THE INCLUSION BEHAVIOR OF SODIUM COMPOUNDS IN SUB-MICRON PARTICLES FORMED DURING COAL COMBUSTION

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Coal, biomass and sewage sludge contains metallic compounds which vaporize during combustion, forming fumes. The formed fumes are emitted from combustion systems together with the exhaust gases. In power plants applications, the hot metallic vapours cause intensive corrosion when in contact with turbine blade surfaces. Efforts to control this behaviour involve mitigating the condensation phase. Among the poisonous and corrosive metallic compounds are the alkali metals like sodium and potassium. Although many researches have been carried out to control the emission of these metals, less has been done to draw a link between alkali metals emissions and the particulates or fumes formed during combustion. In this study, the evolution behavior of these metals was studied in order to establish the conditions and the possible mechanisms by which they appear in combustion exhaust gases via the sub-micron particles using a drop tube furnace and a low pressure impactor (LPI). Four types of coals with deferent chemical properties were tested. The evolution and inclusion of sodium in to the sub-micron particles was studied in relation to the particle size distribution and in particle Sodium fraction distribution. The results suggest that the reaction-controlled mechanism and nucleation via chemical reactions during combustion influence the evolution of sodium in sub-micron particles. At the larger particles of above 0.4 μm, the involved reactions are those which are mainly via gas film diffusion. Besides, the study has shown that the evolution and inclusion of sodium on sub-micron particles is indeed a function of type of coal through the strong influence of composition and the form by which Sodium occurs in coal. This is owed to the way it evolves and included in particles.

Keywords: *Alkali metals, Coal, Sub-micron particles, Combustion & Pollution Control*

INTRODUCTION

Due to the nature of formation process of coal and other biomass fuels, most of the materials involved are subjected into terminal pressures and temperatures. The localities and specifically solids and rocks, where these fuels are formed, on the other hands are composed of mineral matter. These minerals therefore appear in a number of ways (Bryers, 1988, Linak & Peterson, 1986). Barta, *et al* established that for the case of coal, minerals may occur in three forms. The first form is incorporated components in the coal matrix, which is actually part of the coalification process. The second one is the minerals inclusions which enter the coal by sedimentation and is usually the most abundant. The last form is of mineral, which are extraneous ash, usually the mineral matter are liberated by coal grinding. These metals include heavy trace metals and alkali metals, which cause problems of poor performance of power plants, environmental degradation effects, health risks and corrosive effects on the power plant systems. The later is mainly as a result of the alkali metal actions especially at high temperatures of combustion where the metals usually are vaporized (Helbe, *et al,* 1986). On the other hand, alkali metals have the positive effects hidden on the reduction of NO formation by chemical reaction influences (Lissiansky, *et al,* 2001, Sloss, & Smith, 2000). The above positive action has lead to intentional addition of sodium to fuel so as to reduce NO_x especially when co-combustion of coal and sewage is considered. It is necessary therefore in this to understand the mechanisms and behavior of alkali metals during combustion. These are not easily removed from the burning gases at high temperatures.

In the previous work (Naruse, *et al.* 1998), the chemical aspects of the Na evolvement was studied based on the classifications of the chemical nature of the sodium. The type of sodium evolving was classified as water-soluble which evolved mostly. Besides, the influence of alumino-silicates on the sodium evolution was elucidated. The results from this work were in good agreement with other researchers (Mwabe & Wendt, 1996, Wendt, 1994, Gallagher, *et al*, 1996). As an extension of this work, the detailed studies on the particle size distribution and the Na fraction distribution on the particles were necessary to clarify the physical as opposed to chemical reactions occurring with Na during combustion.

In this study, the evolution behavior of these metals have been studied in order to determine the suitable conditions and possible mechanisms by which alkali metals occur in combustion gases and their inclusion in the sub-micron particles. An electrically heated drop tube furnace and a low-pressure impactor (LPI) have been used. Four types of coals with deferent chemical properties were selected. Coal conversion characteristics were first established and correlated to evolution and inclusion of sodium in to the sub-micron particles by analysis of particle distributions and Na concentrations. Furthermore, the particle evolution was analyzed by using the aerodynamic particle diameters.

