FORMALDEHYDE

1. Introduction

Formaldehyde [50-00-0], $H_2C{=}O$, is the first of the series of aliphatic aldehydes. It was discovered by Butlerov in 1859 and has been manufactured since the beginning of the twentieth century. Because of its relatively low cost, high purity, and variety of chemical reactions, formaldehyde has become one of the world's most important industrial and research chemicals (1).

2. Physical Properties

At ordinary temperatures, pure formaldehyde is a colorless gas with a pungent, suffocating odor. Physical properties are summarized in Table 1; thermodynamic values for temperatures ranging from 0–6000 K are given in the *JANAF Interim Thermochemical Tables* (11,12). Other properties are listed in Reference 9.

Formaldehyde is produced and sold as water solutions containing variable amounts of methanol. These solutions are complex equilibrium mixtures of methylene glycol, $CH_2(OH)_2$, poly(oxymethylene glycols), and hemiformals of these glycols. Ultraviolet spectroscopic studies (13–15) indicate that even in highly concentrated solutions the content of unhydrated HCHO is < 0.04 wt%.

Density and refractive index are nearly linear functions of formaldehyde and methanol concentration. Based on available data (16–19), the density may be expressed in g/cm^3 by the following approximation:

$$\text{density} = [1.119 + 0.003(F - 45) - 0.0027\,M]\,[1.0 + 0.00055(55 - t)] \qquad (1)$$

where F and M are the formaldehyde and methanol concentrations, wt%, respectively, and t is in °C.

Table 1. **Properties of Monomeric Formaldehyde**

Property	Value	Reference
density, g/cm^3		
at −80°C	0.9151	2
at −20°C	0.8153	2
boiling point at 101.3 kPa,[a] °C	−19	3
melting point, °C	−118	3
vapor pressure, Antoine constants, Pa[b]		4
A	9.21876	
B	959.43	
C	243.392	
heat of vaporization,[c] ΔH_v at 19°C, kJ/mol[d]	23.3	3,5
heat of formation, ΔH_f° at 25°C, kJ/mol[d]	−115.9	6
std free energy, ΔG_f° at 25°C, kJ/mol[d]	−109.9	6
heat capacity, C_p°, J/(mol · K)[d]	35.4	6
entropy, S°, J/(mol · K)[d]	218.8	6
heat of combustion, kJ/mol[d]	563.5	6
heat of solution at 23°C kJ/mol[d]		7
in water	62	
in methanol	62.8	
in 1-propanol	59.5	
in 1-butanol	62.4	
critical constants		8,9
temperature, °C	137.2−141.2	
pressure, MPa[e]	6.784−6.637	
flammability in air		
lower/upper limits, mol%	7.0/73	10
ignition temperature, °C	430	10

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] $\text{Log}_{10}P_{\text{Pa}} = A - B/(C + t)$; t = °C. To convert $\log_{10}P_{\text{Pa}}$ to $\log_{10\ \text{mm Hg}}$, subtract 2.1225 from A.

[c] At 164 to 251 K, $\Delta H_v = (27{,}384 + 14.56\text{T} - 0.1207T^2)$ J/mol[d] (3).

[d] To convert J to cal, divide by 4.184.

[e] To convert MPa to atm, divide by 0.101.

The refractive index (20) may be expressed by a simple approximation for solutions containing 30−50 wt% HCHO and 0−15 wt% CH_3OH:

$$n_{\text{D}}^{18} = 1.3295 + 0.00125\,F + 0.0000113\,M \tag{2}$$

Viscosities have been measured for representative commercial formaldehyde solutions (21). Over the ranges of 30−50 wt% HCHO, 0−12 wt% CH_3OH, and 25−40°C, viscosity in mPa · s(=cP) may be approximated by

$$\text{viscosity} = 1.28 + 0.039\,F + 0.05\,M - 0.024\,t \tag{3}$$

Significant discrepancies in formaldehyde partial pressures above aqueous solutions (22,23) can occur due to nonequilibrium conditions in the liquid phase. However, these problems have been overcome and consistent results obtained (8,18,22,24−26).

Table 2. **Vapor Pressure above Formaldehyde Solutions, kPa**[a]

Wt %, liquid $HCHO:CH_3OH:H_2O$	40°C			60°C		
	HCHO	CH_3OH	H_2O	HCHO	CH_3OH	H_2O
37:7:56	0.039	0.053	0.308	0.143	0.122	0.851
37:1:62	0.031	0.007	0.322	0.130	0.016	0.891
50:7:43	0.048	0.041	0.265	0.176	0.096	0.749
50:1:49	0.040	0.005	0.283	0.162	0.012	0.795
55:35:10	0.109	0.286	0.095	0.321	0.693	0.285

[a] To convert kPa to mm Hg, multiply by 7.5.

In methanol–formaldehyde–water solutions, increasing the concentration of either methanol or formaldehyde reduces the volatility of the other. Vapor-liquid-equilibrium data (8,27) for several methanolic formaldehyde solutions are given in Table 2. The flash point varies with composition, decreasing from 83 to 60°C as the formaldehyde and methanol concentrations increase (17,18).

