# RAPID EX SITU COLLECTION AND THERMAL BEHAVIOR ANALYSIS OF VOLATILE ORGANIC MATTERS BY THERMAL EXTRACTION CONE CHAMBER FOR HIGH UN-BURNT CARBON COAL FLY ASH

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**Abstract:** A thermal extraction cone chamber system has been modified to measure differential thermal functions and products where overall volatile organic matters are lost to the environment during heating. The aims of the research are to analyze and measure the thermal behavior of high un-burnt carbon coal fly ash derived from textile industrial power in Bandung. Efforts are being made to find the solution in large-scale utilization for alternative energy based on their by product. The sample analysis show that volatile organics matter exceed 30%, which means that others oxides element content are independently favorable. The modified cone chamber can collect the sample up to the total volumes of 30% of the chamber. In contrast to traditional chamber sample collectors, the modified cone extracts volatile organics matter from high un-burnt carbon coal ash divided in two treatments. Results show that the energy of pyrolisis, direct combustion or simple carbonization can be recovered (20%-42%) from wet or dry sample, with extraction efficiency compound-specific. During the direct combustion experimentation, resulted to the embedded energy is pushing up to $279^0$C for the average of volatile organic matters of 34% and for pyrolisis experimentation is $330^0$C for average volatile organic matters of 30%. The maximum thermal productivity values of 80 minutes for the direct combustion is $1022^0$C and for pyrolisis is $1031^0$C, and the contrary of 10 minutes, for the direct combustion is $743^0$C and for pyrolisis is $701^0$C.

## INTRODUCTION

It is evident that with boom of the energy-thirstiness in the textile industrial growth in Bandung, the need for has power increased manifold. With about 3.5 million tons coal supply at Cirebon harbor in 2005 nearly 40% of total Bandung's textile industry has installed power generation capacity is thermal, of which about 95% of its needs of supplied coal, with others making up the rest (http://www.pikiran rakyat.com/cetak/2005/0305/21/0410.htm).

Due to its relatively low operating temperatures, fluidized bed technology is regarded as one of the most promising technologies for utilizing low rank coals for industrial textile power generation. Typical operating temperatures for fluidized bed combustors are between 800 and 900 °C while the flame temperature in pulverized fuel combustors can get as high as 1600 °C. It is important to mention that for thermal textile industrial power generation in Bandung, of about 500.000 tons of coal fly ash that is high un-burnt carbon coal ash and bottom ash are produced every year and this tends to degrade the scarce land and environment. Only about 10 -12 % of coal fly ash is utilized.

Focus on this research is to analyze and measure the thermal behavior of high un-burnt carbon coal ash that is still presence and extent of the embedded energy occurred. Efforts are being made to find the solution in large-scale utilization.

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*Key words: thermal analysis, high unburnt carbon coal fly ash, volatile organics matters, pyrolisis, direct combustion.*

## THEORY

Thermal Behavior Analysis (TBA) is the application of a precision controlled temperature program to a material and measurement of the response of that material. This response may be a weight loss, change of shape or hardness, change in electrical properties or other measurable response which is directly affected by the applied temperature or heating rate.

Thermal 'events' are ubiquitous. Virtually all-chemical and physical processes involve heat and/or temperature changes. Thus thermal methods of analysis will almost always work when other methods fail. On the other hand, for the same reason, thermal methods often lack specificity resulting in interferences. In general, thermal methods involve the measurement of some property *P* as a function of temperature (T).

$$P = f(T)$$

The property *P* may itself be a thermal property (e.g., a change in heat (.Q) or temperature (.T)) or any of a great number of other properties (e.g., mass, magnetic susceptibility, etc.) (Hefter, G. 2004). However, in this unit we will only consider the more analytically useful techniques.

Many researchers employed dilatometry method to measure the onset temperature for particle agglomeration (Siegell, J.H. et. all, 1976). In the test, a small amount of loosely packed particles were placed in a cylindrical sample holder and a shaft with a piston at its end was placed against the sample in the cylinder. A load was applied to the rod and the sample was heated to a desired temperature at a programmed rate of temperature rise. During sample heating, the change in sample length was monitored and plotted as a function of temperature. Initially, the sample increased its length linearly with temperature, due to thermal expansion. As higher temperatures were reached, the rate of expansion decreased. This decrease in expansion rate was attributed to the onset of a separate phenomenon competing with the thermal expansion, i.e. sintering or densification. As the temperature was further increased, a point was reached where the slope of the expansion curve became zero. At that point, the expansion due to thermal effects was just balanced by the contraction due to sintering. This characteristic temperature was defined as *initial sintering temperature*, or *Ts* (Siegell, J.H. et. all, 1976). After this critical point, sample contraction dominated and the length increase became negative. There are two independent variables, sample heating rate and magnitude of the load, in the measurement of the initial sintering temperature.

