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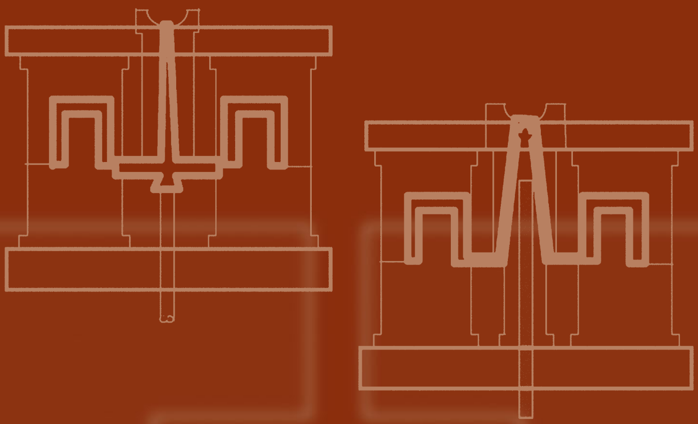

Phenolic Resins: A Century of Progress

Springer

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Louis Pilato
Editor

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Preface

The legacy of Leo Hendrik Baekeland and his development of phenol formaldehyde resins are recognized as the cornerstone of the Plastics Industry in the early twentieth century, and phenolic resins continue to flourish after a century of robust growth. On July 13, 1907, Baekeland filed his “heat and pressure” patent related to the processing of phenol formaldehyde resins and identified their unique utility in a plethora of applications. The year 2010 marks the Centennial Year of the production of phenolic resins by Leo Baekeland. In 1910, Baekeland formed Bakelite GmbH and launched the manufacture of phenolic resins in Erkner in May 1910. In October 1910, General Bakelite began producing resins in Perth Amboy, New Jersey. Lastly, Baekeland collaborated with Dr. Takamine to manufacture phenolic resins in Japan in 1911. These events were instrumental in establishing the Plastics Industry and in tracing the identity to the brilliance of Dr. Leo Baekeland.

Phenolic resins remain as a versatile resin system featuring either a stable, thermoplastic novolak composition that cures with a latent source of formaldehyde (hexa) or a heat reactive and perishable resole composition that cures thermally or under acidic or special basic conditions. Phenolic resins are a very large volume resin system with a worldwide volume in excess of 5 million tons/year, and its growth is related to the gross national product (GNP) growth rate globally. Yet it is a mere 2% of total global production of plastics that amounts to 250 million tons in 2008. Phenolic resins continue to be an important bonding agent for a diversity of uses encompassing the joining of metals, glasses, wood, paper, rubber to other substrates with favorable cost–performance characteristics that surpass most other polymeric resins. As phenolic resins embark into the twenty-first century, the outlook continues to be optimistically favorable.

The global commitment to Nanotechnology has not evaded phenolic resins. Although results are somewhat preliminary, selective phenolic resin mechanical properties are improved and offer promise for continued efforts in this new and exciting technology. Nanotechnology has been applied to phenolic resins, benzoxazines, and cyanate esters using an array of nanomaterials such as nanoclay, carbon nanofiber, carbon nanotubes, POSS® and others. Thus, ablation improvement because of reduced thermal erosion for rocket motors, improved thermooxidative stability of carbon–carbon composites, and better scratch-resistant flooring are current developments that have occurred through Nanotechnology.

The bold commitment of the commercial aircraft manufacturers (Boeing and Airbus) to fabricate the entire fuselage and other critical components involving over 50% of aircraft weight with fiber reinforced composites for reduced weight and greater fuel efficiency has become a “lightning rod” for the re-assessment of product performance with greater emphasis on composites. Although phenolic resin-based composites enjoy an enviable position as the preferred composition for aircraft interiors and cargo liners due to the extraordinary fire, smoke, and toxicity (FST) characteristics, the quest to develop a “load bearing” phenolic resin composite structure with FST behavior that meets or exceeds the mechanical properties of an epoxy resin based composite is desired. Efforts in closely related phenolic systems such as benzoxazine or phenylene bisoxazolines (PBO) may provide encouragement.

New areas in the use of phenolic resins continue to be developed. Carbon foam is prepared by the carbonization of open cell phenolic foam or by the expansion/cure of mesophase pitch at elevated temperature. These newly developed materials are attractive compositions for high temperature composite tooling and floor paneling clad with fiber reinforced prepreg. Significant efforts have resulted in the commercialization of benzoxazines, a closely related phenolic material, into the preparation of fiber reinforced composites, electronics applications, and prepreg intermediate. Phenylene bisoxazolines are being revisited by reacting them with selected novolaks to yield novel polyaryl ether amide resins that possess performance characteristics equal to or better than high T_g multifunctional epoxies but with improved toughness and hot wet strength. Group appendage involving reactions directed to the phenolic hydroxyl such as epoxy, cyanate ester, or allyl groups or ring formation through the use of formaldehyde with a primary amine to yield benzoxazines expands the versatility of phenolic resin chemistry.

Newly developed novolak process by Asahi (known as Phosphoric Acid Phase Separation (PAPS)) involves the use of a high amount of phosphoric acid as catalyst/phase reactant. Asahi proposes “Phase Transfer Catalysis” as the method and results in a rapid process for novolak preparation. The resulting novolaks are predominately high in para content, possess minimal amounts of free phenol or dimer, slower curing with hexa, and exhibit a lower bulk viscosity than conventional novolak prepared by oxalic acid. The PAPS resins are in the early stage of development and require additional time before Asahi commits to full scale commercial production.

Renewable raw materials, particularly those that would reduce the amount of expensive phenol, continue to be examined and can be used in limited amounts. Materials such as cashew shell nut oil, tannins, soy, and furfural are being examined for an economic benefit without a corresponding unfavorable product performance. Other renewable materials such as tung oil and linseed oil continue to be used in limited amounts in the usual applications such as electrical laminates (tung oil) and friction for linseed oil. The emergence of “Biorefineries” in Europe as well as the

US to process lignocellulose waste into fuels and chemical raw materials will result in the availability of pure lignin as a phenolic-like material for utilization in phenolic resin preparation. Lignin economics will be a factor for its potential use in phenolic resins.

The escalating cost of energy and its impact on phenolic resin raw materials, resin production, and processing of phenolic resins by customers is of paramount importance. Low energy systems are stressed by resin customers in spite of cure limitations of phenolic resin chemistry. Efforts directed to the use of resorcinol and tannins as well as newly developed latent cure catalyst of Bac2 in fast cure systems may provide some benefit in energy reduction. Economic value versus energy reduction will need resolution. The current shift to more offshore oil exploration and in greater depths will require the manufacture of more fire resistant composite platforms, deluge pipe, and other items closely related to offshore oil activities. Pultrusion of platforms, phenolic foam paneling for thermal insulation are expected to be in great demand.

Selective non-formaldehyde or non-hexa curing agents are being examined and consist of glyoxal, oxazolidine, solid resole, epoxy, resorcinol, and tannins. In some cases these non-formaldehyde curing agents require less energy for full cure of phenolic resins.

Yet there are some concerns as they relate to large volume applications of phenolic resins. Wood adhesives and mineral fiber binders for thermal insulation are application areas under intense pressure for all formaldehyde containing resins (UF, MF, and PF) due to the environmental movement to reduce or eliminate formaldehyde containing resins in wood and thermal insulation consumer products. Coupled to these considerations is the uncertainty of the status of formaldehyde – whether formaldehyde will be classified as a human carcinogen. These potential shifts in these large consumer markets will surely impact and reduce volume sales of liquid phenolic resins. Thus, gains in increased sales in many of the newly emerging areas mentioned above may be offset by reduced sales in wood adhesives and mineral fiber binder areas.

It is appropriate to acknowledge several individuals who endorsed initially the outline of the book and provided key personnel as authors. These are Harald Steindl, Kazuhisa Hirano, Larry Gollob, James Lamb, William J. McKillip, and Shinichi Ozeki.

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Chapter 1
Introduction

Louis Pilato

The title of this book is selected appropriately to describe a century of progress for phenolic resins. The contributions of Leo Hendrik Baekeland are immense! He was not easily discouraged as he attempted to harness the reaction of phenol and formaldehyde into a manageable, commercial product. In spite of some of the great organic chemists who examined the reaction of phenol and formaldehyde and obtained intractable, useless materials, he prevailed. The legacy of Leo Hendrik Baekeland and his development of phenol formaldehyde resins are recognized as the cornerstone of the Plastics Industry in the early twentieth century whereby phenolic resins and other polymeric systems continue to flourish after a century of robust growth. On July 13, 1907, Baekeland filed his “heat and pressure” patent related to the processing of phenol formaldehyde resins and identified their unique utility in a plethora of applications. Bakelite as coined by Baekeland was considered “the material of a thousand uses!” Phenol formaldehyde resins or Bakelite as they were commonly referred to became the first truly synthetic polymer to be developed. The perseverance and diligence of Baekeland and those who followed him in the ensuing years attest to their significant contributions that are identified with a variety of thermosetting and thermoplastic polymeric materials within the Plastics Industry. Further, it is remarkable that after a century of existence phenolic resins continue their preferred status in a number of applications that were developed during Baekeland’s era to this very day.

Previous phenolic resin publications and commemorative conferences were successful largely due to the global interest and successful business activities of phenolic resin technology. The more recent centennial conference, “Baekeland 2007 Symposium: Thermosets, 100 Years after Bakelite,” held from September 23–26, 2007 in Ghent, Belgium where Baekeland was born and educated, was a resounding success. It is indeed a hallmark of achievement that, after a century of

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existence, phenolic resins are an important component in those industries where it is best qualified.

Since the publication of the phenolics resins book by Springer in 2000, phenolic resins remain a versatile resin system featuring either a stable, thermoplastic novolak composition that cures with a latent source of formaldehyde (hexa) or a heat reactive and perishable resole composition that cures thermally or under acidic or special basic conditions. It is a very large volume resin system with a worldwide volume in excess of 5 million tons/year, and its growth is related to the gross national product (GNP) growth rate globally.

During the early twenty-first century, there has been a rationalization of phenolic resin businesses whereby venerable Bakelite AG, a company that traced its origin to Baekeland and identified as the first phenolic production location in Germany in May 1910, was acquired by Apollo Management and merged with Borden Chemical to form Hexion Specialty Chemicals, one of the large global phenolic resin manufacturers. Further rationalization occurred within Dynea when the Dynea North American phenolic resin operation was sold to Teachers' Private Capital (Ontario, Canada) and renamed Arclin. Another business unit of Dynea, Vyncolit, the phenolic resin molding powders technology, was sold to Sumitomo Bakelite of Japan. Thus, more rationalization is anticipated as phenolic resin technology expands in China, Russia, and India.

As phenolic resins embark into the twenty-first century, the outlook continues to be extremely favorable. However, there are some vigilant activities that relate directly to phenolic resin consumption. The concern over free formaldehyde emissions and their presence as one of the components in the binder for wood panels have resulted in newly proposed rules by California Air Resources Board (CARB) for lower formaldehyde emissions in wood panels in two distinct phases: Phase I (by January, 2009) a reduction of FF value to 0.08 and 0.18 ppm. in hardwood plywood and particle board respectively, and reduced further to 0.05 and 0.09 ppm for the same panels for Phase II by January 2011. These CARB proposals will involve some production modifications when using phenolic resins but is expected to result in additional phenolic resin opportunities by displacing possibly urea formaldehyde resin in particle board panels. The use of phenolic resins as wood adhesives is undergoing many changes due to new wood composite processes coupled with continuous line equipment that are placing greater performance standards on improved wood adhesives. These increased improvement demands coupled with volatile emissions reductions are providing great challenges to wood adhesive manufacturers, many of which are discussed in the wood chapter. As it will be mentioned in wood adhesive area, hybrid resins such as MUF and PMUF are being developed to reduce the amount of formaldehyde emissions in wood panels ensuring the use of UF resins with reactive co-reactants and thus reducing formaldehyde emission.

By contrast, Johns Manville has commercialized a fiber glass insulation product which is "formaldehyde free" and involves a binder that is based on a cured acrylic resin system. It is uncertain whether these modified acrylic binders will lead to a substantial shift in the use of phenolic resins as binders for fiber glass insulation.

It should be noted that once formaldehyde is incorporated into the phenolic resin structure, it is permanently bonded to phenol and no formaldehyde is emitted during processing of the resin. Yet in those instances when the level of free formaldehyde (unattached formaldehyde) in the resin is reduced by the addition of a formaldehyde scavenger like urea, some formaldehyde can be emitted during processing due to a shift in the equilibrium reaction of formaldehyde and urea. In a perceptive manner, some of the benefits of selective basic catalysts used to prepare mineral wool binders with reduced crystalline dimer are mentioned in the mineral wool insulation binders chapter as well as the multiplicity of roles that ammonium sulfate experiences in the final mineral wool binder mixture.

