J. Mater. Environ. Sci. 7 (8) (2016) 2929-2937 *Ibeto et al.*
ISSN: 2028-2508
CODEN: JMESC

Evaluation of Pollution Potentials and Fuel Properties of Nigerian Sub-Bituminous Coal and its blends with Biomass

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Received 26 Nov 2015, Revised 04 Jun 2016, Accepted 09 Jun 2016
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Abstract
The improvement of the combustion properties of coal and biomass by blending and carbonization was investigated. Proximate and ultimate analyses of coal, sawdust, corn cobs and their blends were carried out using ASTM methods. The proximate and ultimate analyses were repeated on the five blends after carbonization at 500^{o}C for one hour. Pollution potential of the fuel samples were derived using simulated parameters for a hypothetical coal/biomass fired power plant. The quantities of CO_2, NO_2 and SO_2 that would be emitted per hour in a 20MW power plant were calculated. The results of the proximate analysis showed that the carbonized blends of both the coal-sawdust and coal-corn cob blends had an improved fixed carbon content and volatile matter, relative to the uncarbonized. The calorific values and other fuel properties were of similar trends. The results of the ultimate analysis showed that corn cob and sawdust had no sulphur content, while the uncarbonized coal-sawdust and coal-corn cob blends showed decreasing carbon content. This study revealed that the fuel properties of coal and biomass can be improved by blending and carbonization. The simulated power plant analysis of the fuel showed that blending of coal with biomass reduced the SO_2 and NO_2 emissions. For SO_2, the value of coal-sawdust blends reduced from 60.5 kg/hr in coal to 5.6 – 50.4 kg/hr in different coal-sawdust blends. Therefore, blending of coal with either sawdust or corn cob should be encouraged in coal fired power plants to reduce environmental pollution.

Keywords: Coal, Biomass, Carbonization, Fuel, Environmental pollutants

1. Introduction
Global energy demand is increasing at an enormous rate, whilst the industry is expected to reduce CO_2 emissions due to global warming. Solid fuels like coal and biomass are widely used energy resources, especially for combustion where heat energy is needed. The market for solid biofuels has grown from 2 million to about 18 million tons per year during the last decade as European power providers are under pressure from their governments to reduce the CO_2 emissions [1]. There is that increasing concern regarding the potential global environmental impacts of fossil fuels used for power generation and other energy supplies. The fossil fuels include coal, petrol, diesel and natural gas. Coal is one of the most abundant energy resources on earth. In many countries, coal continues to be the major fuel for electricity generation. While coal is advantageous, its major drawback is environmental pollution. Greenhouse gas emissions, acid rain and respiratory diseases result from using coal for electricity generation. On the other hand, biomass is indisputably the most abundant energy source on earth. It is represented by plants, animals, waste and by-product of both plants and animals. The interest in biomass as a raw material for producing energy has emerged rapidly in many countries [2]. Utilization of these two solid fuels is quite challenging, despite their wide availability. Some studies have been carried out on Nigerian coals. Sonibare et al., [3], studied the burning and volatile profiles of Nigerian coals with a view of assessing their suitability as future source of energy. The apparent activation energies of the combustion and pyrolysis reactions of the coals varied from 68.5 to 90.9 kJ mol^{-1} and 34.1 to 57.2 kJ mol^{-1} respectively. The trace metals contents of Nigerian Sub bituminous coal from Benue Trough was investigated by Adedosu et al., [4], using energy dispersive X-ray fluorescence Spectrophotometer (EDXRF) and subsequently used for geochemical studies and preliminary investigation of mineral present in Nigerian coal.

ISSN: 2028-2508
CODEN: JMESC

The levels of some metals such as nickel, iron, titanium and copper in these samples indicate that the ash residue of these coals after burning could be a very good source of the metals. However, the presence of some trace elements like copper (Cu) and nickel (Ni) that causes corrosion of the turbines and also poison catalyst in the coals necessitate incorporation of the removal procedures of these metals before refining stage. In another study by Adekunle et al., [5], proximate and ultimate analyses of biocoal briquettes were undertaken with the aim of ascertaining the optimum biomass composition for use as composite domestic fuel. It showed further that all the 50/50% coal and sawdust blends of the two coal samples were suitable as fuel but 90/10% coal and sawdust blend had the highest calorific value. Co-firing of coal and biomass blends has been suggested as a means of mitigating the difficulty of their individual use. Also, pretreatment of coal and biomass before co-firing is expected to reduce the negative properties of coal-biomass blends. There are different pretreatment methods such as torrefaction and carbonization. Torrefaction process is thermal decomposition of raw biomass, in inert atmosphere, at low temperature of 200-300^{o}C [6], this drives out moisture, light volatiles and hydrocarbon especially in the biomass. Carbonization is the heating of the solid fuel at higher temperature in the absence of air to give char. Carbonization can be low temperature (500-700^{o}C) and high temperature (900-1100^{o}C). A modified process, hydrothermal carbonization (HTC) have used as a pretreatment process for making pelletized biomass more homogeneous and energy dense [7].

