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Health Hazard of Smoke Production in Thermal Decomposition of Polymer: A Review

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***Abstract*—**This paper reviews the smoke toxicity in the polymer combustion and the toxicity tests that has been widely used in the polymer industry, which focusing on the polyurethane products. The study has been done by reviewing 98 journal papers that reporting on the thermal decomposition of polymer products. When a polymer burnt, the aliphatic fuels are cracked to smaller alkyl radicals which forming polyenes or polybenzenoids that may be radical, ionic or neutral. These intermediates will react with other unsaturated species and condensed to form soot or char residues. The combustion gases contain varieties of toxic gasses such as carbon monoxide (CO), hydrogen cyanide, nitrogen oxides, hydrogen chloride, sulphur oxides and many other toxic organics. It also produces oxidative pyrolysis products, such as oregano-aldehydes, and particulates. The presence of fluorine, chlorine and bromine would be expected to generate hydrogen halides and halogenated organics. Hydrogen cyanide and other organic cyanides are released during thermal decomposition of polyurethane foams used in the manufacture of furniture, and contribute to mortality in smoke inhalation. Prolonged or excessive exposure will lead to cyanide toxicity and metabolic acidosis. Based on this review, it is obvious that the burning of polyurethane will bring destructive effect to the environment especially to human. All the findings in the study show that there are so many toxic products produced during the pyrolysis of polymer. Each and every product of the pyrolysis has certain effect on the human body. This review has also proven that the burning of the polymer, whether in the process of production or in its pyrolysis, can give out an unhealthy environment to the human body. This result should be taken in consideration by the employer during the planning for a safe environment to the workers in the process of producing polymer products. Some safety measures should be taken, so that the workers will not expose to these toxic products. This problem should also be well taken care by the fire brigade to ensure that the best method of avoiding smoke poisoning among firefighters and fire victims during a fire.

Keywords-*smoke toxicity; polymers combustion; health hazard*

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I. INTRODUCTION

In a modern environment, a wide range of highly combustible materials such as natural and man-made polymers are used. Principle types of plastics that found in the markets are polyethylene (PE) which used in trash bags, grain storage bags and shopping bags; polyvinylchloride (PVC) that be used in bottles, packaging and containers; polyethyleneterephthalate (PETE) which used predominantly in beverage bottles and similar containers; polystyrene (PS) is a light spongy material that be used in meat, eggs and miscellaneous product trays and hot beverage cups; and polypropylene (PP) which used in yogurt containers, straws, margarine tubs and special bags. Most of these plastics are discarded after a single use and become garbage, thrown and burnt in the dumping sites. Studies have also reported that the use of synthetic building materials and furnishings has led to an increase in inhalation injuries causes by fires where they produce more toxic smoke. It is recognized that compared with natural materials (e.g.: cotton, wood, wool) plastics generate heat more swiftly, spread flames faster, generate large amounts of denser visible smoke and release more toxic and greater concentrations of invisible products of thermal decomposition [1]. The information on the toxic and injurious effects of smoke generated from uncontrolled fires is rare where each fire generates its own variety of smoke, depending on the nature of the combusting materials and the burning conditions [2].

The objective of this paper is to review on the studies that have been made on the smoke that is produced during the thermal decomposition of a polymer. It is well known that polymer is widely used in many industrial applications such as automotive, upholstered furniture, mattresses and insulating panels for building. The risk of these flammable materials did not only occur to the end users, but also through the occupational exposure. During the manufacturing process, this material is also exposed to thermal decomposition and has their effect to the workers involved with the manufacturing process. This study is to investigate the toxic component in the smoke during the pyrolysis of this material. It is expected to be composing a variety of toxic components. This is due to the variety of physiological interactions between fire gases and smoke. It is very hard to study the smoke toxicity of polymer combustion due to it contains hundreds of different chemical species even from the burning of a simple polymer. Even so, it is also important to study the toxicity because many of the fatalities in fire are contributing the effects to the atmosphere rather than burns and other injuries.

