CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Advance Oxidation Processes (AOPs) has been viewed with great interest as a promising method for the removal of organic contaminants from water. They rely on the formation of reactive and short-lived oxygen containing intermediates such as hydroxyl radical (OH•) and they exploit the high reactive of these species. Hydroxyl radical is a powerful oxidant and a short-lived, highly reactive, and non-selective reagent that is easy to produce. It has electroplilic properties and its reactions with appropriate substrate molecules are kineticcally controlled usually exhibiting very high second order rate constants, which are often close to (or even above) the diffusion-controlled limit (Sonntag C. V., 1996). Kenetic reaction control refers to competing irreversible reactions in which the product composition is determined by the relative rates of product formation. The reaction of OH• radicals with substrates will be discussed in section 2.2.
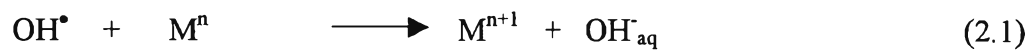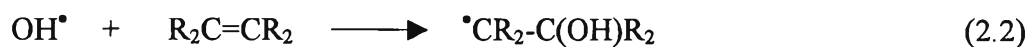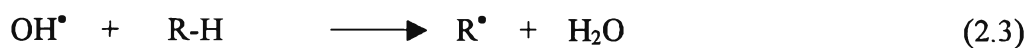
Fenton and Modified Fenton oxidation processes are among the AOPs. Fenton oxidation uses ferrous iron and hydrogen peroxide and modified Fenton processes employ diverse methods to enhance the oxidation efficiency. Particularly, photo-Fenton oxidation has recently emerged as a very promising technology because of its high efficiency and cost-effectiveness compared for wastewater treatments (Maletzky and Bauer, 1999; Ruppert et al., 1994; Bauer and Fallman, 1997; Chen et al., 1997). From these reasons, in this study, Fenton and photo-Fenton processes were conducted for treating formaldehyde and methanol. For further understanding, the mechanism of Fenton and photo-Fenton processes will be described in section 2.3.

2.2 Hydroxyl Radicals

As mentioned earlier, hydroxyl radicals are extremely reactive, short lived and non-selective transient species. This radical with a standard reduction potential of 2.8 V vs. NHE (Table 2.1) is able to oxidize almost organic compounds to carbon dioxide and water. The mean lifetime of $OH^\bullet$ radicals depends on their chemical environment and was estimated to be in the order of 10 μs in the presence of dissolved natural organic matters, bicarbonate and carbonate (Hoigné J., 1998). Hydroxyl radicals can oxidize organic and inorganic substrates by different type of reactions, electron transfer, electrophilic addition, and hydrogen abstraction, as illustrated in Equations (2.1) to (2.3) (Legrini et al., 1993; Hoigné J., 1998):

Table 2.1 Standard reduction potentials of some oxidants

Oxidants	Standard reduction potential [V vs. NHE]
Fluorine (F_2)	3.03
Hydroxyl radical ($OH^\bullet$)	2.80
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.78
Chlorine (Cl_2)	1.36

Electron Transfer

$$OH^\bullet \quad + \quad M^n \quad \longrightarrow \quad M^{n+1} \quad + \quad OH^-_{aq} \qquad (2.1)$$

Electrophilic Addition

$$OH^\bullet \quad + \quad R_2C=CR_2 \quad \longrightarrow \quad {}^\bullet CR_2\text{-}C(OH)R_2 \qquad (2.2)$$

Hydrogen Abstraction

$$OH^\bullet \quad + \quad R\text{-}H \quad \longrightarrow \quad R^\bullet \quad + \quad H_2O \qquad (2.3)$$

