Formaldehyde: history and importance

1. 0INTRODUCTION

Formaldehyde is the first member of the aldehyde family (CH2O) and is the most important aldehyde in the environment. 3 It is a naturally occurring chemical and a by-product of most organisms, including human, industrial and natural processes. Formaldehyde forms from the incomplete combustion of carbon-containing materials; smoke from forest fires, in automobile exhaust, and in tobacco smoke. Atmospheric formaldehyde is formed by the action of sunlight and oxygen on methane and other hydrocarbons. 2 Due to its simple nature, metabolic processes break formaldehyde into carbon dioxide. Formaldehyde does not accumulate in the environment or within plants, animals or people, as it quickly breaks down in the body and the atmosphere. 1 It has a pungent odour and is an irritant and is an irritant to eyes, nose and throat, even at low concentrations. The recommended odour detection limit is between 0. 05 – 1ppm. 3

Formaldehyde is an important industrial chemical and is employed in the manufacture of many industrial products and consumer articles. More than 50 branches of industry now use formaldehyde, mainly in the form of aqueous solutions and formaldehyde-containing resins. In 1995, the demand for formaldehyde in the three major markets – Northern America, Western Europe, Japan – was 4. 1Ã-106 t/a [Chem. Systems Inc.: “ Formaldehyde” (April 1996).].

History of Formaldehyde

Research in the early 1800s by Liebig discovered the chemical composition and nature of various aldehydes excluding formaldehyde due to the ease with which methanol was oxidized to formic acid and further synthesized to carbon dioxide and water. 5

In 1859, Alexandra Mikhailovich Butlerov inadvertently discovered formaldehyde as a result of his proposed synthesis of methylene glycol [CH2 (OH)2]. During his laboratory experiment, Butlerov observed the distinctive odour of the formaldehyde solution while hydrolysing methylene acetate, which decomposed to form formaldehyde and water. 5

He also produced formaldehyde in other forms which led him to publish a detailed report of formaldehyde solution, its gas and polymer. He gave additional evidence of its structure and described the chemical reactions together with the creation of hexamethylenetetramine, [(CH2)6N4] on reacting with ammonia, (NH3).

The main way by which formaldehyde is still being produced till date was discovered by A. W. Hofmann but with other catalysts. In 1868, Hofmann made a successive breakthrough by passing a mixture of methanol and air over a heated platinum spiral. This process is currently industrialised by use of a metal catalyst. Over two decades later, the isolation and purification of formaldehyde was achieved by Friedrich Von Stradonitz (1892). 4

1882 marked two significant improvements in formaldehyde research. Kekule then described the preparation of pure formaldehyde and Tollens discovered a method of regulating the methanol vapour: air ratio, thereby affecting the yield of the reaction. 6

The spiral platinum catalyst was replaced with more efficient copper gauze in 1886 by Leow. Commercial manufacture of formaldehyde was initiated by a German firm, Mercklin and Losekann in 1889 with the first use of silver catalyst patented by Hugo Blank, another German company in 1910. 6

Industrial development continued from 1900 to 1905, when plant sizes, flow rates, yields, and efficiency were increased. In 1905, Badische Anilin&Soda-Fabrik (BASF) started to manufacture formaldehyde by a continuous process employing a crystalline silver catalyst. Formaldehyde output was 30 kg/d in the form of an aqueous 30 wt% solution. The methanol required for the production of formaldehyde was initially obtained from the timber industry by carbonizing wood. The development of the high-pressure synthesis of methanol by BASF in 1925 allowed the production of formaldehyde on a true industrial scale. 6

Importance of Formaldehyde

For several decades, formaldehyde has been used consistently in a wide range of products, ranging from personal hygiene, to medicine, to building products and much more. Many different resins are created from formaldehyde, which are in turn used to create other materials having different properties. Formaldehyde derivatives are used as preservatives in personal hygiene products because they kill bacteria or they are used to make other products more effective in terms of foaming action such as soaps and detergents. Its versatile chemistry and unique properties have created applications for use of formaldehyde in all kinds of every day products such as plastics, carpeting, clothing, resins, glues, medicines, vaccines and the film used in x-rays.

One of the first benefits you derive from formaldehyde chemistry is as a child, when you received your vaccinations for childhood diseases. These include diphtheria, polio and influenza, to name a few. Since it also acts as a preservative, formaldehyde plays a critical role in our medical schools, preserving cadavers used in teaching human anatomy. It has been used for tissue and organ preservation for more than a century and has greatly assisted the advance of biological science. 1

Importance of Green Processes

The concept of Green Chemistry helps reduce or eliminate the use or generation of hazardous substances in the design, manufacture and application of chemical products. This helps in dealing with the ever growing increase to protect the environment and the concept of sustainability.

