Formic Acid

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1. Introduction

Formic acid [*64-18-6*] HCOOH, M_r 46.03, is a colorless liquid with a pungent odor, which is completely miscible with water and many polar solvents but only partially miscible with hydrocarbons. Formic acid derived its name from the red ant, *Formica rufa*, in which it was discovered around 1670. Formic acid has been detected in the poison or defense systems of ants, bees, and other insects and also of cnidarians.

Formic acid is used primarily in dyeing, in the textile and leather industries; in rubber production; and as an intermediate in the chemical and pharmaceutical industries. The use of formic acid as an aid in the ensilage of green forage has increased sharply.

The worldwide production of formic acid is about 260 000 t/a in 1987 and 390 000 t/a in 1995 [1]. Formic acid is produced by hydrolysis of methyl formate or formamide or from its salts. In addition, formic acid is a byproduct of acetic acid production by liquid-phase oxidation of hydrocarbons.

2. Physical Properties

Formic acid, *mp* 8.3 °C [2], *bp* 100.8 °C (at 101.3 kPa) [3], is a colorless, clear, very corrosive liquid with a pungent odor. With a pK_a of 3.739, formic acid is the strongest unsubstituted fatty acid, about ten times stronger than acetic acid [4]. Pure formic acid is hygroscopic.

The temperature dependence of the *density* of formic acid is given in Table 1. The density of formic acid – water binary mixtures, as a function of formic acid concentration, is shown in Table 2.

Table 1. Density of pure formic acid as a function of temperature [5]

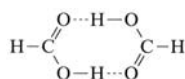| t, °C	ϱ, g/cm^3	t, °C	ϱ, g/cm^3
0	1.244*	40	1.195
10	1.232	50	1.182
15	1.226	60	1.169
20	1.220	70	1.156
25	1.214	80	1.143
30	1.207	90	1.130
		100	1.117

* Supercooled liquid.

Table 2. Density of aqueous formic acid solutions at 20 °C [6]

Formic acid content, wt %	ϱ, g/cm^3	Formic acid content, wt %	ϱ, g/cm^3
2	1.003	50	1.118
5	1.011	60	1.141
10	1.024	70	1.163
20	1.048	80	1.185
30	1.072	90	1.204
40	1.095	100	1.221

The *freezing point* diagram for the formic acid – water binary mixture exhibits a eutectic point (Table 3) at −48.5 °C and 41.0 mol % of formic acid [2]. Formic acid does not increase in volume when it solidifies and has a tendency to undergo supercooling.

Table 4 shows the *vapor pressure* curve of pure formic acid. The vapor of formic acid deviates considerably in behavior from an ideal gas because the molecules dimerize partially in the vapor phase. At room temperature and normal pressure, 95 % of the formic acid vapor consists of dimerized formic acid [8]:

Table 3. Freezing points of various formic acid – water mixtures [2]
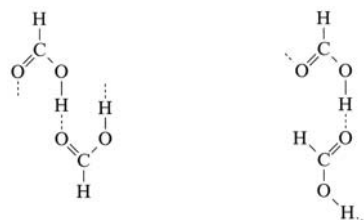
Formic acid molar fraction, %	fp, °C	Formic acid molar fraction, %	fp, °C
100.0	8.3	41.0	−48.5
80.0	−5.6	39.8	−46.8
74.8	−8.2	37.0	−43.0
69.5	−13.0	31.7	−33.5
64.5	−17.3	28.0	−29.3
59.0	−23.2	23.1	−22.8
54.2	−28.3	20.0	−19.7
50.0	−35.3	12.0	−10.3
44.6	−42.0		
42.0	−46.7		

Table 4. Vapor pressure of pure formic acid [7]

Liquid		Solid	
t, °C	p, kPa	t, °C	p, kPa
−5.23	1.083	−5.07	0.664
0.00	1.488	0.00	1.096
8.25	2.392	8.25	2.392
12.57	3.029		
20.00	4.473		
29.96	7.248		
39.89	11.357		
49.93	17.347		
59.98	25.693		
70.04	37.413		
79.93	52.747		
100.68	101.667		
110.62	135.680		

The enthalpy of the gas-phase dimerization is −63.8 kJ/mol [8]. The thermodynamic properties of monomeric and dimeric formic acid have been investigated by WARING [9].

The ring-type dimeric structure exists both in the vapor phase and in solution. Liquid formic acid consists of long chains of molecules linked to each other by hydrogen bonds. Solid formic acid can also be isolated in two polymorphic forms (α and β) [10]:

Portion of the chain in an α-type formic acid crystal

Portion of the chain in a β-type formic acid crystal

The thermodynamic properties of monomeric and dimeric formic acid have been investigated [10].

Vapor – liquid equilibrium data for formic acid – water mixtures and for mixtures of formic acid with organic compounds have been collected in [11]. Formic acid and water form a maximum-boiling azeotropic mixture whose boiling point is 107.6 °C at 101.3 kPa; it consists of 77.6 wt % formic acid and 22.4 wt % water. The composition and boiling point of formic acid – water azeotropic mixtures are shown as a function of pressure in Table 5. Formic acid can form

Table 5. Azeotropic data for the formic acid – water system

p, bar	bp of azeo-tropic mixture, °C	Formic acid content, wt %	Reference
0.093	48.6	66.2	[12]
0.267	72.3	70.5	[12]
1.013	107.6	77.6	[12]
2.026	128.7	84	[13]
3.140	144	85	[13]

Table 6. Dynamic viscosity of pure formic acid as a function of temperature [16]

t, °C	η, mPa · s
10	2.262
20	1.804
30	1.465
40	1.224
50	1.025

azeotropic mixtures with many other substances [14].

The variation of dynamic *viscosity* with temperature is shown in Table 6. The dynamic viscosity of formic acid – water mixtures decreases approximately linearly as the water content of formic acid increases [15]. The *thermal conductivity* of formic acid is markedly higher than that of comparable liquids, because of its pronounced polarity.

The variation of specific *heat capacity* with temperature is shown in Table 7. The specific

Table 7. Specific heat capacity of formic acid as a function of temperature at constant pressure [17]

t, °C	c_p, J g^{-1}K^{-1}	t, °C	c_p, J g^{-1} K^{-1}
Solid		*Vapor*	
−150	0.921	25	1.058
−100	1.114	100	1.192
−75	1.193	200	1.348
−50	1.285	300	1.480
−25	1.411	400	1.589
0	1.800	600	1.757
		800	1.870
		1000	1.953
		1200	2.037
Liquid			
20	2.169		
50	2.202		
100	2.282		

heat capacity of formic acid – water mixtures decreases approximately linearly as the concentration of formic acid increases [6].

The physical properties of formic acid are listed below:

Heat of fusion		276 J/g [7]
Heat of vaporization (at bp)		483 J/g [7]
Dielectric constant		
	Liquid (at 20 °C)	57.9 [21]
	Solid (at −10.1 °C)	11.7
Refractive index n_D^{20}		1.37140 [19]
Surface tension σ		
	(at 20 °C)	37.67×10^{-3} N/m [20]
	(at 40 °C)	35.48×10^{-3} N/m
	(at 60 °C)	33.28×10^{-3} N/m
	(at 80 °C)	31.09×10^{-3} N/m
Heat of formation $\Delta H H_f^0$		
	Liquid (at 25 °C)	−425.0 kJ/mol [22]
	Vapor (at 25 °C, monomer)	−378.57 kJ/mol [8]
	(at 25 °C, dimer)	−820.94 kJ/mol
Heat of combustion ΔH_c^0		
	Liquid (at 25 °C)	−254.8 kJ/mol [22]
Entropy S^0		
	Liquid (at 25 °C)	129.0 J K^{-1} mol^{-1} [10]
	Vapor (at 25 °C, monomer)	248.88 J K^{-1} mol^{-1} [8]
	(at 25 °C, dimer)	332.67 J K^{-1} mol^{-1} [8]
Heat of neutralization		56.9 kJ/mol [23]
Critical data p_{crit}		7.279 MPa [18]
	T_{crit}	581 K [18]
	ϱ_{crit}	0.392 g/cm^3 [18]
Thermal conductivity λ		
	Liquid (at 20 °C)	0.226 W m^{-1} K^{-1} [18], [24]
	(at 60 °C)	0.205 W m^{-1} K^{-1}
	(at 100 °C)	0.185 W m^{-1} K^{-1}
	Vapor (at 50 °C)	0.0136 W m^{-1} K^{-1}
	(at 100 °C)	0.0176 W m^{-1} K^{-1}
	(at 200 °C)	0.0267 W m^{-1} K^{-1}
Electrical conductivity (at 25 °C)		6.08×10^{-5} Ω^{-1} cm^{-1} [25]
Coefficient of cubic expansion α		0.001 [3]
	(at 30 °C)	

In 1968, GALLANT reported the important physical properties of formic acid and other low molecular weight fatty acids as a function of temperature [18].