II. SMOKE TOXICITY OF POLYMERS

A. *Polymer Combustion*

The manufacturing of plastics involves various chemical processes and utilizes a variety of chemical compounds and additives including phenols, amines and esters, antioxidants, ultraviolet (UV) and light stability improvers, antistatic agents and heat stabilizers that impart the finished product specific characteristics for its intended use. The finished product that is the plastic itself is environmentally quite stable. However, the additives, their chemical reaction and degradation products incorporated into the polymeric material have the potential to be released into the environment and cause significant health and environmental concerns.

It is complicated to study fire behavior of polymer during combustion. Thus, it is important to understand initially the processes occurred during the combustion of polymer. The polymer combustion is divided into two processes which are 1) the combustion in gas phase and 2) fuel generation in the condensed phase [3] (refer to Fig. 1).

From the condensed phase, the polymer combustion can be initiated by three stages such as 1) heating, 2) thermal decomposition or pyrolysis and 3) ignition [4]. In the heating process, the temperature of the solid polymer is raised either due to an external heat source namely 1) radiation or flame or 2) the thermal feedback which was produced by the exothermic process of the flame (refer Fig. 2).

In the gas phase, the volatile molecular species produced the pyrolysis process. The combustible gasses, liquid products and solid charred residue will be the source of fuels for the combustion process. These flammable products will mix with the oxygen from the surrounding air (Fig. 1), and furthermore will act as fuel to sustain the flame. This process will produce combustion products such as smoke and charring residue. This is an exothermic process and if the energy is high enough, it will override the endothermicity required for the polymer pyrolysis. This will further elevate the temperature of polymeric materials and accelerates the rate of burning, resulting in the flame spread of the polymer.

In the pyrolysis step, large quantities of small molecules are produced and most of them are combustible. In this process, the polymer is heated and energy (Q_1) is consumed (refer to Fig. 2). It is an endothermic process. In the ignition step, the temperature is elevated high enough to allow polymers to degrade and ignited [5]. Thermoplastic polymers that have a linear chain structure will soften or melt and start to flow during the initial exposure. On the other hand, the thermosetting polymers have a three-dimensional cross-linked molecular structure which prevents softening or melting. Higher temperature will cause both types of polymer to pyrolyse and develop smaller volatile molecular species. These molecular species can be in the form of non-combustible gasses, combustible gasses, liquid products and solid charred residue depending on its chemical compounds [4].

B. *Toxic Products of Polymer Combustion*

Generally, smoke is considered to be a cloud of invisible particles that is opaque as a result of scattering and absorbing a visible light. It is necessary to distinguish between smoke, combustion gases and visible smoke where both can have different effects to the environment. Combustion gases contain varieties of toxic gasses such as carbon monoxide (CO), hydrogen cyanide, nitrogen oxides, hydrogen chloride, sulphur oxides and other very toxic organics [4]. The visible smoke in burning polymers is a result from an incomplete burning. Fig. 3 shows the smoke evolution in polymer pyrolisis. When a polymer burnt, the aliphatic fuels are cracked to smaller alkyl radicals forming polyenes or polybenzenoids that may be radical, ionic or neutral. These intermediates will react with other unsaturated species and condensed to form soot or char residues.

Polymers containing only carbon, hydrogen, (H_2) and oxygen (O_2) will give carbon dioxide (CO_2) and water when burned to completion. But if the combustion is incomplete, it will also give a mixture of pyrolysis products e.g. carbon monoxide, hydrocarbons (HCs), oxidative pyrolysis products such as organo-aldehydes and particulates. The presence of fluorine, chlorine and bromine would be expected to generate hydrogen halides and halogenated organics [6].