Nigeria has an abundance of agro-forestry biomass waste generated each year. The negative effects of solid waste to the human and the environment have been considered as a serious problem [8]. Sawdust is a byproduct of the wood/furniture industry and piles of it are often burnt off at dump sites. Corn cob is also discarded after the kernel has been removed. These biomass materials that are widely available in Nigeria can be blended with Nigerian coal in order to evaluate their performance. Maize, also known as corn, is the most important cereal crop in sub-Saharan Africa and an important staple food for more than 1.2 billion people in this region and Latin America. More maize is produced annually than any other grain. Worldwide production of maize is 785 million tons, the largest African producer being Nigeria with nearly 8 million tons, followed by South Africa [9]. Saw dust is readily available in several sawmills across the country. For instance, a study on one hundred sawmills in Ijebu area of Ogun State, South west Nigeria, showed a potential availability of wood wastes in excess of 212,220 m^2 (about 66,000 tons) generated per annum [10].

Although coal has its threats to the environment and man, its utilization cannot be totally abandoned since there are limited alternatives to coal as fuel. It has been estimated that Current coal reserves in Nigeria are as high as 2.75 billion metric tonnes and the nation's proven reserves stand at 639 million tonnes. However, the coal reserves have not been fully explored or even marginally developed despite the long history of the coal industry. The locations of the coal deposits in Nigeria, mostly sub bituminous are in the eastern parts of the country [11]. With increased awareness of the damaging effect of coal combustion, and stiffer regulations to reduce specific pollutants to the atmosphere, co-firing could be a remedy. Co-firing with biomass residue brings about additional greenhouse gas mitigation by avoiding CH_4 release from the otherwise landfilled biomass. Also, biomass generally contains no sulphur [12]. Therefore, this reduces the overall pollutants released when the fuel is used, as the biomass contains lower amount of pollutants.

Coal-biomass blends need to be carefully prepared so as not to reduce the heating potential of the blends in an attempt to reduce pollutants. Cofiring a variety of biomass substance, in various ratios with coal can be used to determine a balance point, where the pollutant would cause no environmental damage, and the coal-biomass blend is still viable to release sufficient heat during combustion. Also, while it is expected that carbonization should improve a solid, the degree of such improvements on the fuel properties and pollutant needs to be determined. Therefore, this study was carried out to determine the effect of carbonization on the fuel properties of carbonized sub-bituminous Nigerian coal and biomass. As of the time this study was carried out, no literature was found on blending of Nigerian coal with biomass material to evaluate its pollution potential. This study also seeks to evaluate the environmental pollutants in Nigerian coal, and determine the effect of blending with sawdust and corn cob in reducing the pollutants as well as maintaining the coal's heating capacity.

2. Experimental

2.1 Collection and Preparation of the Coal and biomass (sawdust and corn cobs)

Samples of Sub-bituminous coal were obtained from Onyeama mine, Enugu State, South-Eastern Nigeria. The coal was sundried and later crushed with a grinding machine. Sawdust was gotten from a Saw mill, while the corn cobs were collected from Local Maize sellers. The biomass were dried, the corn cob was crushed with a mill. Both sawdust and corn cob were sieved to give a uniform particle size of less than 1mm.

Five blends each of coal-sawdust and coal-corn cob was prepared by combining coal with the biomass (sawdust and corn cob) in percentage ratios of 80:20, 60:40, 50:50, 30:70 and 10:90.

***2.2** Carbonization*

Coal-corn cob (CC) and Coal-sawdust (CS) blends in ratios 80:20, 60:40, 50:50, 30:70, 10:90 were carbonized in a muffle furnace. The blends were weighed (with strict adherence to the ratios) into porcelain crucibles and heated in a muffle furnace in the absence of air at 500^{o}C. After 1 hr., the carbonized corn cob and saw dust (CCC and CCS) were taken out and quickly transferred into a desiccator to cool.

2.3 Characterization of Subbituminous Coal and biomass

2.3.1 Proximate Analysis

Moisture content, volatile matter, ash and fixed carbon were determined using the American Society for Testing and Materials, ASTM D-3173 for coal and ASTM D5142 for biomass respectively. The volatile matter determination was slightly modified because of the high volatility of the biomass. It was determined at 600^{o}C. Calorific values were determined using a Hewlett Adiabatic Bomb Calorimeter model 1242 at the National Center for Energy Research and Development, University of Nigeria, Nsukka.

