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STUDY OF PATICLE SIZE, DENSITY AND CRYSTALLINITY OF COAL FLY ASH PARTICLES FOR USE AS FILLERS IN PAPER AND PAPERBOARDS

Abstract

Industrial solid waste handling and its processing for reuse in industry is very important for sustainable industrial growth and conservation of natural resources and environment. Pulverized coal fly ash obtained from the burning of pulverized coal in thermal power plants is one of the most prominent solid wastes in most of the countries at global scale. The fly ash can be beneficiated by different mechanical and chemical processes to give suitable properties as fillers. In this direction, a novel experimental study has been done for use of pulverized coal fly ash as filler in colored laminate base paper. The particles of fly ash are higher in size in comparison to conventional fillers. So grinding is one of the best options to improve its property as filler material. The ball mill grinding has been studied for reduction of particle size and improvement of surface area. The mechanical strength properties, optical properties like brightness, opacity and surface properties of paper hand-sheets were studied. Chemical compound analysis of fly ash sample using X-ray fluorescence (XRF) has shown its potential for use as wet end filler in laminate base paper. Carbon percentage in fly ash using CHN analyzer and Loss on Ignition (LOI) method has been carried out to see the effect of grinding on carbon percentage as the brightness of fly ash decreases with increase of carbon percentages and deteriorates its quality as filler. The increases of grinding causes lowering of carbon due to oxidation and results in increase of brightness. Laser particle size analysis for particle size distribution and density distribution of fly ash along with X-ray diffraction (XRD) analysis of fly ash for crystalline structure before and after grinding are done. Comparison of properties of paper samples prepared using unbleached pulp and bleached pulp with fly ash filler loading have been studied. The opacity of fly ash loaded paper was better than conventional fillers. Strength properties were also comparable. Utilization of coal fly ash will result in sustainable industrial development and environment friendly handling of waste materials.

Keywords : Pulverized coal fly ash, Fillers, Pulp, Specialty Paper, Opacity, and Grinding.

Introduction

The sustainability concepts of industrial ecology advocate that the by-product generated in a particular industrial process should be assimilated by other industrial activities to conserve and optimize natural resource consumption. A large amount of fly ash is dumped in the near-by landfills or impounds of power plants where it mixes in air, water and soil. This causes a lot of pollution to the environment due to its fineness. Current annual production of fly ash from coal based power plants is 112 million tons in India. The principle components of fly ash are silica, alumina, ferrous oxide, and calcium oxide with varying amounts of carbon as measured by a LOI test [Nugteren, 2007]. The American Society for Testing and Materials (ASTMs) group coal fly ash (CFA) into two classes: C and F. The class F CFA has a combined SiO_2, Al_2O_3, and Fe_2O_3 content of greater than 70% compared to greater than 50% for Class C coal fly ash. Density classification of an ash is a useful technique in optical characterization because the optical properties (more specifically, the complex refractive index) of a fly ash particle depend on its composition, and since density and composition are correlated, this technique helps in detecting the distribution of infrared-active oxides. The scattering and absorption characteristics of a fly ash particle also depend on its geometry [Stanislav et al., 2004; Ghosal and Sidney, 1995]. The grinding of fly ash will result in the size reduction and uniformity of different particles. A sustainable industrial growth depends on effective and environment friendly use of natural resources and industrial waste materials. The beneficiation of fly ash can be done by using magnetic separation as the magnetic fraction will constitute of iron oxide and other magnetic constituents to higher extent. The non magnetic fraction will retain lower amount of iron oxide (70-75% reduction). Rice straw, a solid agro waste material has been used as fiber source. Acetic acid based chemical pulping process converts the agro waste in to a resource for natural fibers. Wheat straw and rice straw are the new promising natural fiber sources available in abundant quantities throughout the world (Sinha *et al.* 2012, Sinha 2012). Preliminary study of coal fly ash as filler without grinding has been done resulting in high opacity but lower brightness with comparable strength properties. But the effect of particle size reduction by grinding and its effect on paper properties has not been studied till now (Sinha *et al.* 2010). *The ground fly ash* can prove to be a very good filler for specialty grade papers like laminate base where very high opacity is sought but whiteness is not important. It will provide the environment friendly use of fly ash and reduction of cost of paper.