In the case of flashover, every polymer released up to 20% of its mass as carbon monoxide which leading to highly toxic smoke. Fire gases result from the pyrolysis, oxidative pyrolysis and flaming combustion of organic materials, and can contain a complex mixture of many different compounds. The temperature and oxygen concentration are significantly different during a fire and between different fires, resulting different gases produced in different stages of a fire [6]. For example, upon burning, polyurethanes produce aromatic isocyanates, amines and aldehydes [4].

At about 400^{o}C, the nitrogenous compounds generated by the thermal decomposition of polyurethane foams may comprise isocyanates and organo-nitriles [6]. As the temperature increases, hydrogen cyanide will be the majority at higher temperatures (example at 800^{o}C). For higher ventilation rates, nitrogen oxides will be the main product.

During thermal decomposition of polyurethane foams used in the manufacture of furniture, hydrogen cyanide and other organic cyanides are released and contribute to environmental toxicities and mortality in smoke inhalation [7]. Hydrogen cyanide and other organic cyanides are released during thermal decomposition of polyurethane foams used in the manufacture of furniture, and contribute to mortality in smoke inhalation. Prolonged or excessive exposure will lead to cyanide toxicity and metabolic acidosis.

Another industrial application of polyurethane (PU) is in the manufacturing of car paints. For a pyrolysis of certain car paint, the temperature was gradually increased to 800^{o}C isocyanic acid; methylene isocyanate, ethylene isocyanate, propyl isocyanate and butyl isocyanate were detected. During the thermal degradation of the polyurethanes car paint at the reference body temperature of the 473^{o}C isocyanic acid, all linear isocyanates are ranging from methyl isocyanate to n-hexyl isocyanate, all alkenyl isocyanates are ranging from propylene to octylene isocyanate and many structural isomers of these compounds were detected [8]. Thermal degradation of car paints can also occur during many industrial processes such as welding and cutting. Emissions of methyl isocyanate and isocyanic acid were detected during these operations in car repair shops [9].

The UK Naval Engineering standards 713 (NES-713) is one of the methods used to study the smoke contents and constituents. The NES-713 has offered the concentration from 14 different toxic gasses which expressed as a factor of the concentration fatal to human at a 30 min exposure time (refer to Table 1) [10]. It is used for the testing of cables, composite materials, insulation materials and interior finish materials in many countries. The UK Building Research Establishment (BRE) also uses the test for building materials and products (United Kingdom Accreditation Service). In [10] has studied the toxicity characteristics of four commercially manufactured insulation materials, which according to NES-713 and colorimetric analysis. The various colorimetric gas reaction tubes were used to measure toxic constituents and contents. Afterwards, the toxicity index (TI) was calculated to evaluate the combustion characteristic of the specimens. The TI of the test materials vary in the range 5.386-18.239 such as

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polyethylene (18.239) > polyurethane (12.35) > rock wool (6.949) > fiberglass (5.386). It showed that the toxicity characteristics of these insulation materials were worse than the untreated wood (TI $\leq$ 2.5). These results indicated that organic foamy materials, polyethylene foam and polyurethane foam did not meet the requirements of the low fire hazard material and were unfavorable in the building's fire prevention.

TABLE I. THE TOXIC CONCENTRATION FATAL (C_F) TO HUMAN AT 30 MIN EXPOSURE TIME WITH NES-713 [10]

Gas	C_f (ppm)
Carbon dioxide (CO_2)	1 x10 ^{5}
Carbon monoxide (CO)	4 x10 ^{3}
Hydrogen sulphide (H_2S)	750
Ammonia (NH_3)	550
Formaldehyde (HCHO)	500
Hydrogen chloride (HCl)	500
Sulphur dioxide (SO_2)	400
Acrylonitrile (CH_2CHCN)	400
Nitrogen oxides (NOx)	250
Phenol (C_6H_5OH)	250
Hydrogen cyanide (HCN)	150
Hydrogen bromide (HBr)	150
Hydrogen fluoride (HF)	100
Phosgene ($COCl_2$)	25

There are many studies that have been made to produce the better fire resistance polymer. One of the appropriately flame-retardant compounds are phosphorus-containing compounds, which can avoid the release of toxic gases into the atmosphere. They mainly act on condensed phase flame-retardant mechanism during burning, that produces much incombustible char residue and release less toxic gases than halogen-containing compounds [20].