Renewable raw materials, particularly those that would reduce the amount of expensive phenol, continue to be examined and are discussed in several chapters. Materials such as cashew shell nut oil, tannins, soy, and furfural are being examined for an economic benefit without corresponding unfavorable product performance. Other renewable materials such as tung oil and linseed oil continue to be used in limited amounts in the usual applications such as electrical laminates (tung oil) and friction (linseed oil). The emergence of “Biorefineries” in Europe as well as the US to process lignocellulose waste into fuels and chemical raw materials may result in the availability of pure lignin as a phenolic-like material for utilization in phenolic resin preparation. Lignin economics will be a factor for its potential use in phenolic resins.

The escalating cost of energy and its impact on phenolic resin raw materials, resin production, and processing of phenolic resins by customers is of paramount importance. Low energy systems are stressed by resin customers in spite of cure limitations of phenolic resin chemistry. Efforts directed to the use of resorcinol and tannins in fast cure systems may provide some benefit in energy reduction. Economic value versus energy reduction will need resolution.

The global commitment to Nanotechnology has not evaded phenolic resins. Although results are somewhat preliminary, some attractive phenolic resin mechanical properties are improved and offer promise for continued efforts in this new and exciting technology. Thus, ablation improvement due to reduced thermal erosion for rocket motors, improved thermooxidative stability of carbon carbon composites, and better scratch resistant flooring are current developments that have occurred through Nanotechnology.

The bold commitment of the commercial aircraft manufacturers (Boeing and Airbus) to fabricate the entire fuselage and other critical components involving over 50% of aircraft weight with fiber reinforced composites for reduced weight and greater fuel efficiency has become a “lightning rod” for re-assessment of product performance with greater emphasis on composites. Although phenolic resin based composites enjoy an enviable position as the preferred composition for aircraft interiors and cargo liners, the quest to develop a “load bearing” phenolic resin composite structure that meets or exceeds the mechanical properties of an epoxy resin based composite is desired. Efforts in closely related phenolic systems such as benzoxazine or phenylene bisoxazolines (PBO) may provide encouragement.

The proposal to broaden the recognized FST characteristics of phenolic resins as an additive into thermoplastic resins for UL VO flame retardant behavior is a consideration.

Weight savings for greater fuel efficiency are related to the replacement of metals and ceramics in the auto industry by many of the newly developed phenolic molding compounds involving long glass fiber (for greater toughness/impact) and carbon fiber reinforced phenolic molding compounds. As the auto industry addresses the need for greater fuel efficiency involving corresponding reduction in auto body weight and auto components, the weight of friction parts will also be reduced. Thus, the frictional load applied to the friction element is expected to increase and will necessitate phenolic resins with greater heat resistance.

New areas in the use of phenolic resins continue to be developed. Carbon foam is prepared by the carbonization of open cell phenolic foam or by expansion/cure of mesophase pitch at elevated temperature. These newly developed materials are attractive compositions for composite tooling and for paneling clad with fiber reinforced prepreg. Phenolic foam for thermal insulation is being reassessed in North America by producing fiber reinforced phenolic foam with a pH close to neutral. There is a reported possible opportunity to replace balsa core with pultruded high density phenolic foam in US naval ship structural sandwich panels.

Significant efforts have resulted in the commercialization of benzoxazine resin, a closely related phenolic material, as well as formulation of benzoxazine resin into fiber reinforced composites, electronics applications, and prepreg intermediate. Benzoxazines appear to be versatile in that they can undergo co-reaction with a variety of materials such as epoxy, isocyanates, and BMI.

Phenylene bisoxazolines are being revisited by reacting them with selected novolaks to yield novel polyaryl ether amide resins that possess performance characteristics equal to or better than high T_g multifunctional epoxies but with improved toughness and hot wet strength.

The current shift to more offshore oil exploration and in greater depths will require the manufacture of more fire resistant composite platforms, deluge pipe, and other items closely related to offshore oil activities. Pultrusion of platforms and phenolic foam paneling are expected to be in great demand. Proppants and emulsifiers will grow.

Selective non-formaldehyde or non-hexa curing agents are being examined and consist of glyoxal, oxazolidine, solid resole, epoxy, resorcinol, and tannins. In some cases these non-formaldehyde curing agents require less energy for full cure of phenolic resins.

Co-reaction of phenol formaldehyde with urea, melamine, olefin, and others occurs readily within the PF structure. Group appendage involving reactions directed to the phenolic hydroxyl such as epoxy, cyanate ester, or allyl groups or ring formation through the use of formaldehyde with a primary amine to yield benoxazines expands the versatility of phenolic resin chemistry. Post cure or reaction with B, N, or P type components provides improved thermal stability.

Newly developed novolak process by Asahi (known as Phosphoric Acid Phase Separation [PAPS]) and Sumitomo Bakelite (who later abandoned the method) involves the use of a high amount of phosphoric acid as catalyst/phase reactant. Asahi proposes “Phase transfer catalysis” as the method and results in a rapid process for novolak preparation. The resulting novolaks are predominately high in para content, possess minimal amounts of free phenol or dimer, better thermal stability, slower curing with hexa, and exhibit a lower bulk viscosity than conventional novolak prepared by oxalic acid. This new novolak process is mentioned in the chapter on resin chemistry.

Timely and concurrent information related to the key phenolic resins raw materials, modern analytical techniques used in phenolic resins analyzes/testing, and various application areas are written by experts who are engaged in daily technical problem solving activities. This new phenolic resins book is global in technical content and attempts to provide a worldwide view of phenolic resins technology as it is applied globally in all market sectors.

Part I
Raw Materials

Chapter 2
Phenols

Manfred Weber and Markus Weber

Abstract Up to the end of the nineteenth century, phenol was recovered primarily from coal tar. With the commercialization of the phenolic resins, the demand for phenol grew significantly. Currently, the cumene-to-phenol process is the predominant synthetic route for the production of phenol. It is accompanied by acetone as a co-product. Cumene is oxidized with oxygen to form cumene hydroperoxide. The peroxide is subsequently decomposed to phenol and acetone, using a strong mineral acid as catalyst. The products are purified in a series of distillation columns. The cumene-to-phenol process is described in more detail in this chapter. An overview is given about synthetic routes via direct oxidation of benzene. None of these alternative routes has been commercialized. The chapter also gives an overview of global supply and use of phenol in 2008. Finally, the main natural sources and synthetic routes for cresols, xylenols, resorcinol, and bisphenol-A are described. These components are used as comonomers for special phenolic resins.

Abbreviations

ACP	Acetophenone
AMS	α-Methylstyrene
BP	Boiling point
BPA	Bisphenol-A
BWWT	Biological Waste Water Treatment
CHP	Cumene hydroperoxide
DAA	Diactone alcohol
DCP	Dicumyl peroxide

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DiPB	Diisopropylbenzene
DMBA	Dimethyl benzyl alcohol
H_2	Hydrogen
H_2O	Water
H_2O_2	Hydrogen peroxide
MOX	Mesityloxide
MAK	Maximale Arbeitsplatzkonzentration
MHP	Methyl hydroperoxide
MP	Melting point
MW	Molecular weight
NaOH	Caustic soda
NaPh	Sodium phenate
NH_3	Ammonia
NO_x	Nitrogen oxides
N_2O	Nitrous oxide
PEL	Permissible exposure limit
SADT	Self-Accelerating-Decomposition-Temperature
TriPB	Triisopropylbenzene
TWA	Time weighted averages (over 8 h)

Phenols are aromatic components which contain one or more hydroxyl groups that are attached to an aromatic ring. For the production of phenolic resins, mostly mono-hydroxybenzenes, especially phenol, are of the greatest importance. Besides alkylphenols (cresols and xylenols), resorcinol (di-hydroxybenzene) and bisphenol-A are used sparingly for the production of phenolic resins. In Table 2.1, the main physical properties of these various phenols are summarized. Compared to aliphatic alcohols, phenols are weak acids. Thus, phenols can be easily extracted from organic solutions with aqueous sodium hydroxide. This is the preferred method to recover phenol and cresols from coal tar [1].

Table 2.1 Physical properties of phenols [6, 29, 32, 33]

Name		MW	MP (°C)	BP (°C)	pK_a 25°C
Phenol	Hydroxybenzene	94.1	40.9	181.8	10.00
o-Cresol	2-Methylphenol	108.1	31.0	191.0	10.32
m-Cresol	3-Methylphenol	108.1	12.2	202.2	10.09
p-Cresol	4-Methylphenol	108.1	34.7	201.9	10.27
2,3-Xylenol	2,3-Dimethylphenol	122.2	72.6	216.9	10.54
2,4-Xylenol	2,4-Dimethylphenol	122.2	24.5	210.9	10.60
2,5-Xylenol	2,5-Dimethylphenol	122.2	74.9	211.1	10.41
2,6-Xylenol	2,6-Dimethylphenol	122.2	45.6	201.0	10.63
3,4-Xylenol	3,4-Dimethylphenol	122.2	65.1	227.0	10.36
3,5-Xylenol	3,5-Dimethylphenol	122.2	63.3	221.7	10.19
Resorcinol	3-Hydroxyphenol	110.1	109.8	276.5	–
Bisphenol-A	2,2-Bis(4-hydroxyphenyl)propane	228.3	157.3	–	–

2.1 Phenol

Up to the end of the nineteenth century, phenol was recovered primarily from coal tar. Presently, a small amount of phenol is still obtained from coal tar. Yet in 1898, Felix Hoffmann filed his patent [2] for the synthesis of acetylsalicylic acid (*Aspirin*), which required phenol as starting material.

At the dawn of the twentieth century, the demand for phenol grew significantly with the commercialization of the phenolic resins (*Bakelite*). Leo Baekeland launched his first phenolic resins plant in May 1910 in Germany since phenol was readily available from coal tar. Much later the use for bisphenol-A (polycarbonates and epoxide resins) became an important factor for the substantial market growth of phenol. Synthetic routes were developed at the end of the nineteenth century to meet the increasing demand for phenol.

The first synthetic method for the production of phenol involved sulfonation and later chlorination of benzene. Details are described in [3]. These processes are no longer used for the commercial production of phenol.

After the Second World War, the cumene-to-phenol process (Hock-Process) was developed and commercialized. It is currently the predominate route for the production of phenol. It is accompanied by acetone as a co-product. Details are described in Sect. “Phenol Production from Cumene”.

In the 1960s, the first commercial plant using toluene as the feedstock was launched. The process was developed simultaneously by Dow [4] and the California Research Corp. [5]. The process is described in more detail in [6]. However, all commercial plants were closed in 2006. Currently, there is no commercial production of phenol from toluene.

Several attempts have been explored during the past two decades to synthesize phenol via the direct oxidation of benzene. Unlike the cumene process route, the direct oxidation of benzene does not produce acetone as a co-product and offers the potential for economy of operation without by-product.

One route is the direct oxidation of benzene with nitrous oxide N_2O, which was mainly developed by Solutia in cooperation with the Boreskov Institute of Catalysis in Russia [7, 8]. The oxidation of benzene is made on zeolite catalysts (ZSM-5) in the gas phase at 300°C to 450°C. The greenhouse gas (N_2O) is a main component in the off-gas from the adipic acid production. Its use for the phenol production would therefore be ideally suited to the adipic acid manufacturers. However, the off-gas requires careful purification to remove various nitrogen oxides (NO_x) and oxygen. As an alternative, N_2O could be produced deliberately by catalytic oxidation of ammonia NH_3 with air [8] without relying on it as a by-product from adipic acid plants.

In [9–11], an overview is presented on the use of oxygen or hydrogen peroxide H_2O_2 for the direct oxidation of benzene with various catalysts. When using oxygen, the benzene conversion is limited to only several per cent due to low selectivities. With hydrogen peroxide, higher conversion rates should be possible. For example, Bianchi et al. [12] reported a three-phase process operating at around 100°C using aqueous hydrogen peroxide as a first liquid phase followed by an organic benzene/sulfolane mixture as the second phase, and a titanium silicalite catalyst (TS-1) as the third phase. However, conversion rates of benzene are still low of only around 10% with selectivities to phenol of around 90%.

None of the above described routes via direct oxidation of benzene have been commercialized. The use of either NH_3 or H_2O_2 is questionable since both are valuable chemical intermediates, and their role as oxygen carriers must be considered in any economical assessment of a direct oxidation of benzene to phenol.

2.1.1 Physical Properties of Phenol

Various physical properties of phenol are shown in Table 2.2.

At ambient temperatures, phenol is a solid and appears as a white amorphous material. It possesses a melting point of 40.9°C. In the molten state, pure phenol is a clear, colorless liquid. When exposed to air, phenol rapidly turns to a pink color due to certain trace impurities such as iron and copper that are present in its production process or during storage.

