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BY-PRODUCT FROM PYROLYSIS OF TAR-SAND IN BLEND WITH GRAY-KING ASSESSED NIGERIAN COALS FOR COKE PRODUCTION

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ABSTRACT

Thermochemical decomposition of Ondo tar-sand was carried out at a temperature of between 190–250°C in a constructed metal retort, and a yield of 66.66 % bitumen was obtained. Some important parameters of coal for blend simulation, such as the rheological and agglomerating properties of coal samples from – Garin Maiganga (GMG), Chikila (CHK), Lamza (LMZ), Shankodi-Jangwa (SKJ), Afuzie (AFZ) were determined by Gray-King assay test to assess their suitability for blending in coke making. The results showed that all the coals had poor thermoplastic properties that cannot agglomerate on heating because of their low level of fluidity, even though SKJ had an appreciable coke yield of 82.60 % with coke type C indicating that it was weakly coking. Thereafter, formulation of binary blend of coal-bitumen by weight (10 % bitumen and 90 % pre-heated coal samples at about 150 °C) was carried out. And the feasibility of the blend for industrial coke production was investigated by physico-chemical analysis, which revealed that the coking properties of the blend had been improved: Gieseler fluidity/plastic property in dial division per minute (DDPM) for LMZ = 76; CHK = 15; AFZ = 37; GMG = 18 and SKJ = 390, which might produce metallurgical coke with good chemical and mechanical properties.

Keywords: Bitumen, Blend, Coal, Coke, Physico-chemical, Rheological and agglomerating properties.

Contribution/ Originality

This study is one of very few studies which have investigated the feasibility coal-bitumen blend for production metallurgical coke. It was found that: pyrolysis is a vital tool in processing of tar sand into bitumen; and the bitumen improved the thermo-plastic properties of coal to cokeable level.

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1. INTRODUCTION

1.1. Background Information

Pyrolysis is a thermochemical decomposition of organic material at elevated pressure and temperatures in the absence of oxygen. It involves the simultaneous change of chemical composition and physical phase, and is irreversible. It can be carried out in an open and closed system, resulting in formation of volatiles and char [1, 2]. Pyrolysis involves the simultaneous change of chemical composition and physical phase, and is irreversible. Pyrolysis is a case of thermolysis, and is most commonly used for organic materials, being, therefore, one of the processes involved in charring. The pyrolysis of wood, which starts at 200 – 300 ^{o}C (390 – 570 ^{o}F), occurs for example in fire where solid fuel is burning or when vegetation comes in contact with lava in volcanic eruption. Pyrolysis is usually the first chemical reaction that occurs in the burning of many solid organic fuels, like wood, cloth, paper, and some kinds of plastic. In a wood fire, the visible flames are not due to combustion of the wood itself, but rather of gases released by its pyrolysis. The flame-less burning of a solid or the combustion of the solid residue (char or charcoal) left behind by pyrolysis is called smouldering [3]. In general, pyrolysis of organic substances produces gas and liquid products and leaves a solid residue richer in carbon content, termed. Extreme pyrolysis, which leaves mostly carbon as the residue, is called carbonization. Pyrolysis conditions may influence the fluidity and swelling behaviour of coal [4].

The process is used heavily in the chemical industry, for example, to produce charcoal, activated carbon, methanol, and other chemicals from wood, to convert ethylene dichloride into vinyl chloride for making polyvinyl chloride (PVC), to produce coke from coal, to convert biomass into syngas and biochar, to turn waste into safely disposable substances and for transforming medium-weight hydrocarbons oil into lighter ones like gasoline. These specialized uses of pyrolysis may be called various names, such as dry distillation, destructive distillation or cracking. Pyrolysis also plays an important role in several cooking procedures, such as baking, frying, roasting, toasting, grilling, and caramelizing [3]. Pyrolysis has been assumed to take place during catagenesis, the conversion of buried organic matter to fossil fuels [3, 5].