Formaldehyde itself reacts efficiently with $OH^\bullet$ radicals by the way of hydrogen abstraction with formation of $^\bullet COH$ radicals or their hydrated form (Figure 2.1). The latter are oxidized by dissolved molecular oxygen to yield formic acid and hydroperoxyl radicals. Again, formic acid reacts with $OH^\bullet$ radicals to give formoyl radicals that react with molecular oxygen finally yielding carbon dioxide and hydroperoxyl radicals (Stefan and Bolton, 1998; Heit et al., 1998; Gonzalez and Braun, 1996).
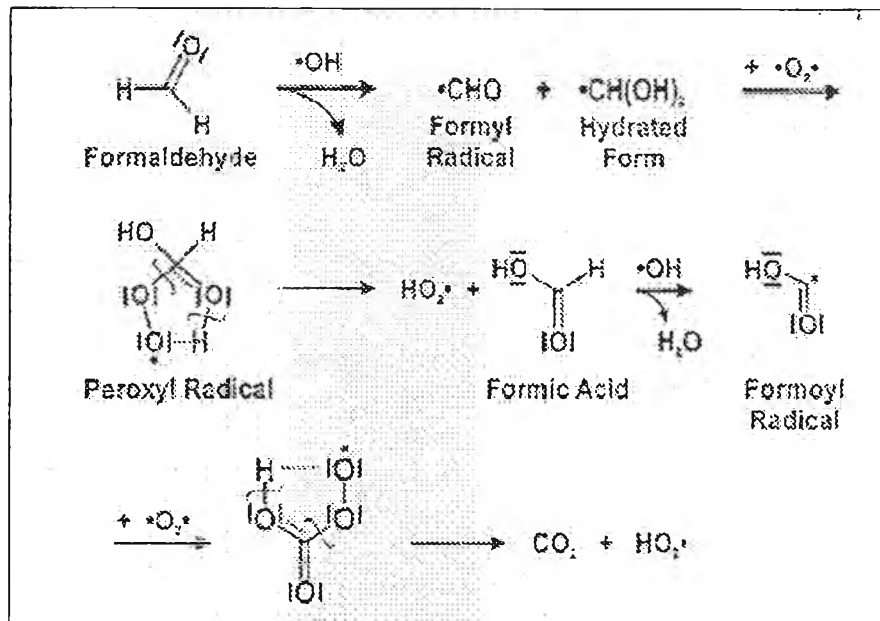
Figure 2.1 Mechanism of the mineralization of formaldehyde by hydroxyl radicals.

2.3 Rate Law and Rate Constants of Hydroxyl Radical Reaction

The reaction of $OH^{\bullet}$ radical with a substrate molecule M to yield a molecule of an oxidation product M^{ox} is a bimolecular reaction according to Equation 2.4.

$$OH^{\bullet} + M \longrightarrow M^{ox} \tag{2.4}$$

The reaction kinetics can be described by the second order rate law of Equation (2.5)

$$r(-M) = -d[M]_t = k_{\bullet OH,M}[M][OH^{\bullet}] \tag{2.5}$$

With r(-M) referring to the rate of diminution of the concentration of M and $k_{\bullet OH,M}$ being the second order rate constant for the reaction of $OH^{\bullet}$ radicals with a substrate molecule M (Hoigné J., 1998). The unit of $k_{\bullet OH,M}$ is usually given in $M^{-1}s^{-1}$.

Since hundreds of rate constant $k_{\bullet OH,M}$ have been measured, mainly by radiation chemical methods applying pulse radiolysis techniques (Buxton et al., 1988). However, the rate constants $k_{\bullet OH,M}$ can also be determined by a competition kinetics method, in which the rate of decay of a target compound is compared with that of a reference compound with known $k_{\bullet OH,M}$. Some examples of second order rate constants $k_{\bullet OH,M}$ for reaction of $OH^{\bullet}$ radicals with various substances M was illustrated in Table 2.2