EXPERIMENTAL SETUP AND PROCEDURES

In order to carry out fundamental studies on coal conversions, an electrically heated drop tube furnace with high heating rate was used. The furnace is operated at a temperature of 1123 K, suited for pulverized coal combustion systems. Under this condition, sampling was carried out at a distance of 1200 mm from the injection port. Shown in Figure 1 is the complete experimental setup, with drop tube, thermo-controllers, heater, vibration feeder, low-pressure impactor and sampling probe. In order to maintain the desired temperature, water cooler system was incorporated in the system. At first the coal conversion and residual fractions of Na were established from these tests. Four types of coals namely, Orchard Valley (OV), Yalloon (Y), Black Thander (BT) and Spring Cleak (SC) were selected for the present work as discussed in Naruse, et al 1998. Table 1 shows the properties of the coals used in this work. It was found OV type has the highest ash and carbon content of the four, while Y (with high Al and Si) and SC coals appear to have apparently higher Na content in the ash. With the LPI, it is possible to determine the particle size distribution and the Na fraction in particles. To determine the Na fraction, the particles were segregated by the LPI, the digested HF and HNO_3 and finally analyzed by a furnace atomic absorption spectrometer. The particle size distributions and the Na fractions are discussed in the context of the four coal types.

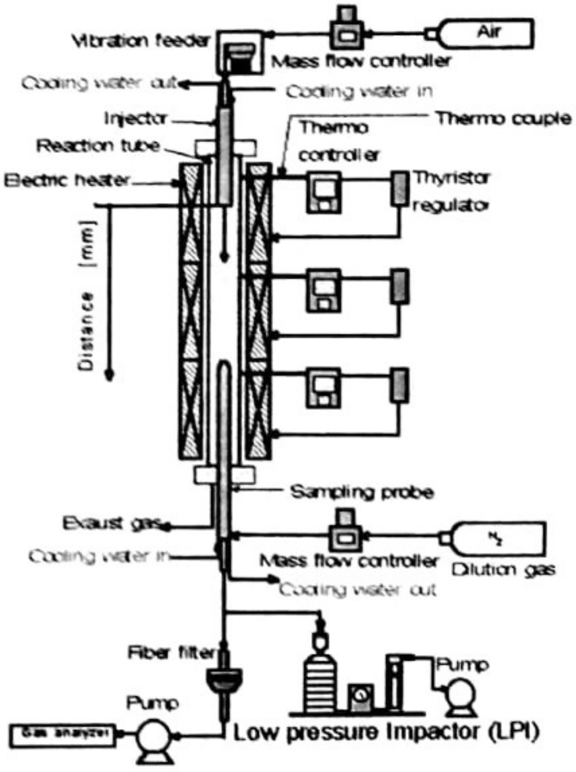


Figure 1: Electrically heated drop tube furnace system

Table 1 Coal properties

Coal			OV	Y	BT	SC
Proximate analysis [mass% , dry]	Ash	mass% dry	8.73	1.05	6.75	4.52
	Volatile matter		36.97	47.99	44.68	45.85
	Fixed carbon		54.3	50.96	48.57	49.63
Fuel ratio [-]			1.47	1.06	1.09	1.08
Ultimate analysis [mass% , dry]	C	mass% d.a.f.	79.1	66.1	74.8	75.7
	H		5.5	4.5	5.2	5.4
	N		1.7	0.6	1.0	0.9
	O		13.3	28.62	18.49	17.61
	Comb.S		0.4	0.1	0.07	0.04
	Total S [dry]		0.44	0.18	0.51	0.39
	Cl [dry]		0.01	0.074	0.019	0.017
Ash compositions [mass% , dry]	SiO_2	mass% in ash	55.84	0.49	27.68	25.64
	Al_2O_3		25.73	0.05	14.66	15.32
	Fe_2O_3		4.4	27.83	3.8	3.81
	CaO		3.54	10.44	25.58	18.74
	MgO		1.1	23.62	5.06	5.71
	Na_2O		1.74	8.67	2.44	8.39
	K_2O		0.59	0.38	0.05	0.37
Content of sodium [mass% , dry]		mass% in coal	0.140	0.057	0.079	0.236

Table 2 shows the experimental conditions adopted in this work. The furnace temperature was maintained at 1123K while the air ratio was kept at 1.2 by maintaining a sample feed of 0.4 g/min. The coal particles used in this work were sieved to mean particle sizes of 0.4 mm with normal distribution.