Pyrolysis differs from other high-temperature processes like combustion and hydrolysis in that it usually does not involve reactions with oxygen, water, or any other reagents. In practice, it is not possible to achieve a completely oxygen-free atmosphere in any pyrolysis system, and hence a small amount of oxidation occurs. Pyrolysis is also a processing technology that will encourage commercial production of bitumen from tar sand. Oil yields from tar sand are in the range of 80 to 89 % of total organics at 400 ^{o}C. Thus, the optimum pyrolysis temperature and residence time of tar sand appears to be about 400 ^{o}C and 40 minutes respectively [6]. Although the chemical processes occurring in tar sand during pyrolysis are most likely numerous and complex, the overall conversion can be viewed simply as given below:

$$\text{Tar sand} = \text{oil/bitumen} + \text{gas} + \text{coke} \qquad (1.1)$$

The tar sand upon heating is converted into three products: oil/bitumen, gas and coke. For more understanding this view requires definition of terms. The bitumen is the total native organic portion of tar sand that is soluble in liquid aromatic e.g. benzene, toluene, etc; Oil is the sum of all liquid products condensable at 0 °C, that volatilizes from the heated tar sand material; gas is the total non-condensable volatile product at 0 °C, that is evolved from the heated tar sand; and coke is the benzene/ethanol insoluble, nonvolatile carbonaceous material remaining with less sulphur, nitrogen, etc after bitumen decomposition [7].

Plasticity refers to the melting and bonding behavior of the coal, and the knowledge of the plastic properties of coal is necessary for a fundamental understanding of coal behaviour and has practical application to the carbonization of coal. Within a limited range of rank, coals soften on heating and re-solidifies as the temperature increases. Concurrent with this phenomenon, thermal decomposition occurs and gas evolves. The fundamental components of coal that are responsible for plastic characteristics are usually obtained by liquefaction (particularly solvent extraction) and through Gray-King assay test. By studying the extract obtained from these processes, knowledge can be gained about the original coal structure [8] and the physical properties and chemical nature of such components may lead to more dependable method of classifying coals and hence utilization.

During the heating of coal an unstable intermediate phase, called metaplast is formed after the moisture is driven from the coal. The metaplast is responsible for the plastic behaviour of coal. On further heating a cracking process takes place in which tar is vaporized and non-aromatic groups are split off. This cracking process is accompanied by re-condensation and formation of semi-coke, and finally coke [9]. This paper is aim at obtaining bitumen that can be used as an additive in blend formulation for production of metallurgical coke by pyrolysis of tar sand. The thermoplastic properties of the formulated blend would also be investigated to determine its viability in the coke making.

2. MATERIALS AND METHODS

2.1. Materials

The materials used for this study were five different coal samples collected from Garin Maiganga (GMG) of Gombe state; Chikila (CHK) and Lamza (LMZ) of Adamawa state; Shankodi-Jangwa (SKJ) of Nassarawa state; Afuzie (AFZ) of Edo state and a sample of Ondo tar sand (OTS) from Ondo state, all in Nigeria.

2.2. Methodology

2.2.1. Pyrolysis of the Tar Sand Sample

An iron facility of rectangular shape (30 cm x 12 cm x 15 cm) was constructed having one end tapered and covered with 1.0 mm diameter wire sieve size of 0.8 mm thickness for filtration. It has four stands tilted downwards at an angle of 25 degrees towards the tapered side (Figure 1).