CFA processing provides the perfect opportunity to increase the awareness of the potential for industrial synergy because of the vast number of potential applications that the CFA or the CFA derived products can be used in. CFA has variety of the components; CFAs are one of the most complex anthropogenic materials that can be characterized. A large number of minerals have been identified in different CFAs [Blissett and Rowson, 2012]. A more up to date estimate would mean that 750 million tonnes of CFA is generated on a global basis each year. Current CFA utilization figures are 39% in the US and 47% in Europe [Vassilev and Vassileva, 2005]. Several reviews of the utilization of CFA have been conducted, but the overviews of multi-component utilization of CFA are only 5 and 10 years old. These overviews address a wide range of sustainability issues within both the fuel and minerals sector [Lior, 2010; Iyer and Scott, 2001].

Materials and Methods

The sample of fly ash was processed in ball mill for 1hr for grinding. The ground fly ash was sieved for 30 minutes in a sieve shaker using sieves no. 36, 60, 85, 150, 300, and 400 (B S 410 1986). The finest fraction, passing through 400 mesh no. (Screen opening size of 38 micrometer) and having average particle size of nineteen micrometer was used as filler in paper making. The sieve analysis of particle size of the fly ash sample was carried out. The compound analysis of original and ground fly ash samples were carried out using X-ray fluorescence spectrometer from IIT Mumbai. CHN analysis for verification of carbon percentage in fly ash was carried out to compare it with the results obtained by LOI method. XRD analysis was done from sophisticated analytical instrument facility, Punjab University, Chandigarh. XPERT-PRO diffractometer system was used with reflection spinner stage maintaining start and end angle position of 5.0084 and 79.9614.

Results and Discussion

Chemical analysis of fly ash is shown in table 1. Silica and alumina are the main constituents. The first four components silica, alumina, iron oxide and titanium oxide comprise nearly 96 percent which are common fillers for specialty grade papers and paper boards.

Table 1: Chemical composition of coal fly ash and rice straw ash (using X-ray Fluorescence Spectrometry Test)

Compounds	Mass Percentage in original Fly ash	Mass Percentage in ground Fly ash	Mass Percentage in rice straw ash
SiO_2	62.33	62.09	90.30
Al_2O_3	26.49	24.72	5.41
Fe_2O_3	5.49	8.53	0.32
TiO_2	1.51	1.32	0.24
K_2O	1.94	1.68	0.13
Na_2O	0.15	0.1	1.97
MgO	0.658	0.76	0.48
CaO	0.448	0.67	0.65
MnO	0.05	0.07	0.02

The important physical properties of fly ash (which are relevant for filler) are shown in Table 2. The grinding of CFA increased the percentage of particles in smaller range. **A grinding time of one hrs results in bringing 90 % of particles in the range below 38 µm.** The major fraction is initially spherical and smooth. By primary crushing, particles break up into pieces. The edges and rough parts of the old and new surfaces will be worn by ongoing grinding.

Table 2: Properties of fly ash used in paper making

Properties	Fly ash
Mean particle size, µm	30
Bulk density, Kg/m^3	897
Brightness, % ISO	28.5
pH	8.5
Specific surface area, M^2/g	1.45
Refractive index	1.7
Color	Grey brown

Residual Carbon analysis and Loss on ignition of fly ash

Residual carbon percentage in fly ash used as wet end filler was measured by CHN analyzer. The grinding improves the brightness of fly ash as very fine carbon particles undergo oxidation and reduces in mass percentage from 6.35 % in original CFA to 4.67% in ground fly ash . Carbon particles are the main reason for dark color of fly ash. LOI is measured according to ASTM standard C 311. LOI value of ground fly ash and original fly ash are 5.10 % and 6.50 %.

Fractionation of fly ash sample using sieve analysis before and after grinding process for different time interval are shown in Table 3 and Table 4.

Table 3: Fractionation of fly ash sample based on particle size before grinding

Fraction	Mesh size (B. S.)	Screen Opening size (10^{-6} m)	Mass Retained (%) of fly ash (without grinding)	Average Particle size (10^{-6} m)
A (retained by sieve no. 36)	36	425	0.071	425
B (retained by sieve no. 60 and passes through sieve no. 36)	60	250	0.37	337.5
C (retained by sieve no. 85 and passes through sieve no. 60)	85	180	0.025	215
D (retained by sieve no. 150 and passes through sieve no. 85)	150	106	11.40	143
E (retained by sieve no. 300 and passes through sieve no. 150)	300	53	55.56	79.5
F (retained by sieve no. 400 and passes through sieve no. 300)	400	38	14.18	45.5
G (retained by pan)	Pan	0	15.89	19