Table 2.2 Representative examples of second order rate constants $k_{\bullet OH,M}$ for reactions of $OH^{\bullet}$ radicals with various substrates M in aqueous solution at T=293 K   (Buxton et al., 1998)
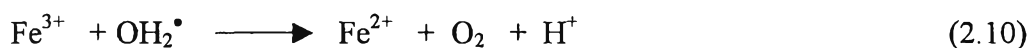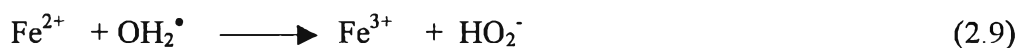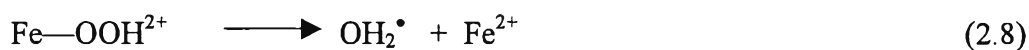
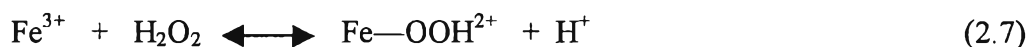| Substance M	Formular of M	Product M^{ox} of thereaction $OH^{\bullet} + M \longrightarrow M^{ox}$	rateconstant $k_{\bullet OH,M}/$ $10^9\ M^{-1}s^{-1}$
Bicarbonate ion	HCO_3^-	$CO_3^{\bullet-} + H_2O$	0.0085
Carbonate ion	CO_3^{2-}	$CO_3^{\bullet-} + HO^-$	0.39
Chloride ion	Cl^-	$^{\bullet}ClOH^-$	4.3
Formaldehyde	HCHO	$^{\bullet}CHO + H_2O$	1
Formate ion	$HCOO^-$	$CO_2^{\bullet-} + H_2O$	3.2
Formic acid	HCOOH	$^{\bullet}CO_2H + H_2O$	0.13
Hydrogen peroxide	H_2O_2	$HO_2^{\bullet} + H_2O$	0.027
Hydroperoxyl radical	$HO_2^{\bullet}$	$O_2 + H_2O$	10
Hydroxide ion	OH^-	$O^{\bullet-} + H_2O$ (pH=11)	12
Hydroxyl radical	$OH^{\bullet}$	H_2O_2	5.5
Methanol	CH_3OH	$^{\bullet}CH_2OH + H_2O$	0.97
Sulfuric acid	H_2SO_4	$SO_4^{\bullet-} + H^+ + H_2O$	0.014
Superoxide radical anion	$O_2^{\bullet-}$	$O_2 + HO^-$ (pH=7.9)	10

2.4 Fenton and Photo-Fenton Processes

Historically, Fe/H_2O_2 oxidations have been of interest mostly from a synthetic/mechanistic perspective and for their relevance to enzyme reactions and free radical-from damage to cell. Recent studies have investigated their potential for waste treatment. Usually ferrous ion (Fenton's reagent) has been used (Pignatello J. J., 1992; Plimmer et al., 1971; Barbeni et al., 1987; Watts et al., 1990), but some studies have employed ferric or ferric oxide. The classical reaction of Fe^{2+} with H_2O_2, known as the Fenton's reaction (Walling C., 1975; Barb et al., 1951), generates $OH^•$ in the rate-limiting step (Equation 2.6). The generated $OH^•$ radicals will react with an organic compound non-selectively.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^• + OH^- \tag{2.6}$$

Fe^{3+} catalytically decomposes H_2O_2 to O_2 and H_2O. The classical "radical chain" mechanism proposed for simple Fe^{3+}(aq) system involves $OH^•$ and the hydroperoxyl radical ($OH_2^•$) are illustrated as follow (Walling C., 1975; Barb et al., 1951)

$$Fe^{3+} + H_2O_2 \longleftrightarrow Fe\!-\!OOH^{2+} + H^+ \tag{2.7}$$

$$Fe\!-\!OOH^{2+} \longrightarrow OH_2^• + Fe^{2+} \tag{2.8}$$

$$Fe^{2+} + OH_2^• \longrightarrow Fe^{3+} + HO_2^- \tag{2.9}$$

$$Fe^{3+} + OH_2^• \longrightarrow Fe^{2+} + O_2 + H^+ \tag{2.10}$$

In the presence of excess hydrogen peroxide, $[Fe^{2+}]$ is small relative to $[Fe^{3+}]$, since Equation (2.7) is generally much slower than Equation (2.6). It is derived that ferrous ions are consumed quickly, but reproduce slowly (Lu et al. 1999; Pignatello J. J, 1992).

By applying UV light to Fenton reaction, photo-Fenton process, can enhance the oxidation rate of many organic compounds (Maletzky and Bauer, 1998; Liou et al., 2003). Photo-Fenton process is already well known in many literatures as an effective and cheap method for wastewater treatment. Production of hydroxyl radicals in a homogenous reaction pathway out of hydrogen peroxide under photocatalytic conditions is the basis of this method. This process utilizes the photoreduction of produced ferric ions (Fe^{3+}) and ferric complexes (Equations (2.11) to (2.12)) (Araña et al., 2001; Kim et al, 1997). In contrast to Fenton reaction (without photo-activation), ferrous ion (Fe^{2+}) is recycled continuously by irradiation of Fe^{3+}-H_2O, and therefore it is not depleted during the course of the oxidation reaction. Hence, the production of hydroxyl radicals is only limited by availability of UV/VIS radiation and H_2O_2.