A lot of emphasis is based on the research and development phase of each chemical or product, to curtail issues affecting human health and environmental pollution. For every chemical or given product, the following guidelines should govern the choice of route: 7

* Choice of feed-stock (costs are relevant of course, but also total resources, energy, waste, etc. in the manufacture of the given feed-stock are important factors)

* Choice of reaction path (minimise energy requirements by use of selective catalysts)

* Choice of catalyst (efficiency, separation from product, recycling of catalyst)

* Down-stream processing/unit operations (minimising the number of stages necessary to obtain the product in the state desired by the customer)

* Minimising not only the amount pollutants, but also the volume of waste streams (effluent/ off-gases and solid waste)

* Recycling of auxiliary, side-, and intermediate products into the process.

This report focuses on physical and chemical properties of formaldehyde (CH2O), its production processes and evolution through time as it tries to conform to some of the principles of green chemistry.

2. 0PROPERTIES OF VARIOUS FORMS OF FORMALDEHYDE

Formaldehyde is more complicated than many simple carbon compounds because it adopts different forms. Formaldehyde is a gas at room temperature, but the gas readily converts to a variety of derivatives. These derivatives generally behave similarly to gaseous formaldehyde and are used in industry. 4

Physical Properties

I. Monomeric formaldehyde: This form of formaldehyde [50-00-0], CH2O is a colorless gas that has a foul, overpowering odour and is an irritant to eyes, nose, throat and skin. Monomeric formaldehyde liquefies at -19°C, and solidifies at -80°C to give a white paste. The liquid and gas phases polymerise readily at low and normal temperatures up to 80°C. Pure formaldehyde gas, on the other hand, does not polymerise between 80 – 100°C and behaves as an ideal gas. Though it is not commercially available in this form, it can be prepared in the laboratory by the Spencer and Wilde method. 6, 3

The molecular formula of gaseous formaldehyde in ambient air is shown below.

II. Trioxane: 1, 3, 5- Trioxane is a stable cyclic trimer of formaldehyde, C3H6O3. It appears as a white solid with a chloroform-like odour but does not cause any form of irritation to living things. The pure form of trioxane melts at 61 – 62°C boils at 11°5C and has a flash point of 45°C. Trioxane is used as a feedstock for some plastics, solid fuel tablet formulas and as a stable source of formaldehyde in laboratories. 8, 3

III. Paraformaldehyde: this is a colourless, granular solid with a pungent and irritating smell. It is prepared by condensation of methylene glycol (HOCH2 OH), and its composition is best expressed by the formula HO- (HCHO) Q-H. Paraformaldehyde melts over a wide temperature range (120-170C), which depends on the degree of polymerization. It has similar uses to formaldehyde; it is commonly used as a source of formaldehyde for disinfecting large areas. 3

IV. Formalin: The primary market for formaldehyde is in aqueous form, Formalin. It is a clear solution with the characteristic odour of formaldehyde. Methanol is normally present, 6-15%, to suppress polymerisation. In aqueous phase, the dominant form of formaldehyde is methylene glycol and polyoxymethlene glycol for concentrated solutions. 3

Chemical Reactions of Formaldehyde

I. Decomposition: In thermal decomposition, formaldehyde is relatively stable. At 150C, formaldehyde undergoes heterogeneous decomposition to form methanol and carbon dioxide. Above 350C, the reaction decomposes to form carbon dioxide hydrogen. Catalysts such as platinum, copper, chromium and aluminum are involved in this decomposition reaction to form methanol, methyl formate, formic acid, carbon dioxide and methane. 6

2HCHO â†’CH3OH+CO

HCHO â†’CO+ H2

II. Polymerisation: At room temperatures and very low pressures, formaldehyde monomer vapours tend to polymerise while at higher temperatures, monomeric HCHO can be maintained readily for several hours without polymerisation at an equilibrium vapour pressure. In the aqueous phase, formaldehyde is oxidized readily by even mild oxidizing agents, such as Ag(NH3)2+, and this property has been exploited in the development of several wet-chemical analytical methods for formaldehyde. 3

III. Reduction and Oxidation Reactions: Formaldehyde is readily reduced to methanol with hydrogen over a nickel catalyst and is oxidized by nitric acid, potassium permanganate, potassium dichromate or oxygen to form formic acid or carbon dioxide, and water. 6, 3

A Cannizzaro reaction occurs when formaldehyde reacts with a strong alkali or heated acid to form methanol and formic acid.

