Effect of biomass ratio on co-firing of biomass with coal on pozzolanic properties

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Abstract. Recently, fly ash from the coal combustion process in power generation has been used in the cement industry as an additive to cement or as partial replacing binder in cement-based structural mortars. The use of fly ash can reduce costs in cement production, including a reduction in the environmental impact. Co-firing biomass with coal is one of the existing technologies for utilizing biomass energy in the power generation system. However, this technology also influences the quantity and quality of the ash produced. The present work, therefore, aims to investigate the pozzolanic properties of ashes obtained from the co-firing of coal with corncob. Pozzolanic and physical properties of such ashes were investigated by varying the percentages of corncob at 20, 30 and 40 during combustion. The Pozzolanic compounds (SiO₂+ Al₂O₃+ Fe₂O₃) according to ASTM C618 were determined by using X-ray fluorescence spectroscopy (XRF). Scanning electron microscopy (SEM) was used to investigate the structure of ash samples. The results show that content of pozzolanic compounds in ashes produced from cofiring corncob with coal decreased when increasing ratio of corncob and became stable when ratio of corncob was higher than 30%. It is observed that the morphology of such ashes illustrated in the form of small spherically shaped particles which can improve rheological behavior, viscosity and flow performance. Considering the requirements for pozzolanic-cementitious material, it is found that the ashes produced in this study has lower content of pozzoolanic compounds than the standard specification for pozzolan class C.

Keywords: Coal–biomass fly ash, Corncob, Cement substitute, Pozzolan, Pozzolanic activity

1. Introduction
Coal is one of the most important energy sources for electricity production because coal has many advantages such as abundant reserve, low-cost, and guarantees inexpensive electricity prices. Despite these benefits, coal is mostly carbon, which, when burned it releases a considerable amount of carbon dioxide, airborne toxins, and pollutants. A large amount of carbon dioxide emissions comes from the power generation process and cement industry. The combustion of coal for power generation is responsible for about 40% of the world’s carbon dioxide emissions [1]. In the cement industry, nearly 1.46 gigatonnes of carbon dioxide were released to the atmosphere in 2016 for cement production [2]. To the reduction of carbon dioxide emissions, usage of biomass is an attractive technology in the areas of renewable energy utilization for power production. Biomass fuels are considered environmentally
friendly, these are no net increase in carbon cycle for combustion of biomass if it is replanted. Biomass consumes the same amount of carbon dioxide from the atmosphere during plant growth stage as is released during combustion stage.

Ash from coal combustion process is one of significant by-products in power generation. It has been used in the cement industry as an additive to cement or as partial replacing binder in cement-based structural mortars. The use of ash has a number of advantages such as a lower water demand, improving the long-term strength development and can reduce costs in cement production, including a reduction in the environmental impact. The impact of co-firing of biomass with coal on ash formation is an important consideration. Many researchers investigated the use of agricultural waste ashes as constituents in cement, including sugar cane bagasse ash, rice husk ash, elephant grass, and corn cob ash. Those ashes, containing a large amount of silica in amorphous form, have potential for use as pozzolanic materials replacing cement in concretes, mortars, and pastes. Martirena et al. [3], used ash from sugar cane straw as pozzolanic materials in lime-pozzolan binders. They found that the sugar cane straw ash could be classified as a good pozzolanic material. Singh et al. [4] showed that the presence of 10% sugar cane bagasse ash by weight of cement in concrete provided a higher compressive strength than the control concrete at all ages. Guilherme et al. [5] studied the pozzolanic activity of elephant grass ash. They found that elephant grass ash is an effective pozzolanic material and replacing 20% by weight of cement with elephant grass ash no changes in compressive strength comparable to the reference concrete. While some studies investigated the characteristic of corn cob ash as a Pozzolanic material includes, the effect of corn cob ash content as a partial replacement for cement. Antonio et al. [6] studied an appropriate percentage replacement of corn cob ash that would comply with specific standards of cement production. They found that up to 10% of corn cob ash replacement could be used in cement production without compromising the structural integrity of cement. Moreover, the compressive strength of the resulting concrete could be improved when corn cob ash is added to the mixtures. Raheem et al. [7] found that the thermal conductivity of corn cob ash-blended cement specimens decreased steadily as the corn cob ash percentage replacement increases. Suwanmaneechot et al. [8] studied the development of corn cob ash as supplementary cement replacement materials. They showed that the sum of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ in the chemical composition of corn cob ash satisfies the requirements of ASTM C618. There previous studies have consistently demonstrated the potential of using ash from biomass combustion as a constituent in cement. However, these studies did not mainly investigate co-combustion of biomass with coal. It is not clear whether there is an impact of co-combustion process on ash formation.

