CARBON MONOXIDE

1. Introduction

Carbon monoxide [630-08-0], CO, gaseous in normal atmospheric conditions (15°C and 101.3 kPa), is a colorless, odorless, and highly toxic gas. Lassonne discovered carbon monoxide in 1776 by heating a mixture of charcoal and zinc oxide. It was a source of heat for industrial and domestic purposes, and was used as a primary raw material in the manufacturing of German synthetic fuel during World War II.

Carbon monoxide is produced by the incomplete combustion of carbon in solid, liquid and gaseous fuels. Industrially produced carbon monoxide is used in the chemical and metallurgical industries, for the synthesis of several compounds (eg, acetic acid, polycarbonates, polyketones, etc.), and the creation of reducing atmospheres, respectively. The demand for carbon monoxide as a raw material for chemical synthesis is expected to continue a rapid growth over the next ten years.

Carbon monoxide is also a by-product of highway vehicle exhaust, which contributes about 60% of all CO emissions in the U.S. In cities, automobile exhaust can cause as much as 95% of all CO emissions. These emissions can result in high concentrations of CO, particularly in local areas with heavy traffic congestion. Other sources of CO emissions include industrial processes and fuel combustion in boilers and incinerators. Despite an overall downward trend in concentrations and emissions of CO, most U.S. metropolitan areas still experience high levels of CO. Household appliances fueled with gas, oil, kerosene, or wood may produce CO emissions that if not monitored, can accumulate to dangerous levels. In urban areas, carbon monoxide emissions are strictly controlled and monitored for CO-producing industries, commercial vehicles and private cars. The Environmental Protection Agency (EPA) is the U.S. governmental body responsible for establishing the emission standards.

2. Physical Properties

Gaseous carbon monoxide is colorless, odorless, tasteless, flammable and highly toxic (1,2). It becomes a liquid at 81.62 K. Carbon monoxide is flammable in air over a wide range of concentration: lower limit of 12.5%, and upper limit of 74% at 20°C and 101.3 kPa. Carbon monoxide is moderately soluble in water at low temperatures, and virtually insoluble above 70°C.

Selected physical properties are listed in Table 1. Solubility data are listed in Table 2.

Table 1. **Physical Properties of Carbon Monoxide**

Property	Value
mol wt	28.011
melting point, K	68.09
boiling point, K	81.65
ΔH, fusion at 68 K, kJ/mol[a]	0.837
ΔH, vaporization at 81 K, kJ/mol[a]	6.042
density at 273 K, 101.3 kPa[b], g/L	1.2501
sp gr[c], liquid, 79 K	0.814
sp gr[d], gas, 298 K	0.968
critical temperature, K	132.9
critical pressure, MPa[b]	3.496
critical density, g/cm^3	0.3010
triple point	
temperature, K	68.1
pressure, kPa[e]	15.39
ΔG° formation at 298 K, kJ/mol[a]	−137.16
ΔH° formation at 298 K, kJ/mol[a]	−110.53
S° formation at 298 K, kJ/(mol·K)[a]	0.1975
$C^\circ{}_p$ at 298 K, J/(mol · K)[a]	29.1
$C^\circ{}_v$ at 298 K, J/(mol · K)[a]	20.8
autoignition temperature, K	882
bond length, nm	0.11282
bond energy, kJ/mol[a]	1070
force constant, mN/m = (dyn/cm)	1,902,000
dipole moment, C · m[f]	0.374×10^{-30}
ionization potential, eV	14.01
flammability limits in air[g]	
upper limit, %	74.2
lower limit, %	12.5

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

[b] 101.3 kPa = 1 atm; to convert MPa to atm, multiply by 9.87.

[c] With respect to water at 277 K.

[d] With respect to air at 298 K.

[e] To convert kPa to torr, multiply by 7.5.

[f] To convert C · m to debye, multiply by 2.99×10^{29}.

[g] Saturated with water vapor at 290 K.

Table 2. **Aqueous Solubility of CO at STP, L/L**

Temperature, °C	Bensen coefficient
0	0.03516
5	0.03122
10	0.02782
15	0.02501
20	0.02266
25	0.02076
30	0.01915
40	0.01647
50	0.01420
60	0.01197
70	0.00998
80	0.00762
90	0.00438

3. Chemical Properties

Chemically, carbon monoxide is stable with respect to decomposition (1). The bond energy of 1070 kJ/mol is illustrative of the triple bond configuration described molecular by orbital theory and is the highest observed bond energy for any diatomic molecule. At temperatures of 310–500°C, CO reduces many metal oxides to lower metal oxides, or metals, or produces metal carbides. Carbon monoxide absorbs at 2143 cm^{-1} in the infrared spectrum. The bonding between CO and transition metal atoms weakens the C–O bond, thus allowing the metal bonded CO to react more readily. Carbon monoxide is a reducing agent that reacts with oxidizers and salts such as iodic anhydride, palladium salts, and red mercuric oxide. Catalytic reduction of carbon monoxide produces methane. Catalytic oxidation of carbon monoxide leads to carbon dioxide. Carbon monoxide reacts violently with oxygen difluoride, chlorine produced by phosgene decomposition, and barium peroxide. Hydrogenation of carbon monoxide yields products that vary with catalysts and conditions: methane, benzene, olefins, paraffin waxes, hydrocarbon high polymers, methanol, higher alcohols, ethylene glycol, glycerol, have all been produced.

3.1. Metal Compatibility.

Carbon monoxide is compatible with all commonly used metals at pressures below 3.5 MPa. However, at higher pressures, carbon monoxide reacts with nickel, iron, cobalt, manganese, chromium and gold, to form small quantities of metal carbonyls, which are unstable and highly toxic. The following metals and alloys may be employed with carbon monoxide under pressure: carbon steels up to 10 MPa, aluminum alloys, copper and copper alloys, low carbon stainless steel, and nickel-base alloys. The presence of moisture and sulfur-containing impurities in carbon monoxide increases its corrosive action on steel at any pressure (2). High-pressure plant equipment is often lined with copper for increased resistance to carbon monoxide attack.

3.2. Refractory Material Compatibility.

Table 3 gives the behavior of refractory materials likely to be employed in high temperature furnaces.

Table 3. **Compatibility of Refractory Materials with Carbon Monoxide**

Material	Compatibility[a]
magnesia	A
zircon	A
bonded alumina	A
fused cast alumina	A
bubble alumina	A
stabilized zirconia	silicon carbide A: $t < 810°C$; B: $t > 1150°C$
silicon nitrite + silicon carbide	A: $t < 810°C$; B: $t > 1150°C$
magnesite	B–C
fosterite	A
synthetic mullite	A
converted mullite	B–C
silica	A
superduty fireclay	A

[a] A = no reaction, material satisfactory; B = slight reaction, material generally satisfactory; and C = reaction, material satisfactory in certain cases.

Table 4. **Compatibility of Elastomers and Plastics with Carbon Monoxide**

Material	Compatibility[a]
Teflon	A
natural rubber	C
neoprene	C
Hypalon	B
butyl rubber	C
Kel-F	A
Buna N	C

[a] A = good resistance; B = fair resistance; and C = poor resistance.

3.3. Compatibility with Elastomers and Plastics. The chemical resistance of certain elastomers and plastics to carbon monoxide is given in Table 4.

4. Reactions

4.1. Industrially Significant Reactions of Carbon Monoxide.

Reppe Chemistry. Chemicals including acetic acid, acetic anhydride, formic acid, propionic acid, dimethyl carbonate, and methyl methacrylate are examples of final products derived from Reppe chemistry (3–6).

Acetic Acid. Acetic acid is synthesized by carbonylation of methanol by the following reaction:

$$CH_3OH + CO \xrightarrow{\text{catalyst}} CH_3COOH \qquad (1)$$

The catalyst can be cobalt iodide, rhodium iodide, or iridium iodide. Other syntheses can be used to manufacture acetic acid, such as oxidation of *n*-butane or naphtha, oxidation of acetaldehyde, and terephthalic acid coproduct. However, methanol carbonylation has been the preferred process for new capacity over the last ten years because of its favorable raw material (methanol) and energy costs. The CO purity required for methanol carbonylation is in the range of 98 to 99% pure, with low concentrations of methane, hydrogen, nitrogen and argon. The feed pressure of CO in the reactor is approximately 35 MPa The primary use for acetic acid is feedstock for the production of vinyl acetate monomer (VAM). It is also a solvent for the air-based oxidation of *p*-xylene to terephthalic acid (see also ACETIC ACID AND DERIVATIVES).