3. Chemical Properties

To some extent, formic acid reacts differently from its higher homologues because it is both a carboxylic acid and an aldehyde.

Aldehyde Reactions. In some reactions, formic acid behaves like an aldehyde. Thus if

an aqueous solution of formic acid is heated with a silver nitrate solution, metallic silver is deposited. Mercury, gold or platinum ions are reduced in solution, as are organic compounds. For example, formic acid reduces triphenylmethanol to triphenylmethane. The reduction of imines (Schiff bases) by formic acid has been known for a long time. Primary amines can be prepared from ketones, ammonia, and formic acid (Leuckart reaction). Like other aldehydes, formic acid has bactericidal properties.

Carboxylic Acid Reactions. Magnesium, zinc, and iron dissolve in formic acid with the evolution of hydrogen. Because of its strongly acidic nature, many alcohols can be esterified by formic acid, without the addition of mineral acids. Primary and secondary alcohols are esterified in pure formic acid 15 000 – 20 000 times more rapidly than in pure acetic acid [26]. The rate of esterification of primary, secondary, and tertiary alcohols in formic acid has been determined [27], [28]. Because of its extremely reactive carboxyl group, amines can be formylated by formic acid, with high yields, for example, the yield of N-methylformanilide [93-61-8] is 93 – 97 %. Formic acid adds to the double bonds of olefins to form esters. Acetylenes react with formic acid in the vapor phase to yield vinyl formates [29].

Formic acid may also be used as a source of carbon monoxide. Thus, carboxylic acids can be prepared from olefins and formic acid in the presence of sulfuric or hydrofluoric acid (Koch carboxylic acid synthesis). Formic acid and tertiary organic bases form addition compounds (3 : 1 and 2 : 1 ratio of formic acid : base). If, for instance, 1 mole of gaseous triethylamine is passed in 3 moles of anhydrous formic acid, the addition product is obtained in quantitative yield. In these compounds formic acid is present in an extremely active form. Addition compounds of formic acid and trimethylamine or triethylamine can be used as liquid reducing agents in many selective reductions. The reduction of sulfur dioxide to sulfur is approximately quantitative [30].

Formic acid reacts with hydrogen peroxide in the presence of an acidic catalyst to form unstable performic acid [107-32-4] (HCOOOH); performic acid ($\rightarrow$ Peroxy Compounds, Organic) may decompose explosively when heated to 80 – 85 °C. Performic acid exhibits typical per-

oxide properties [31]. The reactions of formic acid were summarized by GIBSON in 1969 [32].

Although formic acid is not very stable, it can be distilled at atmospheric pressure in the absence of catalysts. Formic acid may decompose into either carbon monoxide and water (dehydration) or carbon dioxide and hydrogen (dehydrogenation); the nature of the decomposition and the reaction rate depend strongly on the presence of catalysts, the temperature, and the concentration of formic acid. *Dehydrogenation* is catalyzed preferentially by metals (platinum sponge, copper, nickel, silver). *Dehydration*, on the other hand, is catalyzed by aluminum oxide, silicon dioxide, and charcoal. Dehydration is promoted by mineral acids but inhibited by water; it also occurs on activated metal surfaces which must be considered during the preparation and processing of formic acid, as well as during transportation and storage of the highly concentrated acid. Tables 8 and 9 show the formation of carbon monoxide as a function of formic acid concentration and temperature [33]. A summary of the catalytic decomposition of formic acid has been published by MARS [34], along with an extensive list of references. The temperature dependence of formic acid decomposition at low temperature (between 40 – 100 °C) has been investigated [35].

Table 8. Volume of carbon monoxide produced per liter of formic acid (99 wt %) as a function of storage time and temperature [33]

Time, d	V, L		
	at 20 °C	at 30 °C	at 40 °C
15	0.012	0.064	0.303
30	0.024	0.128	0.597
60	0.049	0.255	1.161
90	0.073	0.381	1.700

Table 9. Volume of carbon monoxide produced per liter of aqueous formic acid as a function of storage time and concentration [33]

Time, d	V, L ($t = 40$ °C)		
	90 wt %	98 wt %	99 wt %
15	0.010	0.110	0.303
30	0.019	0.220	0.597
60	0.039	0.437	1.161
90	0.058	0.653	1.700

4. Production

The worldwide installed capacity for producing formic acid was about 330 000 t/a in 1988. The installed formic acid processes can be classified in four groups:

1. methyl formate hydrolysis,
2. oxidation of hydrocarbons,
3. hydrolysis of formamide, and
4. preparation of free formic acid from formates.

The significance of individual processes has shifted considerably in the last decade because the economic data for production and raw products have changed and new processes have been developed. In the past, a large amount of the formic acid utilized was a byproduct in the manufacture of acetic acid. However, the proportion of formic acid produced by dedicated processes has increased.

Formic acid is a byproduct in the production of acetic acid [64-19-7] by liquid-phase oxidation of butane or naphtha (→ Acetic Acid, Section 4.2.). For many years, oxidation of hydrocarbons was the most important method of producing acetic acid. Over the past decade, however, the preferred process in the establishment of new acetic acid plants has been the carbonylation of methanol [36], which is expected to remain the preferred method in the future. As a result, the proportion of formic acid produced worldwide, which results as a byproduct in the manufacture of acetic acid, will continue to decrease.

The production of formic acid by hydrolysis of formamide [75-12-7] played an important role in Europe; in 1972, about one-third of the world production was obtained by this process [3]. However, the consumption of ammonia and sulfuric acid, along with the unavoidable production of ammonium sulfate, have in many cases made this process economically inferior. As a result, the direct hydrolysis of methyl formate is currently preferred.

Another industrial production method involves formation of the free acid from its salts. Sodium formate [141-53-7] and calcium formate [544-17-2] are used for this purpose.

The economic disadvantages of the methods discussed led to the development of a process specifically dedicated to the production of formic acid, with no undesirable byproducts. In the 1970s, the hydrolysis of methyl formate [107-31-3] to methanol and formic acid was developed commercially by various firms into an economically feasible method. This process involves carbonylation of methanol and subsequent hydrolysis of the methyl formate produced. The methanol resulting from this process is returned to the first stage. Formic acid plants based on this process were started up at BASF (Federal Republic of Germany) in 1981 and Kemira (Finland) in 1982 [37]. Most of the formic acid plants begun in recent years employ this principle of methyl formate hydrolysis.

Table 10 shows the world capacity for various formic acid production processes in 1986. Although other methods for producing formic acid have been patented, they do not appear to have been implemented industrially. Direct synthesis of formic acid from carbon monoxide and water cannot be carried out economically because of the unfavorable position of the equilibrium.
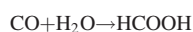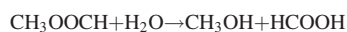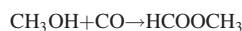
In recent years, various ways of producing formic acid from carbon dioxide and hydrogen have been investigated extensively, but this method has not yet been applied industrially. The oxidation of methyl *tert*-butyl ether [1634-04-4] with oxygen to form *tert*-butyl formate [762-75-4] and formic acid has been described [38]. Various methods have been developed for the electrochemical production of formic acid, but they have not been used commercially [3], [39]. The combined production of formic acid and acetic acid from methyl formate, carbon monoxide, and water with methyl iodide [74-88-4] as promoter and anhydrous rhodium chloride [13569-65-8] as catalyst, has been described by BP [40].

Table 10. Formic acid production capacity in 1986 (without standby plants; BASF assessment)

Process	Capacity, t/a	Percentage of total capacity, %
Hydrolysis of methyl formate	160 000	49
Byproduct in hydrocarbon oxidation	74 000	22
Hydrolysis of formamide	10 000	3
Acidolysis of alkali formates	86 000	26
Total	330 000	

4.1. Methyl Formate Hydrolysis

Synthesis of formic acid by hydrolysis of methyl formate is based on a two-stage process: in the first stage, methanol is carbonylated with carbon monoxide; in the second stage, methyl formate is hydrolyzed to formic acid and methanol. The methanol is returned to the first stage:

$$CH_3OH + CO \rightarrow HCOOCH_3$$

$$CH_3OOCH + H_2O \rightarrow CH_3OH + HCOOH$$

$$CO + H_2O \rightarrow HCOOH$$

Although the carbonylation of methanol is relatively problem-free and has been carried out industrially for a long time [3], [41], only recently has the hydrolysis of methyl formate been developed into an economically feasible process. The main problems are associated with work-up of the hydrolysis mixture. Because of the unfavorable position of the equilibrium, reesterification of methanol and formic acid to methyl formate occurs rapidly during the separation of unreacted methyl formate. Problems also arise in the selection of sufficiently corrosion-resistant materials.

