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Toxicity of Emissions from Combustion and Pyrolysis of Wood

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Summary. Fuels such as wood and forest residuals are becoming important sources of energy; furthermore, wood and wood products are major components of building construction. In both cases environmental impact and health hazard posed by the burning of these materials must be evaluated. Most death and injuries on exposure to burning wood are due to inhalation of toxic gases, smoke, and heat gases, usually carbon monoxide. Any wood or wood products used in building construction must be chosen so as to release the minimum amount of toxic materials as slowly as possible when heated or burned, to allow people time to escape. The emissions from wood burning power plants certainly have local short term and global long term environmental impacts. For example, massive carbon dioxide production from wood burning is believed to affect the earth's energy balance and therefore global climates. This review does not consider this aspect of wood burning, or other environmental hazards due to power plants utilizing wood, about which little seems to be known. The subject of this review is of the literature from 1971–1979 concerned with the toxicity of products of combustion and/or pyrolysis of wood, or wood products, untreated or treated with preservatives.

Introduction

A variety of different woods are used in building construction and, to a lesser extent, furniture and interior furnishing. Wood in common use includes varieties of white and yellow pines, firs, cedars, and hemlocks, etc. However, very little work has been done that explicitly compares the compositions of emissions from different woods subject to combustion or pyrolysis under the same conditions. Halido and his coworkers (1977a, b, c; 1978) compared the combustion products of hardwoods (aspen, poplar, yellow birch, and red oak) and softwoods (western red alder, Douglas-fir, western hemlock, eastern white pine, and southern yellow pine) on toxicity of rats. Jouany et al. (1977) compared Douglas-fir and mahogany combustion products, using as a criterion for comparison the effects upon rats and rabbits. Kishitani and Nakamura (1974) compared the combustion product of Japanese cedar and plywood (untreated and fire retardant treated). However, no other comparative investigations seem to have been carried out even though such studies would be valuable. Other

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literature surveyed typically refers to "wood" or "plywood" without giving specific identifications. Halido and Gall (1977) found no differences between the woods used, and neither did Kishitani and Nakamura (1974). However, Jouany et al. (1977) found Douglas-fir to be more toxic than mahogany. Much of the forest products utilized in building construction today are treated or combined with a variety of chemicals. Preservatives against decay in damp environments are frequently added by impregnation, and a variety of other preservatives are added to the wood for various purposes. Plywoods contain adhesives which are often polymeric in nature. Wood materials are frequently treated with fire retardant materials. Relatively little attention has been paid to the effect of these additives upon the toxicity of burning wood (Kishitani and Nakamura 1974, 1977).

A further major difficulty in making comparisons between different species of wood is that investigators do not use standardized methods and procedures, or define toxicity in a uniform fashion. Important variables in combustion and pyrolysis of wood are temperature, rate of rise of temperature (or time history of temperature), air flow rates, horizontal and vertical combustion, moisture content of the samples, and chemical composition of the wood (aldehydes, terpenes, etc.). Different investigators generally work with different combinations and values of these parameters, thereby rendering comparisons exceedingly difficult. A great variety of experimental configuration are employed, the standard NBS Smoke Chamber being rarely used; Adams (1977) is one of the few workers to use it. Toxicity is generally defined as essentially time to death after onset of exposure (Halido et al., 1978, 1978; Kishitani and Nakamura 1977), or time to incapacitation (cessation of movements) (Kishitani and Nakamura 1974, 1977). These measurements are used to derive LC_{50}'s or TLV's. Boudene et al. (1977) utilized physiological criteria for measuring intoxication and death, based upon the state of the animal as characterized by EEG (electroencephalography) frequency, arterial pressure, and pulse rate. Kishitani compared untreated plywood with plywood treated with fire retardant materials. Dobbs and Grant (1976, 1978) studied CCA (copper-chrome-arsenic) treated wood, and Rappe and Marklund (1978) investigated the chemical mechanisms involved in the burning of chlorophenates, often used as wood fungicides.

A different motivation for studying the composition of gas evolved by burning wood is found in the meat industry, where burning wood is used to smoke meat. Such studies are reported by Borys et al. (1977) and Dikun (1977).