Table 2.2 Physical properties of phenol [6, 34]

CAS registration number	108–95-2
EG registration number	604–001–00–2
MAK limit	2 ppm/7.8 mg/m^3
OSHA PEL (TWA)	5 ppm
MW	94.1
MP	40.9°C
BP	181.8°C
Relative density	1.092 (0°C)
	1.071 (20°C)
	1.050 (50°C)
Specific heat	1.256 kJ/kg K (0°C)
	1.394 kJ/kg K (20°C)
	2.244 kJ/kg K (50°C)
Heat of vaporization	511 kJ/kg (181.8°C)
Vapor pressure	0.02 kPa (20°C)
	0.25 kPa (48.5°C)
	5.0 kPa (98.7°C)
	50 kPa (158.0°C)
	100 kPa (181.8°C)
	500 kPa (247.7°C)
	1,000 kPa (283.0°C)
Mutual solubility of phenol and water	72.16 wt% phenol in phenol phase vs. 8.36 wt% phenol in water phase at 20°C, consolute point at 68.4°C
Lower explosion limit	1.3 vol%
Upper explosion limit	9.5 vol%
Flash point (“closed cup”)	82°C
Ignition temperature (DIN 51794)	595°C

The melting and solidification temperature is lowered considerably by traces of water - approximately 0.4°C per 0.1 wt% water. Phenol becomes liquid at room temperature when around 6 wt% water is added.

At temperatures below 68.4°C, phenol is only partially miscible with water. Phenol is soluble in aromatic hydrocarbons, alcohols, ketones, ethers, acids, and halogenated hydrocarbons. It is less soluble in aliphatic hydrocarbons. Phenol forms azeotropic mixtures with water, cumene, and α-methylstyrene (AMS) as reported in reference [13].

2.1.2 Chemical Properties of Phenol

The chemical properties of phenol are unique. They are due to the presence of a hydroxyl group and an aromatic ring which are complementary to each other in facilitating both electrophilic and nucleophilic type of reactions. Phenol has an extremely high reactivity of its ring toward electrophilic substitution and assists its acid catalyzed reaction with formaldehyde leading to phenolic resins. Further phenol is a weak acid and readily forms sodium phenate (NaPh). In the presence of NaPh, nucleophilic addition of the phenolic aromatic ring to the carbonyl group of formaldehyde occurs. A base catalyzes the reaction by converting phenol into the more reactive (more nucleophilic) phenate or phenoxide ion for reaction with formaldehyde - see Chap. 4, Resin Chemistry. Thus phenol's unique ability to react with formaldehyde under acidic or basic conditions leading either to novolaks resins (via acid conditions) or resole resins (basic conditions), were the resin reactions that fostered the commercialization of phenolic resins, Bakelite, by Baekeland.

The unshared electron pair located on the hydroxyl group is delocalized over the aromatic ring leading to an electron excess at the ortho and para positions. Classical electrophilic reactions are halogenation, sulfonation, and nitration. The reaction of bromine in aqueous solution results in 2,4,6-tribromophenol in high yields.

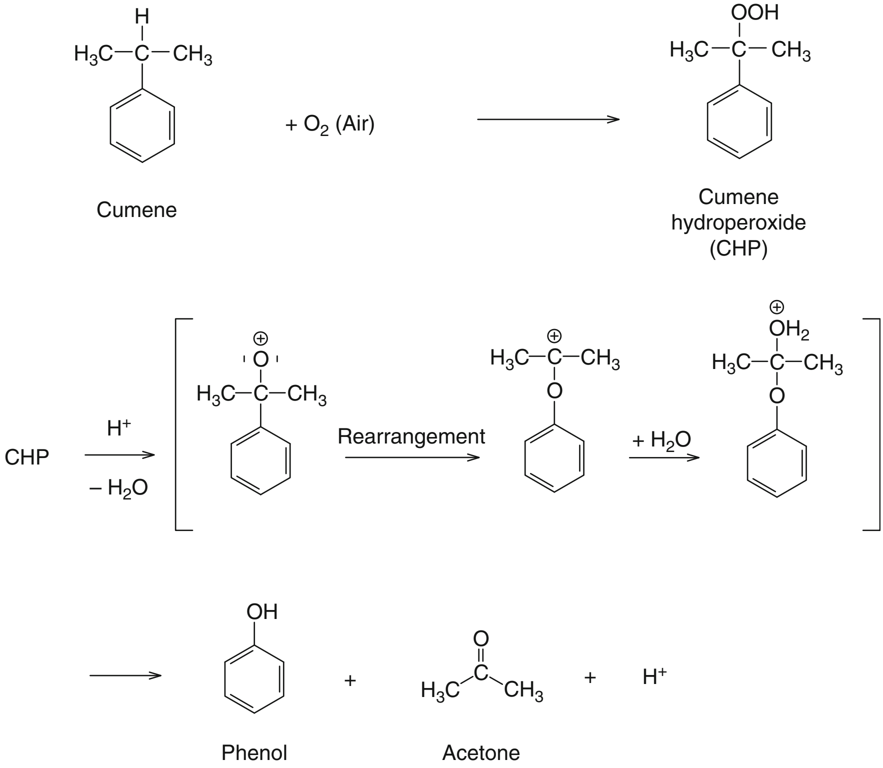
Under special conditions acid catalysts facilitate the conversion of phenol with formaldehyde to bisphenol-F or reaction of acetone to bisphenol-A.

Phenol can be hydrogenated on palladium catalysts to cyclohexanone with high selectivities [14, 15]. Cyclohexanone is the feedstock for the production of caprolactame monomer for Nylon 6.

2.1.3 Phenol Production from Cumene

Presently the cumene-to-phenol process is the predominant route for the production of phenol. In 2008, more than 97% of the phenol worldwide was produced by this process. The process was first reported by Hock and Lang [16], see Sects. "Phenol" and "Alkylphenols" below. Cumene is oxidized with oxygen (from air) to form cumene hydroperoxide (CHP). The peroxide is subsequently decomposed to phenol and acetone, using a strong mineral acid as a catalyst. Figure 2.1 shows the flow sheet of the cumene-to-phenol process.

Cumene as a feedstock for this process is produced from benzene and propylene. Formerly the alkylation reaction was carried out in solution with acidic catalysts like phosphoric acids and aluminium chloride. Currently, most of the cumene is produced commercially with heterogeneous zeolite catalysts. Licensors are UOP, Badger Licensing and CDTech. Details are described in [17].



After World War II, the cumene-to-phenol process was developed on a commercial scale by The Distillers Co. in Great Britain and the Hercules Powder Company in the USA. The first production plant was commenced in 1952 in Shawinigan, Canada. Today, several licensors offer their technology such as KBR or UOP. Although all these processes use the principles of the Hock synthesis, there are differences in the design and operation of the reaction units and the distillation unit.

The world’s biggest phenol producer is Ineos Phenol, formerly Phenolchemie, which constructed the first production plant in Gladbeck, Germany, in the early 1950s. The production was initiated in 1954 with a capacity of 8,000 tons phenol per year. Currently the capacity is 650,000 tons/year. In 1993, a new plant was started up in Antwerp, Belgium. After several expansions, the capacity is currently

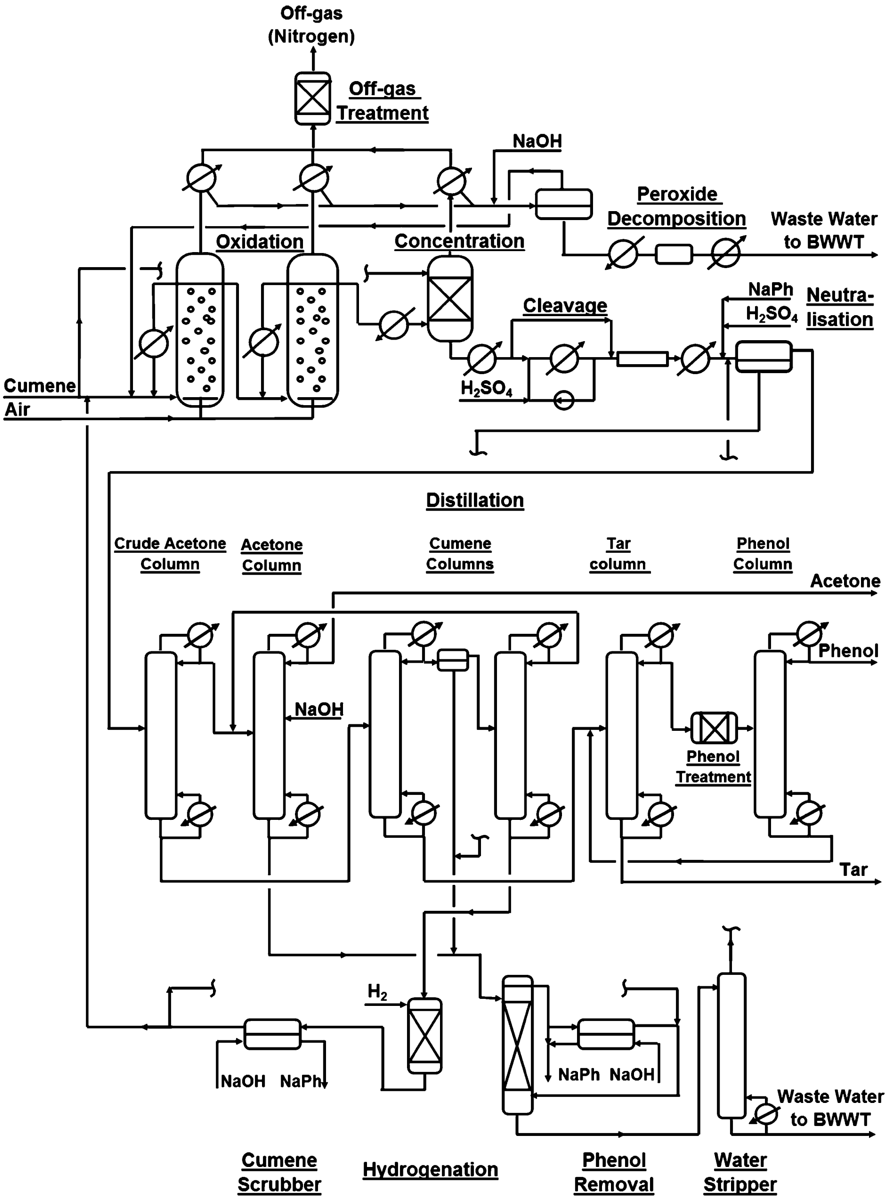


Fig. 2.1 Cumene-to-phenol process flow diagram

680,000 tons/year. In 2000, yet another plant was placed into operation in Mobile, Alabama. The actual capacity there is 540,000 tons/year.

Referring back to Fig. 2.1, cumene is first oxidized with oxygen from air to CHP. Fresh and recycle cumene flow through a cascade of large bubble columns. Air is added at the bottom of each reactor. Oxygen transfers from the air bubbles into the cumene. The reaction in the liquid phase proceeds by a complex radical mechanism [18]. The reaction is auto-catalyzed by CHP. The liquid phase in such large reactors is intensively mixed by the rising gas bubbles. This mixing characteristic plays a critical role in conversion rates and yields [19]. The bubble columns operate at pressures ranging from atmospheric to around 700 kPa. The temperatures are typically in the 80°C–120°C range. The reaction is exothermic with a heat of reaction of -117 kJ/mol. The residence time in the reactors is several hours. The temperature is controlled by internal or external heat exchangers. The final CHP concentration is in the 20–40 wt% range.

Several by-products are formed in the oxidation step. The overall process selectivity is mainly dependent on the formation of dimethylbenzyl alcohol (DMBA) and acetophenone (ACP). DMBA is dehydrated in the cleavage unit to AMS and partially forms high-boiling components. ACP leaves the process with the high boilers from the distillation unit. It can also be recovered as a pure product. Other by-products are formic and acetic acid. Small amounts of methyl hydroperoxide (MHP) are formed and removed with the off-gas. Phenol is a strong inhibitor for the oxidation reaction. Any recycle cumene must be treated to remove even small traces of phenol.

From a safety point of view, great care is required in the design of the air inlet devices (sparger) at the bottom of the reactors. Any backflow of peroxide containing liquid into the air line must be avoided. It is also important to monitor and ensure a low final concentration of oxygen in the off-gas at the top. This is to avoid an explosive mixture in the gas phase and in the subsequent units for the off-gas treatment [20]. Another important aspect is thermal stability of a reactor after a shut-down. It is important to know at what temperature a reactor has to be cooled down to avoid subsequent heating up from the ongoing exothermic decomposition of CHP. This is the so-called *Self-Accelerating-Decomposition-Temperature* (SADT) [19].

The off-gas from the reactors, that is mainly nitrogen and other organics, is cooled to around 0°C to condensate and separate most of the cumene. Residual impurities can be removed from the off-gas with activated carbon adsorbers [21] or with regenerative thermal oxidizers [22]. Off-gas, which is purified under pressure on activated carbon, can be used as *technical grad*e nitrogen for blanketing or venting of process equipment. It can also be used to dry adsorbers after regeneration with steam.