$$Fe^{3+} + H_2O + h\nu \longrightarrow Fe(OH)^{2+} + H^+ \qquad (2.11)$$

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + OH^\bullet \qquad (2.12)$$

$$H_2O_2 + h\nu \longrightarrow 2\,OH^\bullet \qquad (2.13)$$
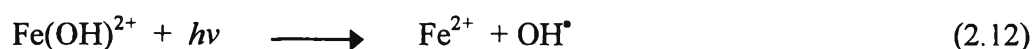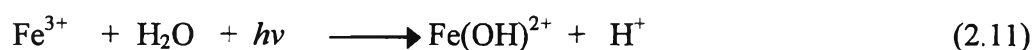
Additionally, a hydrogen peroxide can produce two hydroxyl radicals initiated by UV-light, according to Equation (2.13). Both two routes facilitate the formation of hydroxyl radicals and will promote the degradation rates of organic compounds.

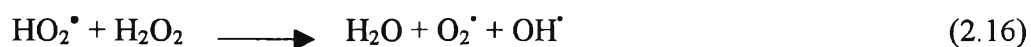## 2.5 Factors Affecting Fenton and Photo-Fenton Efficiencies

Initial pH, concentration of H_2O_2, and concentration of Fe^{2+} are the key factors which can effect Fenton and photo-Fenton reactions. According to Equation (2.14), it indicates that Fenton's reaction is strongly dependent on the solution pH. In fact, only $OH^\bullet$ radicals, the predominant reactive oxidation, is in acidic condition. In addition, at solution pH above 4, the degradation of organic compounds may decrease due to the precipitation of Fe^{2+} (Ghaly et al., 2001; Faust and Hoigne, 1990).

$$2\,Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow Fe^{3+} + 2\,H_2O \tag{2.14}$$
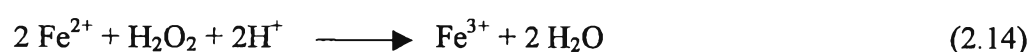
Theoretically, the degradation of organic compounds strongly depends on the amount of H_2O_2 in the system; however, excess amount of H_2O_2 acts as a hydroxyl radical scavenger as illustrated in the following Equation:

$$OH^\bullet + H_2O_2 \longrightarrow H_2O + OH_2^\bullet \tag{2.15}$$
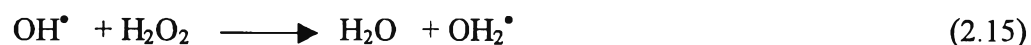
Consequently, low potential radicals, $OH_2^\bullet$, were produced resulting in the decrease of the oxidation of organic compounds (Equations (2.16) to (2.18)) (Schultei et al., 1991; Kochany and Bolton, 1992)

$$HO_2^\bullet + H_2O_2 \longrightarrow H_2O + O_2^\bullet + OH^\bullet \tag{2.16}$$

$$HO_2^\bullet + HO_2^\bullet \longrightarrow H_2O_2 + O_2 \tag{2.17}$$

$$OH^\bullet + HO_2^+ \longrightarrow H_2O + O_2^\bullet \tag{2.18}$$

According to Equation (2.19), in the excess amount of Fe^{2+}, Fe^{2+} may become $OH^\bullet$ radical scavenger because $OH^\bullet$ radicals will oxidize a molecule of Fe^{2+} resulting in the inhibition of the oxidation reaction.

$$OH^\bullet + Fe^{2+} \longrightarrow OH^- + Fe^{3+} \tag{2.19}$$
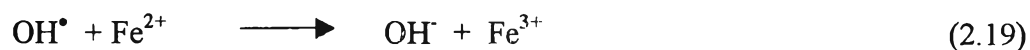
Moreover, it was indicated that hydroxyl radicals were scavenged by inorganic ions, such as CO_3^{2-}, HCO_3^-, PO_4^{3-}, and Cl^-, as expressed in Equations (2.20) to (2.23). Hydroxyl radical scavengers presented in many effluents can drastically reduce the efficiency of pollutant oxidation in direct proportion to their concentration via the reactions as follows (Duguet et al., 1989):

$$OH^\bullet + HCO_3^- \longrightarrow OH^- + HCO_3^\bullet \tag{2.20}$$

$$OH^\bullet + CO_3^{2-} \longrightarrow OH^- + HCO_3^{-\bullet} \tag{2.21}$$

$$OH^\bullet + PO_4^{3-} \longrightarrow OH^- + HPO_4^{2-\bullet} \tag{2.22}$$

$$OH^\bullet + Cl^- \longrightarrow OH^- + Cl^\bullet \tag{2.23}$$

2.6 Application of Fenton and Photo-Fenton Processes

Many researches have reported the decomposition of many refractory organics by Fenton and photo-Fenton processes, which are review as follows.

