

CHEMICAL PROCESS INDUSTRY [CE1705]  
MINI-PROJECT REPORT

# FORMALDEHYDE

## OVERVIEW

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## **EXECUTIVE SUMMARY**

Formaldehyde has been categorized as toxic, suspected carcinogen, teratogen and mutagen compound and widely applied in various industries. Millions ton of formaldehyde is yearly released into environments. Therefore, having enough information about this compound to control its environmental problems is necessary. Although, many articles about formaldehyde production, properties, removal and applications have been published, but access to all of this information in different data bases is not easy and a comprehensive review paper in this area is yet to be published. The aim of this paper is collecting information about toxicology, resources, production and applications of formaldehyde. Formaldehyde can be emitted into atmosphere from natural sources such as atmospheric reactions, fire forest, and biological metabolism. Anthropogenic sources are other important sources of formaldehyde emission. Collecting enough knowledge about common pollutants such as formaldehyde that have been frequently released into environment can make significant contributions to improving environmental quality.

## **HISTORY**

Formaldehyde's public image has always been associated with the funeral homes, doctor offices and biology classes as an embalming fluid, a disinfectant and a preservative. In 1859, Russian scientist Alexander Mikhailovich Butlerov discovered Formaldehyde, accidentally as he investigated the structure of organic compounds. Nine years later, German scientist August Wilhelm Hofmann found a reliable way to make it. Hofmann Passed a mixture of methanol and air over a heated platinum spiral and then identified formaldehyde as the product. This method led to the major way in which the Formaldehyde is manufactured today, the oxidation of methanol with air using a metal catalyst primarily of silver or molybdenum oxide. In 1905, Dr. Leo Baekeland in Yonkers, New York made a major breakthrough in the technology of polymer later named Bakelite after him. The ingredients were Phenol and Formaldehyde, by the 1920's the growth of this resin strained wood alcohol (Methanol) producing capacity, but the revolutionary development of methane reforming route to methanol relieved the situation. Despite the radical shift in methanol technology, the process for formaldehyde based on methanol feedstock has remained virtually unchanged even to today, despite volume growth making it one of the top 25 commodity chemicals.

## **INTRODUCTION**

The development of technologies has made this world a better place to live in than before. But the use of new technologies has also damaged the environment by producing pollutants like waste gases. Formaldehyde vapor is a waste gas that is released in the air worldwide from chipboard production, burning processes, synthesis of resin production and chemical factories. Some researchers have estimated a global emission of thirty-two million tons of formaldehyde in 2006 and it keeps increasing year by year [1]. Michailowitsch Butlerow discovered formaldehyde in 1855. Then, a German chemist "August Wilhelm von Hofmann" achieved technical synthesis of formaldehyde using dehydration of methanol in 1867. The versatility

that makes formaldehyde suitable for use in wide number of factories applications was soon recognized, and it was soon indexed by CAS (Chemical Abstracts Service). During the first 30 years (1900 to 1930), formaldehyde was one of the basic parts of adhesives for wood and wood composite. Germany and Britain were the first countries that had made some factories for producing of commercial particle boards since 1939. Use of particle boards has been becoming an attractive building material for the manufacture of furniture and partition construction for housing since 1950. Adverse health effects due to release of formaldehyde in houses, such as irritation of the eyes, was reported in the 1960s. Formaldehyde emission from urea-formaldehyde resin (UFR) was recognized by researchers as the cause of adverse health effects. As a result, in some countries such as Germany, Denmark, and the United States of America a Criteria was proposed to limit human exposure to formaldehyde in houses during 1981 to 1985. In 1985, first regulations were issued in the USA. In USA and Germany, a lot of actual scale tests were performed on the study of formaldehyde emissions. For evaluation of formaldehyde in this study, chamber method was used. The method of chamber is exceedingly accurate, but this method is expensive and too time-consuming. For these reasons, there was urgency for simple and reliable laboratory test method for measuring of formaldehyde. Discussion about the dangers of formaldehyde dangers started in 1980 by reports about the carcinogenicity of formaldehyde in rats and mice. Consequences of studies on animals and humans about formaldehyde exposure triggered an avalanche of scientific studies. Although the authors had a good electronic databases and a lot of review papers, but reviewing all articles in the medical and technical journals was difficult. The review confirmed formaldehyde is one of the best-known pollutants of air. Over the years, by finding new environmental friendly components, formaldehyde release from produced materials such as particle board has been decreasing. On the other hand, concentration of formaldehyde emitted in outdoor air is increasing, especially in the urban centres or industrial areas. For this reason, formaldehyde has slipped out of the primary focus of air pollution studies. However, discussions about formaldehyde were taken up again in 2004, when it was recognized as a matter carcinogen. As a result, new air guidelines have been proposed and a prioritized listing of chemicals matters and exposures that because concern has been stated. In this prioritized ranking formaldehyde is a compound of concern in the air and that is why knowledge about formaldehyde is very important. The aim of this study is to collect all characteristics of formaldehyde to have a better strategy to control this pollutant.

## **PHYSICAL AND CHEMICAL PROPERTIES**

### **PHYSICAL PROPERTIES**

#### **Formaldehyde**

Formaldehyde is soluble in water and some other chemical solutions. Rapid absorption of formaldehyde in the respiratory and gastrointestinal systems is because of its high solubility in water. Formaldehyde is generally known as formalin. Formalin is 37% formaldehyde solution in water. For preventing polymerization of formaldehyde, it is mixed with ten percent of methanol as a stabilizer. In the table 1 the characteristics of formaldehyde are shown.