Older publications suggest the reaction of methyl formate and a dicarboxylic acid, with subsequent distillation of formic acid from the higher-boiling esters [3]. Degussa suggested hydrolyzing methyl formate at 200 °C above atmospheric pressure and then reducing the pressure suddenly to less than 0.1 MPa. Separation of the methyl formate –methanol mixture flash-evaporated from the aqueous formic acid can then take place in a liquid separator [5].

Industrial methods involving carbonylation of methanol and hydrolysis of methyl formate, followed by isolation of the formic acid, were developed by (1) the Leonard Process Company (United States), (2) BASF (Federal Republic of Germany), (3) Halcon – Scientific Design – Bethlehem Steel (United States), and (4) the Scientific Research Institute for the Chlorine Industry of the Ministry of the Chemical Industry (former Soviet Union).

Key patents relating to the carbonylation of methanol and the hydrolysis of methyl formate are listed in [43].

Basic Principles. *Carbonylation of Methanol.* In the four processes mentioned, the first stage involves carbonylation of methanol in the liquid phase with carbon monoxide, in the presence of a basic catalyst:

$$CH_3OH + CO \rightarrow HCOOCH_3 \quad \Delta H_R^0 = -29\,kJ/mol$$

This reaction was first described by BASF in 1925 [41]. As a rule, the catalyst is sodium methoxide [*124-41-4*]. Potassium methoxide [*865-33-8*] has also been proposed as a catalyst; it is more soluble in methyl formate and gives a higher reaction rate [44]. Although fairly high pressures were initially preferred, carbonylation is carried out in new plants at lower pressure. Under these conditions, reaction temperature and catalyst concentration must be increased to achieve acceptable conversion. According to published data, ca. 4.5 MPa, 80 °C, and 2.5 wt % sodium methoxide are employed. About 95 % carbon monoxide, but only about 30 % methanol, is converted under these circumstances. Nearly quantitative conversion of methanol to methyl formate can, nevertheless, be achieved by recycling the unreacted methanol. The carbonylation of methanol is an equilibrium reaction, and Table 11 specifies the equilibrium concentrations of methyl formate.

The reaction rate can be raised by increasing the temperature, the carbon monoxide partial pressure, the catalyst concentration, and the interface between gas and liquid:

$$r = C \cdot a \cdot e^{-E/RT} \cdot c \cdot p_{CO}$$

where
r = reaction rate,
C = proportionality coefficient,
a = interface between gas and liquid,
E = activation energy,

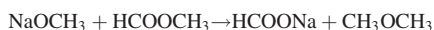**Table 11.** Maximum methyl formate concentration (in weight percent) achievable by carbonylation of methanol (unpublished BASF data)

t, °C	p, MPa			
	1	5	9	17
50	59	95	98	99
60	43	91	96	99
70	31	85	94	98
80	21	78	90	96
90	15	69	85	94
100	10	59	79	91
110	7	49	71	87
120	5	39	62	82

R = molar gas constant,
c = catalyst concentration in solution, and
p_{CO} = CO partial pressure in the gas phase [45].

This equation reveals the dependence of reaction rate on the partial pressure of carbon monoxide. Therefore, to synthesize methyl formate, gas mixtures with a low proportion of carbon monoxide must first be concentrated; this can be achieved by low temperature distillation, pressure-swing adsorption, prism separators (Monsanto), or the Cosorb process (Tenneco).

In a side reaction, sodium methoxide reacts with methyl formate to form sodium formate and dimethyl ether, and becomes inactivated:

$$NaOCH_3 + HCOOCH_3 \rightarrow HCOONa + CH_3OCH_3$$

The substances used must be anhydrous; otherwise, sodium formate is precipitated to an increasing extent:

$$NaOCH_3 + H_2O + HCOOCH_3 \rightarrow 2\,CH_3OH + NaOOCH$$

Sodium formate is considerably less soluble in methyl formate than in methanol. The risk of encrustation and blockage due to precipitation of sodium formate can be reduced by adding poly (ethylene glycol) [46]. The carbon monoxide used must contain only a small amount of carbon dioxide; otherwise, the catalytically inactive carbonate is precipitated.

Basic catalysts may reverse the reaction, and methyl formate decomposes into methanol and carbon monoxide. Therefore, undecomposed sodium methoxide in the methyl formate must be neutralized [47].

Hydrolysis of Methyl Formate. In the second stage, the methyl formate obtained is hydrolyzed:

$$HCOOCH_3 + H_2O \rightleftharpoons CH_3OH + HCOOH \quad \Delta H_R^0 = 16.3\,\mathrm{kJ/mol}$$

The equilibrium constant for methyl formate hydrolysis depends on the water: ester ratio [48]. With a molar ratio of 1, the constant is 0.14, but with a water: methyl formate molar ratio of 15, it is 0.24. Because of the unfavorable position of this equilibrium, a large excess of either water or methyl formate must be used to obtain an economically worthwhile methyl formate conversion. If methyl formate and water are used in a molar ratio

of 1 : 1, the conversion is only 30 %, but if the molar ratio of water to methyl formate is increased to 5 – 6, the conversion of methyl formate rises to 60 %. However, a dilute aqueous solution of formic acid is obtained this way, and excess water must be removed from the formic acid with the expenditure of as little energy as possible.

Another way to overcome the unfavorable position of the equilibrium is to hydrolyze methyl formate in the presence of a tertiary amine, e.g., 1-(*n*-pentyl)imidazole [*19768-54-8*], [49]. The base forms a salt-like compound with formic acid; therefore, the concentration of free formic acid decreases and the hydrolysis equilibrium is shifted in the direction of products. In a subsequent step formic acid can be distilled from the base without decomposition.

A two-stage hydrolysis has been suggested, in which a water-soluble formamide is used in the second stage [50]; this forms a salt-like compound with formic acid. It also shifts the equilibrium in the direction of formic acid.

To keep undesirable reesterification as low as possible, the time of direct contact between methanol and formic acid must be as short as possible, and separation must be carried out at the lowest possible temperature. Introduction of methyl formate into the lower part of the column in which lower boiling methyl formate and methanol are separated from water and formic acid, has also been suggested. This largely prevents reesterification because of the excess methyl formate present in the critical region of the column [51].

The hydrolysis of methyl formate is catalyzed by strong acids, but the efficiency of strong mineral acids [52] is restricted because they also promote the decomposition of formic acid. In the processes described by BASF, Leonhard, and Halcon – Scientific Design – Bethlehem Steel, autocatalysis by formic acid is therefore used. In the Soviet Union, a process has been described in which hydrolysis is carried out in a vertical column reactor divided into two zones [53]; the upper zone is filled with a strongly acidic cation exchanger which partially hydrolyze methyl formate. In the lower part of the reactor, hydrolysis is carried out with autocatalysis by formic acid produced in the upper section.

Dehydration of the Hydrolysis Mixture. Formic acid is marketed in concentrations exceeding 85 wt %; therefore, dehydration of the hydrolysis

mixture is an important step in the production of formic acid from methyl formate. For dehydration, the azeotropic point must be overcome. The concentration of formic acid in the azeotropic mixture increases if distillation is carried out under pressure (Table 5), but the higher boiling point at high pressure also increases the decomposition rate of formic acid. At the same time, the selection of sufficiently corrosion-resistant materials presents considerable problems. A number of entrainers have been proposed for azeotropic distillation [43].

BASF describes various energy-saving processes for the dehydration. One process involves extractive distillation with *N*-formylmorpholine [*4394-85-8*] [54]. Another method of increasing formic acid concentration in dilute solutions without a considerable input of energy is to extract formic acid from water by liquid – liquid extraction. Secondary amides have been proposed [55] as extractive agents. Formic acid binds weakly to the amide; therefore, water can be distilled to overcome the azeotropic point. In a subsequent column, formic acid can then be distilled from the extractant in vacuo. The energy consumed can be reduced further by optimizing the exchange of heat [56].

4.1.1. Kemira – Leonard Process

A 20 000-t/a formic acid plant based on a method developed by the Leonard Process Co. [57] was built at Kemira in Finland and put into operation in 1982. The process has been developed further by Kemira, and licences for it have been issued in Korea, India and Indonesia.

In the Kemira – Leonard process, Methyl formate and carbonylation is carried out at about 4 MPa and a temperature of approximately 80 °C, with additive-containing alkoxides used as catalyst [58]. Hydrolysis is carried out in two reactors with different operating conditions. Methyl formate and water react in the preliminary reactor in approximately equimolar proportions. The formic acid produced catalyzes the hydrolysis in the main reactor. An excess of methyl formate is employed in the main reactor, and hydrolysis is carried out at ca. 120 °C and 0.9 MPa. The reactor discharge is brought to atmospheric pressure in a flash tank; reesterification is largely prevented by the cooling that occurs during flash-evaporation. methanol are separated under vacuum. Although the reverse reaction is attenuated further as a result, condensation of the low-boiling methyl formate in vacuo presents a problem. The formic acid is dehydrated by distillation. If 85 wt % formic acid is desired, dehydration must be carried out at ca. 0.3 MPa. Even higher concentrations can be achieved by connecting an additional dehydration column downstream under atmospheric pressure, and formic acid concentrations up to ca. 98 wt % can then be drawn off as the distillate.