Table 2 Experimental conditions

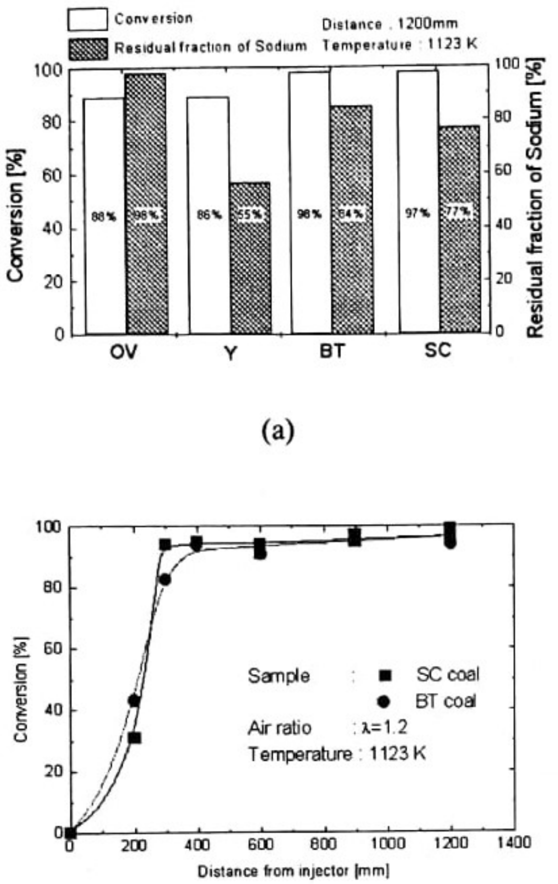
Coal	BT,SC
Furnace temperature [K]	1123
Air ratio [-]	1.2
Sample feed rate [g/min]	0.4
Air flow rate [l /min]	4.0

RESULTS AND DISCUSSIONS

Experiments were carried out and results are presented in two main parts. The first part deals with the fundamental behaviour or the coal conversion in relation to the residual sodium, while the second part dwells on the particle size distribution and the sodium inclusion on the particles.

Fundamental coal conversions and Residual Na

At 1123 K temperatures maintained in the furnace, coal burns with emission of mineral compounds. Coal conversion and residual fraction of Na were measured using the experimental equipment described above. Initial results obtained indicated that for all the tested coals, total coal burnout is registered at a distance of 400 mm, where all the coal is fully converted. From this aspect, the conversion and Na residual fraction of the four types of coals at a distance of 1200 mm are presented in Figure 2. It is evident from Figure 2(a) that coal type OV and Y show comparatively higher and similar conversion fractions while the residual Na differs significantly. This difference in residual Na could be due to the presence of NaCl in coal, which favors the Na vaporization during combustion (Naruse, et al). Furthermore, OV coal has higher Si and Al content which retard the vaporization tendencies of Na in this type of coal. BT and SC coals on the other hand show similar conversion behavior, but difference in the residual Na. From the properties shown in Table 1, the two coals have similar properties in terms of Na and ash content. It is likely that the presence of Al and Si could hinder the evaporation of Na in BT coal thus higher observed residual sodium for this type of coal. The two situations therefore lead to selecting coals BT and SC for detailed study, which is reported in this paper. Figure 2b shows the conversion tendencies of BT and SC coals along the furnace axis. It is evident that the two coals have similar conversion behaviors, with total burnout observed at a distance of 400mm.



(a)

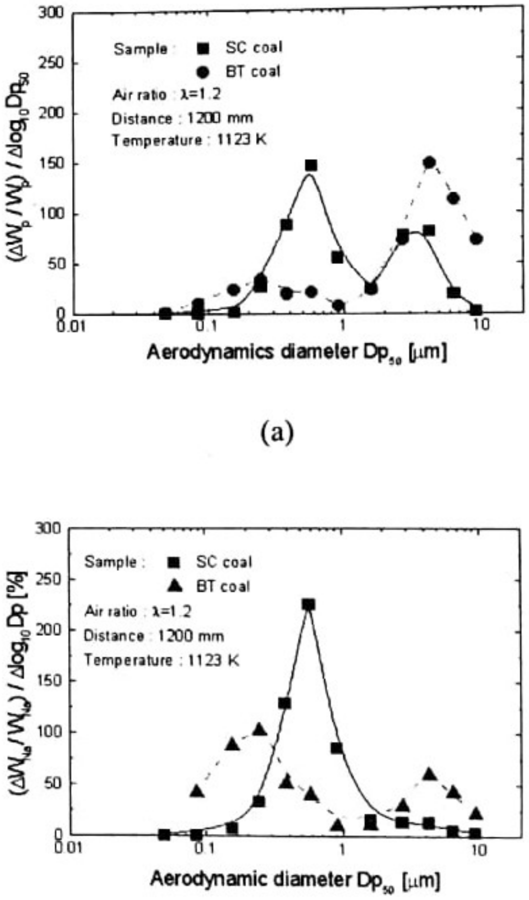
(b)

Figure 2: (a) Coal conversion for SC and BT coals (b) Coal conversion behaviors and Na residual fraction

Particle size distribution and sodium fraction in particles distribution

Resulting from the above observation, there was a need to investigate the particles before and after combustion. In a similar manner, the Na in particles was analyzed and presented in this section with BT and SC.