Wood Combustion

Below 100 °C wood dries, but chemical reaction is insignificant; between 100–150 °C chemical reaction is still very slow and insignificant from the point of view of emission of toxic gases. Between 150–200 °C gases are formed which in general consist of 70% CO_2 and 30% CO. At these temperatures and above, wood will spontaneously ignite after a certain time (Fig. 1 [Metz 1936]). Above 275 °C gases are produced

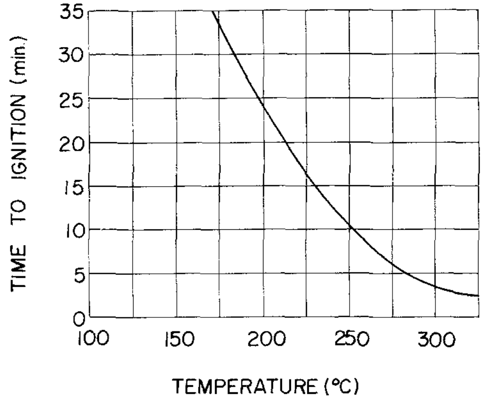

Fig. 1. Dependency of time until ignition of wood on the temperature (from National Fire Protection Association, USA)

rapidly and the amounts of CO_2 and CO decrease; large quantities of hydrocarbons are produced, their production peaking around 450 °C. Figure 2 summarizes the course of events on heating wood (Juon 1907). Differences exist between, for example, coniferous and angiosperm species, possibly due to their different pentosan contents, (Kollmann 1960).

Kishitani et al. (1974, 1977) present curves showing the variation of CO with time of heating treated or untreated plywood of Japanese cedar to 300, 500, or 750 °C. However, the actual CO concentrations are not related to the sample temperature, merely to time and temperature of the heater. Studies on Douglas-fir resulted in shorter time to death than earlier comparable studies on red oak and hemlock; the difference could be possibly due to aging of wood, older wood being more toxic

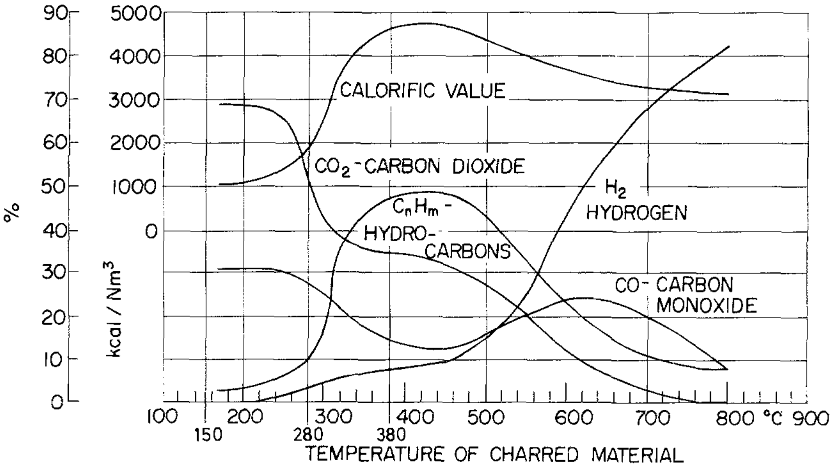

Fig. 2. Course of wood charring in brick-built charring kilns of the Schwartz-type

(Halido and Lopez 1977), a reverse of the trend of some polyurethane foams of decreasing toxicity with age.

Emissions

Carbon monoxide is produced by incomplete combustion of wood. Variation of CO production by different woods might be due to the difference in composition of the wood species, arising from differences in the relative content of cellulose, hemicellulose, lignin, tars, resins, and moisture content. Halido et al. (1978, 1977), who did not find any statistically significant differences between toxicity of nine wood samples, speculated that there might be differences due to species variation (thus violating rules for statistical inference). The earlier work of Halido states that due to the lack of standardization, by a choice of test methods and statistical analysis it is possible to draw any conclusions desired (Halido and Gall 1977). Tests from different types of wood indicated that samples from a combustion chamber ranged from 6400–17600 ppm CO (Halido and Gall 1977). Even though toxicity (time of death) was the same, the CO concentration was significantly different, which suggests that factors other than CO were responsible for death. Further, the large variations in CO production between samples of the same material need to be explained. These variations were probably due to true sample to sample variations or to techniques of manufacture; typical values ranged from 4100-13 000 ppm for asphalt impregnated fiber-board sheathing (Halido et al. 1977). An interesting study by Boudene et al. (1977) investigated the effect of simulated sprinklers on the composition and toxicity of gases produced from Douglas-fir combustion. Both LC_{50} and CO in ppm without water were roughly double that with water. However, a curious finding is that the CO_2 concentration in the presence of water was higher than without water (55 000 vs. 45 000 ppm); the converse would be expected.