Process Description [57–60] (Fig. 1). Compressed carbon monoxide and methanol are converted into methyl formate in reactor (a). Catalyst is fed into the reactor in a methanol solution. The amount of methanol introduced in this way makes up for methanol losses in the process. The discharge from reactor (a) is flashed and fed into the methyl formate column (b) from which methyl formate is drawn off as the distillate. Methanol and the dissolved catalyst are returned to the reactor; inactivated catalyst (primarily sodium formate) is crystallized and discharged.

Off-gas from column (b) and waste gas from reactor (a) are burned. Methyl formate reacts partially with water in the preliminary reactor (c), and discharge from the preliminary reactor is fed into the main reactor (d) along with recycled methyl formate, methanol, and water. The contact time in this reactor is largely sufficient for equilibrium to be established. Reactor discharge is flashed to approximately atmospheric pressure in the flash tank (e); methyl formate, methanol, and small quantities of formic acid evaporated in this process are recycled to the main reactor (d). Methyl formate and methanol are distilled in vacuo in the acid separation column (g). Contact time is minimized by internals with a small liquid holdup. The distillate is separated into methyl formate and methanol in the recycle column (f). Formic acid can be concentrated under pressure in a column; if the pressure is ca. 0.3 MPa, 85 % formic acid is drawn off as the bottom product. Distillation in two columns is more industrially controllable. Water is distilled overhead in the first product column (h). The bottom product is concentrated further in the second product column (i), and formic acid with a maximum concentration of ca. 98 wt % is drawn off as distillate. The bottom product is recycled to the first product column.
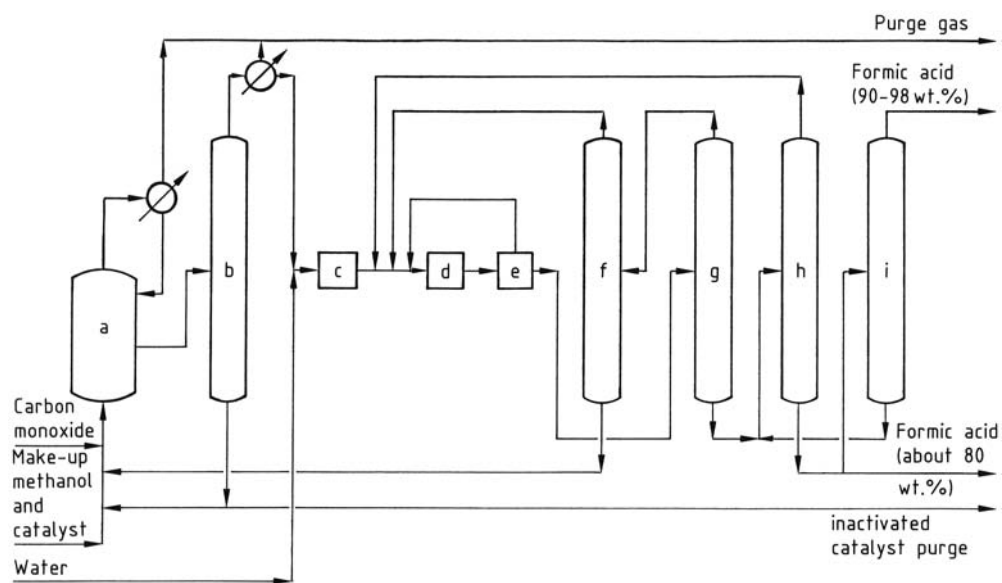
Figure 1. Production of formic acid (Kemira – Leonard process)
a) Methyl formate reactor; b) Methyl formate column; c) Preliminary reactor; d) Main reactor; e) Flash tank; f) Recycle column;
g) Acid separation column; h) First product column; i) Second product column

4.1.2. BASF Process

A 100 000-t/a formic acid plant began operating in Ludwigshafen (Federal Republic of Germany) in 1981. In this plant, a technology for the hydrolysis and dehydration was used for the first time.

The production of methyl formate by carbonylation of methanol has been carried out on a large scale for many years at BASF [41], [61]. The carbonylation stage is largely identical to that of the Kemira – Leonard process, but the hydrolysis stage and the dehydration of formic acid are noticeably different.

In the BASF process, hydrolysis is carried out with a large excess of water (about 5 mol of water per mole of methyl formate) to shift the equilibrium in the direction of formic acid. Much of the water is separated by liquid – liquid extraction with a secondary amide.

Process Description (Fig. 2) Carbon monoxide and methanol react in the methyl formate reactor (a) in the presence of sodium methoxide. Methyl formate is fed, as a distillate, from the methyl formate column (b) into the formic acid reactor (c) together with recycled methyl formate. Methanol and dissolved catalyst are drawn off from the bottom of column (b) and returned to reactor

(a); catalyst decomposition products are discharged by crystallization. In reactor (c), methyl formate is hydrolyzed with excess water at elevated temperature and increased pressure. The reaction product is flashed into the low-boiler column (d). Methyl formate is removed as the distillate, with methanol as a side stream, and dilute aqueous formic acid is drawn off from the bottom into the extraction unit (e). Here, the formic acid and some of the water are extracted by the secondary amide. Most of the water (largely free of formic acid) is recycled to reactor (c). The extract–a mixture of extractant, formic acid, and some water–is distilled in the dehydration column (f). Enough water is distilled via the head for the required formic acid concentration to be obtained in the pure acid column (g). This column is operated in vacuo. The extraction agent is recycled from the bottom of column (g) to the extraction unit.

4.1.3. USSR Process

A 40 000-t/a formic acid plant based on a process [53] developed in the former Soviet Union is being built in Saratov (Ukraine) [62] and is expected to be operational in 1989.
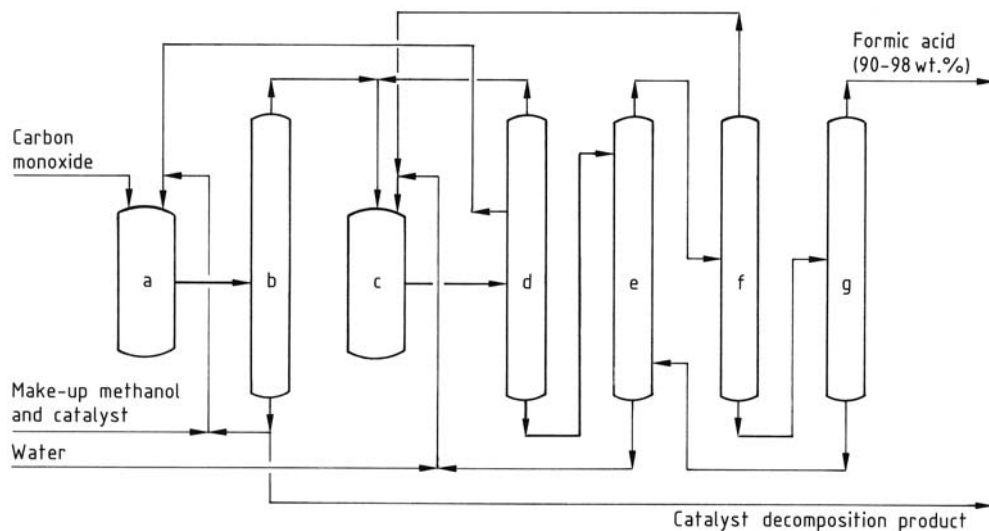
Figure 2. Production of formic acid (BASF process)
a) Methyl formate reactor; b) Methyl formate column; c) Hydrolysis reactor; d) Low-boiler column, e) Extraction unit;
f) Dehydration column; g) Pure acid column

According to published material, this formic acid process differs from the above-mentioned processes [63], [64] in the hydrolysis stage. Hydrolysis is carried out at 80 °C and 0.6 MPa in a fixed-bed reactor equipped with bubble-cap trays in the upper section. Reesterification is prevented by decompressing and cooling to about 45 °C. Formic acid is produced in a pressure column as an azeotropic mixture with water which contains 85 wt % formic acid.

