is decomposed to MIC and HCl. The vapor from pyrolysis reactors is cooled to remove most of the HCl, and condensed to form a mixture of chloroform, MMC, MIC and HCl. That mixture is distilled in a 45-plate column, where about 60% of the methyl isocyanate is recovered as distillate; the remaining 40% is combined with HCl to form MMC and is recycled to pyrolysis section for decomposition. From the bottom of distillation section, chloroform is discharged, evaporated, condensed, and recycled. Heavy ends are discharged for incineration.

The MIC is then run to the storage. ***It is here, in one of the storage tanks, where the highly exothermic hydrolysis of MIC took place in the night of 3 December 1984, leading to Bhopal disaster***.

From the storage tanks MIC is fed to the third reaction section, where it reacts with α-naphthol to form the final product – carbaryl.

The reaction

(3) 

MIC α-naphthol carbaryl (1-naphthyl methylcarbamate)

utilizes anion exchange resin (e.g. Amberlite) catalyst to convert weak base groups to their catalytically active free amine form, while maintaining any strong-base groups in their catalytically inactive salt form. The process is carried out in a continuous flow system. Carbon tetrachloride, CCl_4, is used as a solvent. Generally, the reaction between hydroxy substituted organic compounds and compounds containing isocyanate groups are exothermic in nature and, therefore, some means should be provided to maintain the temperature below the selected upper limit. A typical conditions for the reaction (3) in are given below:

Feed composition, wt%	
1-naphtol	18.0
MIC	7.2
CCl_4	74.8
MIC:1-naphtol mole ratio	1.01
Temperature,ºC, Jacket	83
Reactor Bottom	74
Reactor Middle	93
Reactor Top	88
Product (1-naphtyl methylcarbamate) Yield, %	91.2
Productivity:	
kg Product/ kg resin/ hr	3.2
Product purity:	99.8

Your assignment:

The Bhopal process consists of 3 sections: the MCC synthesis, MCC pyrolysis and the carbaryl synthesis. Each section will be investigated by a different team.

Conduct analysis of the Bhopal plant and develop sustainable alternative(s) of the Union Carbide process assuming the targeted plant capacity as licensed in 1983 (5250 t/yr). The analysis should identify the bottlenecks in the process by applying the generic PI-principles. In the generation of PI-concepts make use of four fundamental approaches of Process Intensification in the spatial, thermodynamic, functional and temporal domains. Consider all scales, from molecular to the scale of processing units. The sustainable alternative(s) should make broad use of process-intensive equipment and methods and should allow to minimize the risk to humans and environment.

<u>Final remark:</u>
Full detailed operational and technical data of the Union Carbide plant in Bhopal are not available to the public. Therefore, in the present assignment data to some parts of the process have been retrieved based on published papers, patent literature and SRI reports on Union Carbide's carbaryl technology. Those data may not reproduce the situation in Bhopal with 100% accuracy. In case of any missing piece(s) of information, the assignees are expected to make reasonable assumptions.