HCHOaq+ NaOH â†’HCO2Na+ H2

H2+ HCHOaq â†’CH3OH

In the presence of aluminum or magnesium methylate, paraformaldehydes react to form methyl formate. This is known as the Tischenko Reaction.

2HCHO polymerâ†’HCO2CH3

IV. Addition Reactions:

V. Condensation Reactions: Formaldehyde is a base product in many synthetic resin product. 9 Formaldehyde condenses with urea, melamine, urethanes, cyanamide, aromatic sulfonamides and amines, and phenols to give a wide range of resins; Amino, Phenolic and Synthetic Resins. 6

3. 0METHODS OF PRODUCING FORMALDEHYDE

Over the years, the starting feedstock for the commercial production of formaldehyde is Methanol. This feedstock has been produced by reacting carbon monoxide and hydrogen, both usually from natural gas or petroleum fractions, under high pressures in the presence of a catalyst. 3

Various patents have been published for the production of formaldehyde but most with no commercial importance. Of all these, the procedure to be discussed is the reduction of carbon monoxide.

3. 1Reduction of Carbon Oxides

This process has been put through a lot of research due to its low cost of raw materials and potential simplicity.

The end-product of this reaction is usually methanol with formaldehyde as an intermediate in the reaction. This process is a two-step reaction; part of the reaction is a simple hydrogenation process and the other, by the Cannizzaro reaction of formaldehyde with itself. The reaction with copper-alumina catalyst forms formaldehyde at temperatures of 282 – 487°C and pressures of 117 – 410 atmospheres. 10

$CO + H_2$ â†” CH_2O

This reduction reaction is highly unfavorable as a means of formaldehyde synthesis due to the following reasons.

* Unreasonable high pressures required to obtain high yields

* To obtain equilibrium at a reasonable rate and avoid hydrogenation, an extremely active and selective catalyst would be required.

3. 2Methanol and Formaldehyde

Formaldehyde is industrially manufactured with methanol through three main processes. 6

1. Partial oxidation and dehydrogenation with air in the presence of silver crystals, steam, and excess methanol at 680 – 720°C (BASF process, 97 – 98 % methanol conversion).

2. Partial oxidation and dehydrogenation with air in the presence of crystalline silver or silver gauze, steam, and excess methanol at 600 – 650°C (77 – 87 % primary conversion of methanol). The conversion is completed by distilling the product and recycling the unreacted methanol

3. Oxidation only with excess air in the presence of a modified iron – molybdenum – vanadium oxide catalyst at 250 – 400°C (98 – 99% methanol conversion).

Process 3, also known as the FORMOX process, a highly exothermic process, occurs at temperatures of about 350°C.

Though this process uses lower temperatures and a cheaper catalyst, the dehydrogenation process is still prevalent in the industry because of its lower operating costs. 2, 3

Production of formaldehyde via conversion of propane, ethylene, propylene, butylene, ethers and butane are not economic therefore have little or no industrial relevance. In addition, the partial hydrogenation of CO and methane oxidation results in lower yields as compared to the former processes. 6

3. 3Development of the Methanol Process

The initial method for the development of formaldehyde was originated from by Hofmann, which is the passing of a mixture of air and methanol over a heated platinum spiral and dissolution of this product to form aqueous formaldehyde, formalin. 10

This process was replaced due to difficulties with explosions in completing the product recovery. Subsequent development involved the replacement of the platinum catalyst with platinised asbestos in a heated tube by Volhard. Further research by Tollens introduced the direct relationship between the methanol-air vapour ratio and the formaldehyde yield; which is still a main principle in today’s industries. 10

Leow refined the two later processes by replacing the platinum catalyst with copper gauze. This initiated the first continuous process for formaldehyde production. The first stage of this process yielded about 15 – 20% formaldehyde, with an additional 30% conversion due to further heating of the reaction gases. 10

Though not aware at the time of the concept of green chemistry, research was carried out covering the preparation of catalysts, reaction times and temperatures, and product absorption during the early years of commercial development of formaldehyde.