Acetic Anhydride. Acetic anhydride is the largest commercially produced carboxylic acid anhydride. Its main industrial application is for acetylation reactions. Over 85% of acetic anhydride production goes into cellulose acetate flake, which is in turn used to make filament yarn, cigarette paper and cellulose ester plastics. Eastman Chemical also uses it as an intermediate to make photographic film base, Tenite cellulose plastics, textile chemicals, and coating chemicals. Acetic anhydride (qv) can be made by carbonylation of methyl acetate, by methanol carbonylation, as follows:

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O \tag{2}$$

$$CO + CH_3COOCH_3 \longrightarrow (CH_3CO)_2O \tag{3}$$

The catalyst system is rhodium and iodide complexes and chromium metal powder on an alumina support.

The CO feed for equation 3 must be anhydrous, of high purity, and pressured at 15–18 MPa.

Vinyl Acetate Monomer (VAM). VAM is currently the most important vinyl ester. It is used mainly for the production of polymers and copolymers for paints, adhesives, textiles, and for the production of poly(vinyl alcohol), and poly(vinylbutyral). VAM can be produced by reacting methyl acetate with CO and hydrogen:

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O \tag{2}$$

$$2\ CH_3COOCH_3 + 2\ CO + H_2 \longrightarrow CH_3CH(OOC{-\!\!-}CH_3)_2 + CH_3COOH \tag{4}$$

$$CH_3CH(OOC{-\!\!-}CH_3)_2 \longrightarrow CH_3COOCH{=\!\!=}CH_2 + CH_3COOH \tag{5}$$

Although viable, this synthetic method has not yet been used in industrial applications. It could become more attractive depending on future raw material prices.

Formic Acid. Formic acid like acetic acid, is produced by methanol carbonylation followed by methyl formate hydrolysis:

$$CO + CH_3OH \longrightarrow HCOOCH_3 \tag{6}$$

$$HCOOCH_3 + H_2O \longrightarrow HCOOCH + CH_3OH \tag{7}$$

Carbon monoxide specifications for this reaction is typically 98% pure, with low levels of methane, hydrogen, chlorine, nitrogen, and a very low sulfur content of less than 1 ppm. The CO feed pressure in the reactor is around 1.5 MPa. Formic acid is a medium volume commodity chemical that has a variety of applications, including processing of natural rubber, textile finishing, production of dyes, flavors and fragrances, and as a chemical intermediate (see FORMIC ACID AND DERIVATIVES).

Propionic Acid. Propionic acid is used in the production of cellulose esters, plastic dispersions, herbicides, and to a limited extent in pharmaceuticals, and in flavors and fragrances. It is gaining importance for the preservation of forage cereals, and animal feeds because many putrefying and mold-forming micro-organisms cannot survive in its presence. Propionic acid can be commercially produced by carbonylation of ethylene, a one-step Reppe process catalyzed with nickel propionate ($Ni(CO)_4$), at 300°C and 22 MPa.

$$CO + H_2C{=}CH_2 + H_2O \longrightarrow CH_3CH_2COOH \qquad (8)$$

Dimethyl Carbonate (DMC). DMC is an extremely versatile chemical. It is used as an organic solvent, additive for fuels, reagent, as a substitute for phosgene, and in the synthesis of other alkyl or aryl carbonates used as synthetic lubricants, solvents, and in methylation and carbonylation reactions for the preparation of isocyanates, urethanes, and polycarbonates. DMC can be commercially produced by oxycarbonylation of methanol catalyzed by copper salts at 150 °C and 1–5 MPa.

$$CO + CH_3OH + \frac{1}{2}O_2 \longrightarrow (CH_3O)_2CO + H_2O \qquad (9)$$

Methyl Methacrylate (MMA). MMA polymerizes to form a clear plastic that has excellent transparency, strength, and outdoor durability. The automotive and construction markets create the largest demand for acrylic sheet. It is also used in the manufacturing of acrylic paints, including latex paints, and lacquers. MMA can be commercially produced from acetone, methanol and high purity CO (99.8%) at approximately 4 MPa.

Koch Carbonylation. The Koch carbonylation is of an olefin in a two-stage reaction. Two main categories of compounds fall under the Koch carbonylation: trialkylacetic acids (monoacids from olefins), and adipic acid (two acidic functions from carbonylation of α-diene) (7).

Trialkylacetic Acids. The lowest member of the series $R{=}R'{=}R''{=}CH_3$ is the C5 acid, trimethylacetic acid, also called neopentanoic acid or pivalic acid. The principal commercial products are the C5 acid and the C10 acid (also known as Exxon's neodecanoic acid, or Shell's Versatic 10). The trialkylacetic acids have a number of uses in areas such as polymers, pharmaceuticals, agricultural chemicals, cosmetics, and metal-working fluids. Commercially important derivatives of these acids include acid chlorides, peroxyesters, metal salts, vinyl esters and glycidyl esters. Pivalic acid (C5), for example, is prepared via Koch's reaction:

$$(CH_3)_2{-}C{=}CH_2 \longrightarrow (CH_3)_3{-}C^+ \qquad (10)$$

where the strong acid catalyst is either a Bronsted acid (H_2SO_4, H_3PO_4, HF), or a Lewis acid such as BF_3.

$$(CH_3)_3\text{—}C^+ + CO \longrightarrow (CH_3)_3\text{—}C\text{—}CO^+ \qquad (11)$$

$$(CH_3)_3\text{—}C\text{—}CO^+ + H_2O \longrightarrow (CH_3)_3\text{—}C\text{—}COOH + H^+ \qquad (12)$$

The C10 tryalkylacetic acid is manufactured using the same process and catalysts. For the C10 acids, a branched C9 olefin is typically used. The resulting C10 acid is typically a mixture of isomers due to chemical rearrangement, olefin dimerization, and oligomerization (see also CARBOXYLIC ACIDS, TRIALKYLACETIC ACIDS).

Adipic Acid. Adipic acid, also known as hexanedioic acid, is the most significant commercially of all the aliphatic dicarboxylic acids. Appearing in nature in only minor amounts, it is synthesized on a very large scale worldwide. The principal use of adipic acid is to produce nylon 6/6, a linear polyamide made by condensing adipic acid with hexamethylene diamine, HMDA. The market for nylon 6/6 is predominantly in fibers. The other uses of adipic acid are in plasticizers, unsaturated polyesters, and polyester polyols (for polyurethane resins). Adipic acid can be synthesized by carbonylation of 1,3-butadiene. This process is attractive from a raw material cost, but requires high operating CO pressure (see also ADIPIC ACID).

Phosgenation. *Phosgene.* Phosgene is an inorganic, intermediate produced by the catalytic reaction of chlorine and carbon monoxide (8). It is a gaseous product, that cannot be stored or conveniently shipped owing to its extreme toxicity. As a result, it is usually produced on demand for intermediate use. Phosgene is an important starting compound in the production of intermediates and end-product in many branches of large-scale industrial chemistry. Most phosgene (80%) is used for the production of diisocyanates. The next largest phosgene application is the production of polycarbonates. The commercial production of phosgene is by the following reaction:

$$CO + Cl_2 \longrightarrow COCl_2 \qquad (13)$$

an activated carbon catalyst is used. This reaction is strongly exothermic. Because of toxicity and corrosiveness of phosgene product, strict and extensive safety procedures are incorporated in plant and operation design. CO purity requirements for this reaction vary considerably depending on the end-products. However, a low content in methane and hydrogen is always required for safety reasons to prevent spontaneous exothermic HCl formation when mixing CO and chlorine. Typically, low sulfur impurities (COS, $CSCl_2$) are also required, as those compounds affect the quality of the end-products.