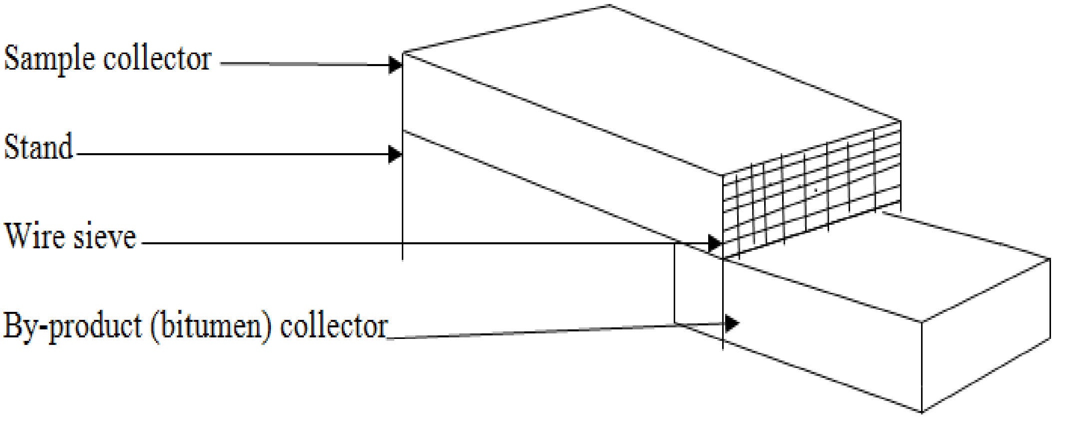

Figure-1. Scheme of pyrolysis

Procedure: Tar sand sample (5.7 kg) was placed into the facility and was heated from the bottom using a Bunsen burner. The heating was done at a temperature range of about 190 °C to 250°C (monitored by a pyrometer), for a period of 3 hours, leading to the complete melting of the sample. The by-product (bitumen) dripped through an embedded sieve which served as a filter. At the end, 3.8 kg of bitumen was collected into a metal container, and kept for binary blend formulation.

2.2.2. Blend Formulation

The preheating of the samples was carried out before blend formulation. Coal sample (9 kg) was put in a retort, then placed into an oven and heated to a temperature of 150 °C for about 1 hour. The coal sample was then taken out and mixed with 1 kg of bitumen in porcelain mortar using pestle for stirring the mass to ensure homogeneity giving 10 % by weight bitumen binary blend.

2.2.3. Physico-Chemical Analysis of Coal and Binary Blend Samples

The physico-chemical analysis determines plastic properties of the organic substance. The standard plasticity tests: crucible swelling number (ASTM, 1992 – D720-83) [10] and Gray-King Assay test of the coal samples [11] and Gieseler plasticity analysis (ASTM, 1992 – D2639-89) [10] of the blends were carried out.

3. RESULTS AND DISCUSSION

3.1. Results

3.1.1. Agglomerating Properties

Table 1 shows the physico-chemical properties of the coal samples, while Figure 2 shows the result of the major coking properties (% coke yield, % tar yield and crucible number) of the coals. The AFZ and SKJ coals had C coking power; LMZ, GMG_B and GMG_{A3} coals had B coking power while CHK coal had the least coke-type of A. The SKJ coal had the highest coke yield of 82.60 % and 14.40 % tar yield, followed by AFZ coal with 57.80 % coke and 15.60 % tar yield. LMZ,

GMG_B and GMG_{A3} coal samples had 18.80 % coke and 13.80 % tar yield; 17.80 % coke and 16.40 % tar yield, and 11.60 % coke and 13.40 % tar yield respectively. The CHK coal recorded no coke yield with the least tar yield of 2.40 %. SKJ recorded a crucible number of 3, both LMZ and AFZ coal sample exhibited a crucible number of 1, while the rest recorded a crucible number of 0.

Table-1. Results of Gray-King assay test and Free Swelling Index (FSI) of the coal samples

S/N	Detail of parameter	Detail of coal samples					
		LMZ	CHK	GMG_B	GMG_{A3}	AFZ	SKJ
1	Coking power	B	A	B	B	C	C
2	Coke yield (g)	0.94	0	0.89	0.58	2.89	4.13
3	Coke yield (%)	18.80	0	17.80	11.60	57.80	82.60
4	Tar + water yield (g)	0.69	0.12	0.82	0.67	0.78	0.72
5	Tar + water yield (%)	13.80	2.40	16.40	13.40	15.60	14.40
6	Crucible number	1	0	0	0	1	3

