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THE EFFECT OF TEMPERATURE ON Na, K, AND Ca EMISSION DURING COMBUSTION OF PINEWOOD SAWDUST

Isack Legonda

The University of Dodoma, Republic of Tanzania
legondaia@gmail.com

Abstrak— Kuantifikasi emisi Na, K, dan Ca dari pembakaran serbuk gergaji kayu pinus telah dikondisikan. Konsentrasi logam-logam ini dalam serbuk gergaji dan abu ditentukan menggunakan spektrometri plasma induktif. Sampel abu dikumpulkan pada suhu 550^{o}C dan 900^{o}C untuk mensimulasikan kondisi operasi aktual untuk proses konversi termal yang terutama adalah pirolisis, gasifikasi, dan pembakaran. Selain itu, sampel tar dikumpulkan dari proses pirolisis yang dilakukan pada suhu 500^{o}C untuk menilai konsentrasi logam tertentu. Hasil analisis menunjukkan bahwa emisi Na, K, dan Ca ditemukan berkisar antara 19-39 ppm, 340-400 ppm, dan 500-550ppm untuk suhu antara 550^{o}C dan 900^{o}C. Kehadiran kandungan logam dalam tar mendukung bahwa mekanisme emisi dapat melalui adhesi selama penguapan hidrokarbon berat dari pembakaran biomassa. Dengan demikian, temuan studi ini menunjukkan bahwa penanganan emisi logam dari api terbuka seperti kompor kayu bakar sangat direkomendasikan.

Kata kunci—logam alkali; emisi; kayu pinus; pembakaran biomassa.

Abstract— *Quantification of Na, K, and Ca emissions from the combustion of pinewood sawdust has been conducted. The concentration of these metals in both sawdust and ashes was determined using inductive coupled plasma spectrometry. Ash samples were collected at 550^{o}C and 900^{o}C to simulate the actual operating conditions for thermal conversion processes which are mainly pyrolysis, gasification, and combustion. Also, tar samples were collected from the pyrolysis process conducted at 500^{o}C to assess the concentration of selected metals. The analysis results showed that emissions of Na, K, and Ca were found to range from 19-39 ppm, 340-400 ppm, and 500-550 ppm for temperatures between 550^{o}C and 900^{o}C respectively. The presence of metal content in tar supports that the emission mechanism can be through adhesion during the volatilization of heavy hydrocarbons from biomass combustion. Thus, the study findings suggest that treatment of metal emissions from the open fire such as that of firewood cookstoves is highly recommended.*

Keywords— alkali metals; emissions; pinewood; biomass combustion.

INTRODUCTION

Recently, there has been growing interest in alarming fossil fuels depletion in addition to climate change. This demand has led to promoting the use of other renewable energy sources including biomass. Biomass can be converted into a useful form of energy through different routes including direct combustion, pyrolysis, and gasification processes. Direct combustion is commonly used in households for cooking while pyrolysis is commonly used in the production of charcoal from biomass. The gasification process converts biomass to gaseous for application in different types of burners and internal combustion engines. Both thermal conversion processes involve heating the biomass to temperatures ranging from 500-1000^{o}C. At this temperature range, trace metals may vaporize in a significant amount to exceed the limit for indoor air quality and other applications [1-3]. Similarly, a high concentration of trace metals in syngas limits its use in internal combustion engines because could increase the wear of mechanical parts such as pistons, piston rings, and cylinder liners. Furthermore, deposition of alkali species such as NaCl, Na_2SO_4, and Na_2CO_3, can poison and deactivate catalysts and fuel cells [4].

Alkali, alkaline, and trace metals concentration in biomass depends on soil mineralogy and plant uptake capacity. Typical metal concentrations in biomass combustion have been reported by past researchers [5]. However, the concentration of these elements has mainly been based on analysis ashes while little has been considered on the interaction of metal emissions with heavy hydrocarbons. Technically, biomass has high inherent volatile maters which evolve during combustion and could impair the indoor air quality in terms of carcinogenic compounds and emitted alkali and alkaline metals. Past research by [6] reported that psychiatric, neurodevelopmental disorders, and Schizophrenia have been associated with abnormal levels of alkali and alkaline metals in human beings. Such findings highlight that there exist impacts when a human is exposed to an elevated level of alkali and alkaline metals.

The main objective of this study was to assess the routes and concentration of Na, K, and Ca at different operating temperatures that could be emitted and pose risks to human health and other applications.

METHODOLOGY

Characterization of pinewood sawdust

Pinewood sawdust was prepared by grinding to 500µm and then dried at 105ºC overnight in a furnace. The resulting sample was used for proximate and ultimate analyses as well as the concentration of Na, K, and Ca elements. Determination of moisture and ash content was determined by heating the sample weighed 1 g to 105 and 550ºC for 2 hrs respectively, while fixed carbon was 900ºC for 7 min. Additionally, ash content was also determined at 900ºC to assess the loss of Na, K, and Ca metals due to temperature. Calorific value was determined in a bomb calorimeter; Parr 6100.

