Promising utilization of fly ash as an eco-friendly sustainable additive for enhancement in flame retardancy of composite production: A review

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Abstract. Fly ash as one of the industrial by-product generated from the coal-based power station will eventually recognized as an environmental pollutant due to their enrichment in potentially toxic trace elements. Hundreds of thousand tons of fly ash every year exist alone were expected from the growth in power plants that use coal as the source of fuel. The present waste is widely been used in concrete industries to replace the usage of cement which is can minimize carbon dioxide footprint, but most will go straightly to the landfill or dump that will be one of the significant matter in environmental concerns and also will soon to be costly due to long term financial burden of maintenance. An economically viable solution to this problem has been proposed by utilization of fly ash as reinforcement in polymer matrix based composite production focusing on construction industry. Several studies proposed that fly ash has great potential as flame retardant in order to develop fire proof products even though not been much examined. This paper will emphasize on reviewing about properties of fly ash with its possible composition and characteristic that can help in fire controlling.

1. Introduction
Nowadays, one of the largest contributions in pollution emissions and global resource use have come from the construction and building industry [1]. Other than minimizing the supply of natural resources, it produces such a vast volume of waste and also contributes to the greenhouse gas effect that required a very proper management control to avoid the destruction for the environment. For this reason, the ‘three-R’ principle which is reduction, reuse and recycles has been introduced to the world as the pollution control problem as well as the resources management that can save and enhance the sustainability of the environment. Reduction concept is more than minimizing the waste production through planning and design, second is reuse which means that the same cycle can be done again by incorporation with the final product and finally the third one is recycling where the utilization of waste produced can be done by chemical and mechanical processing to make another useful product [2-4]. Based on this concept, the recycling of fly ash from coal combustion power plants into construction materials is one of the best idea that has been proposed by the present work.

Fly ash can be defined as the tiny particles that carried out with flue gases during the combustion process from coal-fired power plants. Other combustion products from power plants are bottom ash, boiler slag and Flue Gas Desulphurization (FGD) materials [5]. Other than significantly being used in cement and concrete manufacturing for the better quality products and also for minimizing carbon content production, fly ash also involve directly as a filler of fireproof products or flame retardant...
formulations in composite production of the construction industry. Thermal or fire insulation is one of the significant aspects in the construction industry. Fire can be concluded as a destructive burning related to the effect such as light, flame, heat, and smoke with the existence of the combustible product, an oxidant and also an ignition source [6]. Properties of material or structure that withstand or provide protection against fire or flame are been called as fire resistance which is very important in providing a fire-safe environment. Some commercial products used for fire partition in industrial installation and building sector have properties and chemical composition similar to fly ash [4, 7]. Besides, fly ash also function well as the main component with the residue of waste paper and other industrial waste to make plates which have higher fire insulating properties that can be used to produce fireproof doors, windows or for other fire-resistant products [8]. This fire insulation operated as a wall to prevent the unfavorable effects of fire on the safety of living things and property as well as financial losses can be avoided. Other than that, thermal insulation also can be the most effective way to overcome the global climate change and carbon emission since 30-40% from the building industry is responsible for the global greenhouse gas emissions [9].

The importance of utilization fly ash should not be denied as it can affect the material behavior of fire as well as can help in controlling the thermal activities. The structure and composition of this solid material have the potential in influencing the thermal transport and for this reason, this paper will present the possibility of managing waste like fly ash by utilizing it as a flame retardant in the construction industry.

2. Fly ash
Currently the amount of that solid residue or frequently known as coal combustion products (CCPs) has been increasing globally due to the growth of power plants that using fossil fuel like coal to produce energy and heat. For the last two decades, some big countries like India, China, and USA managed to increase the consumption as well as the demand for the fossil fuel until it can be considered as one of the major source of energy generation at the present time. Besides, the replacement of nuclear sources for energy generation also can be contemplated as one of the reasons why fossil fuel became popular in this time. This is due to the possibility of the nuclear accident such as Fukushima incident that happened in Japan a years ago which is can be one of biggest catastrophe in the world [8]. This trend of development literally has been affected the fly ash generation worldwide substantially and also for the future [10]. Usually, 1 megawatt of electricity as well as 7.65 tons of ash can be generated by the burning of 17 tons of coal. Approximate annual of fly ash production globally is in the range of 600-800 million tons [11].