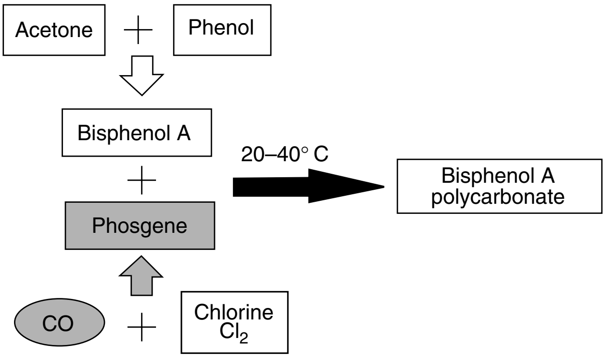
Diisocyanates. Diisocyanates, including toluene diisocyanate (TDI) and 4,4′-methylene diphenyl diisocyanate (MDI), have become large-volume raw materials for addition polymers, such as polyurethanes, polyureas, and polyisocyanurates. By varying the reactants (isocyanates, polyols, polyamines, and others) for polymer formation, a myriad of products have been developed ranging from flexible and rigid insulation foams to the high modulus automotive exterior parts to high quality coatings and abrasion-resistant elastomers unmatched by any other polymeric material. The most common method of preparing isocyanates on a commercial scale is the reaction of phosgene and aromatic or aliphatic amine precursors. The overall reaction is shown below:

$$\mathrm{R{-}NH_2 + COCl_2 \longrightarrow R{-}NHCOCl + HCl} \tag{14}$$

$$\mathrm{R{-}NHCOCl \longrightarrow R{-}N{=}C{=}O + HCl} \tag{15}$$

Nonphosgene routes to isocyanate production have been developed, but none has been commercialized. The term nonphosgene route is primarily used in conjunction with the conversion of amines to isocyanates via the use of carboxylation agents. These approaches are becoming more attractive to the chemical industry as environmental or toxicological restrictions involving chlorine or phosgene are increasingly enforced.

Polycarbonates. Polycarbonates are an unusual and extremely useful class of polymers. The vast majority of polycarbonates (qv) are based on bisphenol A (BPA). The economically most important polycarbonate is the Bisphenol A



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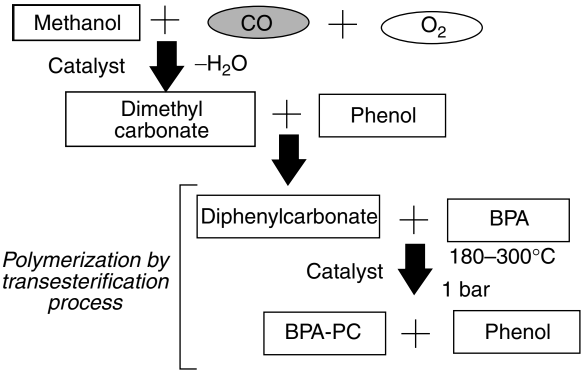

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Fig. 1. Polycarbonate production by the phosgene route (eq. 16) and by the base-catalyzed transesterification of a bisphenol (eq. 17).

polycarbonate (BPA–PC). Its great commercial success is owing to its unique combination of properties: extreme toughness, outstanding transparency, excellent compatibility with several polymers, and high heat distortion resistance. Some of its main uses include coatings, films, fibers, resin for shatterproof windows, computer housings, tape reel housings, gas meter covers, lenses for automobiles and appliances, and pipe. Polycarbonates can be commercially produced by the Schotten-Bauman reaction (interfacial polycondensation): the phosgene route (eq. 16) (Fig. 1) or by base-catalyzed transesterification of a bisphenol with a monomeric carbonate (eq. 17) (Fig. 1).

Ethylene–CO Copolymers or Polyketones. These compounds are defined as polymers with 1:1 molar ratio of carbon monoxide to ethylene (9). Carilon was the first polyketone commercially produced by Shell Chemicals in 1995: it is a new family of polymers called aliphatic polyketone, and results from the polymerization of perfectly alternating structures of CO and olefins (such as ethylene). The product's great strength lies in its broad range of high performance characteristics, allied with its ease of processing. It has a number of properties which make it ideally suited for use in the automotive sector, including: superior energy absorption capacity, dimensional stability at elevated temperature, good impact resistance over a broad temperature range, insensitivity to moisture, and excellent resistance to automotive fuels and their vapors. The polymerization is catalyzed by a single-site late transition-metal (ie, palladium) as follows:

$$CH_2{=}CH_2 + CO \longrightarrow \text{—}(\text{—}CH_2CH_2C\text{—})_x\text{—}\ \text{—}(\text{—}CH_2CH_2\text{—})_y\text{—} \qquad (18)$$

4.2. General Reactions of Carbon Monoxide. *With Hydrogen.* In addition to the reactions already discussed, other products may be obtained from synthesis gas depending on the catalyst used. In a liquid-phase high pressure reaction (60 MPa or 600 atm), a rhodium cluster complex catalyzes the direct formation of ethylene glycol, propylene glycol (see Glycols), and glycerol (qv) from synthesis gas (eq. 19) (10). Mixtures of methanol, ethanol (11), acetaldehyde, and acetic acid (12) are formed by using supported rhodium catalysts at 598 K and 17 MPa (168 atm). Rates of reaction for this latter route appear to be too slow for commercial application.

$$2\ CO + 3\ H_2 \longrightarrow HOCH_2CH_2OH \qquad (19)$$

With Alcohols, Ethers, and Esters. Carbon monoxide reacts with alcohols, ethers, and esters to give carboxylic acids. The reaction yielding carboxylic acids is general for alkyl (13) and aryl alcohols (14). It is catalyzed by rhodium or cobalt in the presence of iodide and provides the basis for a commercial process to acetic acid.

Strong base catalyzes the formation of derivatives of formic acid in the reaction between alcohols and carbon monoxide (15). Methyl formate is made at 443–463 K and 1–2 MPa (10–20 atm) (eq. 20).

$$CH_3OH + CO \xrightarrow{NaOH} HCOOCH_3 \qquad (20)$$

Methanol reacts with carbon monoxide and hydrogen to form ethanol in the homologation reaction. Cobalt carbonyl catalyzes the transformation at 473 K and 30 MPa (300 atm) pressure, and gives yields of less than 75% ethanol. The greatest activity in the homologation reaction is observed for methyl and benzyl alcohols (eq. 21) (16). Reaction between methyl acetate, carbon monoxide, and hydrogen at 408–433 K and up to 10 MPa (100 atm) pressure using a palladium or rhodium iodide catalyst leads to the production of ethylidene diacetate (17) (eq. 22). Ethylidene diacetate can be pyrolyzed to vinyl acetate (eq. 23).

$$CH_3OH + CO + 2\,H_2 \longrightarrow C_2H_5OH + H_2O \tag{21}$$

$$2\,CH_3COOCH_3 + 2\,CO + H_2 \longrightarrow CH_3CH(OOCCH_3)_2 + CH_3COOH \tag{22}$$

$$CH_3CH(OOCCH_3)_2 \longrightarrow CH_2 = CHOOCCH_3 + CH_3COOH \tag{23}$$

With Formaldehyde. The sulfuric acid catalyzed reaction of formaldehyde with carbon monoxide and water to glycolic acid at 473 K and 70 MPa (700 atm) pressure was the first step in an early process to manufacture ethylene glycol. A patent (18) has described the use of liquid hydrogen fluoride as catalyst, enabling the reaction to be carried out at 298 K and 7 MPa (70 atm) (eq. 24).

$$HCHO + CO + H_2O \longrightarrow HOCH_2COOH \tag{24}$$

With Unsaturated Compounds. The reaction of unsaturated organic compounds with carbon monoxide and molecules containing an active hydrogen atom leads to a variety of interesting organic products. The hydroformylation reaction is the most important member of this class of reactions. When the hydroformylation reaction of ethylene takes place in an aqueous medium, diethyl ketone is obtained as the principal product instead of propionaldehyde (19). Ethylene, carbon monoxide, and water also yield propionic acid under mild conditions (448–468 K and 3–7 MPa or 30−70 atm) using cobalt or rhodium catalysts containing bromide or iodide (20,21).

Carbon monoxide also reacts with olefins such as ethylene to produce high molecular weight polymers. The reaction of CO with ethylene can be initiated by an x-ray irradiator (22) or transition-metal catalyzed reactions (23). The copolymerization of ethylene with carbon monoxide is catalyzed by cationic Pd (II) complexes such as $\{Pd[P(C_6H_5)_3]_n(CH_3CN)_{4-n}\}(BF_4)_2$ where $n = 1–3$. With this catalyst, copolymerization can be carried out at 25°C and pressures as low as 2.1 MPa.

Oxidative Carbonylation. Carbon monoxide is rapidly oxidized to carbon dioxide; however, under proper conditions, carbon monoxide and oxygen react with organic molecules to form carboxylic acids or esters. With olefins, unsaturated carboxylic acids are produced, whereas alcohols yield esters of carbonic or oxalic acid. The formation of acrylic and methacrylic acid is carried out in the liquid phase at 10 MPa (100 atm) and 110°C using palladium chloride or rhenium chloride catalysts (eq. 25) (24,25).