Ultimate analysis of pine sawdust was carried out in a CHNSO-IR spectrometry (LECO) analyser to establish elemental composition which is mainly carbon, hydrogen, nitrogen, sulphur, and oxygen (CHNSO). Thermogravimetric analysis was also carried out to investigate the relationship between mass decomposition rate and temperature due to heating in a Simultaneous Thermal Analysis STA-780 series thermal analyser. Helium was used at a flow rate of 20 ml/min to ensure an inert environment while the heating rate was 10ºC/min.

Determination of Na, K and Ca Concentration

The concentration of Na, K, and Ca in pinewood sawdust was analysed using a Perkin Elmer Optima 21000DV inductively coupled plasma spectrometer. About 1.0 g of sawdust was digested with 15 ml of nitric acid. The mixture was heated until brown fumes cleared. It was then cooled before reheating with the addition of 5 ml of hydrogen peroxide. As the solution was not clear, a further 5 ml of hydrogen peroxide was added along with heating to about 250ºC. After the solution was clear, it was allowed to cool before diluting with deionized water to make 50 ml which was later fed to the analyser. Similarly, 0.1 g of ash samples were digested adopting the previously described procedure. For the case of ashes and tar samples, the concentration of Na, K and Ca was determined by Energy Dispersive X-ray spectroscopy (EDX).

Morphology of ash particles

Morphology analysis of ash particles from combustion of pinewood sawdust was analysed by using a ZEISS scanning electron microscope (SEM). Sample preparation and handling were done following standard operating procedures for SEM analysis.

RESULTS AND DISCUSSION

Characterization of the feedstock

Table 1 shows the proximate and ultimate analysis of pinewood sawdust. It can be seen that the fuel is composed of mainly volatile matter with fixed carbon around 14%, while ash content is considered to be of trace amount. The observed low moisture content of 2.47% is a result of preconditioning the fuel through a drying process to increase energy density. The ultimate analysis shows that the elemental concentration in decreasing order is carbon>oxygen>hydrogen>nitrogen> sulphur. Carbon and hydrogen are responsible for heat release while sulphur consumes. The inherent oxygen is normally accounted for the oxidation of combustible elements and trace metals during the combustion process.

Table 1 Proximate and ultimate analysis of sawdust

Proximate Analysis	(%wt)	Ultimate Analysis	(%wt)
Moisture content	2.47	C	49.40
Ash	0.43	H	5.90
Volatile matter	82.73	S	0.02
Fixed carbon	14.37	N	0.30
Total	100.00	O by difference	40.68
Gross calorific value, (MJ/kg)	19.09		

Investigation on the thermal behaviour of sawdust is presented in Figure 1. The figure shows four distinct phases of mass loss. These losses are due to moisture release at temperatures below 105ºC followed by a large loss of volatiles between 200-300ºC as depicted by the 1st and 2nd peaks respectively. Further heating to 300-500ºC results in significant loss of volatile and above 500ºC the loss is considered as a trace amount. The volatiles released at 130-150ºC has been identified as hemicellulose while at 300-500ºC are mixed cellulose and lignin and above 500ºC is mainly lignin [7-8].

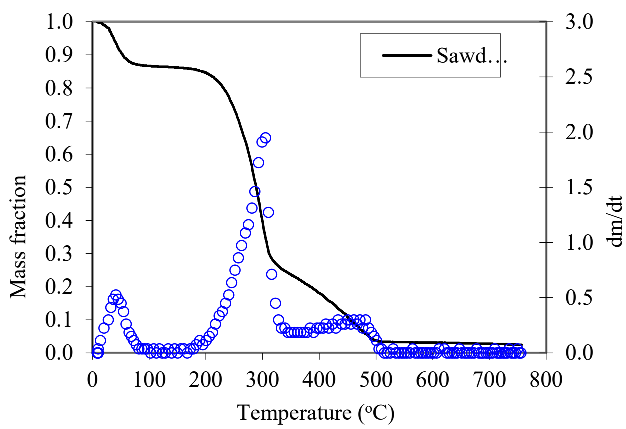


Figure 1 Thermogravimetric behaviour of pinewood sawdust

Alkali and Alkaline Metal Analysis

Table 2 shows selected alkali and alkaline metal concentrations at different temperatures typically found in pyrolysis, direct combustion, and gasification processes. These elements in ash residues occur in form of oxides as reported by [9]. Further explanation on the results show that emissions of Na, K, and Ca were found to be 19-39 ppm, 340-400 ppm, and 500-550 ppm for temperatures between 550 and 900^{o}C respectively. From the table, it can be observed that Na decreased significantly when heated to 900^{o}C. The decrease could be attributed to the vaporization of Na as also revealed by [10] in a study regarding migration characteristics of Sodium during biomass combustion. Another study by [11] also reported that up to 90% K and Na escapes during devolatilization of wood samples at a temperature ranging 200-500^{o}C. Moreover, Ca is among an alkaline group metal that has similar characteristics in vaporization during combustion as for Na and K [12].