Formaldehyde solutions exist as a mixture of oligomers, $HO(CH_2O)_nH$. Their distribution has been determined for 6–50 wt% HCHO solutions with low methanol using nmr and gas chromatographic techniques (28,29). Averages of the equilibrium constants for equation 4 are $K_2 = 7.1$, $K_3 = 4.7$, and $K_4 = 3.4$. The equilibrium constants appear to be nearly independent of temperature over the range of 30–65°C. Methanol stabilizes aqueous formaldehyde solutions by decreasing the average value of n (28,30). Hence, methanolic solutions can be stored at relatively low temperatures without precipitation of polymer.

$$HO(CH_2O)_nH + HOCH_2OH \xrightleftharpoons{K_n} HO(CH_2O)_{n+1}H + H_2O \tag{4}$$

The following approximation was derived from data at 25–80°C (28,30,31) for solutions containing 7–55 wt% formaldehyde and 0–14 wt% methanol:

$$\text{monomer(mol\%)} = 100 - 12.3\sqrt{F} + (1.44 - 0.0164\,F)M \tag{5}$$

where the monomer is the mole percent of formaldehyde present as formaldehyde hemiformal and methylene glycol, F is the wt% HCHO, and M is the wt% CH_3OH.

Commercial formaldehyde–alcohol solutions are clear and remain stable above 16–21°C. They are readily obtained by dissolving highly concentrated formaldehyde in the desired alcohol.

3. Chemical Properties

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 (see ACETAL RESINS).

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. When liquid formaldehyde is warmed to room temperature in a sealed ampul, it polymerizes rapidly with evolution of heat (63 kJ/mol or 15.05 kcal/mol). Uncatalyzed decomposition is very slow below 300°C; extrapolation of kinetic data (32) to 400°C indicates that the rate of decomposition is ca 0.44%/min at 101 kPa (1 atm). The main products are CO and H_2. Metals such as platinum (33), copper (34), and chromia and alumina (35) also catalyze the formation of methanol, methyl formate, formic acid, carbon dioxide, and methane. Trace levels of formaldehyde found in urban atmospheres are readily photo-oxidized to carbon dioxide; the half-life ranges from 35–50 minutes (36).

At ordinary temperatures, formaldehyde gas is readily soluble in water, alcohols, and other polar solvents. Its heat of solution in water and the lower aliphatic alcohols is approximately 63 kJ/mol (15 kcal/mol). The reaction of unhydrated formaldehyde with water is very fast; the first-order rate constant at 22°C is $9.8\ \mathrm{s}^{-1}$ (37).

Formaldehyde is readily reduced to methanol by hydrogen over many metal and metal oxide catalysts. It is oxidized to formic acid or carbon dioxide and water. The Cannizzaro reaction gives formic acid and methanol. Similarly, a vapor-phase Tischenko reaction is catalyzed by copper (34) and boric acid (38) to produce methyl formate:

$$2\,\mathrm{HCHO} \longrightarrow \mathrm{HCOOCH_3} \tag{6}$$

Formaldehyde condenses with itself in an aldol-type reaction to yield lower hydroxy aldehydes, hydroxy ketones, and other hydroxy compounds; the reaction is autocatalytic and is favored by alkaline conditions. Condensation with various compounds gives methylol ($-CH_2OH$) and methylene ($=CH_2$) derivatives. The former are usually produced under alkaline or neutral conditions, the latter under acidic conditions or in the vapor phase. In the presence of alkalies, aldehydes and ketones containing α-hydrogen atoms undergo aldol reactions with formaldehyde to form mono- and polymethylol derivatives. Acetaldehyde and 4 moles of formaldehyde give pentaerythritol (PE):

$$\mathrm{CH_3CHO} + 3\,\mathrm{HCHO} \longrightarrow \mathrm{C(CH_2OH)_3CHO} \tag{7}$$

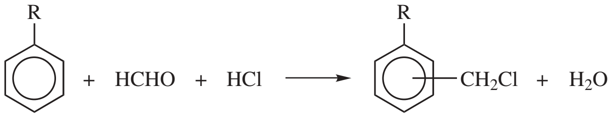
$$\mathrm{C(CH_2OH)_3CHO} + \mathrm{HCHO} + \mathrm{NaOH} \longrightarrow \underset{\text{pentaerythritol}}{\mathrm{C(CH_2OH)_4}} + \mathrm{HCOONa} \tag{8}$$

In the vapor phase at 285°C, acrolein is formed from acetaldehyde (39):

$$\mathrm{HCHO} + \mathrm{CH_3CHO} \longrightarrow \mathrm{HOCH_2CH_2CHO} \longrightarrow \mathrm{CH_2{=}CHCHO} + \mathrm{H_2O} \tag{9}$$

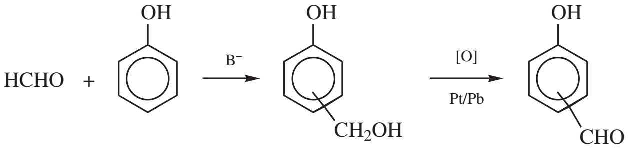
Methylene derivatives are readily formed in the vapor phase with compounds having a hydrogen in the alpha position to an electron-withdrawing group. Acrylic (40,41) and methacrylic (42) acids (or esters) are produced at 300–425°C from acetic and propionic acids (or esters), respectively, using alkali and alkalineearth catalysts. The same catalysts are effective for producing acrylonitrile from acetonitrile (42). With ketones, addition of two formaldehyde units occurs (43); for example, 2-butanone is converted to 2-methyl-1,4-pentadiene-3-one.

Chloromethylation of the aromatic nucleus occurs readily with alkyl and alkoxy substituents accelerating the reaction and halo, chloromethyl, carboxyl, and nitro groups retarding it.



(10)

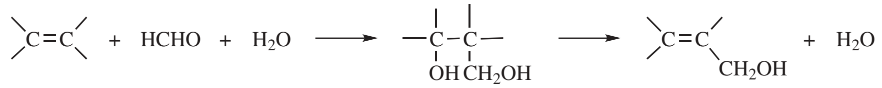
Reaction with phenol gives hydroxymethylphenols as the principal products (44). Through proper selection of reaction conditions and catalyst a 1:1 mixture of *o*- and *p*-isomers is obtained (45):



(11)

Both isomers can be oxidized to the corresponding benzaldehydes in high yield.