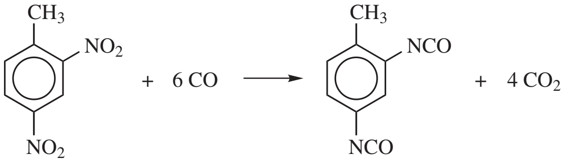
$$CH_2{=}CH_2 + CO + \frac{1}{2}\,O_2 \longrightarrow CH_2 = CHCOOH \tag{25}$$

Dimethyl carbonate and dimethyl oxalate are both obtained from carbon monoxide, oxygen, and methanol at 363 K and 10 MPa (100 atm) or less. The choice of catalyst is critical; cuprous chloride (26) gives the carbonate (eq. 26); a palladium chloride–copper chloride mixture (27,28) gives the oxalate, (eq. 27). Anhydrous conditions should be maintained by removing product water to minimize the formation of by-product carbon dioxide.

$$2\,CH_3OH + CO + \frac{1}{2}\,O_2 \longrightarrow (CH_3O)_2CO + H_2O \tag{26}$$

$$2\,CH_3OH + 2\,CO + \frac{1}{2}\,O_2 \longrightarrow CH_3O_2C\text{—}CO_2CH_3 + H_2O \tag{27}$$

Isocyanate Synthesis. In the presence of a catalyst, nitroaromatic compounds can be converted into isocyanates, using carbon monoxide as a reducing agent. Conversion of dinitrotoluene into toluenediisocyanate (TDI) with carbon monoxide (eq. 28), could offer significant commercial advantages over the current process using phosgene. The reaction is carried out at 473–523 K and 27–41 MPa (270–400 atm) with a catalyst consisting of either palladium chloride or rhodium chloride complexed with pyridine, isoquinoline, or quinoline and yields are in excess of 80% TDI (29,30).



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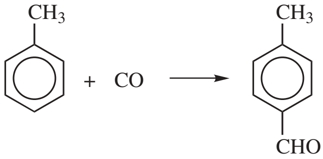
Dimethylformamide. The industrial solvent dimethylformamide is manufactured by the reaction between carbon monoxide and dimethylamine.

$$(CH_3)_2NH + CO \longrightarrow (CH_3)_2NCHO \tag{29}$$

The reaction is carried out in the liquid phase using a sodium methoxide catalyst at 60–130°C and 0.5–0.9 MPa (5–9 atm) (31).

Aromatic Aldehydes. Carbon monoxide reacts with aromatic hydrocarbons or aryl halides to yield aromatic aldehydes (see ALDEHYDES). The reaction of equation 24 proceeds with yields of 89% when carried out at 273 K and 0.4 MPa (4 atm) using a boron trifluoride–hydrogen fluoride catalyst (32), whereas conversion of aryl halides to aldehydes in 84% yield by reaction with CO + H_2 requires conditions of 423 K and 7 MPa (70 atm) with a homogeneous palladium catalyst (33) and also produces HCl.



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Metal Carbonyls. Carbon monoxide forms metal carbonyls or metal carbonyl derivatives with most transition metals (34) (see COORDINATION COMPOUNDS). Metal carbonyls are used in a variety of industrial applications in addition to their use as catalysts. Methylcyclopentadienylmanganesetricarbonyl (MMT), [$CH_3C_5H_4Mn(CO)_3$] was sold as an antiknock additive, but its use in unleaded gasoline was banned by the Environmental Protection Agency (EPA) in 1978; tungsten and molybdenum hexacarbonyls are thermally decomposed to obtain very pure metal films; and numerous carbonyls are used as reagents in organic synthesis (see CARBONYLS).

5. Manufacture

Commercial carbon monoxide is a co-product, along with hydrogen, of synthetic gas (syngas) production. Several technologies, based on steam reforming or partial oxidation processes, are used to produce syngas, with a hydrogen-to-carbon monoxide mole ratio varying from 2 to 0. A ratio of 2 indicates that two parts hydrogen are produced for one part of carbon mononoxide; a ratio of zero indicates pure carbon monoxide without hydrogen. The principal components of the resulting syngas, hydrogen and carbon monoxide are then separated and purified by pressure swing adsorption and/or cryogenic distillation. The purity of the final carbon monoxide product typically ranges from 97% to 99.9% (35). The nature and level of the impurities remaining in the final carbon monoxide product are usually more critical than the total purity for chemical synthesis applications.

5.1. Syngas Technologies.

The principal technologies employed today to produce syngasare (*1*) steam methane reforming, (*2*) naphtha reforming, (*3*) autothermal reforming, (*4*) oxygen secondary reforming, (*5*) partial oxidation of hydrocarbons, petroleum coke and coal, and (*6*) reverse shift of hydrogen and carbon dioxide (36–39).

Steam Methane Reforming. This process involves the catalyzed reaction of steam and methane to yield a mixture of carbon monoxide, hydrogen, and carbon dioxide. The chemical reactions are as follows:

$$CH_4 + H_2O \Longleftrightarrow CO + 3\,H_2 \tag{31}$$

$$CO + H_2O \Longleftrightarrow CO_2 + H_2 \tag{32}$$

Equation 31 is the reforming reaction at 900°C, 3 MPa using a nickel-based catalyst. Equation 32 is the water-shift reaction. The reforming reaction is endothermic and takes place in a primary reforming furnace. The water-shift reaction takes place in a separate reformer, and can be eliminated if a CO-rich mixture is required. The typical hydrogen to carbon monoxide ratio for this technology varies from 3 to 4.9, thus producing a hydrogen-rich stream. Table 5 illustrates typical reformer furnace (890°C, 2.4 MPa) outlet syngas composition.

Naphtha Reforming. This process substitutes naphtha for methane in the reformer. This process presents the advantage of higher hydrogen to carbon monoxide feed content; thus resulting in lower hydrogen to CO rates.

Table 5. **Typical Reformer Furnace Outlet Syngas Composition**

Component	Concentration, vol %
hydrogen	51.0
carbon monoxide	10.4
carbon dioxide	5.0
methane	2.0
water vapor	31.6

Autothermal Reforming. This process is a combination of partial oxidation and steam reforming in one reactor. The exothermic heat of reaction of the partial oxidation of the hydrocarbon feedstock provides the energy required for the (endothermic) steam methane reforming reaction to take place. The chemical reactions taking place in an autothermal reactor are as follows:

In the catalytic steam-reforming zone: reforming (eq. 31) and water-shift (eq. 32) reactions using a nickel catalyst.

In the combustion zone (ca 1,200 °C):

$$C_nH_m + n/2\ O_2 \ \Rightarrow\ n\ CO + m/2\ H_2 \tag{33}$$

$$CH_4 + \frac{1}{2}\ O_2 \ \Rightarrow\ CO + 2\ H_2 \tag{34}$$

$$H_2 + \frac{1}{2}\ O_2 \ \Rightarrow\ H_2O \tag{35}$$

$$CO + \frac{1}{2}\ O_2 \ \Rightarrow\ CO_2 \tag{36}$$

In the steam-reforming zone:

$$CH_4 + H_2O \iff CO + 3\ H_2 \tag{37}$$

$$CO + H_2O \iff CO_2 + H_2 \tag{38}$$

Some of the benefits of autothermal reforming are that no external feed is required, there is flexibility in feedstock selection (from methane-rich natural gas to naphtha), and the ability to produce syngas with low hydrogen to CO ratios. Typically, capital investment for autothermal reforming is lower than for steam reforming. However, operating costs are similar to slightly higher due to the added cost of pure oxygen.

Oxygen Secondary Reforming. This process is a conventional steam methane reformer with a secondary reformer reactor and direct-contact water quench downstream of the primary reactor. Pure oxygen is introduced in the secondary reactor to produce CO-rich syngas. The heavier the hydrocarbon feedstock, the lower the hydrogen to CO ratio.

Partial Oxidation. This process is the nonscatalytic reaction of hydrocarbons, petroleum, coke or coal with steam and oxygen at a high temperature and pressure to produce syngas. The hydrogen to CO ratio depends on the carbon to hydrogen ratio of feedstock. Reactions in partial oxidation are extremely complex. Simplistically, thermal cracking at high temperatures in the reactor produce lowmolecular-weight hydrocarbon fragments. The fragments then react with pure oxygen follows:

$$CH + 1/2\,O_2 \;\Rightarrow\; CO + 1/2\,H_2 \tag{39}$$

Additionally, many of the hydrocarbon fragments are completely oxidized to carbon dioxide and water as follows:

$$CH + 5/4\,O_2 \;\Rightarrow\; CO_2 + 1/2\,H_2O \tag{40}$$

Concurrently, the reversible water-gas shift reaction (eq. 32) takes place, but is incomplete as oxygen is less than stoichiometric, leading to a maximum carbon dioxide content of 2 vol% in the reactor effluent. Reactions 32 and 40 are highly exothermic.