Boudene et al. (1977) also carried out studies to express the toxicity of these gases in terms of meaningful physiological parameters. Rabbits and rats suitably prepared were subjected to toxic gas from combustion of Douglas-fir, and physiological parameters such as EEG, EKG (electrocardiography), blood pressure, CNS activities (cardiovascular-system), and COHB (carboxyhemoglobin) were measured. Similar measurements were carried out using CO for comparison. The study also defined a "Global Index of Intoxication": the animal state is represented as a point in a 3-dimensional space with axes being pulse rate, arterial pressure, and "EEG frequency", (the term "EEG frequency" is unclear and unfortunately not defined). The "Global Index of Toxication" is the distance in space between the actual state of the animal and the control state. Of interest in this work is the difference in responses observed between animals intoxicated with wood smoke and those intoxicated from CO. It is reported that the response to CO and smoke is identical for the first 15 min. However, after 20 min smoke breathing animals suffered irreversible lethal damage (fluid in the trachea), APE (acute pulmonary edema), whereas with CO this did not occur, and the animals were able to recover to some extent. Furthermore, utilizing a water sprinkler simulating system protected the animals from death for a few hours and the indices were similar to those of CO intoxication. But three or four hours after intoxication, APE appeared, which did not occur with CO alone. These results indicate that presence of other substances than CO are responsible for the intoxication. The presence of alkyldiens, acetic acid, propionic acid, and methanol, detected in hemlock gas samples, (Adams 1977) could be responsible for this effect. Other compounds found by Hartung et al. (1977) in Douglas-fir combustion products are small amounts of methane and HCl, HCN, acrolein, and traces of NO_2 and NO. Any or all of these could be responsible for the difference in toxicity reported by Boudene. Jouany et al. (1977) report that an atmosphere of CO is less toxic than an equivalent atmosphere of CO as combustion product from Douglas-fir and mahogany. He hypothetized that this could be due to the presence of other irritant toxicants, such as aldhydes. A comparison between all these results is difficult due to the difference in temperature of combustion, experimental protocol, and different parameters measured.

Compounds from Combustion of Treated Woods

Wood and wood products are often treated with preservatives or fire retardants. Preservatives in common use are pentachlorophenol, coal-tar creosotes, and other oils, chromated and copperized zinc chloride (Kollmann and Côté 1968), CCA (Dobbs and Grant 1978). Fire retardants are commonly ammonium phosphates and sulfate, other compounds such as borates and bromides; potassium and sodium alkali silicates are commonly used as coatings on surfaces. In some cases organic foaming compounds are also utilized, such as mixtures of diammonium phosphate, borax and formaldehyde or dicyandiamide (Kollmann and Côté 1968). When treated wood is heated or burned, products of chemical reactions of the above substances are liberated, and many contribute significantly to the toxicity of the gases. There appears to be little work concerned with the toxicity of these gases. Rappe and Marklund (1978) investigated the mechanisms of formation of PCCDs (polychlorinated dibenzo-P-dioxins) and PCDFs (polychlorinated dibenzofurans) by the burning of chlorophenols. Chlorophenols were found to contain PCCDs and PCDFs as impurities and to produce these substances by a variety of mechanisms when heated. This is a matter of some concern, as many isomers of PCCDs are highly toxic in small amounts. In treating wood, prior to the end use, the outer layers of the treated wood are often shaved and the shavings burned for heating purposes or used for plywood production (Rappe and Marklund 1978). Dobbs and Grant (1978) studied the release of arsenic upon burning of CCA treated wood. An evaluation of the environmental hazards has been published recently by Dobbs and Grant (1976). Typically, a constant 24% of the arsenic in wood is evolved on burning, when the concentration of arsenic in the treated wood is between 8 and 25 mg/g. Hence, increasing the concentration of the salt does increase the amount of arsenic evolved, and very large amounts of toxic arsenic will be released on burning the wood. Much of the lumber used in construction is treated with copper naphthanate; however, no literature has been found dealing with the toxic effects of heating this substance when burning wood.

Influence of Experimental Conditions: Temperature

Halido et al (1977, 1978) simulated developing and fully developed fire by raising the temperature from 200 to 800 °C for the former at a rate of 40 °C/min., and keeping the temperature at 800 °C for the latter. Using nine wood samples, they found no significant differences between the two temperature conditions.