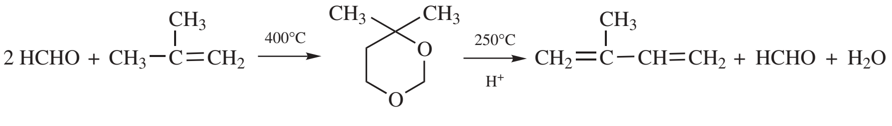
An important synthetic process for forming a new carbon–carbon bond is the acid-catalyzed condensation of formaldehyde with olefins (Prins reaction):



(12)

In acetic acid solvent, ethylene gives 1,3-propanediol acetates (46) and propylene gives 1,3-butanediol acetates (47). A similar reaction readily occurs with olefinic alcohols and ethers, diolefins, and mercaptans (48).

A commercial process based on the Prins reaction is the synthesis of isoprene from isobutylene and formaldehyde through the intermediacy of 4,4-dimethyl-1,3-dioxane (49–51):



(13)

Liquid-phase condensation of formaldehyde with propylene, catalyzed by BF_3 or H_2SO_4, gives butadiene (52,53).

With acidic catalysts in the liquid phase, formaldehyde and alcohols give formals, eg, dimethoxymethane from methanol:

$$HCHO + 2\ CH_3OH \longrightarrow CH_3OCH_2OCH_3 + H_2O \qquad (14)$$

Under neutral or slightly alkaline conditions, only the unstable hemiformal ($CH_3O{-}CH_2OH$, methoxymethanol) is produced. Alpha-chloromethyl ether is synthesized from aqueous formaldehyde, methanol, and hydrogen chloride (54). However, under anhydrous conditions, a carcinogenic by-product, bis(chloromethyl)ether is also formed (55).

Hydrogen cyanide reacts with aqueous formaldehyde in the presence of bases to produce glyconitrile [107-16-4] (56,57):

$$HCHO + HCN \longrightarrow HOCH_2{-}C{\equiv}N \tag{15}$$

This extremely toxic material is an intermediate in the synthesis of nitrilotriacetic acid (NTA), EDTA, and glycine [56-40-6].

Monosubstituted acetylenes add formaldehyde in the presence of copper, silver, and mercury acetylide catalysts to give acetylenic alcohols (58) (Reppe reaction). Acetylene itself adds two molecules (see ACETYLENE-DERIVED CHEMICALS).

$$2\,HCHO + HC{\equiv}CH \longrightarrow HOCH_2C{\equiv}CCH_2OH \tag{16}$$

Primary and secondary amines readily give alkylaminomethanols; the latter condense upon heating or under alkaline conditions to give substituted methyleneamines (59). With ammonia, the important industrial chemical, hexamine, is produced. Tertiary amines do not react.

$$HCHO + (CH_3)_2NH \longrightarrow [(CH_3)_2N{-}CH_2OH \xrightarrow{(CH_3)_2NH} (CH_3)_2N{-}CH_2{-}N(CH_3)_2 + H_2O \tag{17}$$

The well-known Mannich reaction is illustrated by the following example:

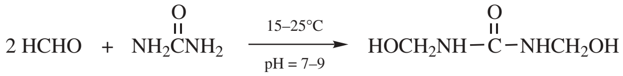
$$CH_3COCH_3 + (CH_3)_2NH\cdot HCl + HCHO \longrightarrow CH_3COCH_2CH_2N(CH_3)_2\cdot HCl + H_2O \tag{18}$$

A detailed account of these reactions has been given (60).

Methylamines are formed by heating formaldehyde with primary or secondary amines or their salts under acid conditions (61):

$$R_2NH\cdot HCl + 2\,HCHO \longrightarrow R_2N(CH_3)\cdot HCl + HCOOH \tag{19}$$

Mono- and dimethylol derivatives are made by reaction of formaldehyde with unsubstituted amides. Dimethylolurea, an item of commercial importance and an intermediate in urea–formaldehyde resins, is formed in high yield under controlled conditions (62):



$$2\,HCHO + NH_2\overset{\overset{\large O}{\|}}{C}NH_2 \xrightarrow[pH = 7\text{–}9]{15\text{–}25^\circ C} HOCH_2NH{-}\overset{\overset{\large O}{\|}}{C}{-}NHCH_2OH \tag{20}$$

Melamine reacts similarly to produce methylol derivatives, which form the familiar melamine–formaldehyde resins on heating (63) (see AMINO RESINS).

Reaction of formaldehyde, methanol, acetaldehyde, and ammonia over a silica alumina catalyst at 500°C gives pyridine [110-86-1] and 3-picoline [108-99-6] (64). This forms the basis of commercial processes for making pyridines (qv) from various aldehydes.

Formaldehyde reacts with syn gas (CO,H_2) to produce added value products. Ethylene glycol (EG) may be produced in a two-stage process or the intermediate, glycolaldehyde, isolated from the first stage (65):

$$HCHO + CO + H_2 \xrightarrow[\substack{30\ MPa \\ 150°C}]{Rh} HOCH_2{-}\overset{O}{\overset{\|}{C}}H \xrightarrow[{[H]}]{Rh,Pd} HOCH_2CH_2OH \tag{21}$$

EG may also be produced via glycolic acid using catalysts containing strong acids (66), cobalt carbonyl (67–69), rhodium oxide (68), or HF solvent (70,71) (see GLYCOLS, ETHYLENE GLYCOL).

$$HCHO + CO + H_2O \xrightarrow{30\ MPa} HOCH_2{-}\overset{O}{\overset{\|}{C}}OH \xrightarrow{[H]} HOCH_2CH_2OH \tag{22}$$

4. Manufacture

Historically, formaldehyde has been and continues to be manufactured from methanol. Following World War II, however, as much as 20% of the formaldehyde produced in the United States was made by the vapor-phase, noncatalytic oxidation of propane and butanes (72). This nonselective oxidation process produces a broad spectrum of coproducts (73) which requires a complex costly separation system (74). Hence, the methanol process is preferred. The methanol raw material is normally produced from synthesis gas that is produced from methane.