Figure 3a shows the particle size distribution and 3b the Na fraction distribution in the particles at a distance of 1200 mm from the injector for BT and SC coals. In the graphs, the vertical axis represents the frequency particle mass coefficient, while the horizontal axis is the aerodynamic particle diameter. It can be observed that the two coals show bimodal particle size distribution with a peak below 1 μm and another one above 1μm. However, comparing the two coals, coal SC shows a higher peak than BT at the sub-micron size, while the peak above 1 μm is higher for BT. Looking at Figure 3b, Na particle distribution shows a mono-peak behavior for the case of coal SC. This suggests that for SC coals, most of the Na occur on the sub-micron particles while BT shows bimodal characteristics. Although the particle size distribution shows a low peak, the Na distribution observed in this type of coal is substantially higher. There is a possibility of the Na been inherent to the particles, or formed through static condensation and chemical reaction likely to have to occur in the probe during quenching.



(a)

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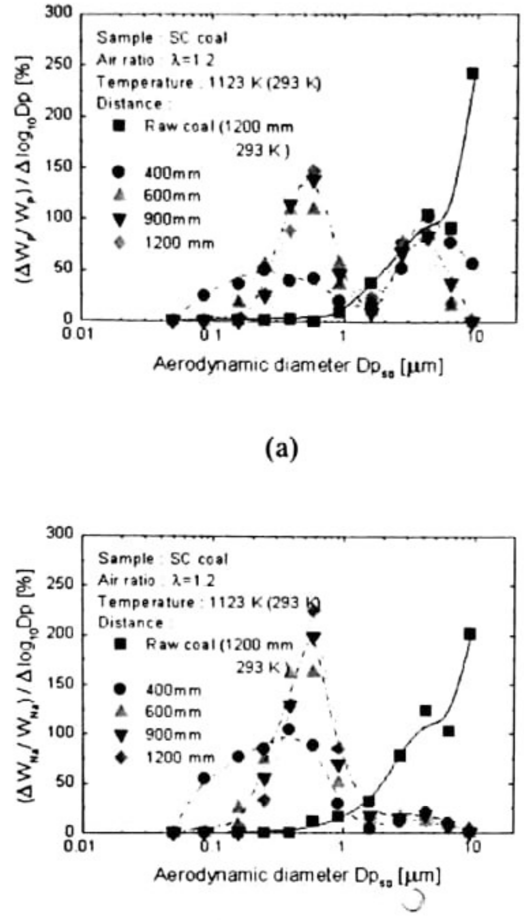
Figure 3: (a) Particle size distribution and (b) Na fraction distribution in the particle



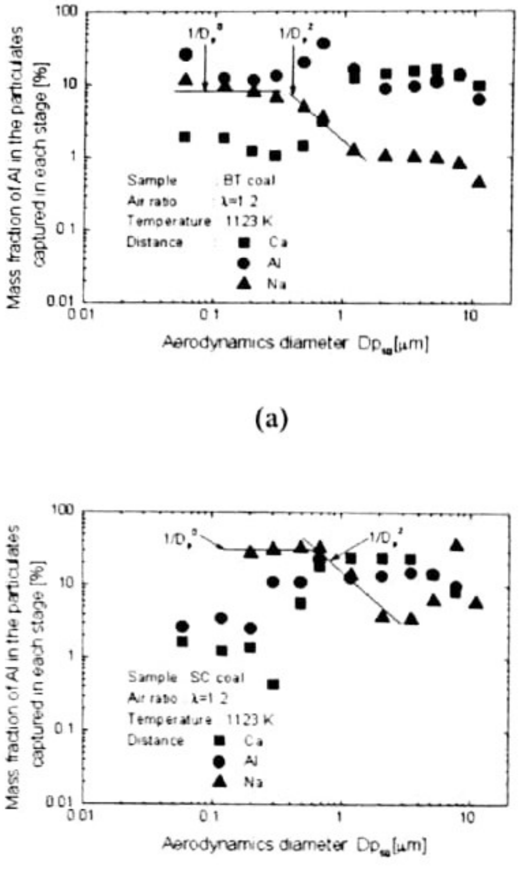
(a)