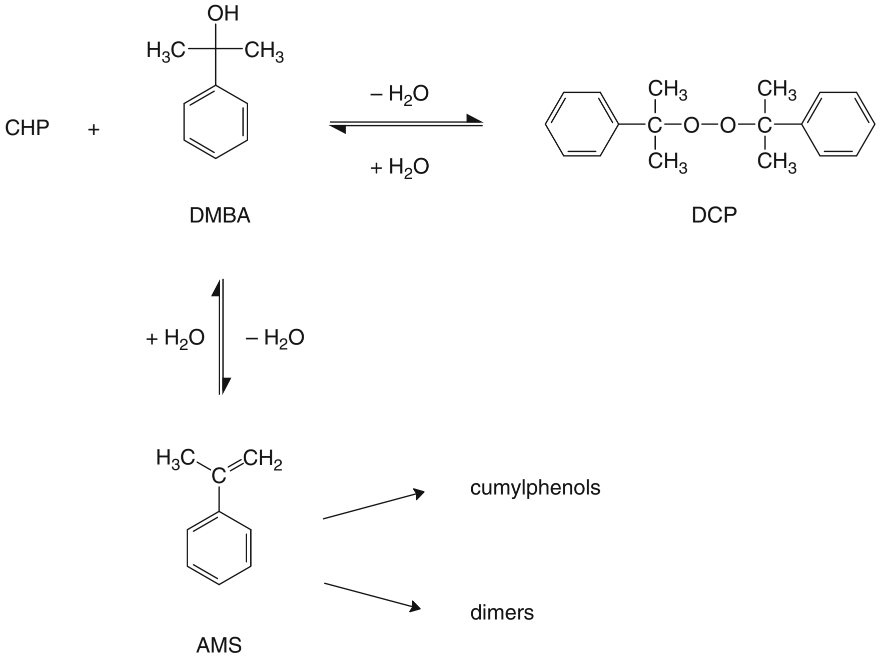
Besides cumene, the water phase is condensed from the off-gas, in which MHP is present. After treatment with diluted caustic soda, the cumene is recycled to the oxidation unit. The water phase is treated at temperatures above 100°C and a high pH to decompose the MHP to methanol. Disposal of MHP in the aqueous stream is not allowed since it is toxic to fish. The water is then sent to a biological waste water treatment (BWWT).

The product from the oxidation unit is concentrated from 65 to 90 wt% CHP. This is accomplished in a one- or multiple-step vacuum distillation, the so-called concentration unit. Cumene is separated at temperatures below 100°C to minimize thermal decomposition of CHP. Highly efficient structured packings are used in these columns. Fresh cumene can be used for reflux. The distilled and recycled cumene is washed with diluted caustic soda to remove organic acids and traces of phenol.

During any shut down, especially in case of a total power failure, the equipment in the concentration unit must be flushed with cumene to avoid runaway reactions of the hot and concentrated CHP. Therefore, a certain amount of pressurized cumene, so-called *flush cumene*, must be available at all times.

The first part of the cleavage unit is a circulation loop. One or several heat exchangers are installed as reactors within the loop. Small amounts of sulphuric acid are used as the catalyst. CHP is added to the loop and is spontaneously diluted with the product from the reaction which is mainly phenol, acetone, and residual cumene. In the event of a shut down, the injection point is flushed with cumene to separate CHP from acidic cleavage product in the loop. CHP decomposes while passing through the heat exchanger. The reaction is exothermic with a heat of reaction of −252 kJ/mol and occurs within 1 min. The temperature is controlled at around 50°C. DMBA is partially dehydrated to AMS, which reacts in consecutive reactions with phenol to high-boiling cumylphenols, see below. AMS also forms high-boiling dimers. DMBA reacts with CHP to dicumyl peroxide (DCP) and water.

Other by-products are hydroxyacetone from the reaction of CHP and acetone, 2-methylbenzofurane (2-MBF) from the reaction of hydroxyacetone with phenol, diacetone alcohol from the self-condensation of acetone, and mesityloxide (MOX) from the dehydration of diacetone alcohol. Some aldehydes are also formed, especially acetaldehyde. All these by-products require special conditions in the distillation unit to separate them from phenol and acetone. An overview of all these reactions is given in [23].



The product from the reaction loop is finally treated in a plug-flow reactor at temperatures above 100°C. The temperature is increased by adding again CHP [24] or by indirect heating with steam. In this reactor, DCP reverts to CHP and DMBA. CHP is cleaved spontaneously to phenol and acetone, while DMBA is completely dehydrated to AMS and water.

The product from the cleavage unit is cooled. All acid-catalyzed reactions from AMS are stopped by adding sodium phenate (NaPh) in the neutralization unit. Additional sulphuric acid may be needed if excess NaPh needs to be decomposed to recover phenol. Salts from organic acids, mainly sodium sulphate from the decomposition of NaPh, are extracted in the aqueous phase. This process water is further treated in the phenol removal unit to recover phenol by liquid-liquid extraction with cumene as the extraction solvent. Phenol is recovered from the cumene as NaPh by washing with caustic soda in a separate scrubber. Parts of the cumene in the phenol removal unit may be refreshed with purified recycle cumene or fresh cumene. NaPh and discharged cumene are routed to the neutralization unit. The process water is finally treated in a water stripper to remove dissolved acetone and cumene.

The product from the neutralisation unit is sent to the distillation unit. In the crude acetone column, acetone and some water are separated as the top product. Pure acetone is recovered in the acetone column as the top product. As an alternative, pure acetone may be separated as an upper side stream to allow removal of light-boilers at the top. Caustic soda is added to this column to convert aldehydes to high-boiling components. The bottom product of this column, which is mainly water, is treated in the phenol removal unit to remove the organic components. It can also be recycled to the neutralization unit.

The bottom product from the crude acetone column is sent to the first cumene column. The cumene with AMS and some phenol as well as water are separated as the top product. The water is separated in a decanter and treated in the phenol removal and in the water stripper to remove phenol, acetone, and cumene. All process water is sent to the final treatment in a BWWT.

The cumene is separated from low boilers, mainly acetone and water, in the second cumene column. The AMS is hydrogenated to cumene in the hydrogenation unit on selective palladium catalysts. These catalysts are highly selective toward the hydrogenation of AMS without any interfering hydrogenation of phenol. Phenol is then separated from the cumene in a cumene scrubber, again using aqueous caustic soda as the extraction solvent. The NaPh is routed to the neutralization unit. The cumene is recycled back to the oxidation unit.

The bottom product from the first cumene column is sent to the tar column. All high-boiling components are separated at the bottom. The tar is typically used as fuel to produce steam. Crude phenol is separated as the top product. As an alternative, crude phenol may be taken as an upper side stream to remove residual amounts of hydrocarbons at the top. Traces of hydroxyacetone, 2-MBF, and MOX in phenol are converted to high-boilers in the phenol treatment unit. Acidic ion exchange resins are used in fixed-bed reactors to accomplish conversion to high boilers [25]. These high-boilers are separated from pure phenol in the phenol column and routed to the tar column. In the phenol column, pure phenol may be separated at an upper side stream to remove light-boilers at the top.

2.1.4 Sources for “Natural” Phenol

The recovery of “natural” phenol from coal tar is still a fully operational method to recover phenol. Coal tar is a complex mixture of condensable organic components, emerging from coal carbonization [1]. During the fractionation of the coal tar, so-called *carbolic oil fraction* is separated and contains 30–35 wt% phenolic components. These phenols are called *tar acids*. The carbolic oil is treated with diluted caustic soda to extract the phenols as sodium phenolate salts. The aqueous phenolate solution is then treated with carbon dioxide to liberate the phenols from the salts.

This crude phenol fraction from carbolic oil consists of phenol, cresols, and xylenols. A typical composition is 30 wt% phenol, 12 wt% *o*-cresol, 18 wt% *m*-cresol, 12 wt% *p*-cresol, 8 wt% xylenols, 15 wt% water, and 5 wt% tar [1].

Phenol and *o*-cresol can be isolated by distillation. The separation of *m*- and *p*-cresol requires more effort due to the similar boiling points, see Table 2.1. Some methods are described in [1]. The xylenol isomers can be separated by combined distillation and extraction steps.

Besides coal tar, other sources of “natural” phenols are the liquid byproducts from gasification processes [26]. Phenol, cresols, and xylenols are recovered from the aqueous phase by solvent extraction, for example with the Lurgi Phenosolvan process. A large source of natural phenols is the liquid by-products from Sasol’s gasification process in South Africa [27]. The phenols are produced and marketed by Merisol, a joint venture between Sasol and Merichem (USA), with a total production of phenols (phenol, cresols, xylenols) of about 110,000 metric tons per year in 2003 [28]. Another large source is the recovery of phenols from the gasification process of lignite coal at Dakota Gasification Company (USA). The annual production of phenol there is about 20,000 metric tons.

2.1.5 Global Supply and Use of Phenol

In 2008, the world-wide phenol capacity for phenol production was around 9.9 million tons, with 98.5% based on the cumene-to-phenol process. The total production in 2008 was around 8.7 million tons. Table 2.3 shows the major phenol producers in the world.

In 2008, the largest use with around 44% was for the production of bisphenol-A, followed by phenolic resins (26%), cyclohexanone/caprolactame (12%), and others like alkylphenols (4%).

Table 2.3 Major phenol producers in the world (2008)

Company	Phenol capacity in thousands of tons per year
Ineos Phenol	1,870
Sunoco	800
Mitsui Chemicals	750
Shell	600
CEPSA Quimica	600
Polimeri Europa	480
FCFC	400
MtVernon Phenol (Sabic)	340
Kumho	330
Dow	300
Taiwan Prosperity	200
Mitsubishi Chemicals	250
Chiba Phenol	230
Georgia Gulf	230
LG Chem	200
Chang Chun PC	200
Rhodia	195
NOVAPEX	180

2.2 Alkylphenols

Alkylphenols are phenols with one or more of the aromatic hydrogens being replaced by an alkyl group. Mixtures are called *cresylic acids*. More specifically, if they are recovered from coal tar, they are called *tar acids*. Cresols are monomethyl derivatives of phenol. Xylenols are dimethyl derivatives.

Higher alkylphenols such as 4-*tert*-butylphenol, 4-*iso*-octylphenol, and 4-nonylphenol are used in phenolic resin production.

2.2.1 Cresols

The three isomers of cresols are *o*-, *m*-, and *p*-cresol. Like phenol, *o*- and *p*-cresol are crystalline solids at room temperature while *m*-cresol is viscous oil. Compared to phenol, they are less soluble in water.

Like phenol, cresols can be recovered from coal tar and other natural sources, see Sects. “Sources for ‘Natural’ Phenol”. Currently synthetic processes are an important route for the production of cresols. These routes are either based on toluene or phenol [29]:

- Chlorination of toluene and hydrolysis of chlorotoluene with caustic soda to sodium cresolate
- Sulfonation of toluene and conversion with caustic soda to sodium cresolate
- Alkylation of toluene with propylene to cymene, oxidizing to cymene hydroperoxide and subsequent cleavage to cresols and acetone

- Methylation of phenol, either in gas phase on aluminium oxide catalysts (350°C) or in liquid phase on aluminium methylate or zinc bromide (350°C, 50 bar).

The chlorination and sulfonation processes are similar to the former production routes to synthetic phenol. The synthesis via cymene hydroperoxide is also similar to the cumene-to-phenol process (Hock process). But the process is more complex, due to the formation of all three cymene isomers. In addition some methyl groups are oxidized to primary peroxides and cause more costly distillation procedures. Mainly *m*- and *p*-cresol are finally recovered from this process. Main product from the methylation of phenol is *o*-cresol.

Besides the use for phenolic resins, other applications for cresols are the production of herbicides, fungicides, disinfectants, and plasticisers.

2.2.2 *Xylenols*

Xylenols or dimethylphenols are available as six isomeric forms, see Table 2.1. They are all crystalline materials at room temperature. Compared to cresols, xylenols are less soluble in water, but can still be extracted from organic mixture with aqueous caustic soda. Xylenols can be recovered from the same natural sources as cresols and phenol.

Besides *o*-cresol, 2,6-Xylenol is the preferred product in the phenol methylation gas phase process [29] and the desired monomer for poly 2,6 dimethylphenylene oxide or PPO and used to make Noryl, a high performance thermoplastic resin. In the phenol methylation liquid phase process, mainly 2,4-xylenol besides 2,6-xylenol is formed.

There are similar routes for xylenols via chlorination and sulfonation as for cresols. Instead of toluene, xylenes are the precursors.

Finally, it is possible to produce 3,5-xylenol via alkylation of *m*-xylene, oxidizing to the corresponding peroxide and subsequent cleavage to 3,5-xylenol and acetone [30, 31].

Besides phenolic resins, other applications for xylenols are their use as solvents and disinfectants.

2.3 Resorcinol

Resorcinol or 3-hydroxyphenol is a white crystalline compound. Compared to phenol, it has significantly higher reaction rate toward formaldehyde.

Resins from resorcinol and formaldehyde (RF resins) are mainly used in the rubber industry. RF resins are used as adhesives for joining rubber with reinforcing materials, for example in tires and conveyer belts. Another important use is the high-quality wood adhesives. Special resins from resorcinol, phenol, and formaldehyde increase the curing rate in structural wood adhesives and allow cure at ambient temperatures. Resorcinol is also used as a light stabilizer for plastics and for the production of sunscreen preparations for the skin (ultraviolet absorbers).