2.3.2 Ultimate Analysis

The carbon, hydrogen, sulphur and nitrogen content of the raw samples were analyzed at the Elemental Analysis Section, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland. Carbon, hydrogen, nitrogen and sulphur analysis were carried out using a Perkin Elmer 2400 series II, CHNS analyzer. The elements were measured as a function of thermal conductivity and the result obtained as a percentage by weight.

2.3.3 Fuel Ratio

The fuel ratios of the samples were determined by dividing the fixed carbon of the fuels by its volatile matter. Before calculating the fuel ratios, the fixed carbon and volatile matter values were converted to dry-ash free (DAF) basis.

2.4 Pollution Potential of Fuel Blends

The CO_2, NO_2 and SO_2 that would be emitted from the combustion of the coal-sawdust and coal-corn cob blends were estimated. A hypothetical coal-biomass fired power plant was used to derive the calculation based on some assumptions. The assumptions made are listed below:

a. A 20 MW (Twenty megawatts) power plant.
b. Complete combustion of carbon, nitrogen and sulphur into carbon (IV) oxide, sulphur (IV) oxide and nitrogen (IV) oxide respectively.

The pollution estimate (CO_2, NO_2 and SO_2) were calculated from the calorific value of the fuel.

1 MW = 1 MWh

1 MWh = 3600 MJ

A power plant of 20 MW would generate 72,000 MJ of energy.

Using coal with calorific value 24261.91 KJ/Kg

i.e 24261.91 KJ => 1 Kg

$$72 \times 10^{6} \text{ KJ} = \frac{72000}{24261.91} = 2,967.6 \text{ Kg of Coal per hour}$$

Quantity of coal required to generate 20MW of electricity in 1hour.

Elemental analysis result of coal: Carbon content- 70.04%, Nitrogen content- 2.03%, Sulphur- 1.02%.

Weight of carbon in coal = $\frac{70.04}{100} \times 2967.6 = 2078.5$ Kg of Carbon

From the chemical equation 1, below

$$C + O_2 \longrightarrow CO_2 \qquad \text{(eq 1)}$$

2078.5 kg of Carbon → ?Kg of CO_2

?Kg of CO_2 = $\frac{2078.5 \times 44}{12}$ (Molar mass of CO_2 = 44 g/mol, C = 12 g/mol) =7621.16 Kg/hr of CO_2

The above calculations were carried out on the entire fuel samples using their calorific value to derive the $CO_{2,}$ $SO_{2,}$ and NO_2 weight emitted.

ISSN: 2028-2508
CODEN: JMESC

2.5 Data Analysis

Data obtained from the proximate and ultimate analysis were analyzed using one way analysis of variance in completely randomized design (CRD) and significance was accepted at $p<0.05$. The SPSS software package 21.0 version was used for the analysis.

3. Results and Discussion

Table 1 shows the results of the proximate analysis of coal, sawdust, corn cob, coal-sawdust and coal-corn cob blends. The results showed that moisture content of uncarbonized samples was lowest in coal at 4.28% and highest in sawdust at 9.45%. Corn cob had a moisture content of 5.27%. The raw samples all had moisture content below 10%. It is expected that moisture content of good fuels should be below 15%. High moisture content of fuel is disadvantageous because it decreases system capacity and increases operational cost [13]. As expected, the biomass (corn cob and sawdust) had a higher moisture content than coal. Both coal-sawdust and coal-corn cob had similar trends, with the moisture content increasing as the biomass content (sawdust and corn cob) increased. Moisture contents of all the blends (coal-sawdust and coal corn cob) were reduced to below 4%, with the highest (3.43%) being carbonized coal and saw dust (CCS)-10:90. There was a significant difference ($P<0.05$) between the carbonized and uncarbonized blends.

The volatile matter of the fuel sample was highest in corn cob at 78.87% and sawdust at 78.15%. Coal had a volatile matter of 36.59%. Raw biomass contains high volatile matter of about 70 – 86%, which makes it a highly reactive fuel, giving it a faster combustion rate [14]. The volatile matter of the coal-sawdust blends increased from 34.83% in CS-80:20 to 71.72% in CS-10:90. This trend is repeated, with the coal-corn cob blends also. CC-80:20 had a volatile matter of 36.01% being the lowest, while the highest volatile matter is 67.31% for CC-10:90. The coal-sawdust blends have slightly higher volatile matter than the coal-corn cob blend. Generally, biomass contains about twice as much volatile matter as fossil fuel (coal), about half as much (or less) fixed carbon, and generally less ash [15]. The high volatile matter would make the fuel smoky with a lot of pollutants during combustion. The utilization of biomass residues in their natural form as fuel is quite challenging due to their low bulk density, low heat release and the excessive amounts of smoke they generate [16]. The volatile matter was also reduced significantly ($P<0.05$) by carbonization.