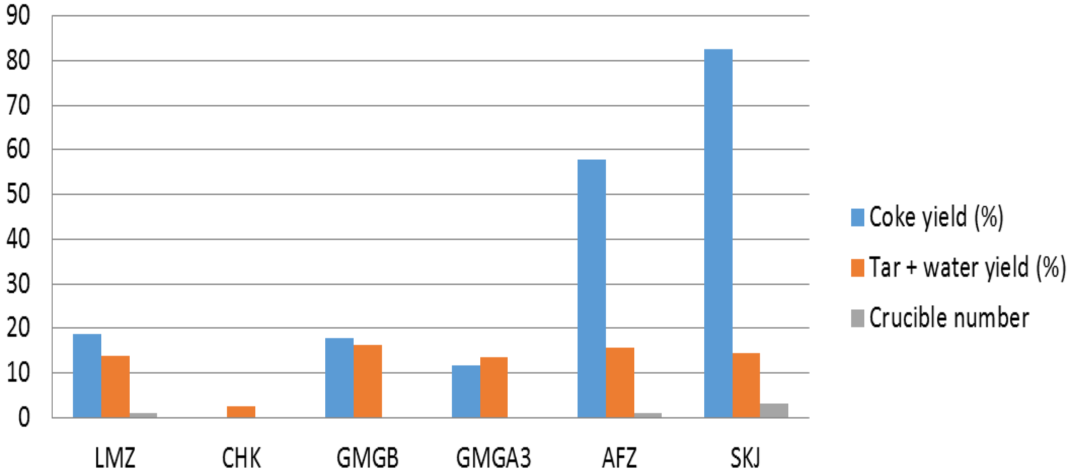

Figure-2. Composition of the major coking properties

3.1.2. Rheological Properties of the Binary Blend

Figure 3 shows the results obtained by Gieseler plastometric analysis of the coal-bitumen blends. The rheological characteristic values like the softening temperature, re-solidification temperature and maximum fluidity of LMZ, CHK, AFZ, GMG_B and SKJ coal-bitumen binary blends were improved by the addition of the bitumen and it was observed that the extent of the thermo-plasticity follow suit of the parent coal. SKJ blend still maintained the best rheological characteristic values: softened at a temperature of 358 °C, attained maximum fluidity of 390 dial division per minute at a temperature of 470 °C and finally re-solidified at a temperature of 477 °C. The temperature range, which is the region between the initial softening and re-solidification temperature of coal, was 119 °C. The LMZ and AFZ blend critical rheological properties are comparatively moderate with maximum fluidity in dial division per minute of 76 and 37, and temperature range (°C) of 87 and 91 respectively. The GMG_B blend has maximum fluidity

(DDPM) of 18 and temperature range of 75 (°C), closely followed by CHK blend with the least thermo-plastic properties of 15 DDPM fluidity and 62 (°C) temperature plastic range.

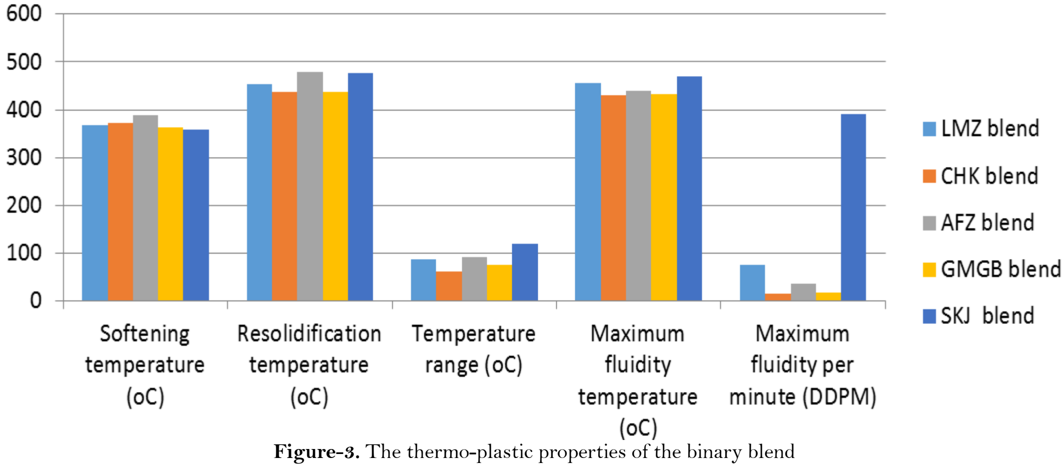

Figure-3. The thermo-plastic properties of the binary blend

3.2. Discussion

3.2.1. Agglomerating Properties of the Coals

Agglomeration is the tendency of a coking coal to be fused into a rounded mass when heated and exhibit caking and swelling characteristics which are physical changes which can be determined by Gray-King assay as well as free swelling test. Most coals with agglomerating properties are in the bituminous rank. All coals undergo chemical changes when heated, but not all coals exhibit physical changes.