Table 4: Fractionation of fly ash sample based on particle size after grinding (10-60 minutes)

Fraction	Mesh size (B.S.)	Screen Opening Size (10^{-6} m)	Mass Retained (%) of fly ash after 10 minutes grinding	Mass Retained (%) of fly ash after 20 minutes grinding	Mass Retained (%) of fly ash after 30 minutes grinding	Mass Retained (%) of fly ash after 40 minutes grinding	Mass Retained (%)of fly ash after 60 minutes grinding	Average Particle size (10^{-6} m)
A	36	425	0.00	0.00	0.00	0.00	0.00	425
B	60	250	0.00	0.00	0.00	0.00	0.00	337.5
C	85	180	0.00	0.00	0.00	0.00	0.00	215
D	150	106	5.76	0.00	0.00	0.00	0.00	143
E	300	53	32.10	17.47	11.1	8.2	8.0	79.5
F	400	38	37.00	21.50	14.65	10.9	10.8	45.5
G	Pan	0	25.14	61.03	74.25	80.9	91.2	19

The fractions obtained by sieve analysis was further analyzed by laser particle size analyzer to find the comparison of density distribution based on particle size of original fly ash (denoted by FA), ground fly ash passing through 38 micron size sieve (denoted by FA (ground)), after burning for one hour time at 900 °C (denoted by FA-ORG-B), ground fly ash passing through 53 micron size sieve (denoted by FA-G53) and ground fly ash passing through 53 micron size sieve and burned for one hour time at 900 °C (denoted by FA-G53-B).

This was analyzed from graph in Fig.1 that grinding provides sharp increase in the particle density especially for medium size particles (from 8 micron to 64 micron). Density of particles increased to nearly double its original value after grinding. This is due to hollow particles in fly ash initially which become dense after breakage of hollow particles in this size range. The most of the particles are below 64 micron size.

The burning of different fly ash samples does not show any significant change in density distribution. The higher size particles have very low density showing presence of lighter and hollow particles like carbon.

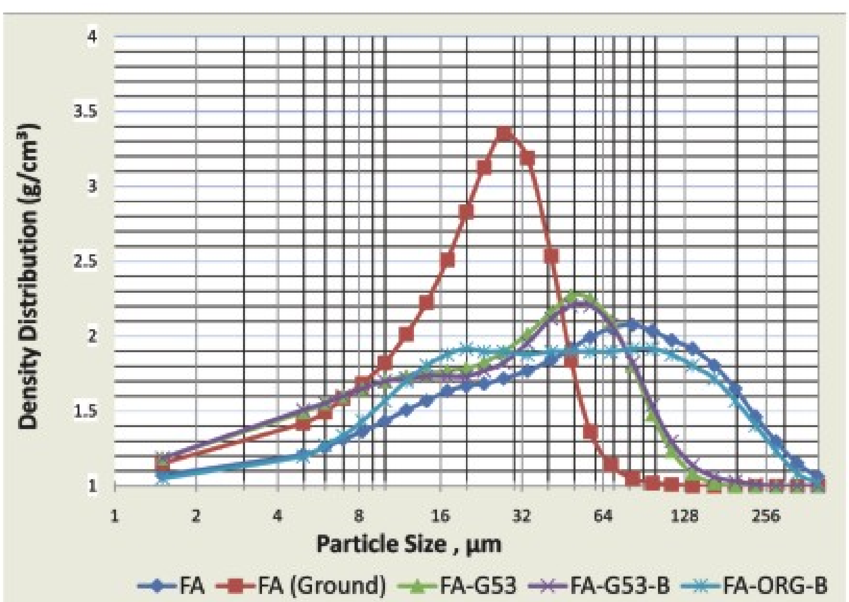

Fig. 1: Comparison of density distribution of original fly ash, ground fly ash and other fractions retained on Screen

The fractions obtained by sieve analysis was again analyzed by laser particle size analyzer to find the Cumulative mass distribution based on particle size of original fly ash, ground fly ash passing through 38 micron size sieve and ground fly ash passing through 53 micron size sieve.

This comparison is given in graph in Fig.2, which shows that original fly ash has particles size from 4 micron to 256 microns where as particles retained on 53 micron sieve has variation from 4 microns to nearly 100 microns. But after grinding all the particles are below 64 microns. The variations of size in different sieve fractions are mainly because of irregular shapes of particles.