The ash content of the coal-sawdust blend showed a reverse trend from the moisture content. It decreased as the biomass (sawdust and corn cob) in the fuel increased: coal ash content was 16.75%, corn cob, 0.21% and sawdust 0.05%. While the ash content of coal is high, those of corn cob and sawdust were very low. The lower the ash content of the fuel, the better its quality. The ash content of a solid fuel is significant to its combustion characteristics. The slagging and fouling in boiler tubes in power plants during combustion is a result of ash. CS-80:20 had the highest ash content of 9.72%, and CS-10:90 had the lowest ash content of 0.3%. Also, CC-80:20 had an ash content of 9.2%. An increase in biomass content of the blend showed a corresponding decrease in the ash content of the coal-sawdust blend. From the result, the ash contents of the blends are all below 10% which is a positive indication of a good fuel. The ash content of the carbonized blends showed that the blend CCS-80:20 had 12.9% ash content, while CCS-10:90 had 7.1% ash content. Also, CCC-80:20 had an ash content of 14.14% and CCC-10:90, 6.8%. The percentage increase in ash content by carbonization is significant ($P<0.05$).

Where CS- Coal-Sawdust
CC- Coal-Corn cob
CCC- Carbonized Coal-Corn cob
CCS- Carbonized Coal-Sawdust

The fixed carbon of the fuels was highest in coal, at 42.38%, and lowest in sawdust at 12.35%. Corn cob had a fixed carbon content of 15.65%. The fixed carbon is the most important thermal property of the fuel, and its value can be directly related to the heating/calorific value of the fuel. Calorific value results as shown on Table 1 indicated that coal had 24261.91 KJ/Kg, corn cob had a calorific value of 15401.58 KJ/Kg and sawdust had 16184.69 KJ/Kg. The calorific value is influenced majorly by the fixed carbon content and volatile matter of the fuel. Coal had the highest fixed carbon content, hence its high calorific value. The fixed carbon content and volatile matter of corn cob and sawdust are relatively close, which may have contributed to their close calorific values. The slightly higher calorific value of the sawdust can be attributed to the lower ash content of sawdust, compared to corn cob. Generally, the coal-corn cob blends showed a higher calorific value than the coal-sawdust blends. This is most likely because of the higher percentage elemental carbon of coal-corn cob blends.

Calorific value of natural fuel can be estimated from its percentage carbon content together with other elements [17].

Table 1: Results of the proximate analysis and calorific values

S/N	Parameters Sample	Moisture Content (%)	Volatile Matter (%)	Ash (%)	Fixed Carbon (%)	Calorific Value (KJ/kg)
1	Coal	4.28	36.59	16.75	42.38	24261.91
2	Corn Cob	5.27	78.87	0.21	15.65	15401.58
3	Saw Dust	9.45	78.15	0.05	12.35	16184.69
			BLENDS			
4	CS- 80:20	5.00	34.83	9.72	50.45	23097.80
5	CS-60:40	6.04	46.76	7.71	39.49	20036.41
6	CS- 50:50	6.84	49.61	6.82	36.73	19636.66
7	CS- 30:70	7.39	64.06	5.13	23.42	18542.06
8	CS- 10:90	9.30	71.72	0.30	18.68	18986.14
9	CC- 80:20	6.53	36.01	9.20	48.26	26056.05
10	CC- 60:40	6.18	46.21	7.50	40.11	20823.48
11	CC- 50:50	6.37	52.73	6.40	34.50	18730.38
12	CC- 30:70	7.45	56.41	4.40	31.74	19446.71
13	CC- 10:90	8.67	67.31	3.20	20.82	16085.65
			CARBONIZED BLENDS			
14	CCS- 80:20	1.73	14.51	12.9	70.86	23703.07
15	CCS- 60:40	1.88	24.39	11.04	62.69	26702.14
16	CCS- 50:50	2.43	15.87	10.70	71.00	22681.86
17	CCS- 30:70	2.62	19.19	9.90	68.29	23986.35
18	CCS- 10:90	3.43	19.06	7.10	70.41	26494.43
19	CCC- 80:20	1.80	13.13	14.10	70.97	25197.17
20	CCC- 60:40	1.93	14.48	13.50	70.09	27132.22
21	CCC-50:50	2.10	15.95	13.10	68.85	26750.11
22	CCC-30:70	2.54	18.80	10.30	68.36	24877.75
23	CCC-10:90	2.84	19.87	6.80	70.49	24299.52

The fixed carbon of the carbonized blends, compared to the raw samples increased significantly after carbonization. The calorific values of the fuel sample are also on Table 1. The carbonized coal-sawdust blends had it highest calorific value blend from CCS-60:40 (26702.14 KJ/Kg) while the carbonized coal-corn cob blend had it highest calorific value blend from CCC-60:40 (27132.22 KJ/Kg). Studies have shown that after carbonization, the calorific value of biomass increase two fold because of the proximate parameters (fixed carbon, volatile matter and ash) and the elements (carbon, hydrogen and oxygen) present in the biomass [18]. It is observed that the effect of carbonization is significant ($P<0.05$) in changing the fuel proximate parameters.