| Country       | Fly ash production (million tons per year) |
|---------------|--------------------------------------------|
| India         | 112                                        |
| China         | 100                                        |
| USA           | 125                                        |
| Europe        | 100                                        |
| Germany       | 40                                         |
| UK            | 15                                         |
| Australia     | 10                                         |
| Canada        | 6                                          |
| Thailand      | 4                                          |

Gross amount of fly ash generation has been shown in table 1 [5, 8, 12]. It is anticipated that the fly ash production in India will exceed around 160 million tons by 2020 [13]. In Malaysia, around 2 million tons of fly ash were produced each year with seven coal-fired power plants [14]. The most well-known application of fly ash that has been thriving for many years globally is in building industry as construction materials. Been shown in figure 1 the involvement of fly ash in the concrete
production cannot be denied as it has become predominant compared to other applications such as in agriculture industry, mining activities, soil stabilizer and many more. This is due to the pozzolanic characteristics own by fly ash because of its fineness and plasticity that may increase the durability as well as the strength of the material [15-17].

3. Effect of fly ash on fire retardancy of composite in construction industry
Other than significantly being used in cement and concrete manufacturing for the better quality products, fly ash also involve directly as a filler of fireproof products or flame retardant formulations in the construction industry. This is due to some characteristics or compositions of fly ash.

3.1. Small particle size (physical)
Basically, the products which manufactured with fly ash tend to have high-temperature performance thanks to the fly ash with the very fine glasslike particles either rounded or spherical made it as powdery material, added with some chemical composition and mineralogy [19, 20].
Figure 2 illustrates the morphology of fly ash observed by SEM imaging. The microstructure is more hollow, spherical particle or calling as cenosphere which is stuffed with smaller amorphous particle and planisphere (crystal). The phrase of cenosphere come from Greek which is kenos means hollow and sphaira is sphere. This combination essentially created by Sinnatt’s research team while investigating pyrolysis activity related to hollow char particles formation [20, 22]. Typically, they are grey in color or can be more to the black. Combustion technology applied with the unburned carbon content inside the coal can affect the color of fly ash [8, 23]. Generally, with the spherical in shape, their size is around the range of 0.5 µm to 300 µm [24]. Other common properties are bulk density which is low (1.01-1.43 gcm$^{-3}$) and specific gravity (1.6-3.1 gcm$^{-3}$). The moisture retention range from 6.1% at 15 bar to 13.4% at 1/3 bar while mean particles densities for a non-magnetic and magnetic particle are 2.7 and 3.4 gcm$^{-3}$, respectively [25]. Low bulk density makes it lightweight, less water absorption, high workability, excellent mechanical strength and also good thermal resistance with low cost since it is kind of waste; these remarkable properties are enough to make the fly ash so popular in various industrial applications like construction and manufacturing lightweight composites [20, 22, 26, 27].

Fly ash has cenosphere or very fine particles as the high surface area will possess cause wide evaporation plateau that will increase the fire resistance as well as thermal and insulating properties [7, 28]. Based on a few researchers previously, the main reason for the excellence of thermal resistance is because there is a diminution of density. When the temperature is rising or the material is exposed to the fire basically more than 100 °C, there will be water evaporation that will produce wide evaporation plateau. This will cause the reduction in density due to the increase in porosity that will bring to better fire resistance and insulating behaviour [7, 29, 30]. Meanwhile, thermal conductivity increase with the ordering of molecules, so based on this reason amorphous and vitreous solid show lower thermal conductivity compared to crystalline materials. Material that reduces heat transfer through the structure against or within which it is installed is called a thermal insulation material. Thermal insulation materials preferably should have a microporous structure in which the size of the pores is of the same size or smaller than, the mean free path of the gas molecules occupying the pores, so that the gas movement is obstructed and the thermal conductivity decrease.

It was found that some of commercial raw materials used for fireproof product in building and construction works which has high insulating and low thermal conductivity have properties like fly ash that exhibit low density as much as one-third less than making them more better in term of thermal behavior compare to conventional mortars [7, 31]. This assertion can be a similar allegation by Celia and her friends where their research related to the preparation of blocks made completely from the combination of Portland cement with fly and bottom ashes [4]. The incorporation of fly ash cenospheres is not restricted to Portland cement only, it also can be lengthened to cementitious materials like geopolymer and magnesium oxychloride cement which is suitable for fire resistant construction applications since by combining with the cenospheres, the density as well as thermal conductivity will diminish eventually [32, 33].