Goi et al. (2002) investigated the kinetics of the degradation of seven nitrophenols with Fenton's reagent, photo-Fenton, and hydrogen peroxide photolysis. The efficiency and operating costs for the studied treatments were evaluated and compared. Fenton's reagent was found to be the most efficient and the cheapest way for the nitrophenols (NPs) degradation. Moreover, Fenton treatment led to the complete detoxification of NPs.

Lu et al. (1999) employed Fenton's reagent to oxidize dichlorvos insecticide. Results showed that the efficiencies were fairly satisfactory. At acidic and saturated dissolved oxygen conditions, only 90 min were needed to push the elimination ratio up to 98%. The dichlorvos decomposition in this system underwent a two-stage reaction. The first stage was the reaction before 30 s in which the decomposition rate of dichlorvos was high, and it was a Fe^{2+} / H_2O_2 reaction. The second stage was the reaction that took place after 30 s. The decomposition rate of dichlorvos in the second stage was slower, and it was a Fe^{3+} /H_2O_2 reaction. The most ideal pH for Fenton reaction to decompose dichlorvos in solution was around 3-4. As the added amount of hydrogen peroxide or ferrous ions increased, the decomposition rate of dichlorvos also increased.

Torrades et al. (2003) reported that the degradation of Bleaching Kraft Mill effluent has been successfully carried out by simultaneously applying Fenton reagent and solar light irradiation. Experimental design was valuable in determining the roles played by the different studied variables. The most important aspect that needed to be considered during the treatment process was the choice of right ratio of Fenton's

reagent. Non-optimal initial concentrations of Fenton's reagent were found to be detrimental. This was apparently due to competitive reaction of H_2O_2 and Fe^{2+} with the hydroxyl radicals. They also indicated that the combination of Fenton's reagent and solar light for the mineralization of Kraft Paper Mill effluents had clear advantages from an applied point of view.

Liou at el. (2003) studied the degradation of explosives by Fenton and photo-Fenton processes. Their results indicated that ferrous ion and ultraviolet light significantly affected the efficiency of explosive destruction. However, UV promoted efficiency of any explosive decreased at higher Fe^{2+} concentration. They also concluded that the $OH^{\bullet}$ inhibition effect occurred in photo-Fenton reaction of the high Fe^{2+} concentration because the large amount of $OH^{\bullet}$ generated from the higher Fe^{2+} concentration decreased the amount of $OH^{\bullet}$ generated from H_2O_2 photolysis.

Goi and Trapido (2002) studied the degradation of 4-NP by advanced oxidation processes such as hydrogen peroxide photolysis, Fenton's reagent and ozonation combined with hydrogen peroxide and UV radiation. It was ascertained that 4-NP can be degraded successfully with Fenton's reagent treatment, where the optimal ratios of hydrogen peroxide to 4-NP and catalyst (Fe^{2+}) to 4-NP were 10:1 and in the range of 1:1 to 1:2, respectively. The further precipitation and filtration could easily remove the residual iron. These processes enabled both degradation 4-NP and elimination of the toxicity as the by-products of advanced oxidation of 4-NP were found to be non toxic, according to Daphnia magna acute toxicity test. Although all these processes led to the degradation of 4-NP, Fenton's reagent was found to be most promising method for the destruction of 4-NP.

Oxidation kinetics and mechanism of trihalomethanes by Fenton's reagent was investigated. This study indicated that the brominated Trihalomethanes (THMs), e.g. bromodichloromethane, dibromochloromethane and bromoform can be oxidized by Fenton's reagent. The oxidation kinetic increased with the increase of the number of

bromine atoms presented in a THM molecule and its concentration. The bromoform experiments indicated that at pH 3.5 the best H_2O_2: Fe^{2+} dose was 3.7-1.9 mM for all initial concentrations of THM. The amount of THM oxidized increased with increasing initial organic concentrations. When H_2O_2 dose was fixed at 3.7 mM and Fe^{2+} dose was increased from 0.19 to 1.9 mM, rate constants were increased due to an increase in available hydroxyl radical generated by the Fe^{2+} (Tang and Tassos, 1997).