Most of the world's commercial formaldehyde is manufactured from methanol and air either by a process using a silver catalyst or one using a metal oxide catalyst. Reactor feed to the former is on the methanol-rich side of a flammable mixture and virtually complete reaction of oxygen is obtained; conversely, feed to the metal oxide catalyst is lean in methanol and almost complete conversion of methanol is achieved.

4.1. Silver Catalyst Process. In early formaldehyde plants methanol was oxidized over a copper catalyst, but this has been almost completely replaced with silver (75). The silver-catalyzed reactions occur at essentially atmospheric pressure and 600 to 650°C (76) and can be represented by two simultaneous reactions:

$$CH_3OH + 0.5\ O_2 \longrightarrow HCHO + H_2O \Delta H = -156\ kJ(-37.28\ kcal) \tag{23}$$

$$CH_3OH \longrightarrow HCHO + H_2 \Delta H = +85\ kJ(20.31\ kcal) \tag{24}$$

Between 50 and 60% of the formaldehyde is formed by the exothermic reaction (eq. 23) and the remainder by endothermic reaction (eq. 24) with the net result

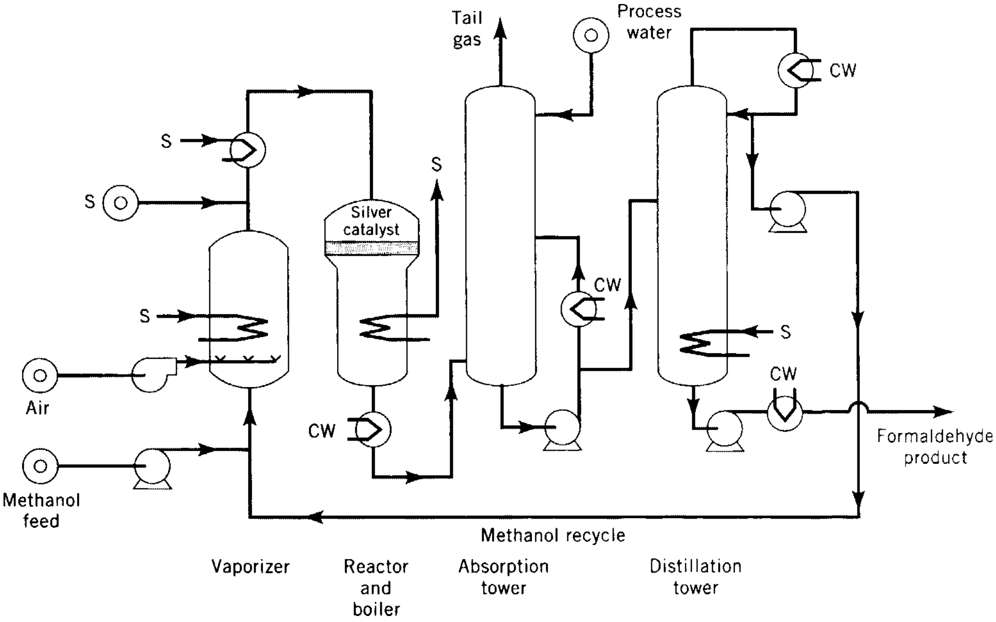


Fig. 1. Flow scheme of a typical silver catalyst process. S = steam; CW = cooling water.

of a reaction exotherm. Carbon monoxide and dioxide, methyl formate, and formic acid are by-products. In addition, there are also physical losses, liquid-phase reactions, and small quantities of methanol in the product, resulting in an overall plant yield of 86–90% (based on methanol).

Figure 1 is a flow diagram of a typical formaldehyde plant (76–79) employing silver catalyst. A feed mixture is generated by sparging air into a pool of heated methanol and combining the vapor with steam. The mixture passes through a superheater to a catalyst bed of silver crystals or layers of silver gauze. The product is then rapidly cooled in a steam generator and then in a water-cooled heat exchanger and fed to the bottom of an absorption tower. The bulk of the methanol, water, and formaldehyde is condensed in the bottom water-cooled section of the tower, and almost complete removal of the remaining methanol and formaldehyde from the tail gas occurs in the top of the absorber by countercurrent contact with clean process water. Absorber bottoms go to a distillation tower where methanol is recovered for recycle to the reactor. The base stream from distillation, an aqueous solution of formaldehyde, is usually sent to an anion exchange unit which reduces the formic acid to specification level. The product contains up to 55% formaldehyde and less than 1.5% methanol.

A typical catalyst bed is very shallow (10 to 50 mm) (76,77). In some plants the catalyst is contained in numerous small parallel reactors; in others, catalyst-bed diameters up to 1.7 and 2.0 m (77,80) and capacities of up to 135,000 t/yr per reactor are reported (78). The silver catalyst has a useful life of three to eight months and can be recovered. It is easily poisoned by traces of transition group metals and by sulfur.