## Formaldehyde monomer

Pure anhydrous formaldehyde is a colourless gas at ordinary temperature and at a molecular weight of 30.26 is slightly heavier than air. It condenses on cooling to  $-19^{\circ}\text{C}$  and freezes to a crystalline solid at  $-118^{\circ}\text{C}$ . The gas is characterized by a pungent odor and is judged moderately irritating to the eyes, nose and throat by 20% of the population exposed to concentrations in the 1.5 to 3.0 ppm range. Dry formaldehyde gas is stable and shows no polymerization tendency at temperature as high as  $100^{\circ}\text{C}$ . However, small amounts of water or other impurities can cause rapid polymerization to poly(oxymethylenes). Anhydrous formaldehyde gas is readily soluble in polar solvents such as water, methanol, and n-propanol. It is only moderately soluble in nonpolar solvents such as ethyl ether, chloroform, and toluene. In water and methanol, its heat of solution is approximately 15kcal/g-mol. A summary of physical properties of monomeric formaldehyde is given in Table 1.1

## Formaldehyde solutions

Formaldehyde is produced and distributed as a water solution, the “standard” strength being 37 wt%, this being a typical concentration and also the basis for making production comparisons. Representative commercially available solutions are shown in Table 1.2

**Table 1.1 Properties of Monomeric Formaldehyde**

Property	Value
Density, g/cm <sup>3</sup>	
at $-80^{\circ}\text{C}$	0.9151
at $-20^{\circ}\text{C}$	0.8153
Boiling point at 101.3 kPa $^{\circ}\text{C}$	-19
Melting point, $^{\circ}\text{C}$	-118
Vapor pressure, Antoine constants, Pa	
A	9.21876
B	959.43
C	243.392
Heat of vaporization, $\Delta H_v$ at $19^{\circ}\text{C}$ , kJ/mol	23.3
Heat of formation, $\Delta H_f$ at $25^{\circ}\text{C}$ , kJ/mol	-115.9
Std free energy, $\Delta G_f$ at $25^{\circ}\text{C}$ , kJ/mol	-109.9
Heat capacity, $C_p$ , J/mol.K	35.4
Entropy, $S^{\circ}$ , J/(mol.k)	218.8
Heat of combustion, kJ/mol	563.5
Heat of solution at $23^{\circ}\text{C}$ kJ/mol	
in water	62
in methanol	62.8

in 1-propanol	59.5
in 1-butanol	62.4
Critical constants	
Temperature, °C	137.2-141.2
Pressure, MPa	6.784-6.637
Flammability in air	
Lower/upper limits, mol	7.0/73
Ignition temperature, °C	430

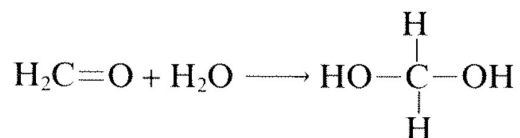
Varying amounts of methanol are included in the solutions as stabilizers and because of the expenses of removal of methanol for uses where it is not harmful. Formaldehyde is highly soluble in water, but in the liquid it reacts readily with water to form the hydrate, methylene glycol, which itself then tends to polymerize to poly(oxymethylene glycols). Also, some hemiformals and a small amount of formic acid are produced. At chemical equilibrium the amount of unhydrated formaldehyde is small, approximately 0.1% at 60°C. In methanol-formaldehyde-water solutions, increasing the concentration of either methanol or formaldehyde reduces the volatility of the other. The flash point varies with composition, decreasing from 83 to 60°C as the formaldehyde and methanol concentration increase. Formaldehyde solutions exist as a mixture of oligomers,  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ . Methanol stabilizes aqueous formaldehyde solutions by decreasing the average value of  $n$ . Hence methanolic solutions can be stored at relatively low temperatures without precipitation of polymer.

**Table 1.2 Typical Analyses and Physical properties of Formaldehyde solutions**

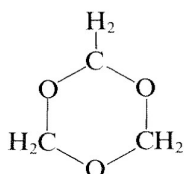
	USP Grades			Low-Methanol Grades	
Formaldehyde (wt%)	37.1	37.1	37.1	44.1	50.3
Methanol (wt%)	7.0	11.0	0.9-1.3	0.9-1.3	0.9-1.3
Acidity as formic (wt%)	0.012	0.012	0.012	0.02	0.018
Iron as Fe (ppm)	0.3	0.3	0.3	0.3	0.3
Turbidity, Hellige	1.5	1.5	2	2	2
Color, APHA	5	5	5	5	5
Density ( $\text{g}/\text{cm}^3$ ), 18°C	1.10	1.09	1.11	1.12	1.13
Boiling point (°C)	97.2	96.7	99.0	99.1	99.5
Viscosity (cP), 25°C	2.5	2.6	2.0	1.7	1.6
Specific heat ( $\text{cal}/\text{g}^\circ\text{C}$ )	0.8	0.8	0.8	0.7	0.7
Flash point (°C)	69	60	83	80	79

## CHEMICAL ACTIVITY/REACTIONS

Formaldehyde is noted for its reactivity and its versatility as a chemical intermediate. It is used in the form of anhydrous monomer solutions, polymers, and derivatives. Anhydrous, monomeric formaldehyde is not, available commercially. The pure, dry gas is relatively stable at 80-100°C but, slowly polymerizes at lower temperatures. Traces of polar impurities such as acids, alkalies, and water greatly accelerate the polymerization. Formaldehyde in water solution hydrates to methylene glycol;



Which in turns polymerizes to poly(methylene glycols),  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ , also called polyoxymethylenes. From these polymers a specific product, paraformaldehyde (or “parafrom”), is obtained commercially. Paraformaldehyde is the name given to polyoxymethanlenes with  $n$  values from 8 to 100. It is produced by the vacuum distillation of concentrated formaldehyde solutions, and is available commercially in powder, granular, or flakes forms. It has the characteristic pungent odor of formaldehyde, and melts in the range of 120 to 170°C. It is flammable, with a flash point of about 93°C. A typical formaldehyde solution may be obtained by dissolving paraformaldehyde in water. Paraformaldehyde may be heated together with a strong acid to produce trioxane, the cyclic trimer of formaldehyde.



This is a colourless crystalline material, melting at 62-64°C, boiling without decomposition at 115°C, and having a flash point of 45°C. Concentrations of trioxane between 3.6 and 28.7 vol% in air are explosive. Formaldehyde may be reduced to methanol over a number of metal and metal oxide catalysts. It may be condensed with itself in an aldol-type reaction to yield lower hydroxyl aldehydes, hydroxyl ketones, and other hydroxyl compounds. Nowadays, factories producing formaldehyde use catalytic oxidation of methanol and methane. At room temperature, formaldehyde gas is flammable, extremely reactive, and colourless. Formaldehyde has a typical electrophile molecule because of its dipolar resonance structure. In the following Figure 1, the formaldehyde structure is shown.