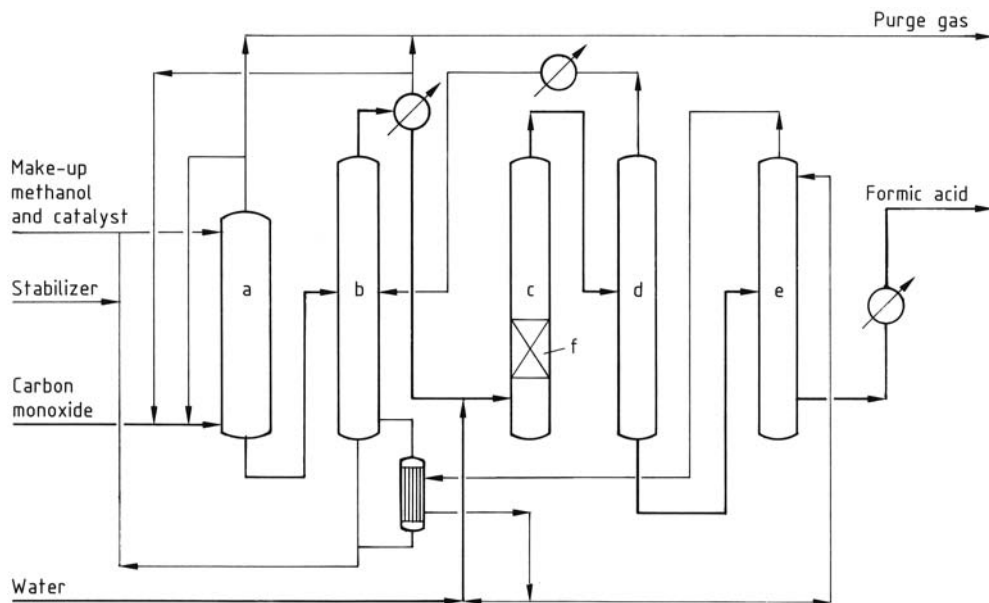**Process Description** [63], [64] (Fig. 3). Carbon monoxide reacts with methanol in column

Figure 3. Production of formic acid (USSR process)
a) Methyl formate reactor; b) Methyl formate column; c) Hydrolysis reactor; d) Low-boiler column; e) Formic acid column;
f) Fixed-bed catalyst

reactor (a), in the presence of the catalyst and a stabilizer, at about 3 MPa, to yield methyl formate. Separation into methyl formate (distillate) and methanol plus catalyst takes place in the methyl formate column (b) at 0.2 MPa. The exhaust gas produced is partially recycled. In reactor (c), methyl formate is hydrolyzed with water in two stages; in the first stage, packed acidic cation exchanger is used as catalyst (f), which partially hydrolyzes the methyl formate. In the second stage, hydrolysis is carried out with autocatalysis by the formic acid produced in stage one. Methanol and methyl formate are distilled from the hydrolysis product in the low-boiler column (d); these compounds are separated, along with the carbonylation reaction mixture, in the methyl formate column (b). Aqueous formic acid is drawn off the bottom of column (d) and further dehydrated in the formic acid column (e) under pressure. Formic acid with a content of 85 wt % is drawn off in the side stream, and the concentration can be increased to about 98 wt % in the column situated downstream.

4.1.4. Scientific Design – Bethlehem Steel Process

The process developed jointly by Scientific Design and Bethlehem Steel [65] has not yet been implemented industrially on a large scale.

The carbonylation stage is essentially similar to the processes described previously. If the concentration of carbon monoxide is higher than 90 mol %, a single back-mixed reactor is provided, but if the carbon monoxide concentration is between 50 and 90 mol %, a two-stage, counter-current, back-mixed reactor system is recommended. If the carbon monoxide concentration is low, however, the total pressure must be increased considerably [66]. The hydrolysis is catalyzed by formic acid, and the dehydration is carried out by distillation alone.

4.2. Other Processes

4.2.1. Oxidation of Hydrocarbons

Formic acid is produced as a byproduct in the liquid-phase oxidation of hydrocarbons to acetic acid (→ Acetic Acid, Section 4.2.). In the United States, butane [106-97-8] is used as the hydrocarbon, and ca. 50 kg of formic acid is produced per ton of acetic acid. In Europe, the oxidation of naphtha is preferred, and up to 250 kg of formic acid is produced per ton of acetic acid in this process. For the mechanism of formic acid production, see [59].

Unreacted hydrocarbons, volatile neutral constituents, and water are separated first from the oxidation product. Formic acid is separated in the next column; azeotropic distillation is generally used for this purpose. The entrainers preferred in this process are benzene or chlorinated hydrocarbons. The formic acid contains about 2 wt % acetic acid, 5 wt % water, and 3 wt % benzene [59]. Formic acid with a content of about 98 wt % can be produced by further distillation.
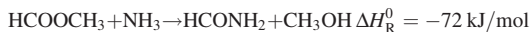
4.2.2. Hydrolysis of Formamide

In 1972, 35 % of the formic acid produced worldwide was still made by the formamide process developed by BASF. However, because of the direct hydrolysis of methyl formate, this process has lost much of its significance (see Table 10).
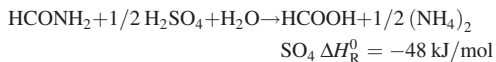
Formic acid is produced this way in a three-stage process. In the first stage, methanol is carbonylated to yield methyl formate:

$$CO + CH_3OH \rightarrow HCOOCH_3 \quad \Delta H_R^0 = -29 \, kJ/mol$$

In the second stage, formamide is produced by ammonolysis of ethyl formate:

$$HCOOCH_3 + NH_3 \rightarrow HCONH_2 + CH_3OH \quad \Delta H_R^0 = -72 \, kJ/mol$$

In the third stage, sulfuric acid is used to hydrolyze formamide to formic acid and ammonium sulfate:

$$HCONH_2 + 1/2 \, H_2SO_4 + H_2O \rightarrow HCOOH + 1/2 \, (NH_4)_2 SO_4 \quad \Delta H_R^0 = -48 \, kJ/mol$$

Methanol is carbonylated as in the first stage of the processes already described (Section 4.1). Conversion to formamide is usually carried out at 0.4 – 0.6 MPa and 80 – 100 °C; methanol is distilled and recycled to the methyl formate stage (see → Formamides). Formamide is hydrolyzed continuously in the third stage by using 68 – 74 % sulfuric acid at temperatures between 85 °C and

the boiling point of formic acid [3]. This reaction is carried out preferably in stirred containers and provides the heat for the distillation of formic acid. A hot slurry consisting essentially of ammonium sulfate and formic acid flows out of the stirred container into a rotary kiln where the residual formic acid is distilled so that dry, pure ammonium sulfate is produced at the kiln end. The yield of formic acid exceeds 90 %. The economic efficiency of this process is determined by the commercial value of ammonium sulfate.

Hydrochloric acid, nitric acid, or phosphoric acid can also be used to hydrolyze formamide [3].
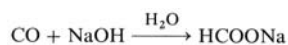
4.2.3. Production of Formic Acid from Formates

The reaction of sodium formate [141-53-7] or calcium formate [544-17-2] with strong mineral acids, such as sulfuric and nitric acids, is the oldest known process for producing formic acid commercially. If formates or sodium hydroxide are available cheaply or occur as byproducts in other processes, formic acid can still be produced economically in this manner.
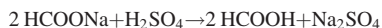
Formates as Byproducts in the Production of Polyhydric Alcohols. Sodium formate and calcium formate occur as byproducts in the production of pentaerythritol [115-77-5], trimethylolpropane [77-99-6], and 2,2-dimethyl-1,3-propanediol [126-30-7] (neopentyl glycol) (→ Alcohols, Polyhydric). The formates unavoidably produced in this manner are used in several plants as feed for manufacturing formic acid.

Formates from Sodium Hydroxide and Carbon Monoxide. The production of sodium formate from sodium hydroxide and carbon monoxide once had considerable significance, but today this process is carried out simply to utilize excess sodium hydroxide solution in low-capacity plants. The economic efficiency of producing formic acid from its salts suffers because one equivalent of a low-value inorganic salt (e.g., sodium sulfate), is produced per mole of formic acid.

Carbon monoxide reacts with alkaline compounds, even in aqueous solution, to yield the corresponding formates:

$$CO + NaOH \xrightarrow{H_2O} HCOONa$$

Carbon monoxide is mixed countercurrently with aqueous sodium hydroxide, for example, in a tower reactor at 1.5 – 1.8 MPa and 180 °C [59]. Sodium formate crystallizes and reacts with strong mineral acids, (e.g., concentrated sulfuric acid) at normal pressure in a cooled, stirred reactor at 35 °C:

$$2\ HCOONa + H_2SO_4 \rightarrow 2\ HCOOH + Na_2SO_4$$

The reaction mixture is separated, for example, in a thin-film evaporator at normal pressure and 100 – 120 °C, to produce formic acid and dry sodium sulfate [67]. The suggestion has been made that reaction with sulfuric acid be carried out in two stages. In this case, the first stage takes place in vacuo in a horizontal tubular reactor with rotating internals, and some of the formic acid is evaporated at the same time. In the second stage, the remaining formic acid is evaporated, also in vacuo, at 30 – 60 °C in a smaller tubular reactor [68].

Norsk Hydro describes the production of formic acid from calcium formate by reaction with nitric acid. The calcium nitrate produced may be used, for example, as a fertilizer.