III. THE HEALTH HAZARD AMONG WORKERS IN PLASTIC INDUSTRIES

There are many potential health hazards associated with the processing of plastics. This led to many studies that reported the harm of plastic to human health, in [11] has reported a study to detect the presence of styrene and/or its metabolites in the workers in one of the Egyptian plastic factories. The study results showed a statistically significant difference between the exposed and the control groups as regard the blood styrene level, urinary mandelic acid level (β2) microgloblin in urine and chromosomal study. The study also showed a statistically significant correlation between the duration of styrene exposure and ventilatory function parameters, and also between the duration of styrene exposure and some detectable chromosomal aberrations.

The raw plastics are rarely used on their own and appropriate precautions should be taken regarding the additives used in the various formulations. In [12] also reported on phthalates. Phthalates or phthalate esters are esters of phthalic acid mainly used as in PVC. PVC is widely used in toys and other children's products such as chewy teethes, soft figures and inflatable toys. This material migrates into the air, food and people including babies in their mother's wombs. The release of phthalates during manufacture, use and disposal of PVC products, in addition to their use as additives in ink, perfumes etc has led to their permanent distribution and abundance in the global environment [13]. Other studies reported phthalates with a variety of bad outcomes such increased adiposity and insulin resistance [14], decreased anogenital distance in male infants [15], decreased levels of sex hormones [16] and other consequences for the human reproductive system in both females and males [17]. Infants and children are more exposed to phthalates where it increased dosage per unit body surface area, immature metabolic system capability and developing endocrine and reproductive system [18].

A study by [19] reported a significant risk of dermatitis from liquids and powders usually from "reactive chemicals" such as phenol formaldehyde, urethanes and unsaturated polyester resins used in the production of glass reinforced plastics (GRP) products. Suitable protective clothing should be worn during direct contact with the material. Fumes can also be generated from the thermal degradation of polymers during hot processing. Although engineering controls can minimize the problem, safety precautions must be taken to avoid inhalation of pyrolysis products under bad conditions. There are cases where operators have been overcome by hydrochloric acid gas and suffered from "polymer fume fever" such as overheating of PVC and polytetrafluoroethylene (PTFE) respectively.

IV. DISCUSSION AND CONCLUSION

There are many toxic gases are produced during the burning of a polymer. Combustion gases contain varieties of toxic gasses such as CO, hydrogen cyanide, nitrogen oxides, hydrogen chloride, sulphur oxides etc. It also produces oxidative pyrolysis products such as organo-aldehydes and particulates. The presence of fluorine, chlorine and bromine would be expected to generate hydrogen halides and halogenated organics. Hydrogen cyanide and other organic cyanides are released during thermal decomposition of polyurethane foams which used in the manufacture of furniture, and contribute to mortality in smoke inhalation. Prolonged or excessive exposure will lead to cyanide toxicity and metabolic acidosis. Based on this review, it is obvious that the burning of polyurethane will bring destructive effect to the environment especially to human. All the findings in this review show that there are so many toxic products produced during the pyrolysis of polymer, especially the polyurethane. Each and every product of the pyrolysis has certain effect on the human body. This study has also proven that the burning of the polymer, whether in the process of production or in its pyrolysis, can give out an unhealthy environment to the human body. This result should be taken in consideration by the employer during the planning for a safe environment to the workers in the process of producing polymer products. Some safety measures should be taken so that the workers will not expose to these toxic products. This problem should also be well taken care by the fire brigade to ensure that the best method of avoiding smoke poisoning among firefighters and fire victims during a fire.