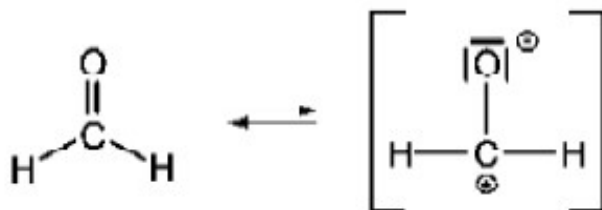
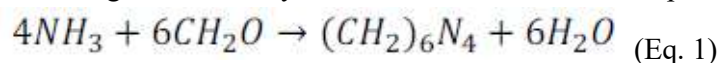


Figure 1: Formaldehyde molecule structure



32,000,000 tons of formaldehyde was released into the atmosphere in 2006, of which 56% was released by Germany, the United States, and China. Nearly 65% of produced formaldehyde is used to synthesize resins [1]. One form of formaldehyde is paraformaldehyde that describes a polymeric structure with 8 to 100 monomers per molecule. The formaldehyde in the form of C<sub>3</sub>H<sub>6</sub>O<sub>3</sub> is named 1,3,5-trioxane. Tang et al. (2006) reported the most important reactions apart from polymerization are as follows [1]:

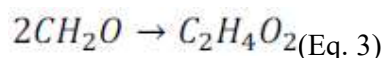
Following is formaldehyde reaction with ammonia and producing hexamethylenetetramine:



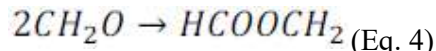
1- Reaction of cannizzaro:



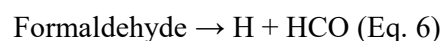
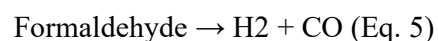
2- Reaction of aldol:



3- Reaction of tischenko:



According to table 1, the formaldehyde constant of Henry's law is  $2.5 \times 10^3 \text{ M atm}^{-1}$  at 24.85 degrees Celsius [5]. Although some scientists and organizations believe that octanol/water partition coefficient (Kow) is equal -0.83, some others such as world health organization (WHO) believe that it is equal -1 [2]. The reaction rate constant with the OH- radical is named KOH and it is for formaldehyde equal  $9.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 24.85 degrees Celsius [4]. With these formaldehyde characteristics and estimate an OH concentration of 10 million molecules per cm<sup>3</sup> are present in the free air. The life time of formaldehyde in the atmosphere is 31 hours. Spectrum among of 260 nm to 360 nm can be absorbed by formaldehyde vapor [7]. The lifetimes against the photolytic processes with two below reactions were calculated for the latitude of 50 degrees Celsius, equals 6.9 and 2.1 h, respectively.



Formaldehyde lifetimes in the air has been calculated with respect to photolysis reaction, reaction with the hydroxyl radical, reaction with the nitrate radical, and reaction with Ozone equal 4 hours, 1.2 days, 80 days and more than 4.5 years, respectively [4]. Braslavsky and Heicklen have performed a study on the reaction of ozone with formaldehyde vapor and found some similar results [8].

## **TOXOCOLGY**

Formaldehyde is soluble in water and this is reason for its rapid absorption in respiratory and gastrointestinal systems of humans and animals. Formaldehyde can be changed to Formate and after that carbon dioxide by oxidation of formaldehyde in human body metabolisms. The biological half-life of formaldehyde in human and animal bodies is exceedingly short at about

60 seconds [9]. Also nucleophilic biogenic compounds in the body can be destroyed by reacting with formaldehyde [10]. Enzyme alcohol dehydrogenase is produced by organisms. It is the cause of formaldehyde produced in small amounts from methanol [11, 12] which is a human metabolite [13, 14]. According to Health Canada's report, mucosa of the upper respiratory tract and irritation of the eyes are some major effects of acute exposure to formaldehyde [15]. RD50 is identified as exposure concentration producing a 50% respiratory rate decrease as an indication of respiratory tract irritation. According to Kuwabara's report, for an exposure time of 5 to 10 minutes, the RD50 values of male mice are 3.1 to 5.3 ppm [16]. Also the lowest observable adverse effect levels (LOAEL) for human sensory irritation range from 0.4 ppm (rhinitis) to 3 ppm (eye, nasal, and throat irritation). Some studies on formaldehyde effects and sensory irritation in humans showed that eye irritation is the most sensitive parameter. A no observed effect level of 0.5 ppm was recognized in the case of constant exposure [17]. Different scientists have identified various threshold values for the odor perception of formaldehyde. According to Devos et al. report, standardized human olfactory threshold of formaldehyde is 1.07 mg/m<sup>3</sup> [18]. Another odor unit is named absolute odor thresholds that is defined as the concentration of compound at which 50% of the panel detects the odor. The WHO has estimated absolute odor thresholds of formaldehyde among 0.06 to 0.22 mg/m<sup>3</sup> (WHO, 1989). In some reports, researchers could have recognized very low odor thresholds of between 0.03 to 0.035 mg/m<sup>3</sup> [10, 19]. European Union, USA, and the International Agency for Research on Cancer classified Formaldehyde as a suspected carcinogen [20]. This decision is based on some evidences regarding the relationship between nasopharyngeal cancer and leukemia related to the exposure to formaldehyde in respiratory air.

## MANUFACTURING

In a lot of industrial processes formaldehyde is used as chemical feedstock. It is used as a biocide, disinfectant, and preservative as applications of formaldehyde. One of the main components in thermosetting adhesives is formaldehyde. Aminoplasts or adhesives that make base urea-formaldehyde are generally used in the wood-based industries due to their low price. By combining urea and formaldehyde (Mannich reaction) monomethylolurea, trimethylolurea and, dimethylolurea will be produced. This reaction is shown in figures 2 and 3. Urea-formaldehyde adhesives are not resistant against water. Urea-formaldehyde adhesives in presence of water will be hydrolyzed and as a consequence, formaldehyde will be released [2].

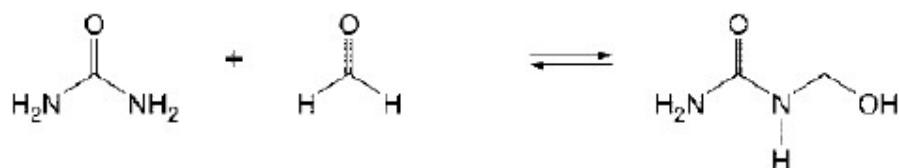


Figure 2: combining of urea and formaldehyde (Mannich reaction)

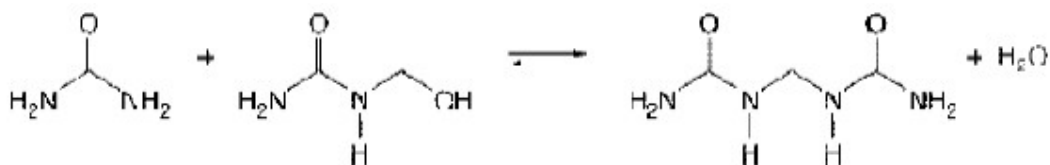


Figure 3: combining of urea and formaldehyde (Mannich reaction)

Adhesive base on Melamine-urea-formaldehyde (MUF) are exceedingly similar to UF adhesives. Industrials produce MUF adhesives using mix UF and melamine-formaldehyde (MF). Figure 4 shows the first step of the melamine-formaldehyde reaction. In all the above explained reactions, formaldehyde vapor can be released into the air [2].