4.2.4. Direct Synthesis from Carbon Monoxide and Water

The simplest theoretically possible method of producing formic acid is to react carbon monoxide with water:

$$H_2O + CO \rightleftharpoons HCOOH$$

As pressure increases and temperature decreases, the equilibrium of this exothermic reaction shifts in favor of formic acid. Below 150 °C, the reaction rate is very slow, and although equilibrium is reached rapidly at higher temperature, the pressure must be increased drastically to obtain acceptable formic acid concentrations. Table 12 lists the calculated equilibrium concentrations at various temperatures and pressures.

Inorganic acids and salts have been described as catalysts in the literature. Unless the reaction rate can be increased markedly by the development of new catalysts, direct synthesis cannot be used for the economical production of formic acid.

Table 12. Calculated equilibrium concentrations of formic acid at different temperatures and pressures [69]

Carbon monoxide pressure, MPa			Formic acid concentration, wt %
at 25°C	at 100 °C	at 217.9°C	
0.027	0.63	6.95	1
0.30	7.15	79.1	10
0.72	16.95	187	20
3.7	85.8	950	50
108	2540	28170	90

4.2.5. Use of Carbon Dioxide

Interesting developments in carbon dioxide chemistry have resulted in formic acid syntheses, but so far these have not been used industrially [70].

Zinc selenide [*1315-09-9*] and zinc telluride [*1315-11-3*] have been proposed as catalysts for the hydrogenation of carbon dioxide [71]. If homogeneous transition-metal catalysts are employed, carbon dioxide, hydrogen, and water can be converted to formic acid. If alcohol is used instead of water, the corresponding ester is produced. Ruthenium and palladium complexes have proved particularly active; either inorganic bases [72] or organic bases [73] (e.g., aliphatic tertiary amines) can be used as the alkaline material.

BP Chemicals has developed a process in which formic acid is produced from carbon dioxide and hydrogen via several process stages [74–76]. In the first stage, a nitrogen base such as triethylamine [*121-44-8*] reacts with carbon dioxide and hydrogen in the presence of a noble-metal catalyst (e.g., a ruthenium complex) to yield the formate of the nitrogen base. In the second and third stages, the formate is separated from the catalyst and the low-boiling constituents. In the fourth stage, the formate reacts with a high boiling base, for example, 1-(*n*-butyl)imidazole [*4316-42-1*], to yield a formate that can be thermally decomposed. Simultaneously, the low-boiling base is liberated and distilled. In the fifth stage, the formate is thermally decomposed, formic acid distilled, and the high-boiling base is returned to the fourth stage.

4.3. Concentration of Formic Acid

Formic acid – water mixtures cannot be concentrated to more than the azeotropic composition by simple distillation ($\rightarrow$ Distillation, 1. Fundamentals). Further dehydration is carried out by ternary azeotropic distillation, extractive distillation, or extraction. Additional concentration can then be achieved by simple distillation. Through suitable choice of distillation conditions, formic acid with a content exceeding 99 wt % can be drawn off as distillate.

Azeotropic Distillation. Propyl and butyl formates have been proposed as entrainers for azeotropic distillation [3]. A particularly economical separation of water from the water – formic acid – acetic acid mixture obtained by oxidizing butane is achieved by azeotropic distillation with ethyl *n*-butyl ether [*628-81-9*] [77].

Extractive Distillation. In extractive distillation, formic acid is extracted in a distillation column by means of a basic extracting agent introduced countercurrently and fed into the bottom of the column. If this mixture is heated in a column downstream, the formic acid is liberated from the salt-like compound and distilled. *N*-Formylmorpholine [*4394-85-8*] has been suggested as extractant [54], and various sulfones have been described as auxiliary liquids for extractive distillation [78].

Extraction. A number of extractants have been proposed for extracting acetic and formic acids [79]. According to BASF, secondary amides are efficient extracting agents [55]; Hüls recommends compounds in the series tri-*n*-octylamine [*1116-76-3*] to tri-*n*-dodecylamine [*102-87-4*] [80].

4.4. Construction Materials

The use of sufficiently corrosion-resistant materials in the individual process stages is part of the expertise of formic acid production. Tests on materials under laboratory conditions do not always guarantee that corrosion resistance can be achieved in practice. A low impurity content or a change in concentration or temperature may produce a decisive change in the corrosion resistance of a material toward formic acid.

If austenitic CrNi steels are used, those that contain molybdenum are preferred to molybdenum-free types [81]. Above 20 °C, stainless steel AISI 304 (Cr 18 wt %, Ni 8 wt %) has only

adequate resistance, if the formic acid concentration is below 10 % or above 90 %. Stainless steel AISI 316 (Cr 18 wt %, Ni 10 wt %, Mo 2 wt %) is resistant up to ca. 50 °C to formic acid below 40 wt % or over 80 wt % [82]. For higher temperatures and formic acid concentrations between 40 and 80 wt %, steels with higher Cr, Ni, and Mo contents (for example, AISI 317 or 317 L) or special nickel-rich alloys must be used. Aluminum ist not sufficiently resistant to formic acid, except at concentrations below 30 wt % or above 80 wt % and at temperatures below 20 °C [82]. Titanium is resistant under oxidizing conditions but is attacked very strongly under reducing conditions [81]. The corrosion behavior of titanium is considerably improved by addition of platinum or palladium. The more exotic metals tantalum, niobium, and zirconium are also corrosion resistant [81].

Of the nonmetallic materials, graphite and glass are sufficiently corrosion-resistant, but their use is limited because of their poor mechanical properties. Among the common plastics, polyethylene is resistant up to about 50 °C. Polytetrafluoroethylene (PTFE) and poly(vinylidene fluoride) (PVDF) are resistant to formic acid. Hard poly(vinyl chloride) (PVC) is resistant only at room temperature, and soft PVC should be used only for formic acid concentration below 10 wt %.

Liquid-crystal polymers (LCP) are recommended as packing materials for columns because their resistance to formic acid is reportedly much better than that of ceramics. A survey of construction materials used in formic acid production is given in [83].

5. Environmental Protection

Like most other simple organic acids, formic acid can be degraded rapidly and completely by biological methods. For this reason, formic acid is totally mineralized in a short time in purification plants and streams. The ecological equilibrium of the streams can, however, be disturbed by a change in pH. For formic acid, the theoretical biological oxygen demand (BOD) is 350 mg/g. The chemical oxygen demand has been determined to be 86 mg/g after 5 d (COD_5) and 250 mg/g after 20 d (COD_{20}). In the modified OECD screening test (OECD method 30 IE), formic acid is degraded to >90 % [84]. If an additional carbon source is available, degradation proceeds more quickly.

Toxicity to fish was tested on the blue gill sunfish (*Lepomis macrochirus*). The lethal dose (TLm 24) was found to be 175 ppm [85]. Toxicity in invertebrates was determined on *Daphnia magna*. The TLm 48 value was 120 ppm [86]. In the Federal Republic of Germany, formic acid is classified among the substances that slightly endanger water (Class 1 of water endangerment, WGK 1) [87].

Formic acid vapor can be removed from exhaust streams by washing with water. Fog results when formic acid vapor is emitted during periods of high humidity. In the Federal Republic of Germany emission is controlled by the technical guidelines for air (TA Luft) [88]. Formic acid belongs to Class 1, which means that for emission rates of 0.1 kg/h or higher, the formic acid concentration must be <20 mg/m^3 in the exhaust gas. Upon filling of formic acid, the displaced air is recycled via a gas-transfer line or it is emitted after purification (e.g., by water washing or passage through an incinerator).

6. Quality Specifications

Formic acid is marketed in concentrations of 85, 90, 95, 98, and >99 wt %. The impurity content depends on the production process. Formic acid produced by oxidation of hydrocarbons still contains a small proportion of acetic acid. A typical specification for formic acid produced by hydrolysis of methyl formate is given in Table 13; this

Table 13. Sales specification for formic acid [89]

Specification	Limits	Analytical method
Content	min. 85 wt %	titrimetric,
	min. 90 wt %	ISO 731/II, 5.2
	99 wt %	
Color number	max. 10 APHA	ASTM D 1209–79
Acetic acid	max. 150 mg/kg	ISO 731/VII
Sulfate	max. 1 mg/kg	ISO 731/V
Chloride	max. 1 mg/kg	ISO 731/IV
Iron	max. 1 mg/kg	ISO 731/VI
Other heavy metals	max. 1 mg/kg	FCC III
Evaporation residue	max. 20 mg/kg	DIN 53 172
Quality	the formic acid complies with DAB 7 and FCC III	

Table 14. Safety data [93] for formic acid

	Formic acid content, wt %				
	85	90	94	99	Method
Flashpoint, °C	59	58	55	48	DIN 51 755
Autoignition point, °C	500	480	480	480	DIN 51 794
Flammable limits in air, vol %	15 – 47	14 – 44	14 – 38	12 – 38	

acid meets the specifications required in the Food Chemicals Codex (FCC) [90].