Resorcinol is produced via sulfonation of benzene to benzene-1.3-disulfonate (INDSPEC Chemical Corp., USA) or via hydroperoxidation of *m*-diisopropylbenzene (Sumitomo, Japan) [32].

In the sulfonation process, benzene reacts with sulphur trioxide at around 150°C. In excess caustic soda, the benzene-1,3-disulfonate is converted into disodium resorcinate at 350°C. The salt is dissolved in water and neutralized with sulphuric acid. Resorcinol is extracted with an organic solvent such as diisopropyl ether.

In the hydroperoxidation process, benzene and a recycled benzene–cumene mixture is alkylated with propylene to diisopropylbenzene isomers. After addition of recycled *p*-diisopropylbenzene (*p*-DiPB) and triisopropylbenzenes (TriPB), the mixture is processed in an isomerisation/transalkylation unit to convert most of the *p*-DiPB and TriPB to *m*-diisopropylbenzene. (*m*-DiPB). The *m*-DiPB is then oxidized to *m*-diisopropylbenzene hydroperoxide. The peroxide is crystallized and dissolved in acetone. The handling of the solid organic peroxide requires special safety measures. The cleavage is carried out under acidic conditions to convert the peroxide into resorcinol and acetone. Usually, sulphuric acid is used as the catalyst in a boiling acetone mixture.

2.4 Bisphenol-A

Bisphenol-A (BPA) or 2,2-bis (4-hydroxyphenyl) propane is used for the production of special resins for coating applications in the phenolic resin area. Presently the main use for BPA is the production of polycarbonates and epoxide resins.

BPA is produced from phenol and acetone in the presence of an acidic ion exchange resin catalyst. Phenol is used in high molar excess. After the reaction, light boilers like acetone and water are separated by distillation. Acetone is recycled to the reactor. BPA is then crystallized in phenol. After mechanical separation and washing of the crystals with phenol, molten BPA is further purified. Excess phenol from the crystallization and from distillation is recycled back to the reactor.

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Chapter 3
Formaldehyde

Stefan Kowatsch

Abstract Formaldehyde, as an aqueous solution ranging from 37 to 50 wt%, continues to be the preferred aldehyde for reaction with phenol for the preparation of phenolic resins. Over 30 million metric tons of formaldehyde represent the global worldwide consumption of formaldehyde for an array of products, besides phenolic resins. These include urea formaldehyde resins, melamine formaldehyde resins, polyacetal resins, methylenebis (4-phenyl isocyanate) , butanediol, pentaerythritol, and others.

The two basic processes to produce formaldehyde from methanol – the silver catalyst process and the metal oxide process – are described along with the strengths and weaknesses of the respective processes. Furthermore, methanol plant siting location is a factor due to raw material (natural gas) and energy costs.

The controversy regarding the classification of formaldehyde as a human carcinogen remains unsettled. In 2004, the International Agency for Research on Cancer (IARC) of the World Health Organization reclassified formaldehyde from a group 2A substance (probable carcinogen to humans) to a group 1 (carcinogenic to humans) substance. Yet no government regulating agency has classified formaldehyde as a known human carcinogen. The studies that acknowledged formaldehyde to be a human carcinogen are being re-analyzed with additional research by IARC to re-examine its current classification of formaldehyde. By end of October 2009, despite strong disagreement among participants of the voting body, who were evenly split at the vote, IARC concluded that there is sufficient evidence in humans of a causal association of formaldehyde with leukemia. Industry disagrees with this conclusion and believes that the weight of scientific evidence does not support such a determination. A review of all of these data is still in process but impact on possible governmental reclassifications expected to be seen in 2010.

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3.1 Introduction

The public is accustomed to products that contain formaldehyde almost every day without any apparent awareness of the presence of formaldehyde in the product. Various industries such as the residential construction industry, the automotive industry, the aircraft industry, and even the health care industry are just a few examples of its broad utility. Even more surprising and unknown to many persons is the fact that human bodies produce formaldehyde, and it occurs naturally in the air we breathe. The use of formaldehyde for embalming purposes was one of the earliest and most widely known applications but represents far less than 1% of consumption.

Products that contain formaldehyde or materials made from formaldehyde enjoy a vital role in world economies, but their dependence on formaldehyde is largely invisible to the public. Statistics are not always well designed to identify or quantify the value of formaldehyde to consumers or the contribution of the formaldehyde industry to the economy in terms of jobs, wages, and investment [1].

3.2 Chemistry

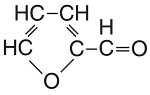
3.2.1 Aldehydes

Formaldehyde is practically the only aldehyde-containing material used in the synthesis of industrial phenolic resins. Special resins are made with other aldehydes, for example, acetaldehyde, butyraldehyde, furfural, glyoxal, or benzaldehyde, but these have not achieved much commercial importance. Ketones are also rarely used. Physical properties of some aldehydes [2–4] are compiled in Table 3.1.

3.2.2 Formaldehyde

Formaldehyde, the first of the series of aliphatic aldehydes, was discovered in 1859 by Butlerov and has been manufactured on a commercial scale since the beginning

Table 3.1 Physical properties of some aldehydes

Type	Formula	MP (°C)	BP (°C)
Formaldehyde	$CH_2{=}O$	−92	−21
Acetaldehyde	CH_3CHO	−123	20.8
Propionaldehyde	$CH_3–CH_2–CH$	−81	48.8
n-Butyraldehyde	$CH_3(CH2)_2–CH$	−97	74.7
Isobutyraldehyde	$(CH_3)_2CH–CHO$	−65	61
Glyoxal	$O{=}CH–CH{=}O$	15	50.4
Furfural		−31	162

of the twentieth century. Because of its variety of chemical reactions [5, 6] and relatively low cost (basically reflecting the cost of methanol), it has become one of the most important industrial chemicals.

Formaldehyde is a hazardous chemical [7–11]. It causes eye, upper respiratory tract, and skin irritation. Significant eye, nose, and throat irritation does not generally occur until concentration levels of 1 ppm. The Environmental Protection Agency (EPA) has classified formaldehyde as a "probable human carcinogen" (group B) under its "Guidelines for Carcinogen Risk Assessment" [12]. However, no evidence exists for identifying formaldehyde as a "probable human carcinogen" (group B). Facilities that manufacture or consume formaldehyde must strictly control workers' exposure following workplace exposure limits. Further information on toxicology and risk assessment of formaldehyde is mentioned in Sect. 3.6 of this chapter.

3.2.3 Chemical Properties of Formaldehyde

At ordinary temperatures, formaldehyde is a colorless gas with a pungent odor. Physical properties are shown in Table 3.2. It is highly reactive and commonly handled in aqueous solutions containing variable amounts of methanol where it forms predominantly adducts with the solvent [5, 6], that is, equilibrium mixtures of methylene glycol (3.1), polyoxymethylene glycols (3.2), and hemiformals of these glycols with methanol (3.3). Even in concentrated solutions, the content of nonhydrated HCHO is very small (<0.04%). MWD of the oligomers was investigated by NMR [13] and GPC techniques. The chemical equilibria of polyoxymethylene glycol formation in formaldehyde solutions in water (and D_20) and of polyoxymethylene hemiformal formation in methanolic formaldehyde solution were examined by ^{1}H and ^{13}C NMR spectroscopy [13]. For similar formaldehyde concentration, the chain length of formaldehyde oligomeric products in aqueous solution is larger than in methanol solution. This fact explains why precipitation of solids (long-chain oligomer) occurs at a lower overall formaldehyde concentration in aqueous solutions than in methanol solution and why solid precipitation from aqueous formaldehyde solution can be avoided by adding methanol. Furthermore, with increasing temperature, the average chain length decreases in solution, whereas in methanolic formaldehyde solution temperature has a negligible effect on chain length. More recent NMR studies of formaldehyde in solution are discussed in Chap. 5, Analyses/Testing.

Table 3.2 Physical properties of formaldehyde [2, 3, 8]

GAS registration number	50–00–0
EG registration number	605–002–01–2
MAK limit	0.5 ppm
OSHA STEL	2 ppm
MW	30.03
MP/BP	−19.2°C/118°C
Dissociation constant, H_20 at 0/50°C	$1.4 \times 10^{-14}/3.3 \times 10^{-13}$
Flash point, 40% solution	60°C
Explosion limits LEL/UEL	7%/173%

In acidic solutions, hemiacetals are transformed into acetals by elimination of water.

$$HO - CH_2 - \ OH \tag{3.1}$$

$$HO - (CH_2 - O)_n - CH_2 - OH \tag{3.2}$$

$$CH_3 - OH + HO - CH_2 - OH \longleftrightarrow CH_3 - O - CH_2 - OH + H_20 \tag{3.3}$$

With the action of basic catalysts, formaldehyde easily undergoes a disproportionation reaction to methanol and formic acid, known as the Cannizzaro reaction (3.4).

A surprising development related to the Cannizzaro reaction was reported by Ashby and coworkers [14]. The Ashby group showed that formaldehyde reacts with NaOH (Cannizzaro conditions) to yield formic acid and hydrogen quantitatively. Typically, conditions exist in which both hydrogen formation and classical Cannizzaro reaction proceed simultaneously. This is far different from the report of Loew in 1887 suggesting a very small quantity of hydrogen as being formed in the Cannizzaro reaction. Ashby showed that the reaction of 4 mol 1^{-1} NaOH with 15 mmol 1^{-1} formaldehyde resulted in the formation of hydrogen from 31% of formaldehyde, the remainder going to normal Cannizzaro products. Chrisope and Rogers [15] point out that with only 0.5 mol 1^{-1} NaOH, 20 mmol l^{-1} formaldehyde solution can be converted into 1–2% hydrogen and the remainder into Cannizzaro products. Depending on ratio of NaOH to formaldehyde, it is possible to generate some hydrogen resulting in potentially hazardous conditions.

Depending on manufacture and storage, formaldehyde solutions always contain trace amounts of formic acid (around 0.05%).

$$2\ H_2C = O + NaOH \longleftrightarrow CH_3OH + H_3C - COONa \tag{3.4}$$

With concentrations ranging from 37 to 56 wt%, aqueous formaldehyde solutions used normally in resin production are unstable. Both formic acid and paraformaldehyde formation depend on temperature, time, and metallic ions (iron) concentration. Low temperature storage lowers the formic acid formation rate, but increases the tendency towards paraformaldehyde precipitation. Commercial formaldehyde grades are, therefore, stabilized with various amounts of methanol up to 15%. Other stabilizers consist of different guanamines, polyvinylalcohol, or isophthalobis-guanamine at concentrations from 10 to 1,000 ppm. Storage containers should be made of stainless steel; iron containers are not suitable. Containers with plastic linings or made from reinforced plastics may also be used. Solutions of formaldehyde higher than 50% are obtained by the addition of paraformaldehyde.

3.3 Manufacturing Processes

There are two basic processes to produce aqueous formaldehyde [16] from methanol by using either a silver or an iron oxide-molybdenum oxide catalyst. Each process possesses many variations, most of which are available to licensees.

3.3.1 Silver Catalyst Process

The silver catalyzed reaction occurs at essentially atmospheric pressure and 600°C–650°C with two parallel reactions:

$$CH_3OH + 1/2\ O_2 \rightarrow HCHO + H_2O \tag{3.5}$$

$$CH_3OH \rightarrow HCHO + H_2 \tag{3.6}$$

In a typical silver catalyst process, the feed mixture is prepared below the flammability limit by spraying air into heated methanol and combining the vapor with steam. The mixture is sent through a super heater to the reactor equipped with a bed of silver crystals or layers of silver gauze. The product is rapidly cooled and fed to an absorption tower. The bulk of the methanol, formaldehyde, and water is condensed in the lower water cooled section of the absorber; the nearly complete removal of the remaining methanol and formaldehyde occurs on the top of the tower by a countercurrent contact with clean process water. Absorber bottoms go to distillation where methanol is recovered and recycled to the reactor. The base stream from distillation, an aqueous solution of formaldehyde, is usually sent to an anion exchange unit where the formic acid is reduced to specification. The product contains up to 55% of formaldehyde and less than 1.5% of methanol. Vented gas can be recovered and used as boiler fuel or recycled.

Formaldehyde yields from the silver catalyst process are lower than from the metal oxide process, but this disadvantage is offset by a lower initial capital investment. The reactors can be very large, allowing producers to achieve economies of scale. Yields range from 80% to 92% of theoretical, with a typical yield of 87–88% of methanol for most well-maintained silver processes, requiring 6.8 Gal of methanol to produce 100 pounds of 37% formaldehyde solution (0.45 metric ton of methanol per metric ton of 37% solution). A slightly lower (82–83%) methanol yield is achieved with more poorly maintained silver processes (Fig. 3.1).

The catalyst for silver-based formaldehyde processes with the conversion of methanol to formaldehyde is electrolytic-generated pure silver crystals (content min. 99.99% Ag) with a typical temperature range of 500°C–700°C for operation. The total of other metal impurities should not exceed a maximum of 100 ppm. The most modern silver catalyst processes use a thin bed of silver crystals (Fig. 3.2).