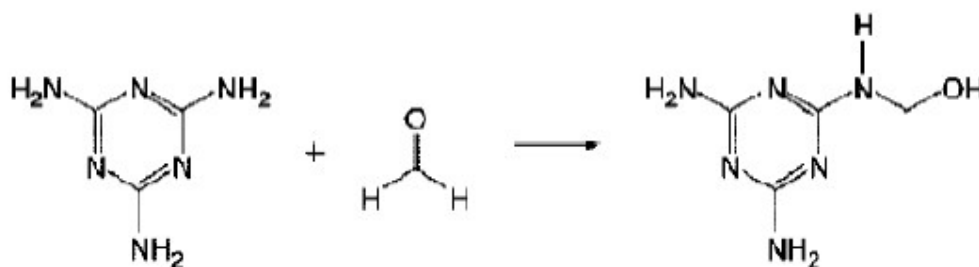


Figure 4: the first step of the melamine-formaldehyde reaction

A category of adhesives is Phenoplasts adhesives that called Phenol-formaldehyde adhesives. To produce of Phenol-formaldehyde, methylol phenol are produced according to the figure 5. The result of this reaction is one of the most stable and water-resistant adhesives that have a good adherence to some materials like wood. Bakelite is a kind of plastic base on Phenol-formaldehyde resins that was used in the past as casings for telephones, radios, etc [2].

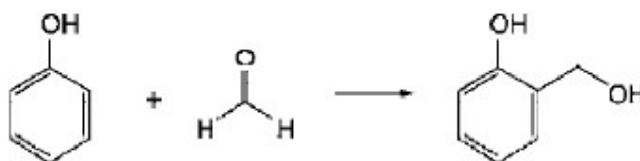


Figure 5: Methylol phenol reaction

Melamine-urea-phenol-formaldehyde (MUPF) adhesives were developed to produce moisture-proof wood. Production of MUPFs adhesives is similar to MUF adhesives. Table 2 provides an overview of formaldehyde applications.

Table 2: Overview of formaldehyde applications

Formaldehyde base production	Urea formaldehyde resins	Particleboard, Fiberboard, Plywood, Paper treatment, Textile treatment, Molding compounds, Surface coatings, Foam
	Phenolic resins	Wood adhesives, Insulation, Foundry
	Melamine resins	Surface, Molding compounds, Laminates, Wood adhesives
	Hexamethylenetetramine	Phenolic thermosetting, Curing agents, Explosives
	Trimethylolpropane	Urethanes, Lubricants, Alkyd resins, Multifunctional acrylates
	1, 4-Butanediol	Tbutyroalacetone, ethahydrofuran, polybutylene terephthalate
	Polyacetal resins	Auto applications, Fuel components
	Pentaerythritol	Alkyd resins, Synthetic lubricants, Tall oil esters, Foundry resins, Explosives
	Urea formaldehyde concentrates	Controlled released fertilizers

A number of authors such as Godish and Pluschke in their reports, have described some formaldehyde applications in the past and present [21, 22]. A list of these applications is given as: Oriented-strand board (OSB), Particle board, flooring materials, high-density fiber board (HDF), medium density fibre board (MDF), plywood, cork products, Insulation materials made of UF foam, mineral wool, coating materials, glass wool, paper products, paints, lacquers containing formaldehyde as preservative, textiles, cleaning, photo processing chemicals, caring products, disinfectants, preservatives, cosmetics, etc.

### **3.1. Outdoor formaldehyde sources**

#### **3.1.1. Formaldehyde as a Natural Compound**

Some synthetic and natural formaldehyde sources are known [23]. Formaldehyde is a biogenic compound. During physiological activities of some plants formaldehyde is released into the atmosphere [24]. A study was conducted by Müller et al. the results of this study showed that formaldehyde is produced by coniferous trees [25]. Similar study in Portugal showed that formaldehyde was produced by degradation of isoprene in a eucalyptus forests [26]. Harder (1927) reported that formaldehyde has the ability for lignin decomposing. Formaldehyde was detected within a remote forest in the Amazon too [27]. Other researchers have been able to detect formaldehyde within or above forests [28, 29]. A report about formaldehyde emission has shown that it can be released by solid wood [30]. Although some researchers believe that formaldehyde can be produced by bio-reaction of OH and NO, some others such as Carter and Atkinson believe that formaldehyde can be produced by methanol oxidation [31, 32]. Other scientists proposed some possible mechanisms for formaldehyde production by plants like reactions of oxidative demethylation, dissociation of 5,10- methylenetetrahydrofolate or decarboxylation of glyoxylate [33]. Although a number of studies was conducted about natural source of formaldehyde, unfortunately exact mechanisms of formaldehyde within plants still remains unclear. Marine environments are another natural formaldehyde source [34].

#### **3.1.2. Atmospheric Reactions**

Biogenic resources emit a lot of organic matters into the atmosphere. Isoprene, sesquiterpenes, monoterpenes, and a number of oxygenated compounds are produced by biogenic resources [4]. These kinds of organic materials react with nitrate, hydroxyl, and ozone radicals. Results of these reactions can play an important role in chemistry of atmosphere (Figure 2-14).