7. Chemical Analysis

The concentration of formic acid is normally determined by titration with sodium hydroxide solution. Volatile impurities can be determined by gas chromatography on packed columns. Polyesters or Carbowax 20 M, both treated with phosphoric acid and adsorbed on chromosorb as a carrier, have proved successful as the stationary phase. Formic acid content is measured with a thermal-conductivity cell because the substance cannot be detected with flame ionization detectors (FID).

Test methods for formic acid have been standardized by the International Organization for Standardization (ISO) [91]. Other standard analytical methods for formic acid are described in [92].

8. Storage and Transportation

Formic acid is stored in tanks made of austenitic CrNi steels (18 % Cr, 10 % Ni, 2 % Mo), for example, AISI 316 L. The use of other materials, such as AISI 304 L, polyethylene-lined carbon steel, glass-lined carbon steel, and polypropylene, is restricted to specific concentrations and low temperatures. Tank cars and tank trucks made of AISI 316 L are used for transportation. Small canisters may be made of polyethylene; glass bottles are used for laboratory quantities. When aqueous formic acid mixtures are stored or transported the melting points at various concentrations (Table 3) should be considered. Tanks are best heated with hot water or subsidiary electrical heating systems. To prevent corrosion, even of AISI 316, wall temperatures above 50 °C must be avoided. Formic acid decomposes to highly toxic carbon monoxide and water. For this reason, formic acid with a concentration of 99 wt % or higher is transported in canisters without gastight seals [3]. Containers of highly concentrated formic acid should be protected against exposure to heat and stored in a well-ventilated place. Before entering ship tanks or storage tanks that have contained highly concentrated formic acid, personnel should monitor the carbon monoxide content of the air. The storage method should ensure that contact with strong alkali solutions (evolution of heat) and strong acids or oxidizing agents (decomposition) does not occur. Table 14 contains important safety data.

9. Legal Aspects

Formic acid is marked according to the regulations of the European Economic Community (council directive 76/907/EEC including the latest amendment) and to the regulations of the Federal Republic of Germany (Gef Stoff V) [94] as: Corrosive, R34 (formic acid content 25 – 90 wt %), R35 (formic acid content > 90 wt %), and S 2–23–26. The EEC numbers of formic acid are 607–001–00–0 (formic acid content >90 wt %) and 607–001–01–8 (formic acid content 25 – 90 wt %). Hazard classifications for the transport of formic acid are listed in the following:

RID/ADR	class 8, item 32 b
Fed. Rep. of Germany: GGVE/GGVS	class 8, item 32 b
ADNR	class 8; item 21 b
IMDG Code (Fed. Rep. of Germany: GGVSee)	8
IATA-DGR	1779
UN Number	1779
DOT Hazard Classification (USA)	corrosive material
HazChem Code (UK)	2 R

Table 15. Applications of formic acid (1988, BASF assessment)

Textiles, leather	25 %
Pharmaceuticals, crop-protection agents	10 %
Latex, rubber auxiliaries	10 %
Silage	35 %
Miscellaneous	20 %

10. Uses

Because of its acidity, its aldehyde nature, and its reducing properties, formic acid is used in a variety of fields (Table 15).

In contrast to mineral acids, formic acid evaporates without leaving any residue. The leather and textile industries, in particular, make use of its strongly acidic nature. Animal skins and hides are acidified with a mixture of formic acid, sulfuric acid, and sodium chloride before chrome tanning (→ Leather, Chap. 6. Chrome Tanning).

Formic acid is used for adjusting the pH of dye baths in dyeing of natural and synthetic fibers. Use is made of its highly reactive nature in the manufacture of pharmaceuticals and crop-protection agents [32], [43]. Formic acid plays an important role in the coagulation of rubber latex.

In Europe, most of the formic acid is used as a silage aid. If freshly mown, damp grass is sprayed with formic acid to establish a pH of ca. 4, such fodder can be used directly for silage. Formic acid promotes the fermentation of lactic acid and suppresses the harmful formation of butyric acid. If formic acid is used, fermentation processes occur more rapidly and at lower temperature so that fewer nutrients are lost [95], [96]. Mixtures of formic acid with formaldehyde or with ammonium formate are also used as silage aids. Silage that utilizes formic acid is restricted largely to Europe, but it should be of interest in all regions where climate makes *green forage* difficult to dry.

Other applications of formic acid are as an additive for cleaning agents (replacement of mineral acid for environmental reasons), in the synthesis of the sweetener aspartame [*22839-47-0*] [97] (→ Amino Acids, Section 5.1.2.), and in the desulfurization of flue gas by the Saarberg – Hölter process (pH stabilization of the wash liquid) [98].

11. Economic Aspects

In 2000 the world consumption of formic acid was about 415 000 t, half of which was used in Europe. The main applications in Europe are in the Silage and animal feed preparation market. About 65% of the formic acid demand in Europe are produced by BASF, Kemira, BP, and Perstorp. Perstorp is the only company using sodium formate as starting material, whereas the other three utilize the methyl formate process.

12. Derivatives

Among the derivatives of formic acid, amides (→ Formamides), various esters, and salts are the most important.

12.1. Esters

Esters of formic acid have the typical physical and chemical properties of esters; they are readily volatile and flammable, and have a sweet, often fruity smell. They are only partially soluble in water. A summary of their chemical properties has been published by GIBSON [32].
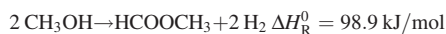
12.1.1. Methyl Formate

Methyl formate [*107-31-3*], $C_2H_4O_2$, M_r 60.05, is an intermediate in the production of formic acid (Sections 4.1, 4.2) and formamide (→ Formamides) in large manufacturing plants. With increasing interest in the production of synthesis gas by coal gasification, methyl formate will become important as a versatile key intermediate. It can also be used as a starting material in the production of high-purity carbon monoxide [99]. Physical properties, safety data, and marking regulations for methyl formate are summarized below.

Boiling point (101.3 kPa)	31.7 °C [17]
Melting point	−99 °C [17]
Specific gravity d_4^{20}	0.975 [17]
Refractive index n_D^{20}	1.3433 [99]
Flash point (open cup)	−20 °C [99]
Ignition temperature	450 °C [99]
Flammable limits in air	5.0 – 23 vol % [99]
MAK value	100 mL/m³; 250 mg/m³
	(category I)

(Continued)

TLV—TWA	100 mL/m^3; 250 mg/m^3
TLV—STEL	150 mL/m^3; 375 mg/m^3
UN number	1243
EEC number	607–014–00–1
Marking according to Gef Stoff V (FRG)	symbol : F R12, S 9–16–33
Hazchem Code (UK)	2 SE
RID/ADR	class 3, item I a
ADNR	class 3, item I a
IMDG Code (F.R. of Germany GGVSee)	3.1
IATA-DGR	1243
DOT Hazard Classification (USA)	flammable liquid

Production. Methyl formate is produced by base-catalyzed carbonylation of methanol (Section 4.1). Processes have been developed for dehydrogenating methanol, but these have not yet been implemented commercially [100]:

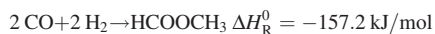$$2\,CH_3OH \rightarrow HCOOCH_3 + 2\,H_2 \quad \Delta H_R^0 = 98.9\,kJ/mol$$

Catalysts containing copper are used.

Mitsubishi Gas Chemical (MGC) has developed highly active catalysts which contain Cu – Zr – Zn or Cu – Zr – Zn – Al. The conversion of methanol is approximately 50 %, with a methyl formate selectivity of ca. 90 % and a space – time yield of 3000 g L^{-1} h^{-1} [101]. Air Products uses a copper – chromite catalyst for the dehydrogenation of methanol [102]. Methyl formate can also be produced by oxy-dehydrogenation of methanol:

$$2\,CH_3OH + O_2 \rightarrow HCOOCH_3 + 2\,H_2O \quad \Delta H_R^0 = -472.8\,kJ/mol$$

Soluble chromium compounds are used as catalyst [103].

The direct synthesis of methyl formate from synthesis gas has been investigated:

$$2\,CO + 2\,H_2 \rightarrow HCOOCH_3 \quad \Delta H_R^0 = -157.2\,kJ/mol$$

The high pressure of 100 – 200 MPa (1000 – 2000 bar) required makes economical implementation impossible [100]. The dimerization of formaldehyde has likewise not been exploited industrially [100]:

$$2\,CH_2O \rightarrow HCOOCH_3 \quad \Delta H_R^0 = -146.4\,kJ/mol$$

Uses. Most of the methyl formate produced is used as an intermediate for the production of formic acid and formamide. Dimethylformamide [*68-12-2*] is produced by reacting methyl formate with dimethylamine [*124-40-3*] ($\rightarrow$ Formamides). A new use has been found for methyl formate in the production of foundry molds. The mold is formed from granular refractory material and a binder consisting of phenol – formaldehyde resin which is cured by exposure to methyl formate vapor. This process makes possible the production of rapidly cured foundry molds at low temperature [104].