The licensees of silver catalyst processes include Derivados Forestales, Dynea, ICI, Josef Meissner,

Mitsubishi Gas, ORKEM and Polimex–Cekop.

3.3.2 Metal Oxide Processes

The metal oxide process involves the catalytic oxidation of methanol by a mixed oxide catalyst containing iron and molybdenum. Other metals, such as chromium,

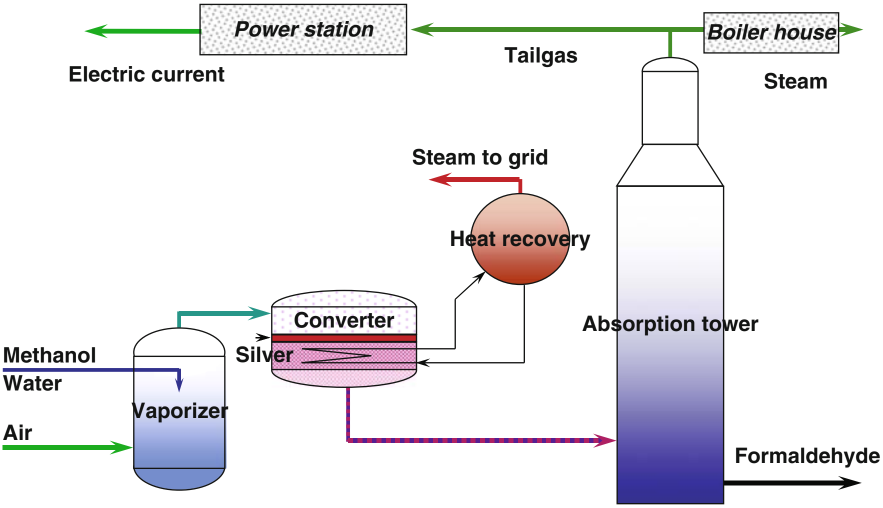


Fig. 3.1 Formaldehyde – Production using silver catalyst (Dynea)

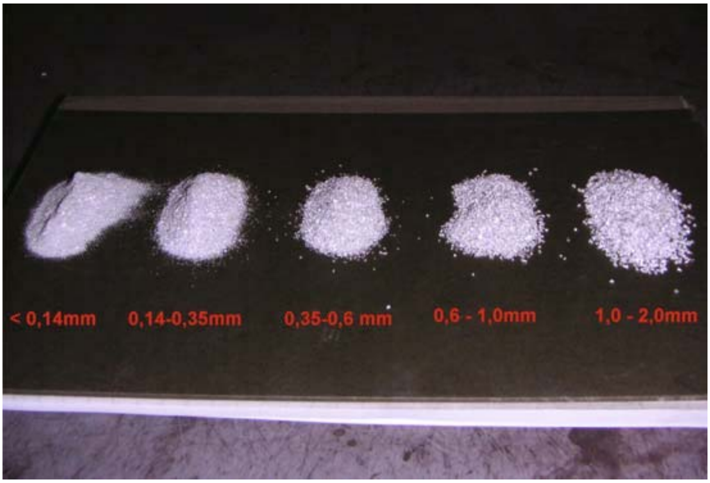


Fig. 3.2 Standard fractions of silver (Dynea)

are often used as catalyst promoters. The reaction is performed at essentially atmospheric pressure (0–6 psig) and approximately 300°C in a recirculation loop. Vaporized methanol is mixed with air and recycle gas to be on the methanol lean side of a flammable mixture, It is preheated to about 250°C and sent to the reactor. Methanol and oxygen react to formaldehyde in the tubes filled with an iron oxide-molybdenum oxide catalyst. The ferric-molybdate catalyst, in the form of spheres, granules, or cylinders, is placed in multiple fixed bed reactors; the shape of the catalyst affects energy costs. Small sized catalyst particles provide higher surface and such a better utilization; however, small-sized particles also increase the flow resistance in the reactor. Thus, the choice of the particle size very much depends on process efficiency as well as reactor geometry. Vaporized methanol and filtered air are fed to the reactors. The tubes of the reactors are surrounded by a boiling heat transfer fluid, usually diphenyl oxide, to which the heat of reaction is transferred and recovered as steam. The reacted gas which exits the reactor at about 290°C is cooled to 130°C before entering the absorber. In the absorber, the formaldehyde is absorbed in water or urea solution. The methanol conversion can be greater than 99%, yielding a product with up to 55% formaldehyde and less than 1% methanol. Formic acid is removed by ion exchange. The tail gas, essentially nitrogen and oxygen, with small amounts of methanol, formaldehyde, dimethyl ether, and carbon monoxide, is incinerated. The absence of a methanol recovery tower is an obvious advantage over the silver process. However, large capacity equipment is used to handle a greater flow of gas (three times greater). The metal oxide catalyst is more tolerant to trace contamination and requires less frequent changes compared to silver. Many metal oxide facilities produce urea-formaldehyde condensates by using urea in place of water at the quenching stage.

The two leading metal oxide processes are Perstorp and D.B. Western. The process was developed by Reichhold Chemicals, Inc. and subsequently sold to Perstorp AB. The Formox® process produces close to 90% yields, requiring 0.43 metric ton of methanol per metric ton of 37% formaldehyde. The D.B. Western process has been in use since 1981 and is employed in over 20 plants worldwide. The conversion of methanol is above 99%, with selectivity to formaldehyde of 91–92%. The D.B. Western process requires 0.42 metric ton of methanol per metric ton of 37% formaldehyde. The other licensees of metal oxide processes include Haldor Topsoe, Josef Meissner, and Nippon Kasei.

There has been significant research activity to develop alternative routes to formaldehyde, but without commercial success. The direct oxidation of methane with air at 450°C and 10–20 bar pressure on an aluminum phosphate catalyst should be mentioned among these processes. However, the process is not commercial.

3.4 Stabilizer

Although methanol is one of the more reasonably priced stabilizers, it is used only for special applications, for example, pharmaceutical industry. For acceptable results, methanol is added to 10%, and in some cases, up to 15%. By contrast, melamine is widely used to stabilize aqueous formaldehyde solution in the range of 40% (weight) and concentrations of melamine used are typically 0.25%–1.0%.

Guanamine such as benzo-guanamine and aceto guanamine is widely used to stabilize formaldehyde solutions with up to 45% w formaldehyde. The required amount depends strongly on the formaldehyde storage temperature and storage duration. Typically, 0.02–0.25% of guanamine is used.

Caprinoguanamine is one of the most effective stabilizing agents for formaldehyde. It is mainly used to stabilize highly concentrated formaldehyde solutions at even low storage temperature. It is effective up to formaldehyde concentrations of 55% w. The required amount depends on concentration, storage temperature, and storage duration. It can be in the range of 0.02–0.25% w. Caprinoguanamine tends to build up a stable foam which can lead to difficulties in resin manufacturing processes, especially when the hardener is added from the top of the reactor.

Finally, industry may use several stabilizers containing polyvinyl acetate and/or polyvinyl alcohol together with various other substances as the active component. Effective concentrations vary between 10 and 500 ppm depending on the stabilizing requirement but typically for lower concentration formaldehyde solutions.

3.5 World Market

Worldwide, most phenol resin producers without a captive phenol source are very often engaged in formaldehyde production for their consumption. Formaldehyde producers represent a rather unique oligopoly industry and a highly competitive one. The availability and access of low-cost methanol feedstock is a very important competitive factor for these resin manufacturers who are backward integrated into formaldehyde production.

3.5.1 Methanol

About 90% of the methanol produced is based on natural gas as feedstock. Others include naphtha, heavier oil fractions, and coal. The cost of natural gas is the most significant factor besides plant size (capital charges) in siting a plant at a specific location [17, 18]. For example, comparing a 200,000 tons per year methanol plant in the Middle East or in Germany, gas and energy costs in the Middle East account for about 10% of the total methanol production cost, whereas in Germany, it is about 40%. Competitive sizes of newer plants are in the range of 700,000 tons per year, leading to a cost decrease of about 20% compared to a 200,000 tons per year plant (German cost situation 1995).

Methanol process [19] consists of three main sections: synthesis gas preparation, methanol synthesis, and methanol purification. Because of extensive heat recovery and recycle streams, there is a considerable interaction between the three. The principal, highly exothermic synthesis reactions are as follows:

$$CO + 2H_2 \rightarrow CH_3OH \tag{3.7}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{3.8}$$

All methanol synthesis processes employ a synthesis loop to overcome equilibrium conversion limitations during typical catalyst operating conditions. The high-pressure process was rendered obsolete when ICI in the United Kingdom and Lurgi in Germany developed a highly active and selective copper-zinc-alumina catalyst. The resulting low-pressure process [20] dominates the methanol production. Four basic reactor types are in use, quench converter, multiple adiabatic, tube-cooled, and steam-raising converter. Crude methanol is purified by conventional distillation with one to three towers depending on the purity required.

Formaldehyde production in the U.S. is reasonably stable, but the production in Southeast Asia is growing and offsets decreases in other parts of the world. The global formaldehyde production is expected to increase at a rate of >2% per year.

Commercially formaldehyde is the most important aldehyde. Urea-, phenol-, and melamine-formaldehyde resins (Urea formaldehyde (UF), Phenol formaldehyde (PF), and Melamine formaldehyde (MF)) accounted for nearly 60% of world demand in the year 2006.

Other large applications include polyacetal resins, pentaerythritol, methylenebis (4-phenyl isocyanate) (MDI), 1,4 butanediol, and hexamethylenetetramine (HMTA). Formaldehyde producers are primarily concerned with satisfying their own captive requirement for forward integrated products rather than supplying local merchant markets.

World trade in formaldehyde is minimal and accounted for less than 5% of the total production in 2006.

The United States, Europe, and China are the largest markets and drove world consumption of formaldehyde (37%) close to 30 million metric tons in 2006. The global capacity utilization was estimated to be 70–80% in 2006. The growth on world consumption is estimated to be 5–6%.

3.5.2 Market Performers

The economic performance of individual countries or regions is still the best indicator of future developments for formaldehyde. However, there are some further aspects to consider, which strongly influence future demand and its impact on success in the market.

The availability and access to low-cost methanol feedstock is one of those aspects, followed by downstream integration into derivatives, and lastly, a continuous striving for sustainable developments in the wood panel industries. Any setbacks in economic developments that influence the growth in construction may result in further consolidations in the formaldehyde industry.

Besides raw material and energy costs, environmental regulations (Kyoto protocol) affect wood logging and the availability of raw wood resources. In some applications, formaldehyde-based wood adhesives are currently being substituted but this substitution is quite price-sensitive. Furthermore, discussions related to health problems caused by formaldehyde [20] (even though scientific opinions are not consistent) [21] are resulting in confusion amongst consumers, followed by erratic buying behavior. Nevertheless, these developments have led to further restrictions on formaldehyde emission levels, which are “in place” already. CARB (California, US) restrictions have become effective January 1, 2009. (See Chap. 8, Wood Composites Adhesives).

3.6 Formaldehyde Uses

The consumption of formaldehyde depends mainly on the construction, automotive, and furniture markets. In the developed world, growth in demand will typically track the gross domestic product, although it will be strongly correlated to the construction industry. In that sense, formaldehyde is an essential component used in the manufacture of numerous daily products such as automobile parts, computer chips, plywood, decorative surfaces, furniture, radio and TV sets, various sports equipment, and much more (Fig. 3.3).

As it was mentioned earlier, it is also used in the health care industry in prenatal diagnostics and in the preservation of vaccines.