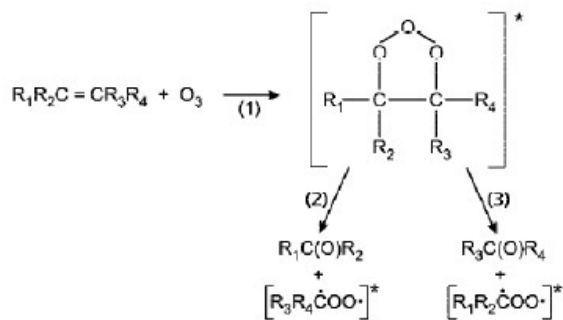


Figure 6: Reaction between alkene and ozone, to produce carbonyl compounds (Finlayson, 2000, Criegee, 1975)

"The gas-phase reaction of ozone with unsaturated hydrocarbons is known to produce aldehydes, ketones, and acids as main components" [2]. Formaldehyde has been identified in a number of reaction between alkenes and ozone [35]. Oxidation reaction of some hydrocarbons in the gas phase have been studied by Grosjean et al. the results of this study show that formaldehyde was formed after completing reaction between ozone and cyclohexane [36]. Formaldehyde production from reaction between ozone and carvone, carveol, citral, and geraniol has been proven[37]. A study has been performed using NMR spectroscopy on the by-products of ozone and terpenes reaction by Griesbaum et al. (1998). In this study formaldehyde has been identified as one of by-products of reaction between ozone and terpenes in the gas-phase [38]. Due to direct release formaldehyde or photochemical reactions in the atmosphere, high concentration of formaldehyde has been found in the megacities air. High relationship between concentration of ozone and formaldehyde in the air, has been observed. In an episode of ozone in the China (Beijing), high concentration of formaldehyde has been detected (36  $\mu\text{gr}/\text{m}^3$ ) in the air [39]. Reaction between methane and hydroxyl radical has a low rate constant. For this reason, formation of formaldehyde from reaction between methane and hydroxyl radical is only important in remote areas.

#### **3.1.4. Formaldehyde Release into the Atmosphere**

According to the world health organization (WHO), formaldehyde release is accrued in industries during all stages of production, use, storage, disposal, or transportation of products with residual formaldehyde. Releasing of formaldehyde has been detected from various industries such as: wood processing factories, chemical factories, coal processing, pulp and paper mills, forestry product plants, tire and rubber plants, textile factories, automotive manufacturing plants, and the metal products industry. According to a report, 70% of formaldehyde emission in Canada is related, because of vehicles traffic aircraft (11%), shipping (7%), the formaldehyde processing industry (10%), and power plants and waste incineration (1%). Determination of global formaldehyde emission is difficult. According to the WHO report, 8960 t/a of formaldehyde was released into the atmosphere by USA in 1992 [2].

#### **3.2. Indoor Sources**

The number of articles on indoor pollution with formaldehyde is more as compared to outdoor. This high number of articles is because of the various resources of formaldehyde and also low air exchange rates in the indoor environment [2]. A relation between wood based products and formaldehyde emission was recognized by scientists during 1960 to 1970. Particle board, could release high concentration of formaldehyde into the homes and offices because of reversibility of reaction between urea and formaldehyde. These reactions are elaborated in equations 1 and 2. Formaldehyde emission from particle boards decrease within time [46]. Throughout the world, due to stricter government regulation emission of formaldehyde from wood base materials was decreased after 1970. Use of environmental friendly adhesives instead of urea-formaldehyde resins also helped in decrease of formaldehyde emission.

### **3.3. Measuring methods of formaldehyde**

A lot of studies can be found about measurement of formaldehyde. Formaldehyde measurement methods are divided into the following three categories: (1) In-Situ Methods; (2) Derivatization Methods; and (3) using of Sensors.

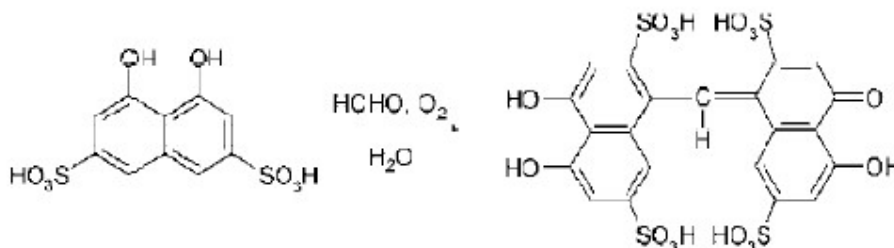
#### **3.3.1. In-Site methods**

Spectroscopic techniques are common methods to measure formaldehyde in outdoor environments. following methods were described to measure formaldehyde in outdoor environments [2]: Differential optical absorption spectroscopy (DOAS), Fourier transform infrared absorption (FTIR), Laser induced fluorescence spectroscopy (LIFS), Infrared diode laser spectroscopy (IDLS), Photoacoustic spectroscopy (PAS), Proton transfer-reaction mass spectrometry (PTR-MS), Selected ion flow tube mass spectrometry (SIFT-MS) and Tunable diode laser spectroscopy (TDLS). Unfortunately In-suit techniques take a long time to performed. For this reason they are not suitable for routine applications. To detect formaldehyde in concentration less than 100 part per billion (ppb) a combination with phot acoustics, FTIR, and diode lasers was developed[47]. Although some scientists believe PTR-MS can be used to determine formaldehyde concentration in outdoor environments, other onesuch as Gouw and Warneke (2007) believe detection of formaldehyde by this method faces problems [48].

#### **3.3.2. Derivatization methods**

Both of the batch and continues sampling methods are useable to take samples of air polluted with formaldehyde. Sometimes formaldehyde is adsorbed on the absorber and after that, adsorbed formaldehyde is extracted by solvent to measure. Extracted formaldehyde can be analyzed by spectrophotometrically or other methods such as gas chromatography (GC). Except GC other methods are not specific for formaldehyde. Several review article can be found about formaldehyde measurement methods [49]. In all of these articles Derivatization methods has been described. The most important of Derivatization methods are:(a) Chromotropic acid method, (b) Acetyl acetone method and (c) 2,4-Dinitrophenylhydrazine (DNPH)method. Some titrimetric methods such as Pararosaniline method has been described in article reviews. A magenta dye will appear by reaction between formaldehyde and Pararosaniline in presence of sodium sulfite. The final solution has a strong absorbance at 570 nm [50, 51]. Under pH more than one other aldehyde can interfere in this reaction, but in pH of less than 1 this reaction is specific only for formaldehyde. Hg(II) can be also used to prevent of SO<sub>2</sub> interfere. In the past Pararosaniline method was used frequently but today we have better methods for formaldehyde measurement.3-methyl-2-benzothiazolinonehydrazone called MBTH is the name of method to measure aliphaticaldehydes. Azide is result of reaction between MBTH and aldehydes. The color of final solution is blue. This solution has a strong absorbance in 628 nm. Pararosaniline method is more sensitive than MBTH method. Other aldehydes can participate in this reaction but the reaction rate is generally lower.

Toda et al. described a method to detect formaldehyde online [52]. 4-amino-3-hydrazino-5-mercapto-4H-1,2,4-triazole (AHMT) can react with aldehydes in high pH. The result of this reaction is detectable using wavelength of 550 nm. Formaldehyde can react with chromotropic acid in present of concentrated sulfuric acid. The result of this reaction is a red-violet hydroxydiphenylmethane. This reaction is shown in Figure 7.