This led to technological development for the use of a silver catalyst by O. Blank in 1910. Thorough investigation with the use of this catalyst proved that higher yields were obtainable as to that of the copper catalyst. 10

Large scale manufacturing welcomed improvements in the method for vapourising alcohol, the scrubbing systems and in the control of the heat of reaction. The copper gauze was observed to disintegrate or fuse together with high air-methanol ratios. To tackle this issue, low ratios were introduced to help keep the catalyst active but this resulted in excess methanol distilled from the formaldehyde. 10 The progress made throughout the years has been achieved by the following:

* Efficient catalysts

* Improved methods of control

* Implicit engineering economies

3. 3. 1Silver Catalyst Process

This route is the classic method for the industrial production of formaldehyde. The two main reactions governed by this process are dehydrogenation and partial oxidation. The dehydrogenation of methanol is a highly endothermic, 650°C, and heat of reaction is usually obtained from the burning of the hydrogen enclosed in the flue gas. These processes are usually carried out by reacting methanol and air over a heated stationary catalyst and scrubbing the off gases with water to obtain aqueous formaldehyde. 6

Addition of inert substances, water or nitrogen, aids conversion by using higher methanol concentrations relative to the oxygen supplied without reaching the explosive phase. A few key reactions take place during methanol conversion to formaldehyde. 3

CH3OH â‡„ CH2O+ H2 âˆ†H= +84kJ/mol

H2 +12O2 â†’ H2O âˆ†H= -243kJ/mol

CH3OH+12O2 â†’ CH2O+ H2O âˆ†H= -159kJ/mol

Methyl formate, methane and formic acid are important by products of the above reactions. Below are a few undesirable reactions that must be avoided by proper control of temperature and other factors to obtain high yields.

CH2O â†’ CO+ H2 âˆ†H= +12. 5kJ/mol

CH3OH +32O2 â†’ CO2+ 2H2O âˆ†H= -674kJ/mol

CH2O +O2 â†’ CO2+ H2O âˆ†H= -519kJ/mol

The usual process for the commercial production of formaldehyde is through the incomplete oxidation of the methanol. So far, this has been proven to be the most optimal process because the distilled methanol is recovered and recycled in the process. This results in higher yield, higher conversion and a high atom economy. 6, 10

The BASF Process

This process involves the complete conversion of methanol to formaldehyde (Reaction 1). This process indirectly applied some of the principles of green chemistry. 6, 10

1. Few reaction steps

2. Recycling of materials within the production system to optimise product recovery resulting in a very high atom economy.

3. Environmental awareness with combusted off-gases having no adverse effect on the environment

4. The use of water as a solvent

5. Incorporation of all materials in the process, maximizing final product with extremely low weight percent of by-products formed

6. Optimum surface reaction with arrangement of catalyst

7. Process conditions adjusted to ensure that in retrieving of the final product, the mixture is easily stripped without scare of an explosion.

Incomplete Conversion and Distillative Recovery of Methanol

In this process, methanol is partially oxidised and distilled to recover formaldehyde. This is the most widely used method of production. It should be noted that an economically feasible process is not necessarily a green process. Partial oxidation of methanol has similar characteristics but differ with the following with respect to green chemistry. 6

1. Two-stage reaction

2. Lower reaction temperatures adopted in the first stage to help suppress the formation of unwanted by-products.

3. Heat of reaction generated from cooling the off gases, recycled in the system reducing energy requirements.

4. Larger amount of methanol is recovered in this process with little presence of the b-products

5. Similar off-gases as produced in the BASF process

6. It also has an alternative route that recycles the tail gas from the top of the absorber. This reduces the amount of feedstock, methanol, required in the process. This produces a more concentrated solution and saves up cost for the distillation process and the yield is relatively high (91-92%).

Factors affecting the yield in methanol oxidation processes

* The higher the temperature in a dehydrogenation reaction, the higher methanol is converted in the process system. 10, 6

* Process air controls the desired reaction temperature and the extent to which the endothermic reactions occur. 10, 6

* Besides catalyst temperature, the inert materials added as stated earlier also affect the yield. 10, 6

Some of the advantages of the silver catalyst process are listed below: 11

* Most cost effective means of manufacturing formaldehyde

* Increased formaldehyde yield, methanol conversion and catalyst life

* Reduced silver requirements

* Greater resistance to plant upsets and poisoning

* Improved formaldehyde product quality

* Technology demonstrated worldwide

3. 2. 2FORMOX Process

The FORMOX process is the direct oxidation of methanol with metal oxide catalysts (iron, molybdenum or vanadium oxide) to produce formaldehyde. Normally, the catalyst used for this process is a mixture of molybdenum and iron in a ratio of 1. 5: 2. 0. Due to the development of this catalyst, a few advantages have been attributed to this process over the silver catalyst processes. This will be discussed in the later part of this report. The FORMOX process can be characterised as follows:

1. Two stage oxidation reaction in gaseous state. This prevents waste that would have been generated by use of a solvent. 6

2. Reaction carried out under atmospheric pressure and at lower temperatures (270 – 400°C), results in an almost complete reaction. 6