Table 2 Concentration of selected alkali and alkaline metals at different temperatures

	Concentration (ppm)				
Element	Sawdust	Ash at 550^{o}C	Ash at 900^{o}C	Emission at 550^{o}C	Emission at 900^{o}C
Na	40.00	20.58	1.00	19.42	39.00
K	415.00	72.68	7.56	342.32	407.44
Ca	671.00	159.51	120.08	511.49	550.92

Figure 2 presents the concentration of Na, K, and Ca metals detected by SEM/EDX in tar samples obtained from pyrolysis at 500^{o}C. Results show that K concentration is four times high compared to Na and Ca. The presence of these metals in tar confirms that Na, K, and Ca escape during devolatilization of biomass which usually occurs at temperatures between 200-500^{o}C as also depicted in Figure 1. These findings are in good agreement with those by [13] who revealed that sodium and calcium emissions occur at the beginning of biomass particle combustion and proceed until the volatilization process stops.

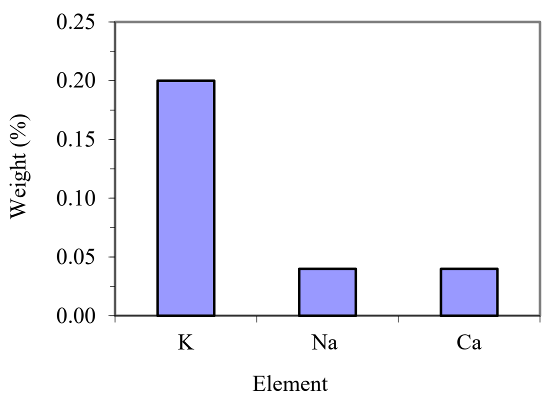
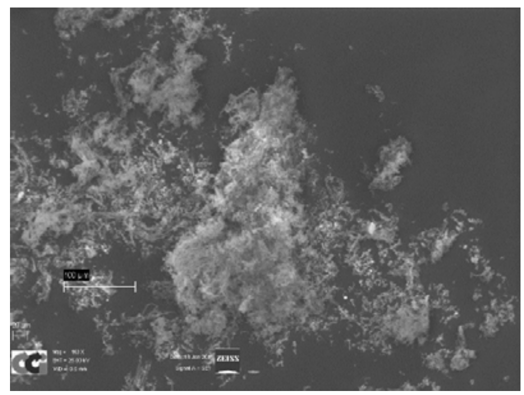


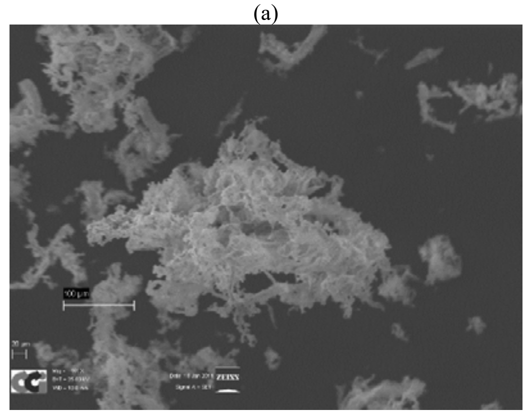
Figure 2 Concentration of Na, K, and Ca in tar samples

Morphology of ash particles

Figure 3 (a) and (b) show the morphology of ash particles from the combustion of pinewood sawdust at 550^{o}C and 900^{o}C respectively. From Figure 3(a) it can be seen that ash particles are loosely scattered with no formation of agglomeration. This finding suggests that escaping route of trace metals in pinewood sawdust at a temperature below 550^{o}C could also be through adhesion during the vaporization of hydrocarbons. In principle, hydrocarbons can act as a carrier of trace metals during devolatilization. Another finding from Figure 3(b) reveals that ash particles are fused forming a chain-like structure which signifies the formation of agglomeration. The observed formation of fusion at 900^{o}C indicates that the possible escaping route of alkali and alkaline metals could be through solid-liquid-gas phase transformation.



(a)



(b)

Figure 3 SEM of ash particles from the combustion of pinewood sawdust (a) ash particles at 550 ^{o}C (b) ash particles at 900 ^{o}C

CONCLUSION

A study on the effect of temperature on selected alkali and alkaline metals during the combustion of pinewood sawdust has been conducted. Emissions of Na, K, and Ca were found to be 19-39 ppm, 340-400 ppm, and 500-550 ppm for temperatures between 550 and 900^{o}C respectively. These emissions exceed the values recommended for indoor air quality and internal combustion engine applications. The presence of metal emissions in tar supports the transport mechanism is through adhesion during the volatilization of heavy hydrocarbons from biomass. Of particular importance, treatment of these emissions from the open fire such as that of firewood cookstoves draws attention to envisaging mechanisms to minimize to the acceptable levels for human health.

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