## MANUFACTURING

Currently, the only production technologies for formaldehyde of commercial significance are based on the partial oxidation and dehydrogenation of methanol using silver catalyst, or partial oxidation of methanol using metal oxide-based catalyst.

**Development of New Processes.** There has been significant research activity to develop new processes for producing formaldehyde. Even though this work has been extensive, no commercial units are known to exist based on the technologies discussed in the following. One possible route is to make formaldehyde directly from methane by partial oxidation. This process has been extensively studied. The incentive for such a process is reduction of raw material costs by avoiding the capital and expense of producing the methanol from methane. Another possible route for producing formaldehyde is by dehydrogenation of methanol which would produce anhydrous or highly concentrated formaldehyde solutions. For some formaldehyde users, minimization of the water in the feed reduces energy costs, effluent generation, and losses while providing more desirable reaction conditions.

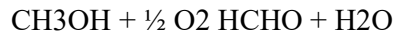
A third possible route is to produce formaldehyde from methylal that is produced from methanol and formaldehyde. The incentive for such a process is twofold. First, a higher concentrated formaldehyde product of 70% could be made by methylal oxidation as opposed to methanol oxidation, which makes a 55% product. This higher concentration is desirable for some formaldehyde users. Secondly, formaldehyde in aqueous recycle streams from other units could be recovered by reacting with methanol to produce methylal as opposed to recovery by other costlier means, eg, distillation and evaporation. Development of this processes is complete.

## **PROBABLE QUANTITATIVE REQUIREMENT**

Basis: 100 kmols of methanol in fresh feed per hour

Molecular weight of methanol = 32 kg/kmole

Weight of methanol in feed = 3200 kg

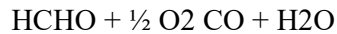


Assume methanol conversion is 97 %.

Hence methanol reacted = 97 kmols

= 3104 kg

Assume that 1% of methanol reacts to form formic acid.



Actual O<sub>2</sub> required = 51.925 kmols = 1661.60 kg

Actual O<sub>2</sub> supplied (250% excess) = 181.738 kmols = 5815.62 kg

Excess O<sub>2</sub> = 181.738 – 51.925

= 129.813 kmols = 4154.02 kg

Assume that 57% of oxygen requirement comes from recycle stream and 43% comes from fresh feed.

O<sub>2</sub> from fresh feed = 181.738 x 0.43

= 78.147 kmols = 2500.70 kg

Corresponding N<sub>2</sub> = 78.147 x (79/21)

= 298.982 kmols = 8371.50 kg

Assume that the percentage composition of recycle stream is

O<sub>2</sub> - 7.78%

N<sub>2</sub> - 88.3%

H<sub>2</sub>O - 3.89%

O<sub>2</sub> from recycle stream = 103.590 kmols = 3314.88 kg

N<sub>2</sub> in recycle stream = 1175.910 kmols = 32925.48 kg

H<sub>2</sub>O in recycle stream = 51.795 kmols = 932.31 kg

Reactor outlet:

Unreacted methanol = 2 kmols = 64 kg

HCHO formed = 92.15 kmols = 2764.50 kg

H<sub>2</sub>O formed = 154.64 kmols = 2783.52 kg

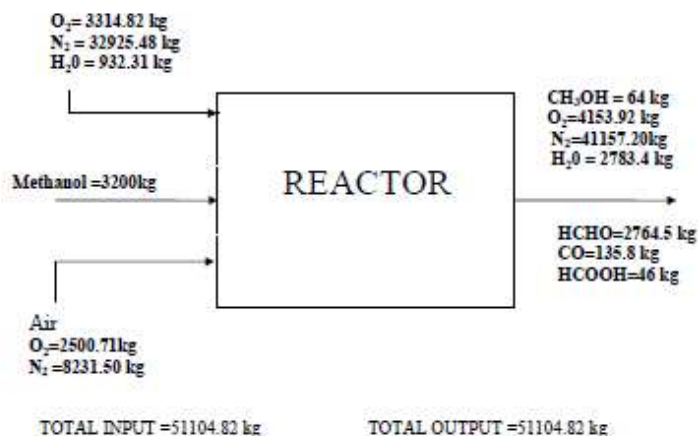
CO formed = 4.85 kmols = 135.8 kg

Nitrogen = 1484.185 kmols = 41157.20 kg

Unreacted oxygen = 129.813 kmols = 4154.02 kg

HCOOH formed = 1 kmole = 46 kg





## **MARKET STANDARD OF MANUFACTURE**

Formaldehyde is sold in aqueous solutions with concentrations ranging from 25 to 56 wt% HCHO. Product specifications for typical grades are summarized in Table 1.3. Formaldehyde is sold as low methanol (uninhibited) and high methanol (inhibited) grades. Methanol is used to retard paraformaldehyde formation.

Procedures for determining the quality of formaldehyde solutions are outlined by ASTM. Analytical methods relevant to Table 1.3 follow: formaldehyde by the sodium sulfite method (D2194); methanol by specific gravity (D2380); acidity as formic acid by titration with sodium hydroxide (D2379); iron by colorimetry (D2087); and color (APHA) by comparison to platinum-cobalt color standards (D1209).

**Table 1.3 Formaldehyde specifications**

Property	Methanol inhibited grades			low methanol uninhibited grades		
Formaldehyde, wt%	37	37	37	44	50	56
Methanol, wt% (max)	6-8	12-15	1.0-1.8	1.5	1.5-2.0	2.0
Acidity, wt% (max)	0.02	0.02	0.02	0.03	0.05	0.04
Iron, ppm (max)	0.5	0.05	0.5-1.0	0.5	0.5	0.75
Color, APHA (max)	10	10				

## **STORAGE AND TRANSPORTATION**

As opposed to gaseous, pure formaldehyde, solutions of formaldehyde are unstable. Both formic acid (acidity) and paraformaldehyde (solids) concentrations increase with time and depend on temperature. Formic acid concentration builds at a rate of 1.5-3 ppm/d at 35°C and 10-20 ppm/d at 65°C. Trace metallic impurities such as iron can boost the rate of formation of

formic acid. Although low storage temperature minimizes acidity, it also increase the tendency to precipitate paraformaldehyde. Paraformaldehyde solids can be minimized by storing formaldehyde solutions above a minimum temperature for less than a given time period. The addition of methanol as an inhibitor or of another chemical as a stabilizer allows storage at lower temperatures and/or for longer times. Stabilizers for formaldehyde solutions include hydroxypropylmethylcellulose, methyl- and ethylcellulose, poly(vinyl alcohol)s, or isophthalobisguanamine at concentrations ranging from 10 to 1000ppm. Inhibited formaldehyde typically contains 5-15 wt% methanol. Most formaldehyde producers recommend a minimum storage temperature for both stabilized and unstabilized solutions. The minimum temperature to prevent paraformaldehyde formation in unstabilised 37% formaldehyde solutions stored for one to about three months is as follows: 35°C with less than 1% methanol; 21°C with 7% methanol; 7°C with 10% methanol; and 6°C with 12% methanol. Materials of construction preferred for storage vessels are 304-, 316-, and 347-type stainless steels or lined carbon steel.