## MATERIAL AND EXPERIMENTAL METHODS

The high un-burnt carbon coal ash were studied and derived from textile industrials power generation in Bandung. It was obtained from dumping sites surrounding industry. Physical analysis was employing screen mesh and portable grind-ball mill, and some determination was acquired. Major element analysis and oxides concentrations by gravimetric measurement and also employed by AAS (Atomic Absorption Spectroscopy) and loss on ignition (LOI) determinations were also acquired.

TBA was studied employing by modified cone chamber and furnace "Stuart Scientific" S1503 PID/D. The cone instruments are coupled via a heated fused silica manually transfer line from inside furnace chamber to the digital analytical balance (figure 1).

All samples size was range between +7 and -100#, and placed in modified cone chamber for about 50 grams. On the next research that comparison will be mixed by $HNO_2$ (pH 4, 5 and 6) 25 ml, pregnancy time was 46 hours, at room temperature and oxygen extinct. The data are in remarkable agreement results also will be compare favorably with high acid solvent $HNO_2$ extracted sample analyses (pH 4, 5 and 6) and can be used to delineate the presence and extent of the embedded energy from high un-burnt carbon coal ash.

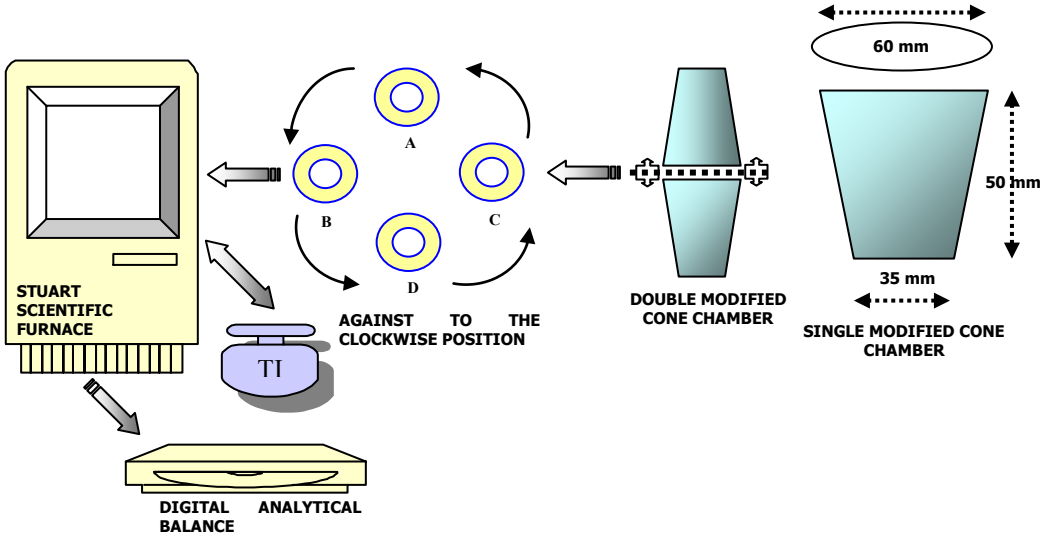


**Figure 1. The Schematic Methods.**

The samples were first heated at a rate up to $20^0$C/m to $1000^0$C, and onset time and peak temperatures were determined. Further characterization was done by rapid ex-situ collection at given time and temperature. Identification of the differential form was determined by calculating the initial ratio to the final products.

## RESULTS AND DISCUSSIONS

Organic matters in coal are microscopically heterogeneous (Yoshioka H., 2003). Its chemical composition is related to biological activity, sedimentation, and diagenetic processes. It is pertinent to note that the un-burnt carbon in the fly ash is quite high as compared to the fly ash of power stations in Indonesia (Table 1). The un-burnt carbon in Bandung coal fly ash is about 30% and in other Indonesians coal fly ash the un-burnt carbon was only 1%.