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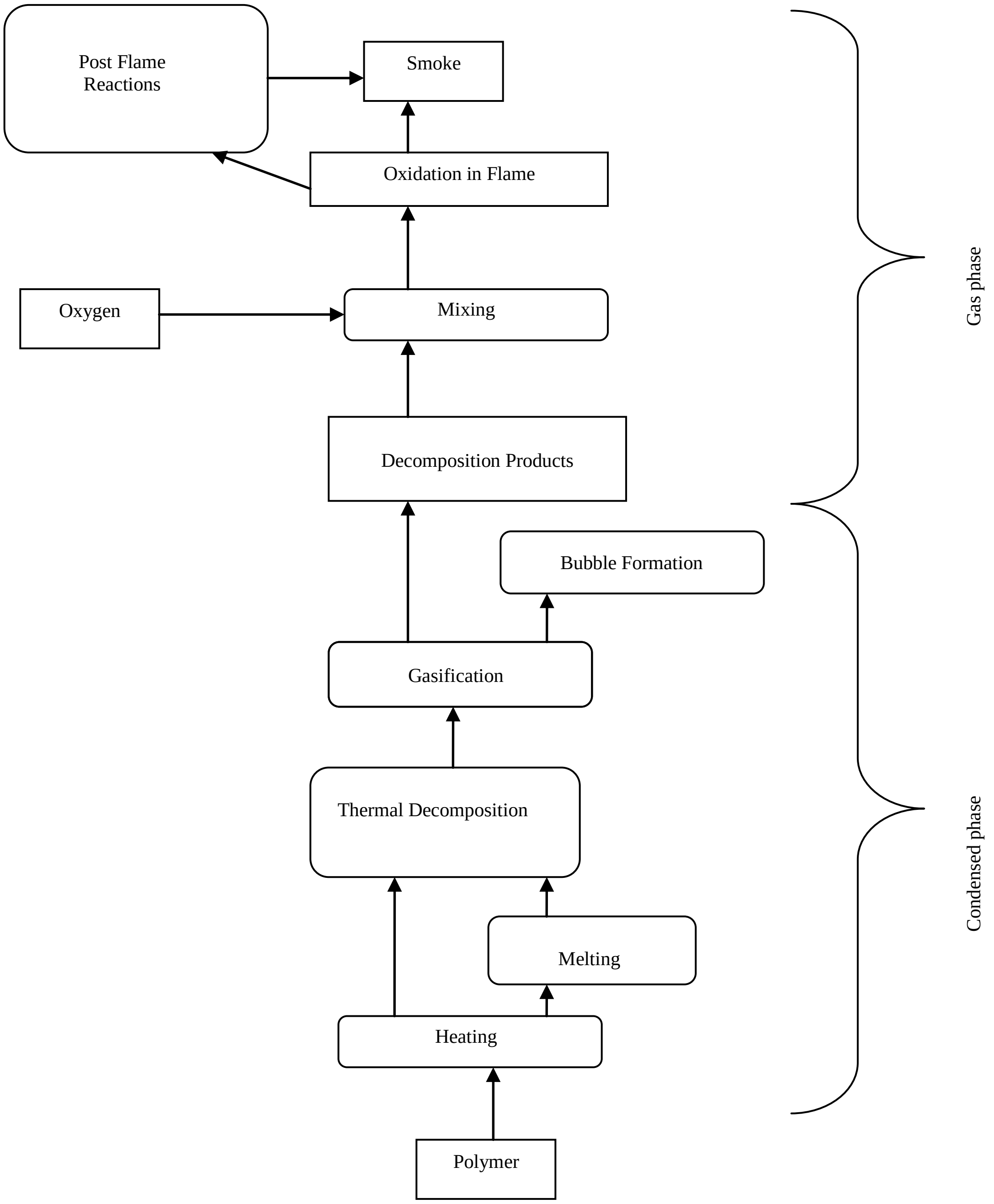

Figure 1. Schematic diagram of flaming combustion of a polymer [3].