The typical reactor temperature is 1250–1500°C and the pressure is between 2.5 and 8 MPa. For heavy hydrocarbon feedstock, a temperature moderator such as carbon dioxide or steam must be used to control the reactor temperature and adjust the hydrogen to CO ratio. Reactor effluent contains carbon monoxide, hydrogen, carbon dioxide (from the water-gas shift reaction), steam, and trace amounts of argon and nitrogen, which enter the system with the oxygen feedstock. If the hydrocarbon feed contains sulfur, hydrogen sulfide and carbonyl sulfide appears in the raw syngas. The high temperature and highly reducing atmosphere in the reactor prevent the formation of NOx and SOx.

The partial oxidation process presents great flexibility with respect to the feedstock (from natural gas to petroleum residue and petroleum coke), as well as the advantage of producing minimal gaseous emissions of NOx and SOx. However, both capital investment and operating costs are high for this process, which makes it prohibitively expensive for light feedstock, from natural gas to naphtha.

Reverse Shift of Hydrogen and Carbon Dioxide. This process uses the reverse water-gas shift reaction:

$$CO_2 + H_2 \;\Longleftrightarrow\; H_2O + CO \tag{41}$$

This reaction can be carried out in: (*1*) a conventional primary reformer with a nickel based reforming catalyst at a furnace outlet temperature of 950°C and 1.4 MPa pressure; (*2*) a simple catalyst-filled reactor that takes advantage of the exothermic methanation reaction to provide the heat needed to drive the simultaneous reverse shift reaction. The down sides of each type of reactor are respectively: (*1*) a fuel stream is required to supply heat to the reaction, and produces export steam; (*2*) methane is a by-product in the syngas effluent. In either case, the production of CO by reverse water-shift reaction requires a large, low-cost source of hydrogen and carbon dioxide feedstock. High purity carbon dioxide is available from ethylene oxide and vinyl acetate monomer units. However, the carbon dioxide produced by these two processes is only available at low pressure and must be compressed for use as feedstock in the reverse-shift process. Typically, the reverse-shift process is not a primary source of carbon monoxide, but rather a supplemental syngas production process that allows petrochemical complexes to adjust the hydrogen to CO ratio to a required level.

5.2. Purification Technologies. All sources of CO are essentially gas mixtures with two primary components, hydrocarbon and CO, as well as other gases including nitrogen, carbon dioxide, methane, and moisture. Purification of carbon monoxide from the syngas effluent is therefore required prior to being used in applications such as organic synthesis. The cost of separation of CO or H_2 contributes significantly to the total production cost of high purity CO. Purification techniques fall into four main categories: cryogenic processes, adsorption process, membrane, and liquid absorption processes (40–44). The choice of the most attractive process is based on the feed conditions, and the final product specifications.

Cryogenic Processes. These processes essentially consist of liquefaction of part of the fuel stream, followed by a phase separation and distillation of the remaining liquid components. In general cryogenic processes are suitable for large capacity high purity CO plants where the nitrogen content of the purified CO stream is tolerated by the downstream application. This method is the oldest, and two principal methods can be used in large-scale processes depending on the required purity: partial condensation cycle; methane wash cycle.

Partial Condensation. Partial condensation allows the liquefaction of CO and methane in several cooling steps, leaving a residual gas stream containing approximately 98% hydrogen and 1 to 2% CO. The liquid phase CO, containing methane and hydrogen impurities is then flashed and distilled to produce a high purity CO stream along with a CO–methane fuel stream. Nitrogen present in the feed remains in the purified hydrogen and CO streams, with a majority staying in the CO product. Figure 2 illustrates a typical process flow schematic.

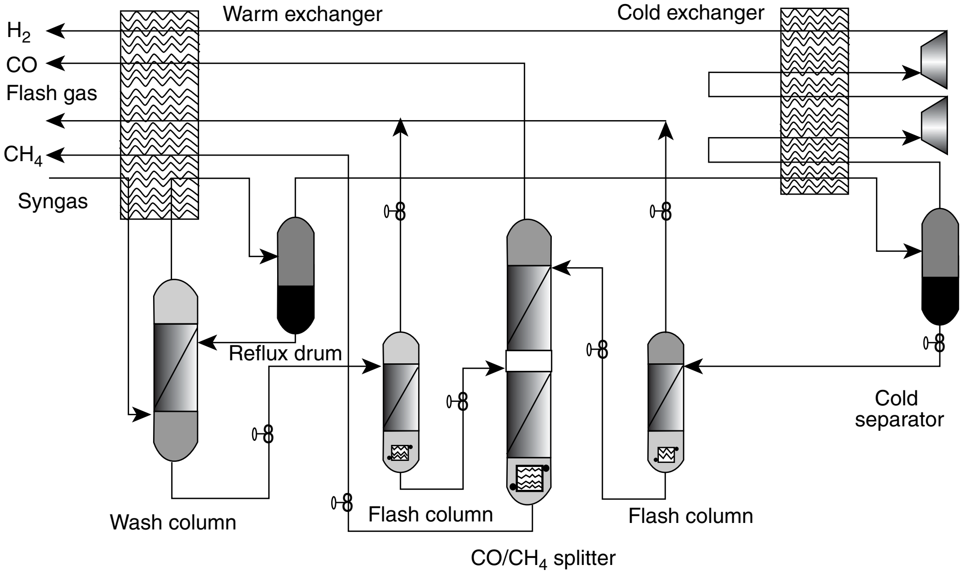

Fig. 2. Process flow schematic for CO/H_2 separation by partial condensation.

The feed gas is compressed and dried to remove residual water and carbon dioxide (that would otherwise freeze in the cold box). The feed gas is cooled against the product stream in the warm exchanger and used to provide heat to the re-boiler of the CO–methane splitter column. Liquid CO and methane are removed in the wash column. Vapor from the wash column is further cooled in the cold exchange. Most of the remaining CO is condensed in the cold exchanger and separated in the cold separator. The final product purity is critically dependent upon the temperature reached at this step. The liquid from the cold separator is a high-purity CO stream used to reflux the CO–methane splitter column. Liquid from the wash column is flashed in the flash column to remove dissolved hydrogen. The vapor from the wash column is rewarmed, compressed and recycled to the feed to recover the contained CO. The liquid from the flash column is directed to the CO–methane column. The CO overhead is rewarmed and recovered as product. The CO–methane liquid is rewarmed and is then available as reformer fuel. Hydrogen from the cold separator is warmed in the cold exchanger and expanded to provide refrigeration for the cycle. Rewarmed in the cold and warm exchangers, hydrogen exits the process at 97–98% purity. The partial condensation is process of choice with high-pressure feed, high H_2/CO ratio, and low hydrogen product purity and pressure requirements.

Methane Wash Cycle. This cycle uses liquid methane to absorb CO from the feed, resulting in a hydrogen stream containing parts per million of CO but 2 to 3% methane. A process flow schematic is presented in Figure 3.

The feed gas is purified by adsorption to remove residual carbon dioxide and water, cooled in the main exchanger and fed to the bottom of the wash column. The column is refluxed with liquid methane to produce a hydrogen stream containing parts per million of CO but saturated with methane (2–3%). The liquid stream from the wash column is preheated and flashed to the flash column where

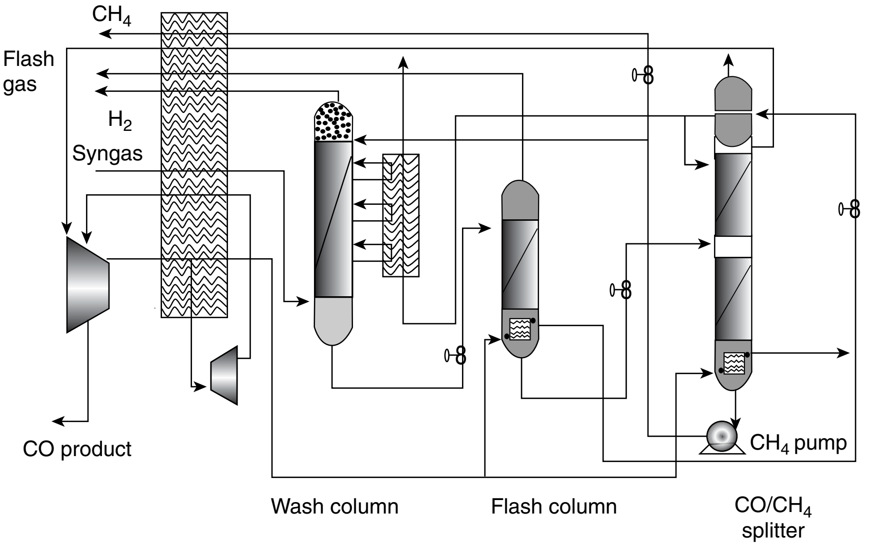

Fig. 3. Process flow schematic CO/H_2 separation by methane wash.

hydrogen dissolved in methane is rejected for use as fuel. To minimize CO losses, the flash column is also refluxed with liquid methane. The hydrogen-free liquid from the flash column is then heated and flashed to the CO−methane splitter column. The CO overhead from the column is rewarmed and compressed. Part of this gaseous stream of CO leaves the process as product, the remainder is cooled and used to reboil the splitter column and preheat the column feeds before being flashed for refrigeration with the liquid used as reflux to the sputter column. The liquid methane from the sputter column is pumped to the wash and flash columns, the excess being vaporized for fuel. The process refrigeration is provided by liquid nitrogen evaporation or by a nitrogen or CO turboexpander recycle system. Methane wash is the process of choice with low feed pressure, low H_2/CO ratio, and a high hydrogen purity with respect to CO.