The LOI and CaO content are different among samples due to variation of melting additive and operation parameters during production. As it is known these losses come from the unburned particles of raw materials. In principle, the homogeneous composition achieved in a long time operation allowed us to propose this slag as candidate for recycling in several materials production. An average sample was taken for full characterisation as secondary material.

Corresponding to the mesh fraction distribution during the experiment (Figure 2), show that +7 mesh is major fraction of 35 – 48 % then the minor fraction of –80 +100 mesh is 1%. Though the specific mesh fraction distribution is rare, may be due to the high porosity and no compactness of powder, the high un-burnt carbon coal fly ash is related to the steam furnace performance itself, which can facilitate the characteristic of this material.

Due to irrelatively worn out of the performance and thermal behavior of "Stuart Scientific" S1503 PID/D, the thermal experimentation was conducted to determine of the given acceleration temperature. As mention on the graphic (Figure 3) that found in an empty chamber for average of 6 $^0$C/m. The thermal conductivity value of the mentioned furnace equipment will be analysed using simple calculation later on.

**Table 1. Chemical compounds of coal fly ash in Indonesia and high un-burnt carbon coal ash.**

| ELEMENT OXIDE (% by Weight) | RAW FLY ASH*) | UBP SURALAYA Indonesia Power | | | HIGH UN-BURNT CARBON COAL ASH |
|---|---|---|---|---|---|
| | | BUKIT ASAM | ADARO | KIDECO | Textile Industries Bandung |
| SiO2 | 37.62 | 75 | 38.73 | 30.87 | 2.06 (2.06) |
| Al2O3 | 32.44 | 33 | 24.66 | 10.32 | 17.60 (17.60) |
| Fe2O3 | 13.35 | 7 | 15.55 | 11.67 | 0.10 (0.14) |
| TiO2 | 1.56 | - | 1.06 | 0.56 | - |
| CaO | 7.25 | 3 | 8.99 | 16.76 | 42.00 (41.99) |
| MgO | 2.51 | 1.5 | 2.28 | 6.56 | 0.03 (0.03) |
| Na2O | 0.51 | 3.5 | 1.12 | 3.15 | 7.90 (7.89) |
| K2O | 0.65 | 0.7 | 0.97 | 1.09 | - |
| P2O5 | 2.22 | - | 0.12 | 0.18 | - |
| SO3 | 1.99 | - | - | - | - |
| LOI | 0.58 | 1.37 | 1.52 | 1.13 | 30.18 (30.20) |

**) Herry Prijatama, 2000*

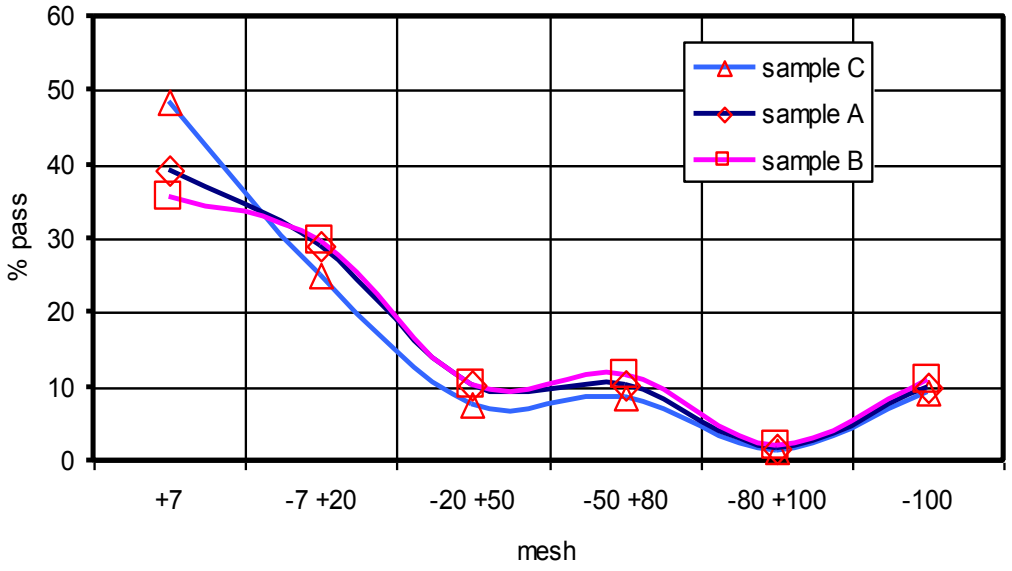


**Figure 2. The Graphic of High Unburnt Carbon Coal Fly Ash Mesh Fraction.**

It is interesting to note that there was a weight loss in the high carbon coal fly ash to the extent between of 30.8% and 35.9% for direct combustion but for pyrolisis of 20.2% and 41.9% when subjected for initial and overall thermal test. The maximum thermal productivity values of 80 minutes for the direct combustion is $1022^0$C and for pyrolisis is $1031^0$C, and the contrary of 10 minutes, for the direct combustion is $743^0$C and for pyrolisis is $701^0$C (Figure 4).