3. Careful adjustments of process conditions help prevent the formation of unwanted by-products. These side reactions occur at temperatures exceeding 470°C. 6

4. The conversion rate for this process is relatively high with a high optimization process.

5. One short-coming of this process is with the tail gas that has lots of impurities and flammable components. The alternative route used instead of combustion is in the addition of fuel to the system which burns the tail gas as a supplement for energy in other start-up processes. 6

In summary, the green advantages of the three commercial processes can be summarised as follows: 7

1. Few unit operations

2. Waste is minimised by a highly selective reaction

3. Use of catalysts to optimise process reactions

4. Water used as the only solvent

5. Reaction carried out at atmospheric pressure

6. Gas-phase reaction for the FORMOX process means that catalyst does not have to be recovered from solution

7. Recovery of energy from exothermic reactions to help reduce environmental and economic impacts.

8. High conversion rates achieved through efficient use of equipment, energy and material

9. Use of air as oxidant instead of chemical oxidising agents reducing the toxicity and by-products formed.

3. 3Development of New Processes

Various research works have been carried out for developing new formaldehyde synthesis. Unfortunately, there has been no existence of commercial units of the techniques discussed below:

1. Partial oxidation of methane to produce formaldehyde which has an advantage of reducing raw material costs of producing the methanol from methane. The inducement for such a process is reduction of raw material costs by avoiding the capital and expense of producing the methanol from methane. 12

2. Production of anhydrous or highly concentrated formaldehyde solutions via dehydrogenation of methanol. In some instances, energy costs are reduced as well as effluent generation, and losses, providing a more favorable condition. 12

3. Formaldehyde production from methylal (produced from methanol and formaldehyde) which is in two phases. Firstly, methylal oxidation which yields up to 70% of the concentrated formaldehyde product as compared to methanol oxidation with 55%. After this, methylal is produced by reacting formaldehyde obtained in aqueous recycle streams from other units with methanol as opposed to recovery by other more costly means, e. g. distillation and evaporation. Development of this process is complete. 12

Further research is still being carried out in the use of bacteria to produce formaldehyde. This will not be discussed in this report.

4. 0ENVIRONMENTAL ISSUES ASSOCIATED WITH FORMALDEHYDE

REFERENCES

1. Formaldehyde Council, I. (2007, November). Formaldehyde: Facts and Background Information. Retrieved May 10, 2010, from http://www. formaldehyde. org/_base/pdf/fact_sheets/11_01_07-FormadehydeFactsandBackgroundInformation. pdf

2. Daily, C. (2004, April 01). The Chemistry Encyclopedia. Retrieved May 07, 2010, from http://www. chemistrydaily. com/chemistry/Formaldehyde

3. Council, N. R. (1981). Formaldehyde and other Aldehydes. Washington, D. C, USA.

4. Wikimedia. (2010, May 02). Formaldehyde. Retrieved May 07, 2010, from http://en. wikipedia. org/wiki/Formaldehyde

5. Harrison, K. (1998, July). Formaldehyde. Retrieved May 07, 2010, from 3d Chem: http://www. 3dchem. com/molecules. asp? ID= 101

6. Wiley, I. (2006). Formaldehyde. Retrieved May 07, 2010, from Ullman’s Encyclopedia of IndustrialChemistry: http://mrw. interscience. wiley. com. resourceproxy. manchester. ac. uk/emrw/9783527306732/ueic/article/a11_619/current/pdf

7. Chuck, R. (n. d.). A Catalytic Green Process for the Production of Niacin. Retrieved May 07, 2010, from Lonza Group: http://www. lonza. com/group/en/company/news/publications_of_lonza.-ParSys-0002-ParSysdownloadlist-0026-DownloadFile. pdf/25_A%20Catalytic%20Green%20Process%20for%20the%20Production%20of%20Niacin. pdf

8. Wikimedia. (2010, April 15). Trioxane. Retrieved May 07, 2010, from http://en. wikipedia. org/wiki/1, 3, 5-Trioxane

9. Smith, S. (2010). What is formaldehyde resin? Retrieved May 07, 2010, from Wisegeek: http://www. wisegeek. com/what-is-formaldehyde-resin. htm

10. Walker, J. F. (1967). Formaldehyde. Wilmington, Delaware: Reinhold Publishing Corporation.

11. GFRT. (Updated 2010). Silver Catalysts. Retrieved May 07, 2010, from Global Formaldehyde and Resin Technologies: http://www. globalformaldehyde. com/silver. htm

12. Kirk-Othmer Encyclopedia of Chemical Technology. Formaldehyde, Vol12. John Wiley & Sons.