## **CONSUMPTION PATTERNS/APPLICATION AND MARKET ANALYSIS**

Formaldehyde is a basic chemical building block for the production of a wide range of chemicals finding a wide variety of end uses such as wood products, plastics, and coatings.

**Amino and Phenolic Resins.** The largest use of formaldehyde is in the manufacture of urea-formaldehyde, phenol-formaldehyde, and melamine-formaldehyde resins, accounting for over one-half (51%) of the total demand. These resins find use as adhesives for binding wood products that comprise particle board, fiber board, and plywood. Plywood is the largest market for phenol-formaldehyde resins; particle board is the largest for urea-formaldehyde resins.

Phenol-formaldehyde resins are used as molding compounds. Their thermal and electrical properties allow use in electrical, automotive, and kitchen parts. Other uses for phenol-formaldehyde resins include phenolic foam insulation, foundry mold binders, decorative and industrial laminates, and binders for insulating materials.

Urea-formaldehyde resins are also used as molding compounds and as wet strength additives for paper products. Melamine-formaldehyde resins find use in decorative laminates, thermoset surface coatings, and molding compounds such as dinnerware.

**1,4-Butanediol.** market for formaldehyde represents 11% of its demand. It is used to produce tetrahydrofuran (THF), which is used for polyurethane elastomer;  $\gamma$ -butyrolactone, which is used to make various pyrrolidinone derivatives; poly(butylenes terephthalate) (PBT), which is an engineering plastic; and polyurethanes.

**Polyols.** The principal ones include pentaerythritol, trimethylolpropane and neopentyl glycol. These polyols find use in the alkyd resin and synthetic lubricants markets. Pentaerythritol is also used to produce rosin/tall oil esters and explosives (pentaerythritol tetranitrate). Trimethylolpropane is also used in urethane coatings, polyurethane foams, and multifunctional monomers. Neopentyl glycol finds use in plastics produced from unsaturated polyester resins and in coatings based in saturated polyesters. The formaldehyde demands for pentaerythritol, trimethylolpropane, and neopentyl glycol are about 7, 2, and 1% respectively, of production.

**Acetal Resins.** These are high performance plastics produced from formaldehyde that are used for automotive parts, in building products, and in consumer goods. The acetal resins

formaldehyde demand are 9% of production.

**Hexamethylenetetramine.** Pure hexamethylenetetramine (also called hexamine and HMTA), the production of hexamethylenetetramine consumes about 6% of the U.S. formaldehyde supply. Its principle use is as a thermosetting catalyst for phenolic resins. Other significant uses are for the manufacture of RDX (cyclonite) high explosives, in molding compounds, and for rubber vulcanization accelerators. It is an unisolated intermediate in the manufacture of nitrilotriacetic acid.

**Slow-Release Fertilizers.** Products containing urea-formaldehyde are used to manufacture slow release fertilizers. These products can be either solids, liquid concentrates, or liquid solutions. This market consumes almost 6% of the formaldehyde produced.

**Methylenebis(4-phenyl isocyanate).** This compound is also known as methyl diisocyanate (MDI). Its principal end use is rigid urethane foams; other end uses include elastic fibers and elastomers. Total formaldehyde use is 5% of production.

**Chelating Agents.** The chelating agents produced from formaldehyde include the aminopolycarboxylic acids, their salts, and organophosphonates. The largest demand for formaldehyde is for ethylenediaminetetraacetic acid (EDTA); the next largest is for nitrilotriacetic acid (NTA). Chelating agents find use in industrial and household cleaners and for water treatment. Overall, chelating agents represent a modest demand for formaldehyde of about 3%.

**Formaldehyde-Alcohol Solutions.** These solutions are blends of concentrated aqueous formaldehyde, the alcohol, and the hemiacetal. These solutions are used to produce urea and melamine resins; the alcohol can act as the resin solvent and as a reactant.

**Paraformaldehyde.** It is used by resin manufacturers seeking low water content or more favorable control of reaction rates. It is often used in making phenol-urea-, resorcinol-, and melamine-formaldehyde resins. It is EPA registered disinfectant, "Steri -dri" sanitizer and fungicide for barber and beauty and for households, ships, bedding, clothing, nonfood/non/feed transporting trucks.

**Trioxane and Tetraoxane.** It is mainly used for the production of acetal resins.

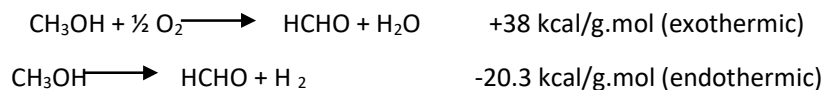
**Other Applications.** Formaldehyde derivatives, such as dimethyl dihydroxyethylene, are used in textiles to produce permanent press fabrics. Other formaldehyde derivatives are used in this industry to produce fire-retardant fabrics, Paraquat made from Pyridine chemicals, are used for agricultural chemicals (Herbicides). Formaldehyde and paraformaldehyde have found use as a corrosion inhibitor, hydrogen sulfide scavenger, and biocide in oil production operations such as drilling, waterflood, and enhanced oil recovery. Other used for formaldehyde and formaldehyde derivatives include fungicides, embalming fluids, silage preservatives, and disinfectants.

**Note:** The requirement of formaldehyde for certain applications like Polyacetal, MDI, 1,4-Butanediol and Neopentylglycol does not exist in India.