The thermal analysis indicated there was a average weight loss for direct combustion of 34% to pyrolisis of 30 % at ± 1000ºC in these

high carbon coal fly ash, indicating the present of chemically bound water in the C-S-H gels thus formed during the autoclaving process especially in pyrolisis experiment. This loss of water took place below 600 ºC confirming that the loss was not due to decomposition of un-burnt carbon. The same was confirmed by the differential thermal analysis investigations of the generated fly ash and high carbon coal fly ash.

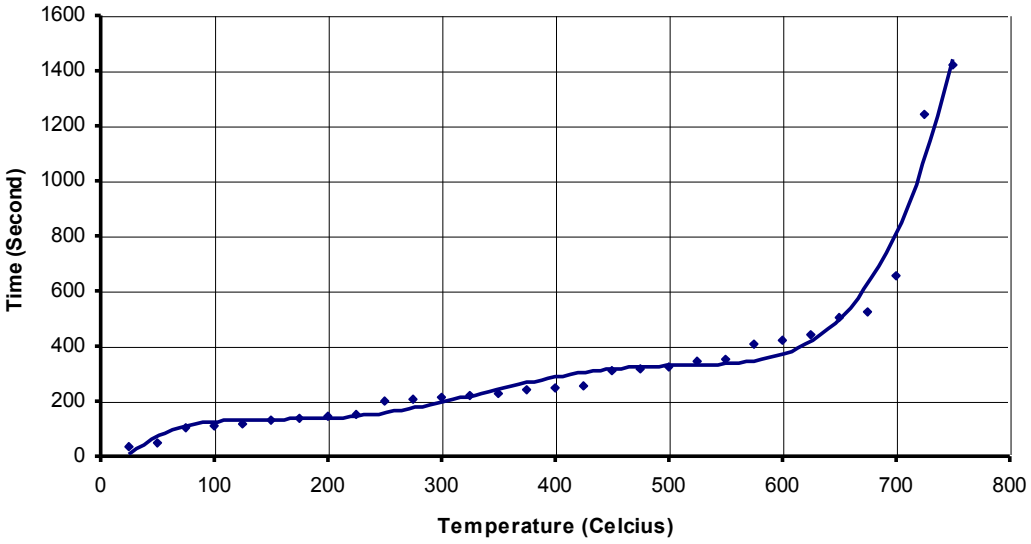


**Figure 3. The Graphic of Temperature VS Time of furnace "Stuart Scientific" S1503 PID/D.**

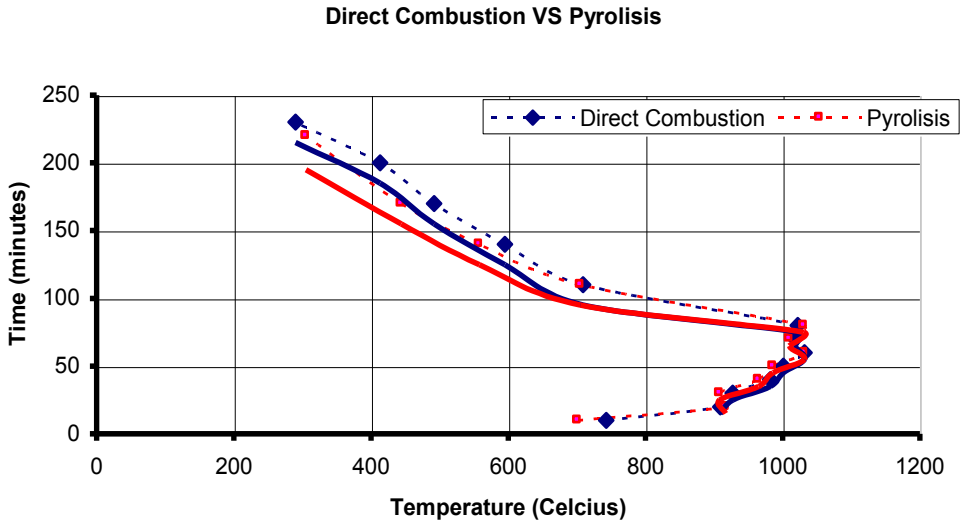


**Figure 4. Graphic of Initial Thermal Productivity and Descending Thermal Profile of High Unburnt Carbon Coal Fly Ash.**