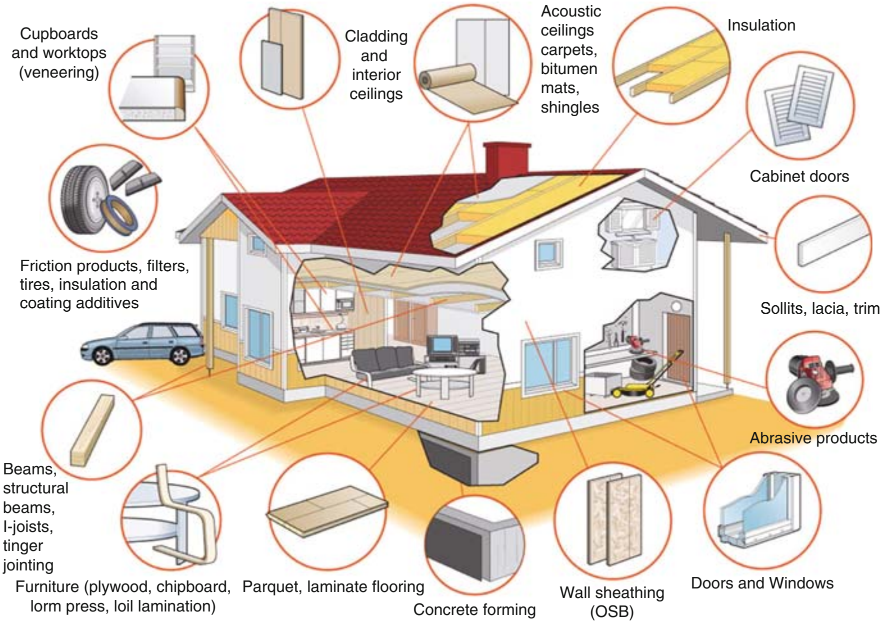
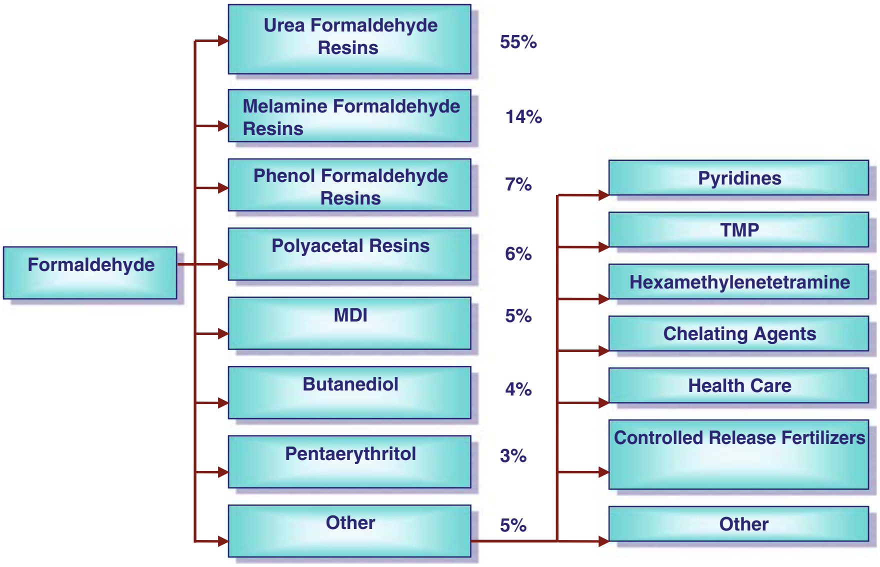


Fig. 3.3 Formaldehyde uses (Dynea)
Source: http://www.formaldehyde-europe.org/common_uses.uses.0.html

Table 3.3 Product tree for formaldehyde, 2004



Source: FormaCare

Formaldehyde is supplied as a 37–50% aqueous solution, with 37% being the most widely used composition which may also contain 0–15% methanol and a polymerization inhibitor (stabilizer, see Sect. 3.3).

Table 3.3 illustrates the array of products or product tree for formaldehyde.

UF resin is one of the mainstays in the building and construction industry. About 95% of UF resins are used as a binder or adhesive in particleboard and medium density fiberboard for composite panels. In these applications, it has a predominant market share. There are substitutes for each application but no substitute material has the broad range of properties of UF resins which consist of low cost, dimensional stability, hardness, clear glue line, and a fast curing process.

MF resin is used widely in the building and construction industries in the form of laminates and surface coatings, which account for more than 95% of its consumption. Its combination of properties allows it to maintain a dominant market position in certain applications, such as high pressure laminates for exterior decorative surfaces, in spite of its higher cost. Other resins, or different materials, may be substituted for MF resin-based products, but are more costly and less appealing to the consumer.

PF resin is another important product for the building and construction industry. Approximately, 60% of PF resins are used in this sector for applications such as insulation binder, wood products, and laminates. Other important end uses include automobile applications (e.g. friction materials) and foundry binders. Like UF resins, it has a predominant market share in its major applications. There are substitutes for each application but no substitute material has the broad range of properties of PF resins where high strength, dimensional stability, the ability to resist water, and thermal stability are required. In addition, current production methods are designed and integrated for the continuing use of PF resins. Other potential competitive substitutes to PF resins would require some/many changes in the existing processes and may lead to different processing/product properties.

Some formaldehyde is used in the preparation of MDI. The majority of MDI is used in the manufacture of rigid polyurethane foams. These products are commonly used in construction applications for their superior insulating and mechanical properties. In addition, MDI rigid foam applications include appliances (e.g., refrigerators, freezers, and air conditioners), packaging for high-end electronics, and transportation. In the absence of MDI, consumers would be required to use less effective materials and would experience significant losses in performance (e.g. inferior insulation properties, increased breakage, or spoilage).

Other materials such as alternate resins can be substituted for formaldehyde-based materials in many uses; but these resins which are frequently more costly, result in reduced consumer benefits because the resulting products with these alternate costly resins are generally inferior to that of formaldehyde-based resins in many instances.

3.7 Health and Safety

Formaldehyde is classified as a chemical irritant. At concentrations above 1 ppm, formaldehyde vapor causes irritation on contact with the eyes, nose, throat, and lungs. Contact with liquid formaldehyde causes eye burns, may cause allergic skin reaction, and is likely to irritate the skin. Moreover, formaldehyde has mutagenic activity in bacterial or mammalian cell culture test systems, but is generally negative in whole animal systems. Concerns over possible human carcinogenicity from exposure to formaldehyde continue to be a controversial issue. Many studies assessing the human risk of flow-level exposure to formaldehyde have been conducted; the interpretation of scientific studies has been variable. The lack of conclusive evidence has led to widespread disagreement among industry, government agencies, and unions regarding the appropriate risk assessment of formaldehyde.

In 1987, the U.S. EPA classified formaldehyde as a probable human carcinogen (group B-l) on the basis of sufficient evidence of animal carcinogenicity and limited evidence of human carcinogenicity. In June 2004, the World Health Organization's International Agency for Research on Cancer (IARC; an advisory board to the World Health Organization) reclassified formaldehyde from a group 2A substance (probably carcinogenic to humans) to group l (carcinogenic to humans). This reclassification was primarily based on the results of a National Cancer Institute (NCI) study of workers with occupational exposure to formaldehyde indicating that formaldehyde causes nasopharyngeal cancer (NPC) and is associated with leukemia. Although an outright ban on formaldehyde use in wood-based products is currently not likely, because industry is depending on current efficient technologies. Nevertheless further restrictions on formaldehyde emissions can be expected. No governmental regulatory agency has, as of yet, classified formaldehyde as a known human carcinogen. Subsequent to the NCI study linking formaldehyde to NPC, a re-analysis of the original study and additional research has led the IARC to re-examine its reclassification. The NCI is updating and re-examining its original studies in an effort to improve the accuracy of its findings as well as conducting new studies. The IARC has reviewed all studies and updates in preparation for a review of its formaldehyde carcinogen classification. End of October 2009, despite strong disagreement among participants of the voting body, who were evenly split at the vote, IARC concluded that there is sufficient evidence in humans of a causal association of formaldehyde with leukemia. FormaCare disagrees with this conclusion and believes that the weight of scientific evidence does not support such a determination. The U.S. EPA has maintained its classification of formaldehyde as a probable human carcinogen and is waiting to examine the results of the NCI update before initiating a review of formaldehyde's cancer classification. Within the European Union, formaldehyde is classified as a substance that has limited evidence of carcinogenic effect, and as such, represents category 3 in the list of carcinogenic substances.

In Western Europe, the exposure levels in the workplace vary from country to country. The United Kingdom sets a limit of 2 ppm, while Germany, Switzerland, and some Scandinavian countries operate within a limit of 0.2–0.8 ppm (SCOEL).

3.8 Other Formaldehyde Materials

3.8.1 Paraformaldehyde

Paraformaldehyde is a white, solid low molecular weight polycondensation product of methylene glycol with the characteristic odor of formaldehyde. The degree of polymerization ranges between 10 and 100. It is obtained by the distillation of formaldehyde solutions under different conditions depending on the temperature, time, and pressure during distillation. Commercial grades contain up to 6% water (Table 3.4).

Paraformaldehyde is seldom used in resin production because of the high costs compared to aqueous formaldehyde solutions, solids handling, and severe problems with the high heat evolution during the start-up phase. Some possible reasons for its use in special instances are resins with high solids content or to avoid distillation of waste water. Paraformaldehyde and/or aqueous formaldehyde is used in the new "PAPS" novolak resin technology (Resin Chemistry, Chap. 3). Paraformaldehyde can be used with acidic catalysts to cure novolak resins or to cure resorcinol

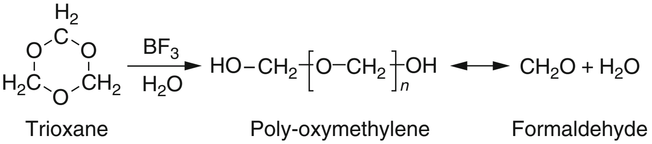
Table 3.4 Properties of paraformaldehyde [22]

Content of formaldehyde	90–97%
Content of free water	0.2–4%
Specific weight	1.2–1.3 g/cm3
Flash point	71°C
Melting range	120°C–170°C

prepolymers in cold setting structural wood adhesives. At low cure temperatures, the separation of formaldehyde is tolerable, and the reaction rate depends on the degree of polymerization.

3.8.2 *Trioxane and Cyclic Formals*

Trioxane, a cyclic trimer of formaldehyde or methylene glycol, is a colorless solid (MP 62°C–64°C, BP 115°C) and can be prepared by heating paraformaldehyde or a 60–65% formaldehyde solution in the presence of 2% sulfuric acid.



(3.9)

Trioxane can be used as a source of formaldehyde in prepolymer formation or as a resin curing agent. Cyclic formals, 1,3-dioxolane, 4-phenyl-1,3-dioxolane, and 4-methyl-1,3-dioxolane, have been recommended [23] as curing agents for novolak resins and high-solids, low-pressure laminating systems, taking into account their action as solvent.

3.8.3 *HMTA*

HMTA is by far the most important compound to cure novolak resins. It is prepared from formaldehyde and ammonia according to (3.10).

$$6\ CH_2O + 4\ NH_3 \longleftrightarrow (CH_2)_6N_4 + 6\ H_2O \tag{3.10}$$

In reverse, HMTA decomposes at elevated temperatures. In aqueous solution, HMTA is easily hydrolyzed to aminomethylated compounds and is often used as a catalyst in the resole synthesis instead of ammonia. HMTA is quite soluble in water (Table 3.5), but less soluble in methanol or ethanol. The aqueous solution exhibits a weak alkaline action with a pH in the range of 7–10. In powder form, HMTA is prone to dust explosions; it is rated as a severe explosion hazard.

Table 3.5 Physical properties of HMTA [24]

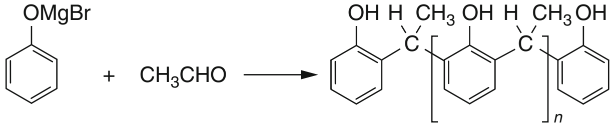
MW	140.2
Relative density	1.39 g/cm3
Behavior at heating	Sublimation at 270°C–280°C
Solubility in 100 g H20, 20°C/60°C	87.4/84.4 g

3.9 Other Aldehydes

Like formaldehyde, acetaldehyde is a gas at ambient temperature (BP 20.8°C). Acetaldehyde is miscible with water in all proportions and most common organic solvents. The liquid phase oxidation of ethylene is the process of choice for the manufacture of acetaldehyde (Wacker - Hoechst Process) using palladium and cupric chloride catalyst at 130°C. It reacts with phenol at considerably lower reaction rates as compared to formaldehyde. C_3 through C_{11} aldehydes [2, 4] are highly flammable and explosive, colorless liquids with pungent odor. They are miscible with most organic solvents, for example, acetone, ethanol, or toluene, but are only slightly soluble in water. Butyraldehyde is produced by the oxo reaction of propylene in the presence of cobalt or rhodium catalysts (3.11).

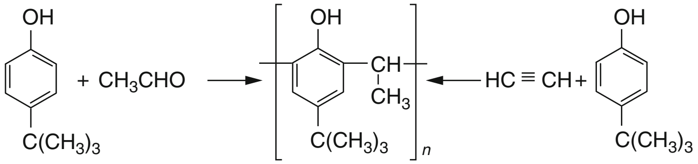
$$H_3CHC = CH_2 + CO \longleftrightarrow CH_3CH_2CH_2CHO + (CH_3)_2CHCHO \qquad (3.11)$$

Higher aldehydes react with phenol at significantly slower rates compared to formaldehyde. The base-catalyzed resole formation is not practical, as higher aldehydes easily undergo aldol and Tischenko condensation and self-resinification reactions. Acidic catalysts are preferred. In particular, non-transition metal phenates (Mg, Zn, or A1) are recommended [25] for the preparation of acetaldehyde phenol novolak resins in an aprotic solvent medium (12 h/120°C). Yields in excess of 90% with an exclusive ortho substitution (3.12) are reported.



(3.12)

The phenol reaction with higher aldehydes is, in general, performed under strong acidic conditions, preferably in a water-free system, by continuous aldehyde addition to the phenol melt. However, only acetaldehyde and butyraldehyde have had limited commercial success, for example, in resins for rubber modification, wood fiber binders, and antioxidants. The structure of novolak resins from acetaldehyde (3.13) corresponds to those obtained by the reaction of acetylene with phenol and cyclohexylamine as a catalyst:



(3.13)

The reaction of unsaturated aldehydes, acrolein, and crotonaldehyde with phenol in acidic medium was studied [26] by ^{13}C NMR and GPC. The alkylation reaction via the double bond seems to be the dominant pathway.