Physical and chemical characteristics of mechanically treated fly ashes have been investigated by other scientists. The grinding of fly ash using laboratory mill for 10 to 60 minutes time have been studied. This is reported as increase of fineness of the samples with grinding time but loss of effectiveness occurred for grinding time longer than 20 minutes. The ground samples showed higher specific gravity (increases from 2.44 to 2.69 g/cm^3) probably due to presence of hollow particles like cenospheres in the original fly ash. The mean diameter decreases from 32.19 to 5.93 micro in 60 minutes. The specific surface area increases from 3980 to 8930 cm^2/ g. In few minutes, the majority of particles with diameter greater than 50 micro meters have been crushed. Only a little change in mineralogical composition of fly ash was reported during grinding process. This little change was due to formation of calcium carbonate resulting by reaction of calcium oxide with carbon dioxide (Paya *et al.* 1995).

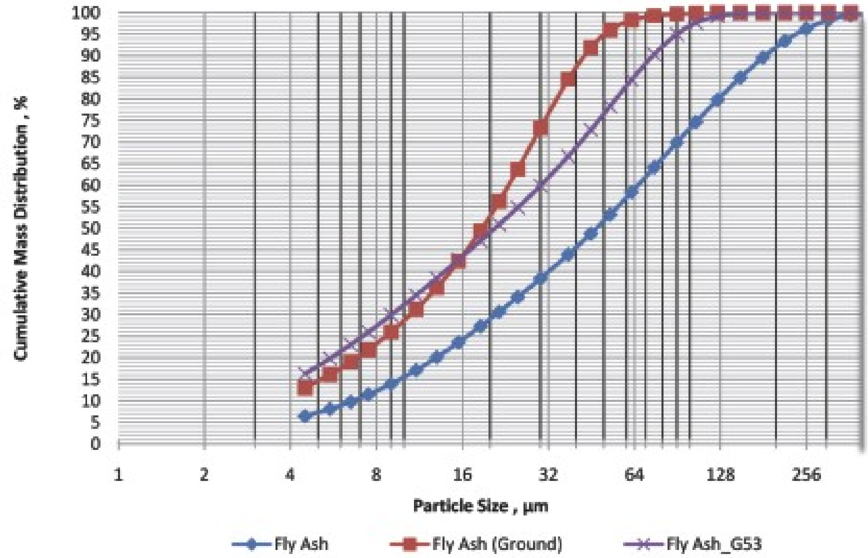

Fig. 2: Comparison of cumulative mass distribution of fly ash, ground fly ash and fly ash retained on 53 micron screen

The fig. 3 shows the effect of grinding (as shown in FA-G) in upper graph. The size of crystallite decreases as compared with original fly ash samples (FA-O).