The reaction occurs at essentially adiabatic conditions with a large temperature rise at the inlet surface of the catalyst. The predominant temperature control is thermal ballast in the form of excess methanol or steam, or both, which is in the feed. If a plant is to produce a product containing 50 to 55% formaldehyde and no more than 1.5% methanol, the amount of steam that can be added is limited, and both excess methanol and steam are needed as ballast. Recycled methanol required for a 50–55% product is 0.25–0.50 parts per part of fresh methanol (76,77).

With increasing energy costs, maximum methanol conversion is desirable, eliminating the need for the energy-intensive distillation for methanol recovery. If a dilute product containing 40 to 44% formaldehyde and 1.0 to 1.5% methanol is acceptable, then the ballast steam can be increased to a level where recycled methanol is eliminated with a significant savings in capital cost and energy (81,82). In another process, tail gas from the absorber is recycled to the reactor. This additional gas plus steam provides the necessary thermal ballast without the need for excess methanol (82–84). This process can produce 50% formaldehyde with about 1.0% methanol without a distillation tower (79,84). Methanol recovery can be obviated in two-stage oxidation systems where, for example, part of the methanol is converted with a silver catalyst, the product is cooled, excess air is added, and the remaining methanol is converted over a metal oxide catalyst such as that described below (85). In another two-stage process, both first and second stages use silver catalysts (86–88). Formaldehyde–methanol solutions can be made directly from methanol oxidation product by absorption in methanol (89).

The absorber tail gas contains about 20 mol% hydrogen and has a higher heating value of ca 2420 kJ/m^3 (65 Btu/SCF). With increased fuel costs and increased attention to the environment, tail gas is burned for the twofold purpose of generating steam and eliminating organic and carbon monoxide emissions.

Aqueous formaldehyde is corrosive to carbon steel, but formaldehyde in the vapor phase is not. All parts of the manufacturing equipment exposed to hot formaldehyde solutions must be a corrosion-resistant alloy such as type-316 stainless steel. Theoretically, the reactor and upstream equipment can be carbon steel, but in practice alloys are required in this part of the plant to protect the sensitive silver catalyst from metal contamination.

4.2. Metal Oxide Catalyst Process. Oxidation of methanol to formaldehyde with vanadium pentoxide catalyst was first patented in 1921 (90), followed in 1933 by a patent for an iron oxide–molybdenum oxide catalyst (91), which is still the choice in the 1990s. Catalysts are improved by modification with small amounts of other metal oxides (92), support on inert carriers (93), and methods of preparation (94,95) and activation (96). In 1952, the first commercial plant using an iron–molybdenum oxide catalyst was put into operation (97). It is estimated that 70% of the new formaldehyde installed capacity is the metal oxide process (98).

In contrast to the silver process, all of the formaldehyde is made by the exothermic reaction (eq. 23) at essentially atmospheric pressure and at 300–400°C. By proper temperature control, a methanol conversion greater than 99% can be maintained. By-products are carbon monoxide and dimethyl ether, in addition to small amounts of carbon dioxide and formic acid. Overall plant yields are 88–92%.

Figure 2 is a flow scheme for a typical metal oxide catalyst formaldehyde plant (99–102). Vaporized methanol is mixed with air and optionally recycled

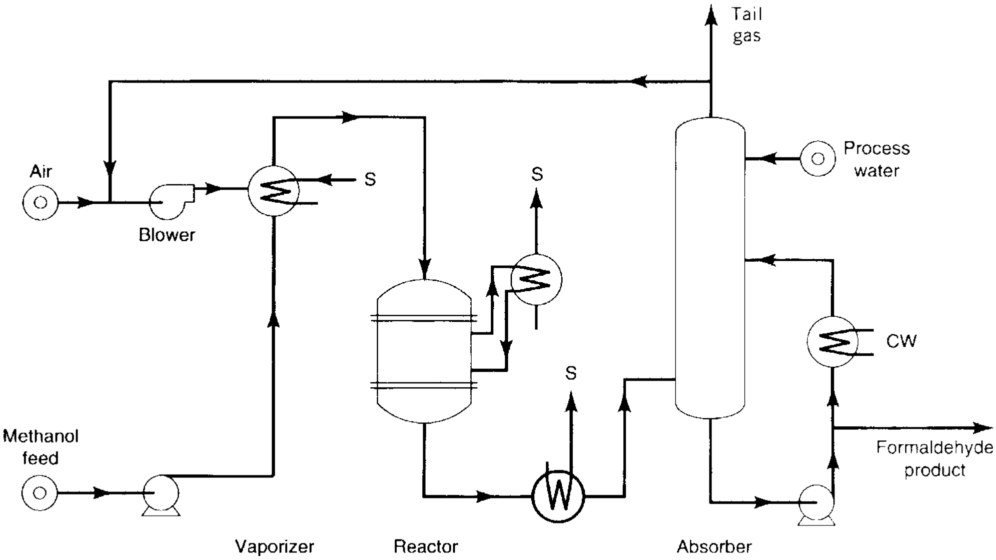


Fig. 2. Flow scheme of a typical metal oxide catalyst process. S = steam; CW = cooling water.

tail gas and passed through catalyst-filled tubes in a heat-exchanger reactor. Heat released by the exothermic reaction is removed by vaporization of a high boiling heat-transfer fluid on the outside of the tubes. Steam is normally produced by condensing the heat-transfer fluid. A typical reactor has short tubes of 1.0 to 1.5 m and a large shell diameter of 2.5 m or more. Product leaving the bottom of the reactor is cooled and passed to the base of an absorber. Formaldehyde concentration in the product is adjusted by controlling the amount of water added to the top of the absorber. A product up to 55% formaldehyde and less than 1% methanol can be made. Formic acid is removed by ion exchange.