Photo-Fenton process was applied to two azo reactive dyes. Results showed that the pH, initial H_2O_2 concentration, the contact time and the effect of irradiation had an important influence on the photodegradation of the selected reactive dyes: C.I. Reactive Yellow 84 and C.I. Reactive red 120[cl]. The results indicated that the oxidation rate increases in an acidic medium, and pH 2-3 was found to be the optimum. The most favorable molar ratio of Fe^{2+}/H_2O_2 was 1:20 for both dyes. The results also showed that no significant difference existed during the first minutes of reaction if the process was carried out in the presence of the UV light or under solar irradiation (Neamtu et al., 2003).

Maletzky and Bauer (1999) studied the degradation of nitrogen containing organic compounds by photo-Fenton process. They concluded that among the AOPs photo-Fenton process was a relatively inexpensive and efficient wastewater treatment process for highly contaminated water. Moreover, it was indicated that the best results were achieved with ferrous sulphate. This corresponds to the results mentioned in the literature (Kochany et al., 1995) where chloride had a greater inhibiting effect than sulphate.

Degradation of ethylene glycol was investigated by applying photo-Fenton reaction. Ethylene glycol loss rate constants of 1.0 ± 0.40 h^{-1} were achieved in photo-Fenton systems containing concentration of 1000 mg/l ethylene glycol. Ethylene glycol was converted to formic acid resulting in a loss of calculated chemical oxygen demand. Iron was not catalytic in the system, which may be due to the formation of

ferric oxalate complexes. The system was inhibited by elevated concentration of sulfate and a phosphate buffer solution. The optimal pH was 3.0, which significant decreases in the degradation rates at pH below 2.8 and above 3.2 (McGinnis et al., 2000).

2.7 Properties of Formaldehyde and Methanol

2.7.1 Formaldehyde

Although formaldehyde is a gas at room temperature, it is readily soluble in water, and it is most commonly sold as a 37% solution (with approximately 10 % of methanol) in water called by trade names such as formalin or formol. Its chemical properties are as follows:

Formula: CH_2O

Molecular weight: 30.03 g/mol

Relative Density : 1.0

Melting Point : -15 ^{0}C (37% solution)

Boiling Point : 97 ^{0}C (37% solution)

As formaldehyde can kill most bacteria, a solution of formaldehyde in water is commonly used as a disinfectant or to preserve biological specimens. It is also used as a preservative in vaccinations. Formaldehyde is a part of the embalming solution about 1.9% concentrations. In order to preserving tissue for long period of time it also acts to inactivate many microorganisms that may reside in the tissue. The permissible exposure limit for formaldehyde is 0.75 ppm (parts per million). Airborne concentrations of formaldehyde above 0.1 ppm can cause irritation of the eyes, nose,

and throat. Higher concentrations can be dangerous to life and health. Skin contact with formaldehyde can also result in various skin reactions, including sensitization.

A high quantity of formaldehyde exposure, for example from drinking formaldehyde solutions, is potentially lethal. Formaldehyde is converted to formic acid in the body, leading to a rise in blood acidity, rapid, shallow breathing, hypothermia, and coma or death. People who have ingested formaldehyde require immediate medical attention. In the body, formaldehyde can cause proteins to irreversibly bind to DNA. Laboratory animals exposed to large doses of inhaled formaldehyde over their lifetimes have developed more cancers of the nose and throat than are usual, as have workers in particle-board mills. However, some studies suggest that smaller concentrations of formaldehyde like those encountered in most buildings have no carcinogenic effects.

2.7.2 Methanol

Methanol, also called methyl alcohol, is the simplest of a long series of organic compounds called alcohols. Its chemical properties are as follows:

Formula: CH_3OH

Molecular weight: 32.042 kg/kmol

Relative Density: 0.79

Melting Point: -97.7 ^0C

Boiling Point: 65 ^0C

Methanol is a colorless liquid, completely miscible with water and organic solvents and is very hydroscopic. It forms explosive mixtures with air and burns with a nonluminous flame. It is a violent poison; drinking mixtures containing methanol

has caused many cases of blindness or death. Methanol is a potent nerve poison. It has a characteristic pungent odor. The permissible exposure limit is 200 ppm in air. Preventing skin contact is to wear nitrile gloves and a plastic apron.