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Chapter 4
Resin Chemistry

Louis Pilato

Abstract During the ensuing years since the last phenolic resins book was published, many new and remarkable developments have occurred in the realm of phenolic chemistry and are given in this chapter.

A critical examination of the first step or addition step (methylolation) in the preparation of resoles is described and how it can be controlled and compared with the typical resole resin preparations. It provides a vision into the preparation of mineral wool/glass insulation resins and ways to minimize the undesirable dimer/oligomer formation.

Different reactivities of the common methylolated phenols and phenol are ranked, and their resulting reactivities differ depending on whether formaldehyde is present or absent in the methylolated phenols.

Use of organic bases such as triethyl amine indicates that a much faster reaction of F with P occurs as compared to the use of NaOH under similar conditions, and primarily ortho directed intermediate 2-methylol phenol is obtained. Further more methylene ether linkages result in the final TEA resole.

Bisphenol F, the simplest oligomer of phenolic novolak, continues to elicit considerable activity related to improved and economical synthetic preparative methods.

A unique, novel novolak process involving heterogeneous/two phase method known as the PAPS process is discussed along with several features and favorable comparisons with existing novolaks. Features such as narrow MWD, high yield, low free phenol, and rapid reaction favor this new process. Current markets that are responding to PAPS novolaks are photoresists and novolak curing agents for epoxy resins.

Nanotechnology is being applied to resoles and novolaks as well as the closely related phenolic materials such as cyanate esters and benzoxazines. With very small

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amounts of nanoparticles ($\leq$5%), these phenolic materials are significantly "upgraded" with resulting nanomodified phenolics exhibiting higher heat strength, higher modulus, T_g, etc., with many of these resin characteristics carrying over into fiber reinforced composites.

A new phosphorous flame retardant additive known as DOPO is reported and is instrumental in providing UL 94 VO behavior to cured novolak epoxy electrical laminates.

Benzoxazines are emerging as a more desirable phenolic resin system available from resin manufacturers as well as formulators such as Gurit (prepreg) and Henkel (FRP matrix). Benzoxazines undergo ring opening without emitting any volatiles during cure and result in a cured product with excellent dimensional stability, low water absorption, and stable, low dielectric properties (many of which are unavailable from typical phenolic resins). These attractive features have been responsible for its large volume use in electronics and FRP.

An overview of all types of natural products used either as partial phenol replacement, solvent or co-reactant, or as a resin modifier are tabulated along with origin/source, role in resin preparation, and different application areas.

An unusual technical development that attracted the interest of the symposium attendees was delivered by Sumitomo Bakelite researchers at the Commemorate Centennial Baekeland 2007 Symposium held in Ghent, Belgium during September 25, 2007. It was proposed that the 3D polymer network of hexa cured phenolic novolak resin can undergo further improvement based on reported curelastomer, T_g values, and DSC data. It is the view of the researchers based on phenolic resin conformations reached by using the Mark-Houwink-Sakarada equation as well as molecular simulations that higher T_g, exceptional strength, and performance driven characteristics of the resulting cured phenolic systems can be attained if an extended, linear novolak with low amounts of branching is cured with hexa. Conventional novolaks possess a "coiled" structure with branching, and during hexa cure, some novolak sites are sheltered or unavailable for cure and result in a 3D polymer network that is not fully cured in spite of the availability of excess hexa.

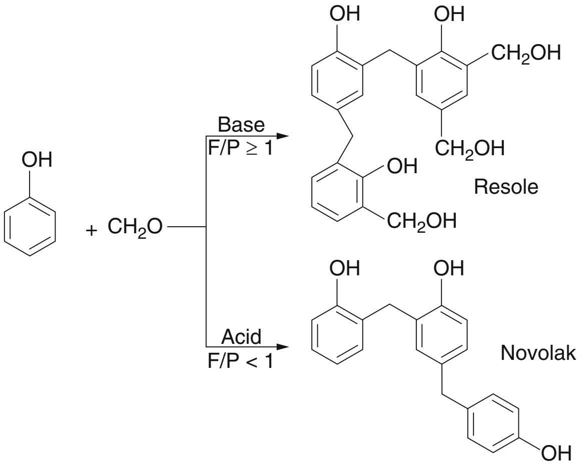
A reaction that is being revisited consists of phenylene bisoxazoline (PBO) reacting with novolak, and this promises to lead to the commercialization of a polyaryl ether amide type polymer possessing high T_g, high strength, and toughness exceeding multifunctional epoxy systems.

The capture and release of formaldehyde by aminoalcohols through the formation of an oxazolidine intermediate to facilitate the cure of phenolic resins has been commercialized as is shown in 2 different application areas. A pultrusion system based on novolak and oxazolidine is claimed to operate at line rates comparable to fast polyester pultrusion speeds. The other application involves the use of oxazolidine with PRF resin in the preparation of fiber reinforced FST duct systems.

The appendage of either an allyl or an ethynyl group to a novolak or resole followed by thermal cure leads to unusually high T_g phenolic materials, close to 400°C and is of interest for ultra high performance organic matrix composites.

4.1 Introduction

A formal understanding of how phenol reacts with formaldehyde under either acidic or basic conditions is necessary to appreciate the variety and versatility of the array of phenolic resins that are available [1]. Further the molar ratio of formaldehyde to phenol with acid or base is a contributing factor. Heat reactive phenolic resins known as resoles are obtained using a base catalyst, and the molar ratio of formaldehyde can vary from below equimolar amount to as high as 3–4 moles of formaldehyde to phenol. However, when less than an equimolar amount of formaldehyde to phenol is maintained under acidic conditions, a novolak resin is obtained.



(4.1)

Besides the use of acidic or basic conditions, the use of a transition metal salt catalyst under mildly acidic conditions yields a uniformly, structured phenolic resin known as high ortho phenolic resin. The salient features for the preparation of these various phenolic resins are best illustrated in Table 4.1.

The table provides a comparison of different catalysts that are utilized in phenolic resin production, resin types, molar ratios of F/P, physical state(s) of the resulting resins, polymer functional groups, resin stability, and method of cure. For the sake of completeness, the rarely used enzymatic coupling of phenol is also listed. Classically individual functionalities of phenol and formaldehyde are recognized as 3 and 2 respectively but deviate as one reacts phenol and formaldehyde under basic or acidic conditions. When a resole is prepared (equimolar or greater amount of formaldehyde to phenol with base catalysis) or when a novolak is desired (less than equimolar amount of formaldehyde to phenol with an acid catalyst), the functionality of formaldehyde is <2 and ≤ 3 for phenol for resoles while values of 2 for formaldehyde and 1.5–1.7 for phenol are reported for novolaks. The apparent difunctionality of formaldehyde applies only in novolak preparation and is less than 2 in resole preparation. The complexity of resole chemistry during resole preparation reduces functionality values of both formaldehyde and phenol. The phenol

Table 4.1 Different catalysts for various phenolic resins

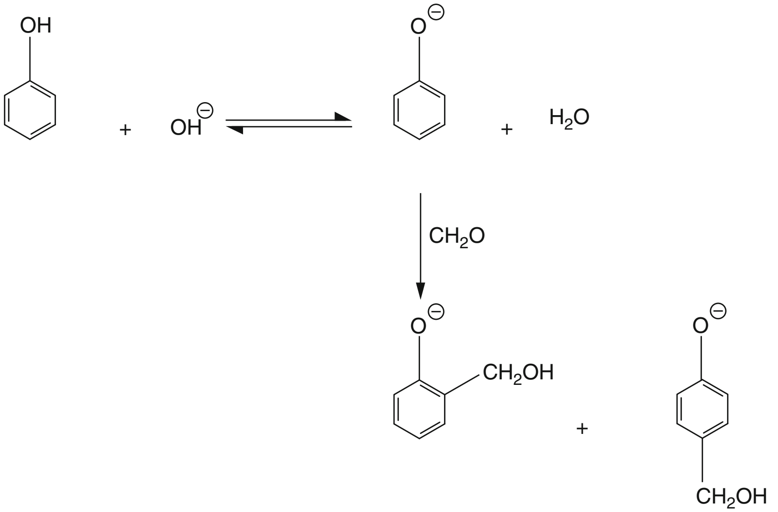
			Functionality f_{actual}					
Catalyst	Resin type	F/P	F	P	Physical state	Product stability (RT)	Functional groups	Mode of cure
Base	Resole	≥1	<2	≤3	Liquid, solid, solution	Limited	Methylol, phenolic	Acid, base, thermal
Acid	Novolak	<1	2	1.49–1.72	Solid	Stable	Phenolic	Hexa (CH_2O)
Metal salt	Resole or novolak	≥1	High	Ortho	Liquid, solid	Liquid-limited solid-stable	Methylol, phenolic	Same as resole or novolak
Enzyme	Pseudo novolak	No (CH_2O)	–	–	Solid	Stable	Phenolic	Resin transformation

functionality value of 1.5–1.7 in novolak preparation is considerably lower than the recognized value of 3 for phenol. The use of a deficient amount of formaldehyde in novolak preparation results in a linear or branched material and not a gelled or potentially cross linked novolak, hence the lower functionality for phenol.

4.2 Resole

4.2.1 Methylol Phenol(s)

Either ortho or para methylol phenol is obtained as phenol and formaldehyde are reacted under basic conditions. They are the simplest phenolic components that can be cured into a phenolic resin. The reaction leading to the *o*- or *p*-methylol phenol involves the addition of F to the phenolate ion as shown in (4.2):



(4.2)

Besides the monomethylol phenols, some dimethylol phenols and trimethylol phenol are obtained when the reaction of phenol is carried with more than an equimolar amount of formaldehyde (Fig. 4.1)

These intermediate methylol phenols are similar to compounds that result from the Lederer–Manasse reaction and one of the forerunner reactions that Baekeland was aware of during his initial experiments. These mono-, di-, and tri-methylolated phenols act as transient intermediates and undergo oligomerization into dimeric, trimeric, and higher oligomers depending on F content, reaction basicity, and temperature during reaction.

Mono, di- and tri-hydroxymethyl phenol (HMP) type intermediates have been examined by Higuchi in a series of papers [2–7] whereby the kinetic fate of 2-HMP, 4-HMP, 2,4-dihdroxymethyl phenol (DHMP) and 2,4,6-trihydroxymethyl phenol

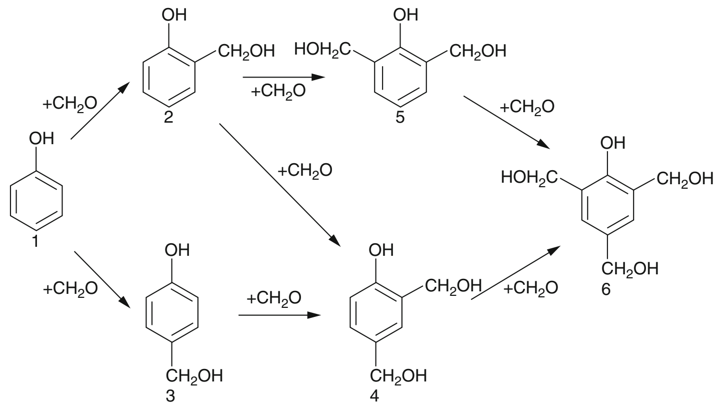


Fig. 4.1 Methylolated phenols

(THMP) was examined: 2-HMP undergoes a first order base catalyzed self condensation involving a quinone methide intermediate; base self condensation of 4-HMP involves simultaneous unimolecular and bimolecular reactions as rate determining steps; and finally both 2,4-DHMP and 2,4,6-THMP undergo simultaneous unimolecular and bimolecular reactions with reaction mechanism changing with the reaction species and, in some cases, with reaction conditions. These model studies were beneficial in understanding the use of propylene carbonate (PC) as an accelerator in the cure of base catalyzed resoles. The authors claim that PC increases the reactivity of 2-HMP through a transesterification of 2-HMP followed by enhanced rate of cure.

Christjanson et al. [8] carried out the melt condensation of 2-HMP and 4-HMP at 120°C with and without NaOH catalyst to determine the fate of these intermediate HMP materials at elevated temperature since they are present within a resole resin. In the absence of NaOH, either of the HMPs is transformed into the corresponding *o,o′* or *p,p′* methylene ether compounds. With a catalytic amount of NaOH and a 50/50 mixture of 2- and 4-HMP, only *o,p′* and *p,p′*-dihydroxy diphenyl methylene (DPM) compounds are obtained. These observations allowed the authors to propose that under resole curing conditions (resole as a wood adhesive), some formaldehyde is expected to be emitted when the bimolecular reaction of either 2- or 4-HMP occurs leading to the DPM materials.

4.2.2 Addition – Methylolation

Resoles are a mixture of methylol phenols, oligomers of varying – mer units, and residual amounts of free phenol and formaldehyde. Depending on reaction conditions (molar ratio of F/P, catalyst concentration/type and temperatures) at low temperatures (60°C) only addition of formaldehyde to phenol occurs. In a