Small quantities of methyl formate are used as solvents and insect control agents. With the anticipated extension of C$_1$ chemistry, methyl formate may be used as an intermediate for a number of products [99], [100].

12.1.2. Ethyl Formate

Ethyl formate [*109-94-4*], C$_3$H$_6$O$_2$, M$_r$ 74.08, *bp* 54.1 °C, *mp* $-80 d_4^{20}$ 0.923, flash point-20 °C, ignition point 440 °C, UN number 1190, has a sharp rumlike smell and taste.

Ethyl formate is produced by carbonylation of ethanol with carbon monoxide or by esterification of ethanol with formic acid.

Ethyl formate is a solvent for acetyl cellulose and nitrocellulose. Ethyl formate is used in alcohol-free drinks, ice cream, chewing gum, and other confectionery as a component of apple-, pineapple-, banana-, and peach-type flavors.

12.1.3. Isobutyl Formate

Isobutyl formate [*542-55-2*], M$_r$ 102.13, *bp* 98 °C, *mp* $-96 d_4^{20}$ 0.88, flash point 5 °C, ignition point 320 °C, UN number 2393, is produced by carbonylation of isobutyl alcohol [*78-83-1*] with carbon monoxide or esterification of isobutyl alcohol with formic acid. Isobutyl formate is used as a solvent for colors, lacquers, adhesives, and cleansing agents.

12.1.4. Miscellaneous Esters

A number of formates produced by esterification of the corresponding alcohols with formic acid are used as perfumes and flavorings ($\rightarrow$ Flavors and Fragrances). Some representative products are citronellyl formate [*105-85-1*], geranyl for-

mate [*61759-63-5*], phenylethyl formate [*104-62-1*], benzyl formate [*104-57-4*], and isopentyl formate [*110-45-2*].

Orthoformates are used in the preparation of acetals and ketals. Chloroformic esters are used as intermediates in organic syntheses.

12.2. Salts

12.2.1. Alkali-Metal and Alkaline-Earth Metal Formates

Sodium formate [*141-53-7*] and calcium formate [*544-17-2*] are byproducts in the synthesis of polyols such as pentaerythritol. However, they are also produced directly from the corresponding hydroxides and carbon monoxide (Section 4.2.3) [3].

Sodium or calcium formate is used to produce formic acid (Section 4.2.3). An important process for manufacturing sodium dithionite [*7775-14-6*] starts with sodium formate. Oxalic acid [*144-62-7*] production employs sodium formate as an intermediate. Sodium formate is used in chrome tanning and as a mordant in the dyeing and printing of fabrics by the textile industry. The reducing power of sodium formate is utilized in electroplating baths and photographic fixing baths. Calcium formate is also used in tanning. Adding calcium formate to concrete reduces the setting time considerably.

12.2.2. Ammonium Formate

Ammonium formate solutions are used as a low-corrosion silage aid; the complex salts ammonium diformate [*64165-14-6*] and ammonium tetraformate [*70179-79-2*] are stable in aqueous solution [105].

12.2.3. Aluminum Formate

Stepwise replacement of the hydroxyl groups in aluminum hydroxide [*21645-51-2*] yields dibasic aluminum formate [*18748-09-9*], $(HO)_2Al(OOCH)$; Almonobasic aluminum formate [*51575-25-8*], $(HO)Al(OOCH)_2$; and aluminum formate [*22918-74-7*], $Al(OOCH)_3$. Aluminum hydroxy acetate formate [*34202-30-7*] $(HO)Al$

$(OOCH)(OOCCH_3)$, is also manufactured commercially. The various formates are produced either directly from the metal or by reaction with an aluminum compound, for example, aluminum hydroxide [106].

Aluminum formates are used to impregnate textiles and to make paper water-resistant. Formates are also employed mordants in the textile industry. Because of the low toxicity and antiseptic, astringent, and basic properties of the aluminum salts, aluminum formates are used in pharmaceuticals.

12.2.4. Nickel Formate

Nickel(II) formate [*15694-70-9*] usually exists in the form of a green crystalline dihydrate Ni $(HCOO)_2 \cdot 2\ H_2O$; it is prepared by dissolving nickel(II) hydroxide [*12054-48-7*] or nickel(II) carbonate [*16337-84-1*] in formic acid or by reaction of nickel(II) sulfate with sodium formate. Nickel(II) formate is used for the production of nickel hydrogenation catalysts.

12.2.5. Copper Formate ($\rightarrow$ Copper Compounds, Section 5.1.)

Copper(II) formate [*544-19-4*] is produced by reacting copper(II) hydroxide [*20427-59-2*], copper(II) oxide [*1317-38-0*], or copper(II) carbonate [*12069-69-1*] with formic acid. It is used as an antibacterial agent for treating cellulose.

13. Toxicology and Occupational Health

Formic acid occurs naturally in small amounts in plants, animal poisons, and higher organisms. In humans, it is formed in toxic amounts during methanol poisoning. After intake of large amounts of methanol, the metabolic capacity to detoxify it to carbon dioxide is insufficient, and the high amount of formic acid that results leads to metabolic acidosis. Under physiological conditions, formic acid which is observed under these conditions in low concentration is a component of human blood and tissues, and plays an important role in the transfer of C_1 compounds during intermediate metabolism. Most of the

formic acid taken up by the body is metabolized; a small portion is excreted unchanged in the urine. After oral intake, the biological half-life of formic acid is about 45 minutes in human blood plasma [107].

The most prominent toxic property of this compound is its corrosive effect upon skin and mucous membrane. When applied to the clipped skin of rabbits, formic acid causes necrosis, which heals slowly [108]. Following oral intake of aqueous dilutions of formic acid, corrosion of the oral cavity and esophagus occurs even at concentrations as low as 6 % [108–110]. The LD_{50} after oral administration is reported to be 1830 mg/kg in rats [111] and 1076 mg/kg in mice [112]. Formic acid, whose solubility in water is good, can be absorbed easily by the skin [107], [108] and causes serious local injuries upon inhalation. In rats, increasing concentrations of aqueous acid solutions, inhaled as saturated vapors (20 °C), lead to death during decreasing exposure times: a 10 % aqueous solution of formic acid is tolerated for 7 h. Eyelid closure and watery nasal discharge as a result of pronounced irritation is no longer observed after termination of the exposure period. A 25 % aqueous solution is lethal after an exposure of more than 3 h; a 50 % aqueous solution, after 30 min; and undiluted (98 %) formic acid, after only 3 min inhalation. In rats, the LC_{50} is 7.4 mg/L after inhalation of the vapor [113]. The predominant symptoms of inhalative intake are irritation of the eyes, irritation and corrosion of the nasal mucous membranes, and corneal opacity.

According to earlier investigations [108], formic acid affects the central nervous system (CNS). In rabbits, intravenous administration of buffered formic acid in the range of 0.46 – 1.25 g per kilogram of body weight leads to CNS depression; higher dosages cause convulsions. Subcutaneously administered doses of 0.8 g/kg in dogs and over 0.4 g/kg in cats lead to staggering, while a dosage of 0.4 g/kg leads to sleepiness in cats. In dogs, lethal doses administered intravenously result in tonic and clonic convulsions [108]. The mechanism of CNS effects was investigated by exposing rats to formic acid vapors (20 ppm) for 6 h a day, five days per week, for two or three weeks. This treatment caused changes in glial cell metabolism, which could be the reason for neurological effects [114].

Rats administered formic acid in concentrations of 0.5 and 1.0 % in feed and drinking water, respectively, showed a slight increase in body weight gain. In addition the weights of liver, kidneys, adrenals, and (for the lower dose group) spleen were lower than those of control animals [111]. In rats, the administration of dosages of 8.2, 10, 25, 90, 160, and 360 mg kg^{-1} d $^{-1}$ in drinking water for 2 to 27 weeks led to a lower intake of food and delay in body weight gain only in the highest dose group [115].

The influence of formic acid on biochemical parameters was investigated in rats by exposing them for 6 h a day to vapors of 20 ppm for three or eight days [116]. This treatment led to a decrease in the concentration of glutathione in the liver and kidneys.

Few experimental results are available regarding the mutagenic effects of formic acid. The substance was weakly mutagenic when tested on *Escherichia coli* [117]. A mutagenic effect was also observed on the germ cells of drosophila [118]. However, no primary genotoxic mechanism of action appears to be involved; rather, the mutagenicity is probably associated with the acidity of the compound, which leads to radical formation after inhibition of the enzyme catalase.

The TLV-TWA exposure limit (ACGIH) for formic acid is 5 ml/m^3 (9 mg/m^3); its MAK value is also 5 ml/m^3 (9 mg/m^3) (short term exposure maximum: category I). Formic acid has a PDK (former Soviet Union) of 0.5 ml/m^3 (1 mg/m^3).

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