The absence of a methanol recovery tower is an obvious advantage over the conventional silver process (Fig. 1). However, the equipment has to be large to accommodate the greater flow of gas. The air–methanol feed mixture must be on the methanol lean side of a flammable mixture. If the oxygen in the total reactor feed is reduced to about 10 mol% by partially replacing air with recycled tail gas, then the methanol in the feed can be increased somewhat without the danger of forming an explosive mixture (103), and for a given quantity of production, gas flow (air plus recycle) can be reduced by 17 to 37% (104). Even with gas recycle, the metal oxide process must handle a substantial volume of gas which is 3.0 to 3.5 times the gas flow of a conventional silver-catalyzed process.

A typical metal oxide catalyst has an effective life of 12 to 18 months (76,100,105). Compared to silver, it is much more tolerant to trace contamination. It requires less frequent change-outs, but a longer down time for each replacement. In contrast to a silver-catalyst plant, there is little economic justification to incinerate the metal oxide plant tail gas for the purpose of generating steam. The tail gas is essentially nitrogen and oxygen with combustible components (dimethyl ether, carbon monoxide, formaldehyde, methanol) representing only a few percent of the total. However, increasing environmental pressures make vent incineration more desirable. With the addition of auxiliary fuel, the vent can be oxidized by thermal incineration at temperatures of 700 to 900°C. As an alternative, the stream can be oxidized at 450 to 550°C in a catalytic incinerator which can be thermally self-sufficient with supplemental fuel required only for startup or abnormal operating conditions (104).

The requirements for the material of construction are the same as for the silver catalyst process except the use of alloys to protect the catalyst is not as important.

4.3. 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 (106–108). 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 the dehydrogenation of methanol (109–111) 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 method for the nonoxidative preparation of formaldehyde from methanol has been described (112).

A third possible route is to produce formaldehyde from methylal that is produced from methanol and formaldehyde (113,114). 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 (113). 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 more costly means, eg, distillation and evaporation. Development of this process is complete (114). Process for the production of formaldehyde from dimethyl ether has been described (115).

5. Economic Aspects

Essentially all formaldehyde is produced as aqueous solutions containing 25–56 wt% HCHO and 0.5–15 wt% CH_3OH. All information on capacity, demand, and prices is reported on a 37 wt% formaldehyde basis.

Table 3 gives the United States producers of formaldehyde and their capacities. Commercial production is from methanol either using a silver or metal oxide catalyst. The major portion of this production (70–80%) is used captively (116).

Seven producers in Canada have a combined production total of about 815×10^3 t. Mexico has 11 producers and their combined production is 230×10^3 t (116).

Table 3. **U. S. Producers of Formaldehyde and their Capacities**[a]

Producer	Capacity × 10^3 t[b]
Borden Chemical, (18 sites)	2086
Capital Resin, Columbus, Ohio	45
Celanese, Bishop, TX; Rock Hill, S.C.	785
D. B. Western, Virginia, Minn.	18
Degussa, Theodore Ala.	98
DuPont, LaPorte, Texas; Parkersburg, W.Va.	408
Geo Specialty Chemicals, (Trimet) Allentown, Pa.	61
Georgia-Pacific (14 sites)	1139
Hercules (Aqualon), Louisiana, Mo.	77
ISP, Calvert City, Ky; Texas City, Tex.	91
Neste Resins (5 sites)	408
New Mexico Adhesives, Las Vegas, N.M.	23
Perstorp, Toledo, Ohio	204
Praxair, Geismar, La.	64
Solutia, Alvin, Texas	91
Wright Chemical, Riegelwood, N.C.	73
Total	*5671*

[a] Ref. 116.

[b] 37% basis.

U.S. demand in 2000 was 4400 × 10^3t and the projected demand for 2004 is about 4580 × 10^3t. Demand equals production minus imports. Imports in 2000 were 28 × 10^3t.

Prices of 37% methanol-free formaldehyde for the period 1995–2000 ranged from $0.06/kg to $0.11/kg. Current (2004) price is $0.10/kg.

Formaldehyde demand is in part related to the housing and construction sector. Decrease in housing impacts the demand for particleboard and plywood made of urea–formaldehyde and phenol–formaldehyde resins. These two types of construction materials consume more than one third of the formaldehyde demand.

Formaldehyde capacity has always exceeded demand and this situation is expected to continue.

6. Specifications

Formaldehyde is sold in aqueous solutions with concentrations ranging from 25 to 56 wt% HCHO. Product specifications for typical grades (18,117–119) are summarized in Table 4. Formaldehyde is sold as low methanol (uninhibited) and high methanol (inhibited) grades. Methanol is used to retard paraformaldehyde formation.

7. Analytical Methods

Procedures for determining the quality of formaldehyde solutions are outlined by ASTM (120). Analytical methods relevant to Table 5 follow: formaldehyde

Table 4. **Formaldehyde Specifications**[a]

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)[b]	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	10	10	10	10

[a] The specification range is the high and low specifications of producers surveyed.
[b] As wt% formic acid.

Table 5. **Specifications and Physical Properties of Formaldehyde–Alcohol Solutions**

Property	Methanol	Methanol	1-Butanol	Isobutyl alcohol
alcohol, wt%	48	55	53	52
HCHO, wt%	43	35	40	40
H_2O, wt%	9	10	7	8
bp, °C	88.0	91.6	104.5	103
specific gravity at 40°C	0.977	1.051	0.963	0.973
flash point, °C	33[a]	44[a]	57[b]	53.8[b]
U_f/L_f, mol %[c]		47.0/7.0	21.0/2.5	19.0/2.0

[a] Tag closed cup (ASTM D56).
[b] Tag open cup (ASTM D1310).
[c] Upper and lower flammable limits in air.

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).