The results of the ultimate (elemental) analysis in Table 2 show that raw samples had higher carbon contents, in comparison to the hydrogen, sulphur and nitrogen content determined. Coal had a carbon content of 70.04%, corn cob had 48% carbon content, and sawdust, 48.78% carbon content. Ragland et al [19], in their study found out that the carbon content of wood is between 47-53%. From the result, the biomass materials had carbon content below 50%, while coal showed the highest percentage carbon content. Fossil fuels like coal have larger carbon content because it had been fossilized through a process of diagenesis and catagenesis. The hydrogen content of the three raw materials is approximately the same. Coal showed hydrogen content of 5.32%, corn cob, 5.79% and sawdust 5.94%. Biomass materials like corn cob and sawdust contains hydrogen in the form of water (H_2O) and other volatile and tars (CH_4, C_6H_6). The carbon and hydrogen content of the sawdust agrees closely with values reported by Akowuah et al [20]. The elemental analysis also showed that coal contains 2.03% and 1.02% nitrogen and sulphur content respectively. Corn cob and sawdust contain only nitrogen, with no sulphur content detected. Corn cob has a nitrogen content of 0.89% and sawdust 1.02%. Nitrogen and sulphur in solid fuels are potential pollutants when combusted. They are capable of contaminating the environment, and affecting man’s health. The zero percent sulphur content of the biomass is an advantage; it can be blended with other solid fuels to reduce aggregate sulphur content.

ISSN: 2028-2508
CODEN: JMESC

Table 2: Results of the ultimate analysis

S/N	Elements Sample	% Carbon	% Hydrogen	% Nitrogen	% Sulphur
1	Coal	70.04	5.32	2.03	1.02
2	Corn Cob	48.00	5.79	0.89	0.00
3	Saw Dust	48.78	5.94	1.02	0.00
		BLENDS			
4	CS- 80:20	65.72	5.45	1.82	0.82
5	CS-60:40	61.54	5.57	1.63	0.61
6	CS- 50:50	59.41	5.62	1.53	0.51
7	CS- 30:70	55.16	5.77	1.32	0.31
8	CS- 10:90	50.91	5.89	1.12	0.10
9	CC- 80:20	65.23	5.42	1.79	0.82
10	CC- 60:40	61.22	5.51	1.58	0.61
11	CC- 50:50	59.02	5.56	1.48	0.51
12	CC- 30:70	51.60	5.66	1.23	0.31
13	CC- 10:90	50.20	5.75	1.0	0.10
		CARBONIZED BLENDS			
14	CCS-80:20	70.26	3.10	1.10	0.12
15	CCS-60:40	69.72	3.93	1.36	0.05
16	CCS-50:50	71.18	3.06	0.79	0.09
17	CCS-30:70	65.27	3.23	1.50	0.40
18	CCS-10:90	76.49	3.24	1.31	0.03
19	CCC- 80:20	71.01	3.66	2.36	0.28
20	CCC- 60:40	68.67	3.18	2.18	0.42
21	CCC- 50:50	74.27	3.37	2.48	0.01
22	CCC- 30:70	78.86	3.66	2.38	0.12
23	CCC- 10:90	77.12	3.72	1.31	0.15

The carbon content of the blends decreased as the coal content of the blends reduced. Coal had a larger contribution to the blends' carbon content because the coal had a carbon content of 70.04%. The carbon content of a fuel is indicative of its CO_2 releasing potential. Blending of coal and biomass is done to reduce anthropogenic CO_2 emissions, especially from non-renewable energy sources like coal. The percentage hydrogen content of the coal-sawdust blends are approximately the same, with CS-10:90 being the highest at 5.89% and CS-80:20, the lowest as 5.45%. However, the percentage nitrogen content of the coal-sawdust blends was highest in CS-80:20 at 1.82% and lowest in CS-10:90 at 1.12%. The sulphur content ranged from 0.82% in CS-80:20 to 0.1% in CS-10:90. The nitrogen and sulphur contents is indicative of the potentials of the coal to cause air pollution during combustion. Infact, the percentage sulphur in these fuel blends are low, and are not expected to lead to acid rain.