The present work, therefore, aims to investigate the pozzolanic properties of ashes obtained from the co-firing of coal with a corn cob. The evaluation of pozzolanic activity is essential to predict the behavior of the partial replacing binder with the used of co-firing fly ash in cement-based structural material. Pozzolanic and physical properties of such ashes were investigated by varying the percentages of corn cob at 20, 30 and 40 during combustion. The Pozzolanic compounds (SiO$_2$+ Al$_2$O$_3$+ Fe$_2$O$_3$) according to ASTM C618 were determined by using X-ray fluorescence spectroscopy (XRF). Scanning electron microscopy (SEM) was used to investigate the structure of ash samples. Results from this work could be used to assess the potential of ash forming by co-combustion of biomass and coal combustion as a raw material for cement.

2. Methodology

Corn cob used in this work was received from a local produce market in Bangkok and coal was obtained from Siam quality work Co., Ltd., the supplier of renewable fuels in Bangkok, Thailand. Coal and corn cob were air-dried in sunlight to reduce its moisture content and subsequently, were pulverized using a ball-milling machine to reduce particle size and then were sieved to remove particles larger than 1 mm. The proximate analyses of the coal and corn cob were evaluated by a thermogravimetric analyser and results were listed in Table 1. The sample was placed into a platinum crucible with a heating rate of 10 °C/min.
The co-combustion of coal and corncob were investigated using a carbolite furnace. The coal and corncob blends were shaken thoroughly with the amount of corncob in the mixture varied at 0, 20, 30, and 40% by mass respectively. Then, each of the four mixture were burnt in a muffle carbolite furnace using a heating rate of 20 °C/min from room temperature to 700 °C for about 4 hours.

Table 1. Proximate analysis of coal and corncob (dry basis)

| Samples     | Proximate analysis (wt. %) |
|-------------|----------------------------|
|             | Moisture          | Volatile matter | Ash   | Fixed Carbon |
| Coal        | 12.21            | 42.39           | 3.23  | 42.18        |
| Corncob     | 6.96             | 73.64           | 0.98  | 18.42        |

The chemical compositions of ash samples were analyzed using X-ray fluorescence (XRF) analyzer. The pozzolanic activity of the ashes was determined using the procedure described in the ASTM C618 standard [9] and the microstructure of ashes was studied using a scanning electron microscope (SEM).

3. Results and discussion

3.1. Chemical properties of ash

Results from TGA in Table 1 demonstrates that the ash content in corncob is significantly lower than that in coal. The same tendency can be observed in the quality of ash after calcination shown in Table 2. The low ash content in corncob leads to the observed decrease in wt% of ashes after calcination. However, the resulting ash formation does not follow a simple mixing rule. The co-combustion of biomass and coal is considered to be one of contributing factors resulting in this non-linear trend.

Pozzolanic compounds were characterized by summing the composition of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ as shown on the last line in Table 3. Coal ash has the content of pozzolanic compounds of 33.33%. The co-combustion of coal and corncob gives rise to a change in the proportion of pozzolanic compounds in the ashes. All samples have such compositions lower than chemical requirement of the standard specification for pozzolan class C according to ASTM C618, in order to present pozzolanic activity (summary of SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ higher than 50%) The percentage by weight of pozzolanic compounds in Table 3 was plotted as a function of the ratio of corncob in the coal-corncob mixture in Figure 1. The variation in the reported chemical compositions could be attributed to coal sample has low SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ content. The CaO and SO$_3$ content of ashes decrease when the ratio of corncob increased which high free CaO and sulfur content may affect volume stability and concrete durability [10].

Table 2. The quantity of ashes after calcination.

| Samples                  | wt.% of ashes after calcination |
|--------------------------|---------------------------------|
| 100% Coal                | 4.48                            |
| 80% Coal with 20% Corncob| 4.08                            |
| 70% Coal with 30% Corncob| 3.35                            |
| 60% Coal with 40% Corncob| 2.65                            |
Figure 1. Percentage by weight of pozzolanic compounds (SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$) with ratio of corncob.