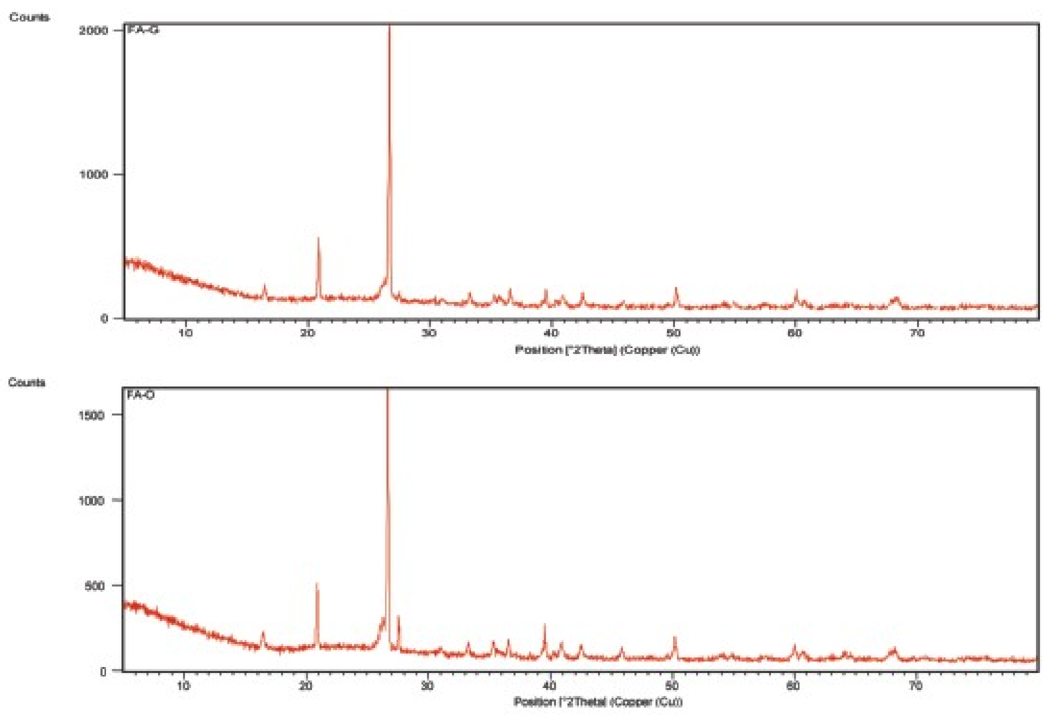

Fig. 3: XRD graph of ground fly ash (FA-G) and original fly ash (FA-O) showing intensity at different angle positions

Crystallite size of original and ground fly ash: The crystallite size is measured at different angles. The crystallite size of ground fly ash shows significant decrease from original fly ash.

$$\text{Crystallite size} = \frac{K \times L}{FWHW \times \cos\theta}$$

Where K = Shape factor,

L= Wavelength of X-ray used in diffraction = 1.5406 Å,

FWHM = Full width at half maximum,

θ = Position angle measured as 2θ

Economics & Benefits of fly ash

First benefit is the negligible cost of fly ash in comparison to other fillers used in paper, so it will decrease cost of paper by 3-5 %. Secondly, it will result in higher opacity of paper for same filler percentage in paper. Mechanical strength properties are superior to that of conventional fillers added paper. Again environmental degradation may be avoided by having proper use of fly ash which is a major solid waste available in all parts of world.

Conclusions

About 10 % of mass has particle size below 6.61 µm and 16% of fly ash has particle size below 10.30 µm. X_{50} of fly ash sample is 47.06 µm. A grinding time of one hrs results in bringing X_{50} of particles at 18.74 µm. The grinding process also affects the shape. The crystallite size decreased with grinding. Silica, alumina and iron oxide are the main chemical constituents making 95% mass fraction of fly ash. Grinding increases the percentage of particles in smaller range. Titanium dioxide, costly filler is present in fly ash in reasonable quantity, 1.5 % on mass basis. Fly ash has the potential to be very good filler for laminate grade colored base papers where very high opacity is required.

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References

H.W. Nugteren. Coal fly ash: from waste to industrial product. *Part Part Syst Charact.*, 24(1):49–55, 2007.

V. Stanislav, R.S. Vassileva, G.B. Angeles, D.S. Mercedes, and M.T. M. Rosa. Phase-mineral and chemical composition of coal fly ashes as a basis for their multi component utilization & Characterization of magnetic and char concentrates, *Fuel*, 83:1563–1583, 2004.

S. Ghosal and A.S. Sidney. Particle size-density relation and cenosphere content of coal fly ash. *Fuel*, 74(4): 522-529, 1995.

A. S. K. Sinha, M. Singh, S. P. Singh. Acetic acid pulping and ECF bleaching of rice straw and effect of acid concentration on pulp characteristics. *IPPTA* 24(2):151-158, 2012.

A. S. K. Sinha. Environment friendly removal of silica from wheat straw and Sacchrum Munja using Urea. *IPPTA* 24(3): 165-168, 2012.

A. S. K. Sinha, M. Singh, S. P. Singh. Study on use of non magnetic fraction of pulverized coal fly ash. *IPPTA* 22(2): 117-120, 2010.

R.S. Blissett, N.A. Rowson, A review of the multi-component utilisation of coal fly ash. *Fuel.* 97(1): 1-23, 2012.

S.V. Vassilev, C.G.Vassileva. Methods for characterization of composition of fly ashes from coal-fired power stations: a critical overview. *Energy Fuels.* 19(3): 1084–98, 2005.

N. Lior. Sustainable energy development: the present (2009) situation and possible paths to the future. *Energy.* 35(10): 3976–3994, 2010.

R.S. Iyer, J.A. Scott. Power station fly ash – a review of value-added utilization outside of the construction industry, *Resources. Conserv Recycl.* 31(3): 217–28, 2001.

J. Paya, J. Monzo, M.V. Borrachero, E. Peris-Mora. Mechanical treatment of fly ashes. Part I: Physico-chemical characterization of ground fly ashes. *Cement and Concrete research 25*(7): 1469-1479, 1995.