Removal of nitrogen from the CO stream requires an additional column and cryogenic distillation step. Separation of nitrogen and CO by cryogenic process is difficult as the difference in their boiling point is only 6°C.

Adsorption Process. Also known as vacuum swing adsorption (VSA), the adsorption process is suited to the production of high purity product with a high yield of CO. Adsorption is the binding of molecules from a gaseous phase to the surface of a solid (the adsorbent). Physical forces that are dictated by the type of molecules and the characteristics of the solid cause this binding. Generally, the adsorbent load capacity increases with the partial pressure of the gas component and with a decreasing temperature. The process consists of passing the syngas mixture (H_2/CO) sequentially through first and second adsorptive beds, each of which adsorbs H_2 more readily than CO. Typically, a minimum of three adsorptive beds are used, as the process involves three cyclical steps: production (selective adsorption), regeneration of the adsorber (evacuation of the adsorbed gas), and repressurization of the bed with a portion of the purified stream. The number of beds is increased for higher flow rates or higher CO recovery rates. In general, CO-selective absorbents are available to only a very limited extent. Sodium-type mordenite active-carbon-supported carbon and activated carbon are the most common absorbents. Active carbon copper is a chemical absorbent based on the selective binding capability of Cu^+ to CO. Several adsorbents consisting of porous carriers, such as activated carbon or zeolite, and supported Cu^+, have been developed for CO adsorption. These adsorbents exhibit selectivity for CO; however, their adsorption capacities and selectivity depends significantly on the properties of the carrier. Sample performance data of a commercial VSA plant for recovery of CO is pesented in Table 6. The VSA cycle yield decreases as the desired CO purity is increased.

Table 6. **Example of Operating Performance of a CO VSA Plant**

Feed gas components	Concentration, (%)	Purified CO stream
H_2	2	flow rate: 150 Nm^3/h
CO	68	purity: 99−99.9%
CO_2	16	yield: 80−90%
N_2	13	
O_2+ Ar	1	

Membrane Processes. Membrane gas separation was first introduced in the mid-1970s. The first application of membrane processes in syngas separation was to adjust the H_2/CO ratio of natural gas-reformed syngas using the PRISM polysulfone separator (45). A membrane system selectively removes hydrogen and moisture from a compressed syngas feed, leaving a carbon monoxide rich stream as the primary product. This separation is accomplished utilizing hollow fiber polymeric membranes housed in modules with no moving parts. An individual fiber is about the size of a human hair (approximately 0.1 mm in diameter) and each module houses thousands of these fibers. Syngas molecules fed under pressure to the center of the hollow fibers partially dissolve in the polymeric membrane material, diffuse to the low pressure side outside of the fibers, and desorb at the lower pressure. Each component in the syngas stream dissolves in the polymer to a different extent and permeates at a different rate. "Fast" components with a high permeation rate, such as hydrogen and moisture, diffuse through the membrane, flow out through the hollow fiber interior and are channeled into the residue stream. "Slow" molecules, such as carbon monoxide, methane, carbon dioxide, and nitrogen, are held in the high-pressure stream, flow around the walls of the fibers and are removed from the membrane as the dry product gas. Feed gas is sent to a coalescing filter to remove liquids, and is preheated before entering the permeator. Membrane systems offer several advantages over competing separation technologies, such as eliminating: (*1*) the need for a drier and extended equipment; (*2*) cooling time required in cryogenic processes. Also, variations in flow, pressure and composition associated with the VSA technology are nonexistent with membrane processes. One key element in the membrane process is the selection of a selective material. For both syngas H_2:CO ratio adjustment and pure CO production, cellulose acetate membranes were found to provide higher selectivity and permeability compared to polysulfone membranes under similar operating conditions. In membrane processes, impurities such as methane, nitrogen and carbon dioxide, remain with the treated CO, while hydrogen and water are permeated. Subsequent purification of CO to remove the methane and carbon dioxide impurities can be made by VSA processes. New developments in membrane technology focus on improving H_2:CO selectivity. Recent studies (46,47) show that polyimide membranes exhibit competitive H_2:CO selectivity as high as 350. A new strategy to increase selectivity is to cross-link a transition metal complex (ruthenium and niobium-based) to the cellulose acetate membrane to decrease CO permeability.

Liquid Absorption Processes. These processes are based on the selective and reversible complexation of CO with metal-based complexing compounds in a liquid solution. Liquid absorption processes include: ammoniacal copper liquor process:

$$\mathrm{CO} + \mathrm{Cu(NH_3)_2}+ \iff \mathrm{Cu(NH_3)_2(CO)^+} \tag{42}$$

COSORB process:

$$\mathrm{CO} + \mathrm{ArX} \iff \mathrm{COX} + \mathrm{Ar} \tag{43}$$

Where ArX = copper(I)tetrachloroaluminate(III) aromatic solution (benzene or toluene).

Other gases, such as hydrogen, carbon dioxide, methane, and nitrogen are chemically inert to this solvent, but are slightly soluble in benzene or toluene. Water, ammonia, hydrogen sulfide, sulfur dioxides, and oxides of nitrogen are poisons to the complex, and therefore must be removed in a pretreatment step (ie, molecular sieve adsorption system). The COSORB process works well to produce high-purity CO from a variety of gas mixtures, including a nitrogen-rich feed. Separation of nitrogen from CO by the COSORB process is easier and more economical that by cryogenic distillation.

In a typical process, CO produced by COSORB technology is 99% pure with a 99% yield. COSORB is also less capital intensive than the ammoniacal copper liquor process. However, due to degradation of the absorbent in the COSORB process, this process is seldom used.

New CO-complexing compounds have been studied for liquid absorption applications, including iron complexes, palladium complexes, selenium and secondary amine systems (48–50).

6. Production

Carbon monoxide and hydrogen are generally produced simultaneously by syngas plants. Carbon monoxide production for relatively large users typically falls into one of three cases. They are (*1*) a plant on the user's property owned and operated by the user; (*2*) a plant that is on or adjacent to the user's property, owned and operated by an industrial gas company per a long-term contract between the industrial gas supplier and the CO user; and (*3*) a plant owned and operated by an industrial gas company that supplies carbon monoxide to several users. In the first two categories, carbon monoxide is generally supplied to the user's site via a pipe. In the last case, carbon monoxide is distributed via a pipeline with branches to several users' sites. In most cases, pure hydrogen produced from a syngas plant is distributed similarly to CO. For most applications, an average capacity of a CO plant is approximately 4000 to 8000 Nm^3/h. Some of the largest plants built can produce up to around 25,000 Nm^3/h.

7. Shipment

Gas by pipeline is a cost-effective way to manufacture and supply CO to the user. Losses and distribution costs are minimized. Carbon monoxide pipeline networks are found in heavily industrialized areas such as the Gulf Coast in the United States, and in the Rotterdam area in Europe.

When the syngas plant belongs to an industrial gas company, then excess carbon monoxide and hydrogen roan be stocked in liquid and/or gaseous phase and supplied to smaller customers by cryogenic trucks (liquid phase), or high pressure tube trailers (gas phase). Cryogenic liquid tanks of appropriate size are permanently installed at the customer's site. Tank and piping isolation and design are critical to minimize the inevitable boil-off of the liquid CO to reduce losses. Extreme precautions must be taken when handling liquid CO. Refer to the *Handbook of Compressed Gases* by the Compressed Gas Association

(2) for more detail on liquid CO handling, and to the ASME Boiler and Pressure Vessel Code and ANSI/ASME B31.3 for proper selection and maintenance of cryogenic CO vessels. The Type 300 series stainless steels, 9% nickel steel, and aluminum alloys are suitable for inner vessel material construction.