Initially thermal behavior analysis of high carbon coal fly ash found that exponentially increased as function of pregnancy times for 80 minutes at $1000^0$C are:

$$t_{di} = 0.0465e^{0.007T_{di}} \quad \text{..... 1)}$$

for direct combustion experiment and

$$t_{pi} = 0.1161e^{0.0061T_{pi}} \quad \text{..... 2)}$$

for pyrolisis, where $t_{di}$ is initially pregnancy time of direct combustion (minutes), $T_{di}$ is initially thermal productivity of direct combustion ($^0$C) and for $t_{pi}$ is initially pregnancy time of pyrolisis (minutes), $T_{pi}$ is initially thermal productivity of pyrolisis ($^0$C).

Descending thermal function profile is also concerned to summaries on the utilization process later on. It is interesting found that the descending thermal function is relatively closed to the linearly excessive of embedded energy during the experimentation are:

$$t_{dd} = -0.293T_{dd} + 316.44 \quad \text{..... 3)}$$

for direct combustion and

$$t_{pd} = -0.2736T_{pd} + 297.62 \quad \text{..... 4)}$$

for pyrolisis, where $t_{dd}$ is descending pregnancy time of direct combustion (minutes), $T_{dd}$ is descending thermal productivity of direct combustion ($^0$C) and for $t_{pd}$ is descending pregnancy time of pyrolisis (minutes), $T_{pd}$ is descending thermal productivity of pyrolisis ($^0$C).

During the direct combustion experimentation, resulted to the embedded energy is pushing up to $279^0$C for the average of volatile organic matters of 34% and for pyrolisis experimentation of $330^0$C for the average volatile organic matters of 30%. Respectively, when subjected to different processing conditions has also different result. As shown on Figure 3 at the descending function on both experimentations was starting at the same point, which is pregnancy time for 110 minutes and temperature between of $705^0$C and $709^0$C. More attention due to the final descending temperature function of direct combustion resulted on $290^0$C is longer than for pyrolisis of $305^0$C at delta time of 10 minutes. Along the oxygen influences in direct combustion process, which does burning of volatile organics matters cause, which is freely fused. Also, the calcinations have occurred during the process, which has gradually decreasing of temperatures. Therefore, pyrolisis experimentation, which is oxygen extinct, has higher temperature than direct combustion, and caused by barrier calcinations in modified cone chamber.

## CONCLUSION

An investigation into TBA has been carried out as a potential technique for characterizing the thermal behavior of high unburnt carbon coal fly ash at elevated temperatures. Results show that, when applied to the obtained material at a heating rate of more than 6 $^0$C/min. at max temperature of 1000 $^0$C, the technique can successfully detect the point at which the material change its descending energy characteristics at direct combustion on $290^0$C and for pyrolisis of $305^0$C at delta time of 10 minutes. Contrary to previous findings, however, this characteristic point does not seem to correlate with the onset temperature of particle agglomeration and calcinations of oxides from calcium.

From the analysis study of high unburnt carbon coal fly ash results it can be concluded that, in principle, it can be an useful as raw material for the production of solid fuel as briquettes as alike, building materials, as well as raw cements material, which is the objective of the work now carried out. Results will be given in next papers.

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## REFERENCES

Hefter G., 2004, "Thermal Methods", Murdoch University School of Mathematical & Physical Sciences Murdoch, WA 6150 Australia.

Prijatama H., 2000, "Production and Utilization of Synthetic Zeolithes from Coal Fly Ash", Ph. D Thesis, Univ. of Leeds, UK.

Siegell, J.H. et al, 1976, "Defluidization Phenomena in Fluidized Beds of Sticky Particles at High Temperature", PhD Thesis, City University of New York.

Stuart Scientific, 1994, "The Equipments Handbook", Bibby Sterilin Ltd.

Yoshioka H., Takeda N., 2003, "Analysis of Organic Compounds in Coal Macerals by Laser Micropyrolisis", Goldschmidt Conference.

http://www.pikiran-rakyat.com/cetak/2005/0305/21/0410.htm