(b)

Figure 4: Characteristics particle size distribution along the distance from the injector: (a) particle distribution (b) Na fraction distribution in particles

In order to verify the evolution of the Na in the particles, the particle size distribution and Na particle distribution was measured along the furnace axis. By this measurement, it is possible to discuss the kinetic evolution of the particles. Figure 4 shows the results obtained from these measurements are shown for coal type SC. For reference purposes, the characteristics for the raw coal at a temperature of 293K are included in the results shown in Figure 4 (a) the particle size distribution and (b) Na fraction in particles. From Figure 4a, it can be observed that a bimodal peak is observed where as the distance from the injector increases, the peak also increases. This suggests that as the conversion proceeds, the particles confined in the sub-micron particle size increases. However, at a distance of 400 mm, the peak is higher at the particle sizes d_p>1 μm. As the distance increases, the second peak does not show distinct feature as observed on the first peak. Figure 4b on the hand shows the sodium particle distribution along the axis distance for the SC coal, taken as a representative of the others. Unlike the particle size distribution, the Na fraction distribution seems to be confined on the sub-micron particles. As the distance from the furnace increases, the peak Na fraction distribution increases too. It is probably owing to condensation on the already formed minute particles that the peak is increased with distance.

To elucidate the evolution phenomenon of Na, fraction of Na in particle for the case of Al, Ca and Na are mapped together. Main purpose here is to



(a)

(b)

Figure 5: Characteristics of Na fraction with aerodynamic diameter at 1200 mm for (a) BT and (b) SC coals

isolate the influence of other alkali metals (Wittholm, *et al*, 1988, Hartinger, *et al*, 1994). Figure 5 shows the tendency of fraction of Na in particle size distribution for (a) BT and (b) SC coals. It is evident from the two figures that below 0.4μm, the Na fraction is proportional to $1/Dp^0$ while within 0.4 and 1 μm, the trend follows a proportion of $1/Dp^2$. This is in agreement with the trends observed by Wendt, 2001 regarding the behavior of trace metals during incineration processes. The first stage could be the Na evolution on particles, which involves reaction-controlled phenomenon, specifically observable during the combustion processes involving the minute particles formed by nucleation (Mizohara, 2001, Raask, 1985, Smoot & Smith, 1985). The second stage on the other hand, could be considered to be a result of gaseous diffusion, emanating from the Na vapors formed during combustion. The fractions of Ca and Na on the other hand, indicate that in both cases, the Ca is lower in amount and probably of the same magnitude. In this case, its presence could be the same for the two coals. However, Al appears to be higher for the first stage of Na on particle for BT coal than for SC. This probably could have relation to the occurrence of Na on the particles (Shadman, *et al*, 1990, Ahluwalia, *et al*, 1984). It is therefore possible that the observed Na fraction could be a result of chemical reaction which more related to the Al. For the case of SC on the, the Al concentration is lower, thus the vaporization and subsequently release of Na higher than that of BT. This suggests that the role of Al and probably chemical reaction could be insignificant, in which case, the evolvement of Na could be more as a result of condensation Takuwa, *et al*, 2000).

CONCLUSIONS

The evolution of sodium has been studied in relation to particle size distributions for raw and converted coals. The discussions of the particle size distribution and the sodium fraction in coal particles have shown that;

- Although the vaporization of Na in coals during combustion is a function of coal type, the evolvement of Na on particles shows some similarities. In this case, Na evolves as a result of chemical reaction. This phenomenon is comparable to the observed Al concentration.
- Owing the devolatilization behaviors, Na may also evolve as a result of gaseous diffusion and condensation. This is significant especially at the inter-region between the sub-micron particles and larger particles.
- The particle size distribution has its peak increasing with distance from injection point. This phenomenon is likely due to partitioning of large particles in to smaller ones and the condensation behavior, which could predominates as the distance increases.
- The presence of volatilization inhibiting species such as Al (Yossif, *et al*, 1998, Seeker,). This is likely to be as a result of retarded volatilization of the coal. This is valid with the higher residual fractions observed for coal type Y, with higher amount of Na appearing chemically bound to Al and Si. Under this phenomenon, Na is retained in the coals as a result of these species present in the coal.

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