8. Storage and Handling

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 (17,18). Trace metallic impurities such as iron can boost the rate of formation of formic acid (121). Although low storage temperature minimizes acidity, it also increases 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 (122–125) include hydroxypropylmethylcellulose, methyl- and ethylcelluloses, poly(vinyl alcohol)s, or isophthalobisguanamine at concentrations ranging from 10 to 1000 ppm. Inhibited formaldehyde typically contains 5–15 wt% methanol.

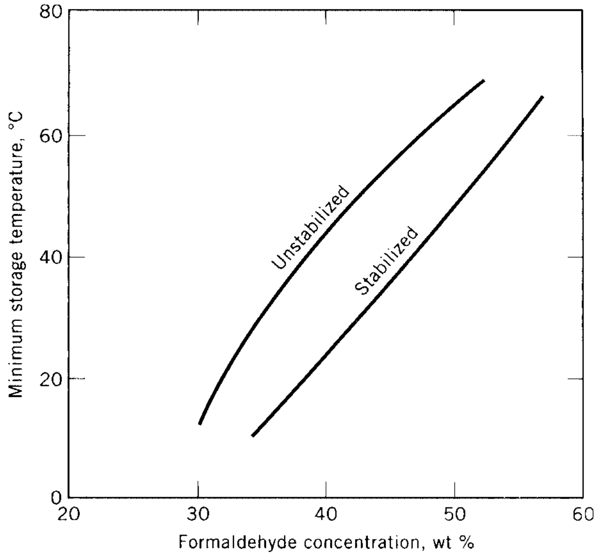


Fig. 3. Storage temperature vs formaldehyde concentration (< 2.0 wt%; CH_3OH).

Most formaldehyde producers recommend a minimum storage temperature for both stabilized and unstabilized solutions. Figure 3 is a plot of data (17,18,122,126) for uninhibited (<2.0 wt% methanol) formaldehyde. The minimum temperature to prevent paraformaldehyde formation in unstabilized 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 (127).

Materials of construction preferred for storage vessels (17–19,128) are 304-, 316-, and 347-type stainless steels or lined carbon steel.

9. Health and Safety Factors

Sources of human exposure to formaldehyde are engine exhaust, tobacco smoke, natural gas, fossil fuels, waste incineration, and oil refineries (129). It is found as a natural component in fruits, vegetables, meats, and fish and is a normal body metabolite (130,131). Facilities that manufacture or consume formaldehyde must control workers' exposure in accordance with the following workplace exposure limits in ppm: action level, 0.5; TWA, 0.75; STEL, 2 ACGIH TLV TWA, 1 ppm. (132). In other environments such as residences, offices, and schools, levels may reach 0.1 ppm HCHO due to use of particle board and urea–formaldehyde foam insulation in construction.

Formaldehyde causes eye, upper respiratory tract, and skin irritation and is a skin sensitizer. Although sensory irritation, eg, eye irritation, has been reported at concentrations as low as 0.1 ppm in uncontrolled studies, significant eye/nose/throat irritation does not generally occur until concentrations of 1 ppm, based on controlled human chamber studies. Odor detection has commonly been reported to occur in the range of 0.06–0.5 ppm (133–135).

Formaldehyde is classified as a probable human carcinogen by the International Agency for Research on Cancer (IARC) and as a suspected human carcinogen by the American Conference of Governmental Industrial Hygienists (ACGIH). This is based on limited human evidence and on sufficient evidence in experimental animals (136). Lifetime inhalation studies with rodents have shown nasal cancer at formaldehyde concentrations that overwhelmed cellular defense mechanisms, ie, 6 to 15 ppm. No nasal cancer was seen at 2 ppm or lower levels (137).

Formaldehyde is not considered a teratogen and has not been reported to cause adverse reproductive effects (138,139). *In vitro* mutagenicity assays with formaldehyde have yielded positive responses, while *in vivo* assays have been largely negative (130).

10. Uses

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. U.S. distribution of formaldehyde production according to use is as follows: urea-formaldehyde resins, 24%; phenol–formaldehyde resins 16.5%; polyacetal resins, 13%; 1,4-butanediol (BDO), 11%; methylene diisocyanate (MDI), 7%; pentaerythritol, 5%; controlled release fertilizer, 3.5%; hexamethylenetetramine (HMTA), 3%; melamine–formaldehyde resins, 3%; miscellaneous, including chelating agents, trimethylolpropane, pyridine chemicals, nitroparaffin derivatives, textile treating and trimethylolethane, 14%.

10.1. Amino and Phenolic Resins. The largest use of formaldehyde is in the manufacture of urea–formaldehyde, phenol–formaldehyde, and melamine–formaldehyde resins, accounting for a major portion of the total demand (115). 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. Under certain conditions, urea–formaldehyde resins may release formaldehyde that has been alleged to create health or environmental problems (see AMINO RESINS AND PLASTICS).

Phenol–formaldehyde resins are used as molding compounds (see PHENOLIC RESINS). 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.

10.2. 1,4-Butanediol. 1,4-Butanediol [110-63-4], made from formaldehyde and acetylene, is a significant market for formaldehyde. It is used to produce tetrahydrofuran (THF), which is used for polyurethane elastomers; γ-butyrolactone, which is used to make various pyrrolidinone derivatives; poly-(butylene terephthalate) (PBT), which is an engineering plastic; and polyurethanes. Formaldehyde growth in the acetylenic chemicals market is threatened by alternative processes to produce 1,4-butanediol not requiring formaldehyde as a raw material (140) (see ACETYLENE-DERIVED CHEMICALS).