Products of carbonized coal showed structural properties similar to an ordered graphite-like component [21]. Thus, carbonization significantly increased ($P<0.05$) the carbon content of the blends. The sulphur content in the carbonized fuel was all below 1% and ranged from 0.01 to 0.42%. The result revealed that CCS-30:70 had the highest sulphur content (0.4%) and CCS-10:90 had the lowest sulphur content (0.03%). In the case of nitrogen content, the carbonized blends showed reduced sulphur content, compared with the coal's sulphur content. The blend with the highest nitrogen content is CCC-50:50 (2.48%) and the lowest is CCC-10:90 (1.31%). Nitrogen content of the coal-corn cob sample increased after carbonization. The values of the nitrogen and sulphur contents are relatively moderate and should not cause significant environmental pollution. They are below the maximum sulphur acceptable limits of 1.5 – 1.6% [22].

Table 3 shows the fuel ratios, which is an indication of the combustion characteristics of solid fuels. Coal has a fuel ratio of 1.12 which is above 1. This indicates that the fixed carbon in it is more than the volatile matter. Corn cob and Sawdust have a fuel ratio of 0.23 and 0.21 respectively.

Based on its fuel ratio, coal would burn for a longer time during combustion than both corn cob and sawdust. A fuel blend with a higher amount of volatile matter (i.e lower fuel ratio) would emit smoky pollutants than a fuel with a higher fuel ratio. Only CS-80:20 showed a fuel ratio above 1. Thus, CS-80:20 is the best fuel among the coal-sawdust fuel blends in terms of smoky pollution during combustion. The fuel ratio of the coal-corn cob blend ranged from 1.28 (CC-80:20) to 0.37 (CC-10:90). CC-80:20 showed a good quality fuel ratio above 1. The carbonized coal-sawdust blends showed a significant improvement than the raw samples. CCS-60:40 showed the lowest fuel ratio (2.24), while CCS-80:20 had the highest fuel ratio (3.58). All the blends had fuel ratio above 1. Carbonization of the fuel blends significantly ($P<0.05$) reduced the volatile matter content and increased the fixed carbon content. This is the reason for the improved fuel ratio of the carbonized fuel. Thus, a carbonized fuel blend would emit much less pollutants during combustion.

Table 3: Results of Fuel Ratios

S/N	Parameters Samples	Fixed Carbon (DAF) %	Volatile Matter (DAF) %	Fuel Ratio
1	Coal	52.90	47.11	1.12
2	Corn Cob	18.39	81.61	0.23
3	Saw Dust	17.10	82.90	0.21
		BLENDS		
4	CS-80:20	57.81	42.19	1.37
5	CS -60:40	46.37	53.64	0.86
6	CS -50:50	43.56	56.44	0.77
7	CS -30:70	29.68	70.32	0.42
8	CS -10:90	23.48	76.52	0.31
9	CC-80:20	56.13	43.88	1.28
10	CC-60:40	46.95	53.05	0.89
11	CC-50:50	40.89	59.12	0.69
12	CC-30:70	31.67	62.34	0.60
13	CC-10:90	26.75	73.25	0.37
		CARBONIZED BLENDS		
14	CCS-80:20	78.18	21.83	3.58
15	CCS-60:40	69.15	30.85	2.24
16	CCS-50:50	77.57	22.43	3.46
17	CCS-30:70	74.55	25.45	2.93
18	CCS-10:90	75.68	24.32	3.11
19	CCC-80:20	78.92	21.08	3.74
20	CCC-40:60	77.81	22.20	3.50
21	CCC-50:50	76.45	23.55	3.20
22	CCC-30:70	74.78	25.22	2.90
23	CCC-10:90	75.31	24.69	3.05

Results of the pollution potential simulation of coal, corn cob, sawdust and blends are shown in Table 4. The biomass released a greater amount of carbon (IV) oxide than the coal per hour, this is because biomass has a lower calorific/energy value compared to coal, and would need a larger quantity of the biomass (sawdust and corn cob) to produced 20 MW power capacity of the power plant. Thus, despite its lower carbon content, it still produced a higher amount of carbon (IV) oxide. This shows that the combustion of corn cob and sawdust, would contribute more carbon (IV) oxide to the environment than coal.

However it is known that the carbon (IV) oxide emitted is the same taken in by the plant during photosynthesis. The nitrogen (IV) oxide of coal, corn cob and sawdust per hour were 198 kg, 137 kg and 149 kg respectively. Coal had higher nitrogen (IV) oxide pollution, followed by sawdust and corn cob. While the value was largely moderate, the potential for the formation of nitrous oxide was based on power plant operating conditions. The coal would emit 60.5 kg of SO_2 per hour. The result showed both corn cob and sawdust would not emit any sulphur (IV) oxide. This is because they do not have any sulphur content. The combustion of these fuels aid in reduction of SO_2 pollution to the environment.