3.2. Silica content (chemical)

Fly ash mainly consists of silica [7]. As an alternative to the use of halogenated flame retardants, which control flammability by modifying the gas-phase chemistry in the flame, the family of silicon compounds such as silanes, silsesquioxane, silica and silicate has been explored as potential flame retardants to polymeric materials. Silica for instance, has been acting as a protective role when loaded one of its forms of silica nanoparticles or layered silicates in addition of silica affect the thermal stability of thermoplastic polymers. During combustion, it created an inorganic barrier on the surface that reduces heat transfer and also protects the underlying polymer from oxygen [34, 35]. It is well known that phosphorus-based flame retardant can act in both condensed and gas phase; actually it is effective in the condensed phase only in polymers, which contain oxygen and nitrogen and are self-charring. Fumed silica acts in condensed phase and reduces heat release rate and mass loss rate thus improving flammability properties.
Table 2. Chemical composition typical of fly ash.

| Chemical component       | Class C (wt%) | Class F (wt%) |
|--------------------------|--------------|--------------|
| Silica oxide ($\text{SiO}_2$) | 40           | 55           |
| Aluminium oxide ($\text{Al}_2\text{O}_3$) | 16           | 26           |
| Ferric Oxide ($\text{Fe}_2\text{O}_3$) | 6            | 7            |
| Calcium Oxide ($\text{CaO}$) | 24           | 9            |
| Magnesium Oxide ($\text{MgO}$) | 2            | 2            |
| Sulfate Oxide ($\text{SO}_3$) | 3            | 1            |
| Loss of Ignition (LOI)   | 6            | 6            |

Basically, coal fly ash consists of Silicon (Si), Alumina (Al), Iron (Fe), Calcium (Ca), Magnesium (Mg), Sodium (Na) and Potassium (K), and Sulphur (S) with some of them such as Si, Al, and Fe have been classified as major matrix element [37]. There is two types of fly ash based on silica, alumina and iron oxide content according to American Society for Testing and Materials (ASTM). They are categorized as Class F and Class C as their chemical composition has been shown in table 2 generally. Class F defined as low in lime while Class C with the high in lime [36, 38].

The flammability characterization and synergistic flame retardant mechanism of fumed silica in the ethylene-vinyl acetate/magnesium hydroxide (EVA/MH) blends were studied by Mouzheng [39]. The results showed that the addition of a given amount of fumed silica apparently increased the LOI value and decreased loading of MH in EVA blends while keeping the V-0 rating in the UL-94 test. The data obtained from the DSC analysis indicated that the addition of fumed silica not only greatly reduced the heat release and mass-loss rates, but also depressed the smoke released during the combustion of EVA/MH blends. The morphological and TGA data showed further evidence that this synergistic flame retardant mechanism of fumed silica in the EVA/MH materials is mainly due to the physical process of fumed silica acting as enhanced char/silica layers in the condensed phase which prevents the heat and mass transfer in the fire.

In addition, the thermal decomposition products of the polycarbonate with added fly ash has been quantitatively analyzed and the result shows the reduction in total quantity of thermal decomposition gas about 60%. This is because of the existence of silica in fly ash that diminished the generation of phenols and bisphenol A in the middle-molecular-weight portion in the thermal decomposition of the polycarbonate. Decomposition mechanism of the polycarbonate has changed by the presence of silica and at the same time, the decomposition products are established as a char through the dehydration condensation reaction instead of undergoing the gasification process, signifying that the polycarbonate has become more flame retardant [40]. Besides, the higher content of acidity in silica-alumina also help in promote charring since it can increase its effectiveness as a solid acid catalyst thus will enhance the flame retardancy.

4. Conclusion
In this review, can be concluded that the composition and characteristic of fly ash have potential to act as a flame retardant in composite production to overcome one of the major weakness in the construction industry which is the vulnerability to fire even though there is only a little research has been done to identify the related performance. The fact that fly ash is a kind of waste that must be taken seriously in the future literally will offer a range of sustainability benefits that meet current industry trends in the utilization of waste materials due to environmental awareness.

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