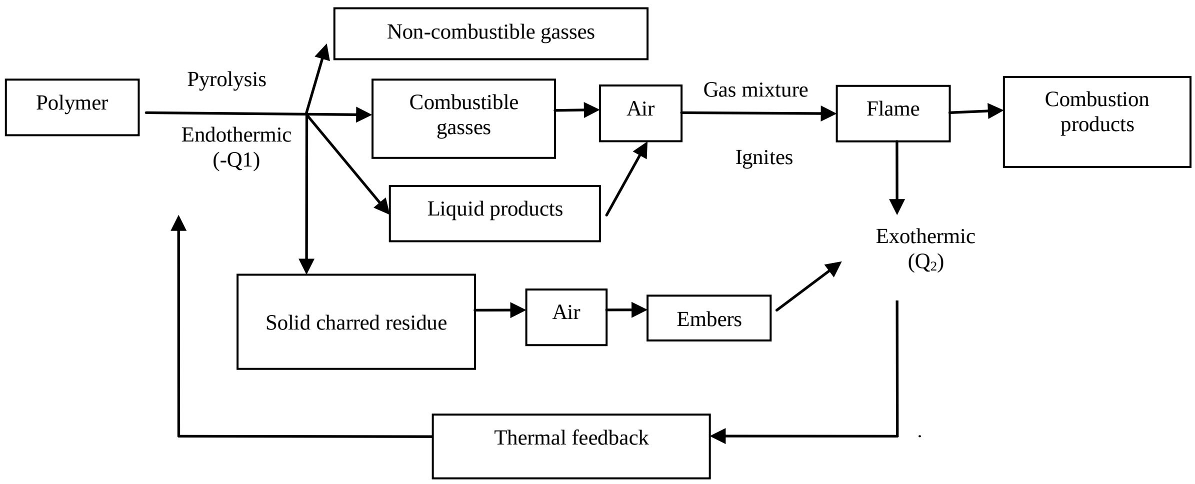

Figure 2. Schematic diagram of processes involved in polymer combustion [4].

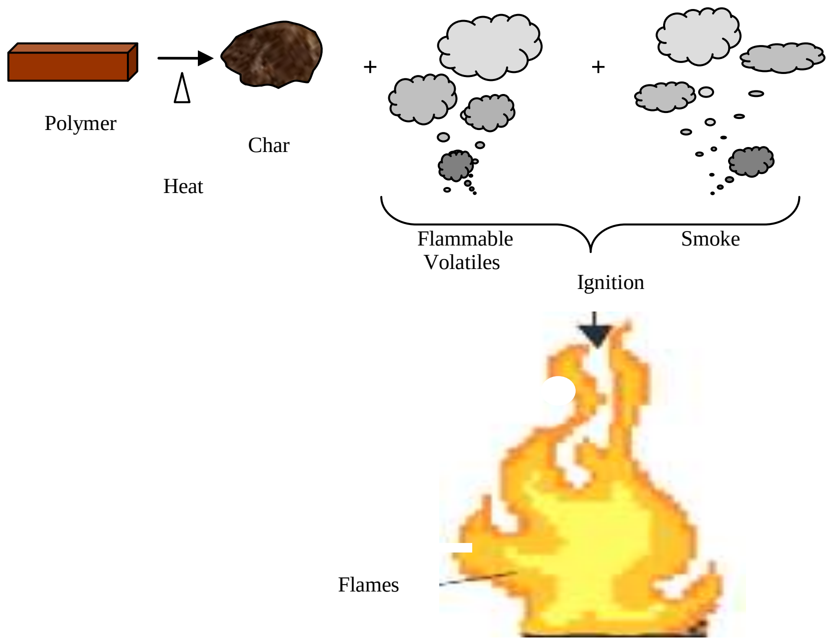

Figure 3. Polymer pyrolysis, burning and smoke evolution [4].