10.3. Polyols. Several important polyhydric alcohols or polyols are made from formaldehyde. The principal ones include pentaerythritol, made from acetaldehyde and formaldehyde; trimethylolpropane, made from *n*-butyraldehyde and formaldehyde; and neopentyl glycol, made from isobutyraldehyde and formaldehyde. These polyols find use in the alkyd resin (qv) and synthetic lubricants markets. Pentaerythritol [115-77-5] is also used to produce rosin/tall oil esters and explosives (pentaerythritol tetranitrate). Trimethylolpropane [77-99-6] is also used in urethane coatings, polyurethane foams, and multifunctional monomers. Neopentyl glycol [126-30-7] finds use in plastics produced from unsaturated polyester resins and in coatings based on saturated polyesters.

10.4. Acetal Resins. These are high performance plastics produced from formaldehyde that are used for automotive parts, in building products, and in consumer goods. Acetal resins (qv) are either homopolymers or copolymers of formaldehyde. Typically, the resin is produced from anhydrous formaldehyde or trioxane.

10.5. Hexamethylenetetramine. Pure hexamethylenetetramine [100-97-0] (also called hexamine and HMTA) is a colorless, odorless, crystalline solid of adamantane-like structure (141). It sublimes with decomposition at >200°C but does not melt. Its solubility in water varies little with temperature, and at 25°C it is 46.5% in the saturated solution. It is a weak monobase; aqueous solutions are in the pH 8–8.5 range (142). Hexamethylenetetramine is readily prepared by treating aqueous formaldehyde with ammonia followed by evaporation and crystallization of the solid product. The reaction is fast and essentially quantitative (142).

Its principal 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. Some hexamethylenetetramine is made as an unisolated intermediate in the manufacture of nitrilotriacetic acid.

10.6. 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. (see CONTROLLED RELEASE TECHNOLOGY, AGRICULTURAL).

10.7. Methylenebis(4-phenyl isocyanate). This compound is also known as methyl diisocyanate [101-68-8] (MDI) and is produced by the condensation of aniline and formaldehyde with subsequent phosgenation. Its principal end use is rigid urethane foams; other end uses include elastic fibers and elastomers.

10.8. 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 [60-00-4] (EDTA); the next largest is for nitrilotriacetic acid [139-13-9] (NTA). Chelating agents find use in industrial and household cleaners and for water treatment.

Table 6. **Specifications of Commercial Paraformaldehyde**[a]

Property	Prills	Powder[b]
formaldehyde, wt%	91.0–93.0	95.0–97.0
water, wt%, max	9.0	5.0
acidity as formic, wt%, max	0.03	0.03
iron, ppm, max	2	2
ash wt%, max	0.01	0.01

[a] Ref. 117.

[b] 10 wt% max retained on 74 mm (200 mesh) sieve.

10.9. Formaldehyde–Alcohol Solutions. These solutions are blends of concentrated aqueous formaldehyde, the alcohol, and the hemiacetal. Methanol decreases the average molecular weight of formaldehyde oligomers by formation of lower molecular weight hemiacetals. These solutions are used to produce urea and melamine resins; the alcohol can act as the resin solvent and as a reactant. The low water content can improve reactivity and reduce waste disposal and losses. Typical specifications for commercially available products are shown in Table 5 (117).

10.10. Paraformaldehyde. Paraformaldehyde [9002-81-7], or paraform, is a solid mixture of linear poly(oxymethylene glycols) of fairly short chain length, $HO(CH_2O)_nH$ (143) (the range of n is 8–100). The average degree of polymerization is only roughly given by the formaldehyde content. The specifications of commercial paraformaldehyde are given in Table 6 (117). Gaseous formaldehyde can be generated from paraformaldehyde by heating (144). A current process for paraformaldehyde is based on continuous, staged vacuum evaporations, starting with 50% aqueous formaldehyde (145,146).

The rate at which paraformaldehyde dissolves (hydrolyzes) in water is at a minimum pH 3–5; it increases rapidly at lower or higher pH and at higher temperatures. Once dissolved in water, paraformaldehyde behaves like methanol-free formaldehyde of the same concentration.

Paraformaldehyde 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.

10.11. Trioxane and Tetraoxane. The cyclic symmetrical trimer of formaldehyde, trioxane [110-88-3], is prepared by acid-catalyzed liquid- or vapor-phase processes (147–151). It is a colorless crystalline solid that boils at 114.5°C and melts at 61–62°C (17,152). The heats of formation are -176.9 kJ/mol (-42.28 kcal/mol) from monomeric formaldehyde and -88.7 kJ/mol (-21.19 kcal/mol) from 60% aqueous formaldehyde. It can be produced by continuous distillation of 60% aqueous formaldehyde containing 2–5% sulfuric acid. Trioxane is extracted from the distillate with benzene or methylene chloride and recovered by distillation (153) or crystallization (154). It is mainly used for the production of acetal resins (qv).

A practical synthesis has been claimed for the cyclic tetramer of formaldehyde, 1,3,5,7-tetraoxane [293-30-1], which has a boiling point of 175°C and a melting point of 112°C (155). It has found some use in textile treatment in Japan.

10.12. Other Applications. Formaldehyde is used for the manufacture of a great variety of other chemicals. Formaldehyde derivatives, such as dimethylol dihydroxyethylene, are used in textiles to produce permanent press fabrics. Other formaldehyde derivatives are used in this industry to produce fire-retardant fabrics. Pyridine chemicals, made from formaldehyde, acetaldehyde, and ammonia, are used for agricultural chemicals. 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 uses for formaldehyde and formaldehyde derivatives include fungicides, embalming fluids, silage preservatives, and disinfectants. A scavenger for reducing the amount of free formaldehyde in microbiocidal articles has been described.

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