Kishitani et al. (1974, 1977) heated building materials from room temperature to 350, 500, and 750 °C in 15 min. In addition they also heated samples more rapidly, raising the temperature to the final value over 6 min. In the former case natural draft was used, and in the latter an air flow rate of about 28 l/min was used. They recorded the movements of mice, using cessation of movements by either a tread mill, or a strain gauge detecting the motion of the mice in the cage. However, cessation of movement is not a good measure of toxicity. The mice could be temporarily incapacitated and be able to recover afterwards. The strain-gauge is capable of detecting the breathing movements, and would be more reliable; it was employed in their later work (Kishitani and Nakamura 1977). The time of exposure used is roughly comparable to the time required to evacuate a multistoried building. Boudene et al (1977) and Jouany et al. (1977) heated Douglas-fir and mahogany in an annular furnace using 400 °C to simulate smoldering conditions and 850 °C to simulate fully developed fire. It is not clear whether these temperatures represent the sample or the heater temperature. In both cases the air flow was 120l/h. Hartung et al. (1977) exposed rats to nonflaming decomposition products from Douglas-fir, using a radiant heater to char the wood, but they do not provide any information about temperatures, rate of increase in temperature increase, or gas flow rates. Adams (1977) also used a radiant heater in the NBS chamber, but did not report any temperatures, and since the chamber was sealed, no air flow rate. Dikuns et al. (1977) pyrolyzed sawdust by superheated steam at 400 °C, with 10 and 14 g of steam/g of wood. Rappe and Marklund (1978), in their study of the products of burning chlorophenates and wood, merely allowed birch leaves or wood wool to burn freely in air in a glass bowl.

It is virtually impossible to make meaningful comparisons between the results of different workers due to differences in temperatures, rate of temperature, increase and different gas flow rates. Borys et al. (1977) found a linear relationship between combustion rate of sawdust and the product of temperature and air flow rate for particular particle size and moisture content. They also present without discussion an empirical exponential relationship between combustion rate and air flow rate. The linear relationship shows a high correlation coefficient, but no support was given to the exponential relationship. A linear correlation such as that observed by Borys et al. (Dikun et al. 1977), if firmly established, could be of use in comparing different sets of results, provided adequate data are available. Unfortunately many workers in this field fail to report, or often even control, relevant variables.

Conclusions

This field at present suffers from a lack of standard procedures and methods in all aspects, rendering all comparisons exceedingly difficult. It is necessary to be able to make comparisons between, for example, different types of wood, different combustion conditions, and different experimental parameters. The ultimate goal must be the accurate and reliable determination of the specific hazard posed by different wood and wood products used commercially.

The basic mechanisms of wood pyrolysis and combustion are known, but details are lacking concerning variation between species, and influence of combustion conditions, such as air flow, orientation (horizontal vs. vertical or inclined), natural or oxygen starved, rate of rise of temperature, and temperature. A body of work exists concerning wood combustion from the point of view of fire science and fire prevention (Bush et al. 1976), but not gas emission and toxicity. For a realistic and practical approach to toxicity of combustion production, integration between these two fields is needed. Borys et al. (1977) have taken a step in this direction, but better empirical correlations are needed relating, for example CO production and air flow, temperature and temperature rise rate, etc.

Evaluation of toxicity is very much a matter of individual choice, ranging from the sophisticated and physical "degree of intoxication" of Boudene and Jouany, to the cessation to treadmill activity used by Kishitani. A meaningful evaluation of toxicity must use standardized methods and possibly adaptations of those used for drug toxicity evaluations (Mantegaza and Piccinini 1966; Mathews 1972).

Carbon monoxide is a major toxicant, produced by incomplete combustion of all woods. However, studies of Jouany and others have shown the toxicity of combustion gases is greater than can be attributed to the CO content of the gases alone. There are speculations that other irritants contribute markedly to toxicity, even though they are present in small amounts, for example aldehydes from Douglas-fir pyrolysis. In fact, Kollmann (1960) lists over 200 organic chemicals found in pyrolysis emissions. Further, the possibility of a synergistic effect between compounds present in small amounts cannot be neglected. If it could be determined that certain specific minor constituents of combustion products contribute significantly to toxicity and enhance irreversible physiological effects, then the possibility exists of retarding the emission of these specific constituents by treatment of the wood.

Another area that needs further work is that of toxicity of emission from burning wood treated with preservatives and/or fire retardant. There is an extensive literature concerning fire retardants per se (McKinon 1976; Bhatnager 1977), but very little has been reported concerning the toxicity of emissions from wood treated with fire retardants. Although there is in existence an NBS Standard Smoke Chamber, it has been used only by few investigators and then with some modifications. All experimental apparatus and procedures vary from group to group. More standardization of experimental conditions and methods of measurements is needed to facilitate comparisons between results of different workers in this field. More detailed investigations are required to establish a mean LD_{50}, as a function of concentration and time at the concentration of gases produced from burning wood.

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