For small-volume customers involved with applications such as CO-lasers, high-pressure cylinders are the supply mode of choice. The maximum pressure authorized for carbon monoxide cylinders is 6.9 MPa at 21°C if the gas is dry and sulfur-free, the cylinders can be charged to 5/6 the service pressure but never more than 13.7 MPa at 21°C. A high pressure carbon-steel cylinder holds approximately 175 scf of pure CO. Under present regulations, the cylinders authorized for carbon monoxide service, per TC/DOT specifications, must be requalified by hydrostatic test every five years.

8. Economic Aspects

Carbon monoxide is manufactured as a syngas mixture or as purified gas by a number of chemical and industrial gas plants. A large majority of the carbon monoxide produced is used immediately downstream and at the plant site for chemical synthesis, or steel manufacturing. Consequently, published production data are not readily available. Based on the development and growth of some of the applications in chemical synthesis (see Uses), carbon monoxide production has grown over the last few years and is expected to continue to grow over the next ten years.

Carbon monoxide pricing is dependent upon several factors: the price of by-product hydrogen, feedstock price, purity requirement (which determines the manufacturing and purification processes, thus determining capital and operational costs), location (which impacts the distribution cost), mode of supply, and volume. On-site carbon monoxide is the most economical supply method.

Carbon monoxide can also be delivered via high pressure tube trailers, typically containing 50,000 to 100,000 scf each. Liquid carbon monoxide is available only from a very small number of suppliers due to the safety and health risks associated with handling and stocking the product under liquid form.

Prices for bulk CO in the Gulf Cost area would typically range from \$0.35/m^3 (\$1.00/100 scf) for “over the fence” supply of approximatly 25,000 m^3/day to \$0.85/m^3 (\$2.40/100 scf) for high pressure tube trailers containing.

For smaller volume requirements, carbon monoxide can be supplied in high pressure steel cylinders with top pressures of (11–13.7 Mpa) and at purities ranging from 99.0% to 99.995%. The price variance between the lowest and highest grades can be in the 1:20 ratio, as extra purification steps are required.

9. Specifications

Typically the purity of the carbon monoxide stream from a commercial production and purification unit is in the range of 97 to 99.9%. Higher purity, of up to 99.995% can be achieved for electronic grades and applications. For most applications involving carbon monoxide, the nature and concentration of the

CO stream impurities are more critical than the total purity value. The typical impurities are hydrogen, methane, carbon dioxide, moisture, nitrogen, oxygen, and argon. The level of these impurities is dependent upon the manufacturing process, the feedstock and the purification process. The chemical reaction using the CO stream drives the purity specifications: ie, in addition to the impurities mentioned above, the commercial process to synthesize formic acid demands less than one part per million mole of sulfur contamination. Consequently, the manufacturing and purification process design must be geared towards the particular application(s) the carbon monoxide is to be used for.

For electronic applications, minimum purity of 99.98–99.995% is required. At 99.995% purity, the typical levels of contaminants are as follows: N_2 <10 ppm, O_2 <3 pm, Ar <10 ppm, CO_2 <1 ppm, H_2 <1 ppm, H_2O <3 ppm, CH_4 <2 ppm (51).

As gas purity and grade names are not standardized across the industrial gas industry, it is important for the end-user to consider the supplier's published guaranteed specifications when performing purity versus price value comparisons.

10. Analytical Methods

Carbon monoxide can be analyzed by a number of procedures based on the reducing properties of CO. Qualitative detection of CO is made by passing the gas through palladium chloride ($PdCl_2$): black metallic palladium appears in the presence of CO. This technique is able to detect levels down to 100–1000 ppm. However, hydrogen, hydrogen sulfide, ethylene, and acetylene also reduce palladium chloride, thus interfering with CO detection. Detection and quantification of CO is also possible via infrared spectrophotometry. The CO infrared stretching frequency is at 2143 cm^{-1}. Electrochemical oxidation of CO to CO_2 is another viable method. Gas chromatography is a method of choice to analyze CO, as it allows both separation of the CO product from its impurities, and quantification. Thermal conduction detectors (TCD) are appropriate for high level concentrations (< 500 ppm). Flame ionization detectors (FID) or discharge ionization detectors (DID) are necessary for low part per million concentration levels. Analysis by a FID necessitates the reduction of CO to CH_4 on a palladium-based catalyst in the presence of high purity hydrogen. Atmospheric CO emissions are measured by continuous emission monitoring systems (CEMS), typically based on infrared, or gas chromatography methods.

Impurities in carbon monoxide are typically analyzed using the following gas chromatography techniques: nitrogen, argon, carbon dioxide, and hydrogen by TCD, methane by FID, moisture via electrical hygrometers based on the direct amperometric method on the piezoelectric sorption detector.

11. Health and Safety Factors

Hazard associated with the use of carbon monoxide derive primarily from: its toxicity; and its flammability.

11.1. Toxicity. Carbon monoxide is a chemical asphyxiant and acts toxically by combining with the hemoglobin of the red blood cells to form a stable compound called carbon monoxide–hemoglobin. This stable compound prevents the hemoglobin from taking up oxygen, thus depriving the body of the oxygen needed for metabolic respiration. The affinity of carbon monoxide for hemoglobin is approximately 300 times than affinity of oxygen for hemoglobin. The inhalation of concentration as low as 0.04% causes headaches and discomfort within 2 to 3 hours. Inhalation of a 0.4% concentration in air is fatal in less than 1 hour. Carbon monoxide is odorless and colorless, which gives no warning of its presence, and inhalation of heavy concentration can cause sudden, unexpected collapse. The current eight-hour time-weighted average threshold limit value (TLV) adopted by the U.S. Occupational Safety and Health Administration is 35 ppm (or 40 mg/m^3) for exposure to carbon monoxide, and a ceiling limit of 200 ppm (229 mg/m^3) (2,52).

According to the *Journal of the American Medical Association*, carbon monoxide is the leading cause of poisoning death in the United States. In concentrations of 12,800 parts per million (ppm) or 1.28 vol% unconsciousness is immediate with the danger of death in 1 to 3 minutes if not rescued. Domestic sources of CO are typically associated with home gas appliances (ovens, water heaters, clothes dryers), generators, furnace, fireplaces, charcoal grills, automobile exhaust fumes, power tools, etc. Only carbon monoxide detectors can detect lethal levels of CO in households. Industrial environments where carbon monoxide is used or stored should also be monitored for CO concentrations with CO detectors and alarms.

11.2. Flammability.

Carbon monoxide is flammable in air over a wide range of concentration: lower limit of 12.5%, and upper limit of 74% at 20°C and 101.3 kPa. In an industrial environment, special care should be taken to avoid storing carbon monoxide cylinders with cylinders containing oxygen or other highly oxidizing or flammable materials. It is recommended that carbon monoxide cylinders in use be grounded. Additionally, areas in which cylinders are in use must be free of all ignition sources and hot surfaces.

12. Environmental Concerns

Carbon monoxide is highly toxic and with the single exception of carbon dioxide, its total yearly emissions of CO exceed all other atmospheric pollutants combined. Some of the potential sources of CO emission and exposure are foundries, petroleum refineries, kraft pulp mills, carbon black manufacturers, steel mills, formaldehyde manufacturers, coal combustion facilities, fuel oil combustion operations (ie, power plants, industrial, commercial and domestic uses, charcoal manufacturer, sugarcane processing operations, motor vehicles). In the U.S., two-thirds of the carbon monoxide emissions come from transportation sources, with the largest contribution coming from highway motor vehicles. In urban areas, the motor vehicle contribution to carbon monoxide pollution exceeds 90%. In 1992, carbon monoxide levels exceeded the Federal air quality standard in 20 U.S. cities, home to more than 14 million people.

The Clean Air Act of 1990 gives state and local government primary responsibility for regulating pollution from power plants, factories, and other "stationary sources". The U.S. Environmental Protection Agency (EPA) has primary responsibility for "mobile sources" pollution control (53).