The coal-sawdust blend with the highest CO_2 emission per hour is CS-60:40 (8104.80 kg) and the lowest is CS-10:90 (7074 kg). The result showed that the CO_2 emission values of coal-sawdust blends was a relative average of raw coal and sawdust. The calorific values of the fuel have an impact on the CO_2 emission of the fuel since it is measured, per hour (energy consumed) basis. A fuel with high calorific value would have moderate CO_2

emission per hour, depending on it carbon content. Table 4 also shows the nitrogen (IV) oxide and sulphur (IV) oxide of the coal-sawdust blends.

Table 4: Pollution estimate of the fuels and their blends

S/N	Parameters Sample	CO_2 (Kg/hr)	NO_2 (Kg/hr)	SO_2 (Kg/hr)
1	Coal	7618.00	198.00	60.50
2	Corn Cob	8224.10	137.00	-
3	Sawdust	7952.00	149.00	-
		BLENDS		
4	CS-80:20	7560.00	185.40	50.40
5	CS-60:40	8104.80	190.80	43.20
6	CS-50:50	7972.80	183.30	36.00
7	CS-30:70	7812.00	167.76	24.05
8	CS-10:90	7074.00	138.24	7.20
9	CC-80:20	6606.00	162.40	45.00
10	CC-60:40	7754.40	179.28	42.16
11	CC-50:50	8316.00	186.48	39.60
12	CC-30:70	7002.00	149.56	22.90
13	CC-10:90	8236.00	146.88	8.88
		CARBONIZED BLENDS		
14	CCS-80:20	7815.60	109.44	7.27
15	CCS-60:40	6890.00	120.50	2.69
16	CCS-50:50	8272.00	82.80	5.60
17	CCS-30:70	7180.00	147.60	23.99
18	CCS-10:90	7614.00	117.00	16.20
19	CCC-80:20	7437.60	221.04	15.95
20	CCC-60:40	6681.60	189.72	22.29
21	CCC-50:50	7329.00	218.88	0.54
22	CCC-30:70	8366.00	224.08	6.94
23	CCC-10:90	8377.20	127.52	8.88

Where CS- Coal-Sawdust
CC- Coal-Corn cob

The SO_2 and NO_2 pollution potential decreased in the blends from CS-80:20 to CS-10:90. The blend with the highest SO_2 is CS-80:20 (50.4 kg/hr). The decline in sulphur (IV) oxide content in the blends as sawdust content increase is because sawdust has no sulphur, hence, it reduces the aggregate sulphur content. The coal-corn cob blend with the highest CO_2 emissions was CC-50:50 (8316 kg/hr). The fuel blend with the lowest emission is CC-80:20 (6606 kg/hr). The kilogrammes of NO_2 and SO_2 emissions per hour respectively for all the coal-corn cob blends are CC-80:20 (162.4), (45), CC60:40- (179.28), (42.16), CC-50:50 (186.48), (39.6), CC-30:70- (149.56), (22.90), CC-10:90 (146.88), (8.88). The result shows that coal-corn cob blends have a higher nitrogen (IV) oxide emission than the coal-sawdust blends. While the average CO_2 and SO_2 gases released from the coal-corn cob blend are lower than those released from coal and coal-sawdust blends. In an experimental analysis, the co-firing of coal and bio-waste had no adverse effect on boiler efficiency but reduced SO_2 emissions [23].
The carbonized blends showed an irregular pattern in coal-sawdust blends for both SO_2 and $NO_{2.}$ CCS-30:70 showed the highest nitrogen (IV) oxide, and sulphur (IV) oxide values (147.6 and 23.99 kg/hr). While the blend with the lowest nitrogen (IV) oxide is CCS-50:50 (82.8 kg/hr), the blend with the lowest sulphur (IV) oxide value is CCS-60:40 (2.69 kg/hr). Overall, the results revealed a significant reduction in the nitrogen (IV) oxide that would be emitted from raw coal or sawdust. Carbonization therefore reduces the quantity of obnoxious gases in solid fuels. The coal-corn cob blend with the highest CO_2 emissions was CCC-10:90 (8377.20 kg/hr). The fuel blend with the lowest emission is CC-80:20 (6606 kg/hr). The coal-corn cob blends showed close emission pattern to the coal-sawdust blends. The kilogrammes of CO_2 emission per hour was influenced by the calorific value of the individual fuels. CCC-80:20 (221.40), (15.95), CCC-60:40 (189.72), (22.29), CCC-50:50 (218.88), (0.54), CCC-30:70 (224.08), (6.94), and CCC-10:90 (127.52), (8.88). The result shows that coal-corn cob blends have a higher nitrogen (IV) oxide emission than the coal-sawdust blends. While the average CO_2 and

SO_2 gases released from the coal-corn cob blend are lower than those released from coal and coal-sawdust blends.