## **PROCESS DESCRIPTION/REACTIONS INVOLVED**

Fresh methanol, which is free from iron carbonyls and sulfur compounds (catalyst poisons) is combined with recycle methanol and diluted with equal amount of water, which is then pumped to a evaporator, where methanol is vaporized along with water. Methanol-water vapor mixture

is then superheated to 650°C in a steam superheater using low pressure steam. Air is drawn via, a filter and compressed in a blower for feed to the process. Filtered air is preheated with outgoing reactor effluent gases and then superheated to 650°C in a additional superheater. Superheated air and methanol water vapor is mixed in a mixer, the mixture is then passed into a Fixed bed tubular catalytic reactor which is nothing but a 1-1 shell and tube heat exchanger, the reactor tubes is packed with silver grains as catalyst, where the below mentioned reactions takes place i.e formaldehyde is produced both by oxidation and by dehydrogenation of methanol. About half of the methanol goes to each reaction, hence the combination is net exothermic.

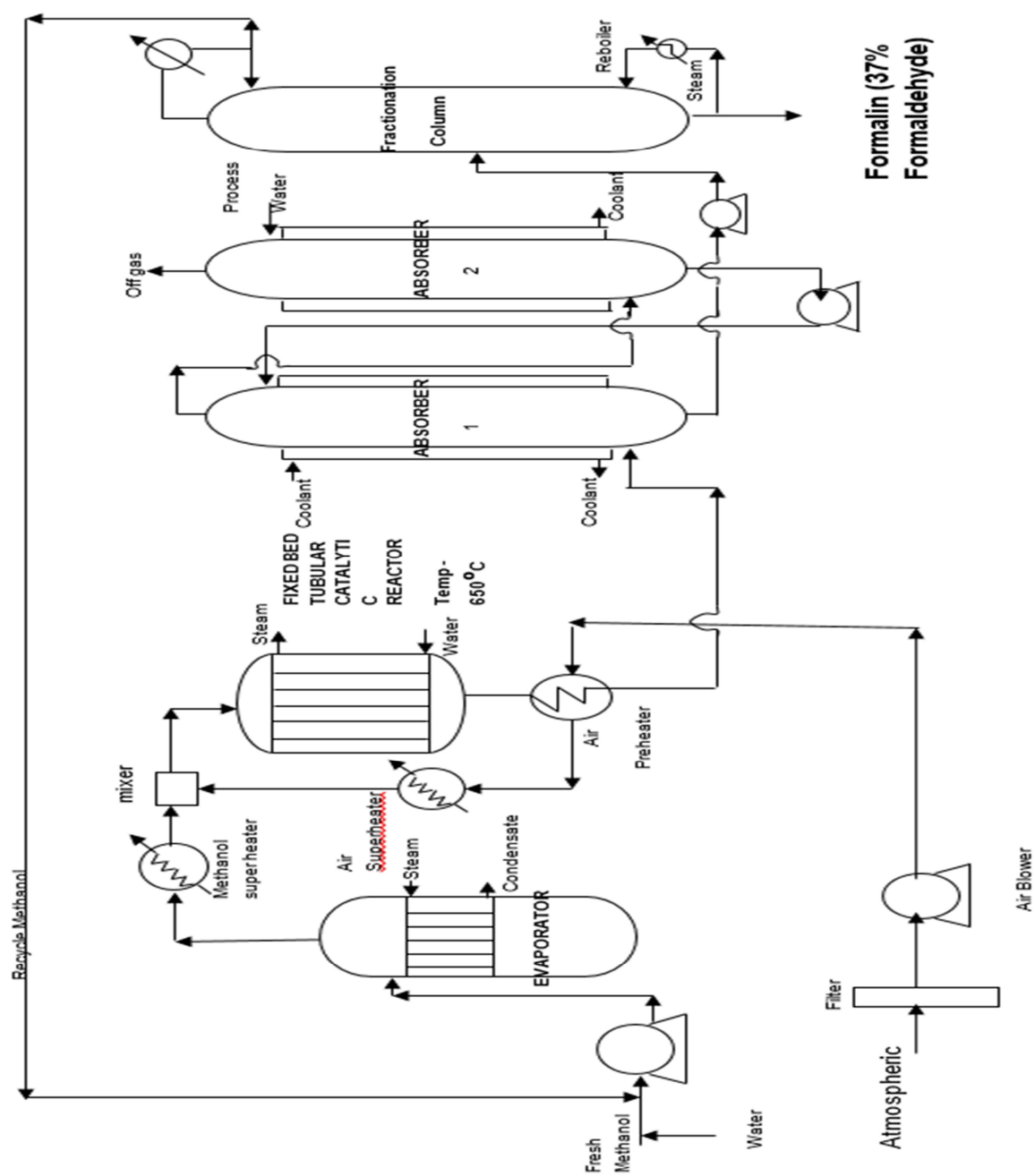


The conversion of methanol is 90% and the reactor pressure is kept slightly above atmospheric. Methanol-air ratio in reactor is kept above the rich side of the explosive limits (6.5 to 36.5 vol% in air), i.e, above 36.5%. Since the reactor temperature is to be maintained at 650°C the net exothermic heat of reaction is removed by circulating water through the shell side of the reactor, which in turn takes away net exothermic heat of reaction to give low pressure steam. The reactor effluent gases, at 650°C is brought down to 120°C by preheating the feed air in a air-reactor effluent gases preheater. The reactor effluent contains oxygen, nitrogen, hydrogen, HCHO, water, and unreacted methanol. The effluent gases enters the packed bed absorbers (2nos.) in series where dilute formalin and water are used for absorption, here HCHO is cooled and gets dissolved in water, heat of solution is evolved due to absorption, assuming heat of solution to be negligible. Some amount is required to vaporize water which passes via the vent. Heat given out by the entering gases to reach a temperature of 25°C from 120°C is removed by using a coolant which is circulated via tower external circulation. The bottom material from 2<sup>nd</sup> absorber contains HCHO-methanol water solution which is sent to a fractionation column. The fractionation column is sieve plate column containing 17 trays where the feed is introduced on 8<sup>th</sup> tray from top. The column overhead temperature is maintained around 65°C and bottom reboiler temperature of 93°C, methanol is condensed in the overhead condenser as top product and recycled back to evaporator. The bottom contains 37% wt of HCHO and less than 1% of methanol and remaining water. The water content of the bottoms is controlled by the amount of makeup water added at the top of the absorber. The tail gas coming out of 2<sup>nd</sup> absorber contains hydrogen which is used a source of fuel in boiler for steam generation. The formalin product tapped out of the distillation still is cooled and sent for storage.

## RAW MATERIAL REQUIPMENTS

(For 10 Tones Per Day)

1. METHANOL	-	4389.50kgs/ Day
2. AIR	-	4735.2kgs/Day
3. CATALYST	-	90.72kgs/day



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