Table 3. Chemical composition of coal ash and co-firing of coal/corncob blends ash

| Chemical composition (%) | Sample       | 100% Coal | 80% Coal | 70% Coal | 60% Coal |
|--------------------------|--------------|-----------|----------|----------|----------|
| Silicon dioxide (SiO$_2$) | 14.70        | 10.80     | 11.80    | 9.98     |
| Aluminum oxide (Al$_2$O$_3$) | 5.83      | 5.32      | 4.96     | 5.04     |
| Iron oxide (Fe$_2$O$_3$)   | 12.80        | 13.00     | 10.80    | 12.50    |
| Calcium oxide (CaO)        | 27.00        | 27.50     | 25.20    | 26.80    |
| Magnesium oxide (MgO)      | 4.95         | 5.46      | 5.07     | 5.50     |
| Potassium oxide (K$_2$O)   | 1.04         | 3.73      | 5.11     | 6.51     |
| Sodium oxide (Na$_2$O)      | 0.836        | 0.729     | 0.93     | 1.22     |
| Sulfur trioxide (SO$_3$)   | 10.90        | 10.90     | 10.30    | 10.40    |
| Phosphorus pentoxide (P$_2$O$_5$) | 0.07 | 0.46 | 0.76 | 1.00     |
| Manganese(II) oxide (MnO)  | 0.49         | 0.53      | 0.46     | 0.49     |
| Titanium dioxide (TiO$_2$)  | 0.43         | 0.37      | 0.36     | 0.33     |
| Barium oxide (BaO)         | 0.25         | 0.26      | 0.22     | 0.22     |
| Strontium oxide (SrO)      | 0.13         | 0.12      | 0.01     | 0.12     |
| Chloride (Cl)              | 0.046        | 0.048     | 0.054    | 0.05     |
| Nickel(II) oxide (NiO)     | 0.02         | 0.02      | 0.02     | 0.018    |
| Chromium(III) oxide (Cr$_2$O$_3$) | 0.02 | 0.02 | 0.02 | 0.02     |
| Copper(II) oxide (CuO)     | 0.01         | 0.02      | 0.02     | 0.02     |
| Zinc oxide (ZnO)           | 0.01         | 0.02      | 0.02     | 0.03     |
| SiO$_2$+Fe$_2$O$_3$+Al$_2$O$_3$ | 33.33 | 29.12 | 27.56    | 27.52    |
3.2. Scanning electron microscopy (SEM)
The morphology of the material particles was determined using scanning electron microscopy (SEM) analysis. The particle shape can predict the rheological behavior, viscosity and flow performance [11]. Figure 2 shows scanning electron micrographs (SEM) of coal and coal/corncob ashes obtained by co-firing, it can be observed that ashes are composed of the particle with different shapes and sizes. In figure 2a, the shape of coal ash is similar to a sponge (particles had rough surfaces with high porosity) and large surface area, which seems to be mainly composed of CaO and MgO. This is consistent with the results reported by Telma et al [12]. The “sponge” shape indicates that an additional water was absorbed during the particle size reduction process and this can have a detrimental effect on flow and viscosity [13]. The particle shapes of coal/corncob blend ashes shown in figure 2b, 2c and 2d were relatively smaller particles and contains more spherical particles with rough and porous surfaces. The spherical shape is expected to provide the good rheological behavior.

4. Conclusions
This study aimed to determine the pozzolanic activity of co-firing corncob with coal ashes. Based on the results, the followed conclusions can be drawn:

(1) X-ray fluorescence analysis shows that co-firing corncob with coal ashes decreases the pozzolanic activity of ashes and stable when the ratio of corncob more than 30%
(2) CaO and SO$_3$ content of ashes decreases when the ratio of corncob increased which this feature can improve pozzolanic activity according to ASTM C618
(3) The morphology of co-firing corncob with coal ashes could be seen, small and forming spherically shaped particles more than coal ashes improve rheological behavior, viscosity, and flow performance.

(4) In terms of physical and chemical characteristics, the ashes produced from co-firing corncob with coal in this study cannot be considered a pozzolanic-cementitious material according to requirements in ASTM C618 because coal sample has low SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ content.

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