Conclusion

This study has been able to authenticate the efficacy of pretreatment by carbonization as a means of improving solid fuel properties. Beyond the fuel properties, carbonization also reduced the quantity of polluting elements (sulphur and nitrogen) in the blends; this would lead to a reduced sulphur (IV) oxide and nitrogen (IV) oxide pollution. Blending of coal with sawdust and corn cob improved certain fuel properties. The ash content was reduced in both coal-sawdust and coal-corn cob blends. The proximate analysis and fuel ratios of both coal-sawdust and coal corn cob blends were very close, though the coal-corn cob blends showed a slightly higher average calorific value than the coal-sawdust blends. The pollution estimate revealed the coal-corn cob blends to be a better range of fuel, because they would emit averagely, lower amounts of CO_2, NO_2 and SO_2. Further studies on pollution potentials of other Nigerian coal types should be carried out.

Acknowledgements-The authors are grateful to the National Centre for Energy Research and Development (NCERD), University of Nigeria, Nsukka for assisting in the collection of the coal samples. Technical assistance of the Laboratory staff of NCERD is also gratefully acknowledged.

References

1. Demirbas M.F., Balat M., Balat, H., *Energy Conver. and Manag*. 50 (7) (2009) 1746-1760.
2. Van derStelt M.J.C., Gerhauser H., Kiel J.H.A., Ptasinski K.J., *Biomass Bioenergy*, 35(9) (2011) 3748-3762.
3. Sonibare OO., Ehinola OA., Egashira R., KeanGiap L., *J. Appl Sci*, 5 (2005) 104-107.
4. Adedosu TA., Adedosu HO., Adebiyi, F.M., *J. Appl. Sci.*, 7(20) (2007) 3101-3105.
5. Adekunle JO., Ibrahim JS., Kucha EI., *Bri. J. of Appl. Sci. & Technol.* 7(1) (2015) 114-123.
6. Baonongbua D., Soponpongpiapat N., Wasananon S., *Journal Sci Technol MSU.* 32 (1) (2013) 73-83.
7. Sui J., Xu X., Zhang B., Huang C., Lv J., *Energy and Power Engineering*, 5 (2013) 1-5. doi:10.4236/epe.2013.54B001.
8. Sabeen AH, Norzita N., Zainura ZN., *J. Mater. Environ. Sci.* 7 (5) (2016) 1819- 1834.
9. Joseph KO., Labunmi LJ., Sustainable Energ & Environ., 4(2013) 77-84.
10. Bello RS., Onilude MA., Adegbulugbe TA. *International Letters of Chemistry, Physics and Astronomy*, 54 (2015) 88-97.
11. Emodi NE., Kyung-Jin B., *Renewable and Sustainable Energy Reviews*, 51 (2015) 356–381.
12. Sami M., Annamalai K., Wooldridge M., Co-firing of Coal and Biomass Fuel Blends. *Progress in Energy and Combustion Science*, 27 (2001) 171–214.
13. Jauro A., LAP Lambert Academic Publishing, Saarbrucken, 2011.
14. Loo S.V., Koppejan J., Earthscan, London, 2008.
15. Jean-Francois H., U.S Department of Agriculture, Forest Service, 1982.
16. Amaya A., Medero N., Tancredi N., Silva H., Deiana C., *Bioresour. Technol*. 98(8) (2007) 1635–1641.
17. Demirbas A., Mechanism of Liquefaction and Pyrolysis Reactions of Biomass. *Energy Conser. Manag*. 41(2000) 633-646.
18. Sugumaran, P., Seshadri, S., Evaluation of selected biomass for charcoal production. *J. of Sci. and Ind. Res*. 68 (2009) 719-723.
19. Ragland K.W., Aerts D.J., Baker A.J., *Bioresource Technol.*, 37 (1991) 161-168.
20. Akowuah J.O., Kemausuor F. Mitchual S.J., *Int. J. of Energy and Environ. Eng.* 3 (2012) 20.
21. Kuznetsov P.N., Kamenskii E.S., Kolesnikova S.M., Kuznetsova L.I., *Solid Fuel Chemistry.* 48(1) (2014) 51-57.
22. Mason D.M., Gandhi K., *American Chem Soc Div of Fuel Chem.* 25 (1980) 235–245.
23. Zuwala J., Sciazko M., *Biomass Bioenerg*. 34 (2010) 1165-1174.

(2016) ; http://www.jmaterenvironsci.com