The EPA motor vehicle program has achieved considerable success in reducing carbon emissions from the 1970s until 1990. EPA standards in the early 1970s prompted automakers to improve basic engine design. By 1975 catalytic converters, designed, to convert CO to CO_2, appeared and reduced CO emissions upwards of 80%. In the early 1980s, automakers introduced more sophisticated converters, plus on-board computers and oxygen sensors to help optimize the efficiency of the catalytic converter. Today's passenger cars are capable of emitting 90% less carbon monoxide over their lifetimes than their uncontrolled counterparts in the 1960s. As a result, ambient carbon monoxide levels have dropped, despite large increases in the number of vehicles on the road and the number of miles they travel. However, with continued increases in vehicle travel projected, the increasing number of more pollutant vehicles (utility vehicles, pick-up trucks), it is expected that CO levels will climb again. This increase has already started in the most populated urban areas. CO emissions from automobiles increase dramatically in cold weather because cars need more fuel to start at cold temperatures. The addition of oxygen-containing compound to gasoline in cold temperature improves the air-to-fuel ratio, thereby promoting complete fuel combustion, and reduced CO emission. The 1990 Clean Air Act requires oxygenated fuels in designated CO non-attainment areas where mobile sources are a significant source of CO emissions. In other urban areas of Europe and industrialized Asia, automotive CO emissions create similar issues, but local environmental protection agencies have not been as active over the past decade. However, the historically high fuel gas prices in these geographic areas lead to the manufacturing of cars and trucks that are more fuel efficient than in the U.S., which in turn contributed to less CO emissions on a per vehicle basis.

CO emitted from stationary sources, such as refineries, is under the EPA Clean Air Act 1990 regulation but enforced by state and local environmental agencies. For example, refineries are required to monitor CO stack emissions on a periodic basis, ie, daily. Typically two certified calibration standards (one of higher concentration that the expected value, and one of lower value than the expected level), are required to validate the concentration of emitted CO. Additionally, on a quarterly basis, a calibration gas audit with EPA Protocol gases is required. EPA Protocol gases are gas standards manufactured by industrial gas suppliers in accordance with an established U.S. EPA Standards that dictate how to manufacture and certify the gaseous $CO{-}N_2$ mixture. Plants that emit more than permitted are penalized by fines or have the option of buying emission credits from the plants that have emitted less CO than allowed. Authorized CO emission levels are lower in nonattainment areas.

13. Uses

13.1. Chemical Synthesis.

Pure carbon monoxide is used in a number of chemical syntheses: eg, acetic acid, acetic anhydride, polycarbonate and diisocyanates (via phosgene), formic acid, propionic acid, methyl methacrylate, polyketones (see Fig. 4). Commercial petrochemical processes using pure CO are based on four principal classes of chemical reaction: Reppe chemistry, Koch carbonylation, phosgenation, and ethylene–CO copolymers (see section Industrially

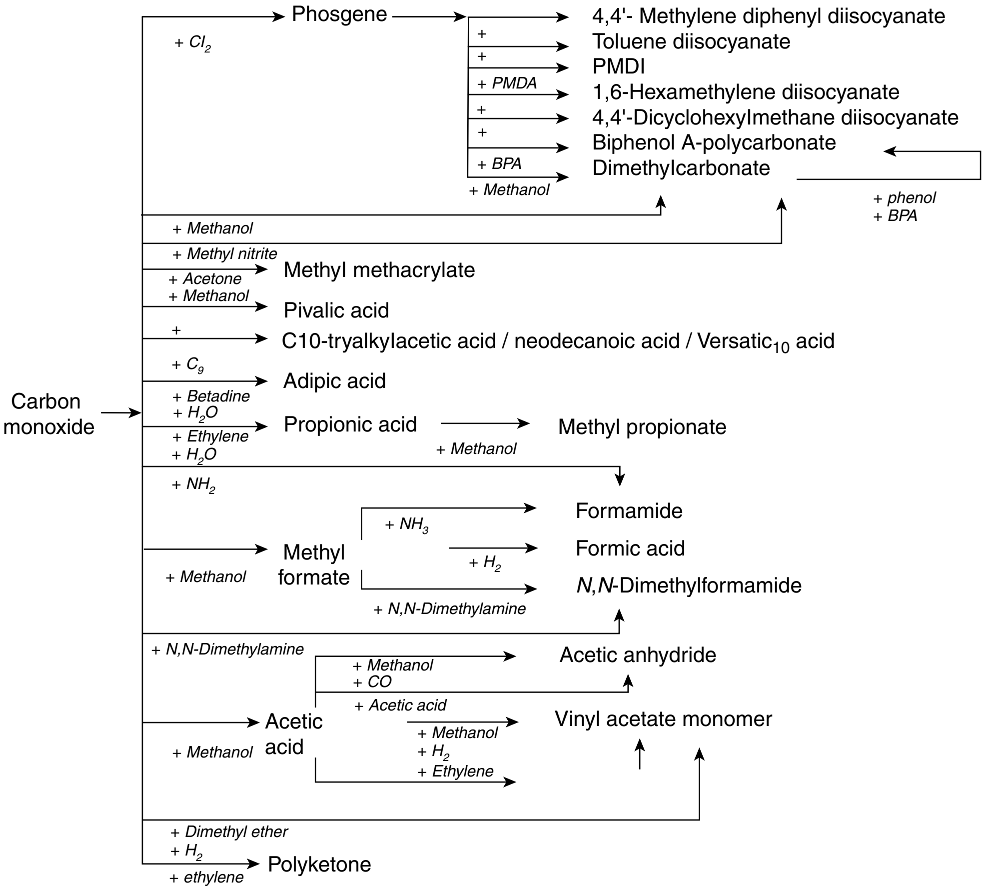

Fig. 4. Carbon monoxide applications in chemical synthesis.

Significant Reactions of Carbon Monoxide, for specific information on these processes and uses for the chemicals produced). Figure 5 provides a summary of the end-use of the various chemicals produced by synthesis involving carbon monoxide.

13.2. Other Application. With applications of carbon monoxide include the following:

Fuel gas alone or in mixes as waste gas or producer gas.

Metallurgy as a reagent for manufacturing special steels, as a reagent for reducing refractory oxides.

As a reagent to make high grade zinc white pigment for paints and varnishes.

Electronics in dielectric etch recipes: a new chemistry, CF_4–CO–CHF_3–N_2, was developed for enhanced selectivity to underlayer and/or overlayer film (54).

Infrared gas lasers (CO laser wavelength range is 5.2–6.0 μm) used in solid state and molecular spectroscopy, nonlinear optics, laser studies.

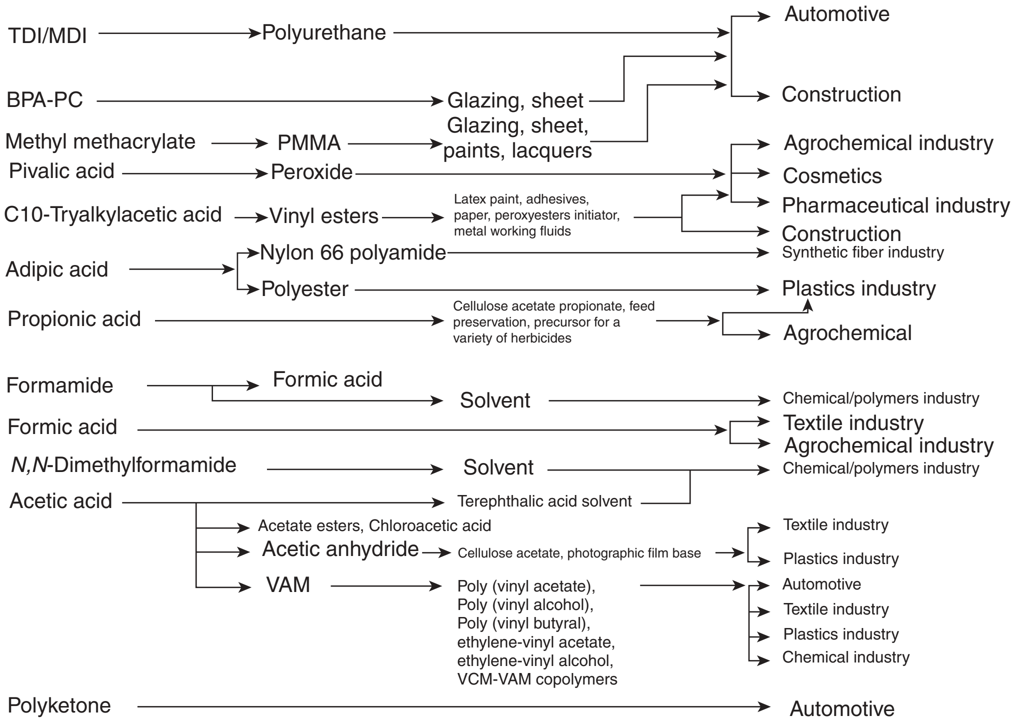

Fig. 5. End-use of chemicals derived from CO synthesis.

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