Gray-King assay test is considered as low temperature carbonization of swelling coal that is used to assess the coking characteristics of coals by comparing the coke obtained from the test with a standard profile: A if the residue remained is powder; B is non-coking; C and D are weakly coking; E, F and G are medium coking while G_1, G_2 ……. to G_{10} are strong coking coals that swell [11].

The Gray-King assay determines the percentage of tar (condensed volatiles) and coke yield by weight (to assess the extent of fluid level and conversion of coal to coke). The tar yield is of paramount importance in the selection of coals suitable for low temperature carbonization which produces smokeless fuel. It has been widely posited that the yield of tar is closely related to the volatile matter and moisture of the coal: that the tar yield decreases with increase in volatile matter and moisture content. This assertion is confirmed in these coal samples as the tar yields are generally poor, which implies low rheological properties; cannot on their own be used for either smokeless or metallurgical coke production without bonding substance (additive). And this creates room for coking technology, utilization of the coals of which is in line with this study. The bitumen obtained from the processing technique (pyrolysis) which has a good yield of 66.66 % was used as blend additive to improve the coking properties of these poor coals. The low tar (plastic property) exhibited by these coals is of advantage for use in combustion as energy source because of the low caking tendency.

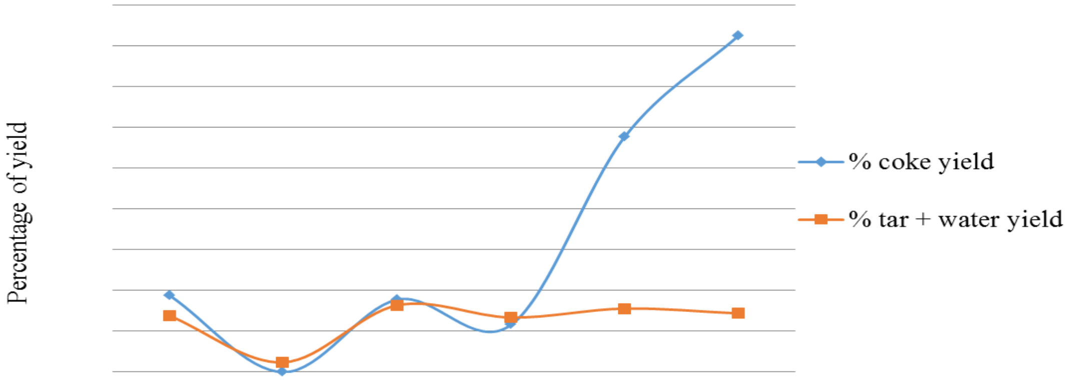

Figure-4. Plasticity and cokability of coal samples

Among the coal samples only AFZ and SKJ had C coking power of the Gray-King assay, indicating that they are weakly coking, suitable for blending in coke making. In terms of coke yield, only SKJ coal has appreciable conversion ability to the extent of 82.60 % (Figure 4). The LMZ, GMG_B and GMG_{A3} coals had B coking power indicating that they are non-coking and may only be used in formed coke and smokeless briquette production. CHK coal had least or no coking property as the residue remained is powder. Gray-King assay coking power and free swelling crucible number are important tools for ISO classification which are used as sub-group and group parameter respectively.

Free swelling index (FSI) gives a measure of the extent of swelling of a coal and its tendency to agglomerate when heated rapidly. This swelling property determines whether a coal would cake or not. The crucible swelling number depends on both rank and coal type [12, 13]. The free swelling index standard profile has increasing swelling index number by half units from 1.0 – 9. Coal with a high index of ≥ 6.5 [14] is said to be coking while that with low value is said to be free burning. Meyers [13] posited that if a single coal is to be used for coke manufacture, an intermediate value of 4 – 6 is appropriate. Of all the coal samples, only SKJ coal has a value of 3 with appreciable caking properties, concurring with Gray-King coke type as weak coking. However, Reduction of the ash content in further study may improve the potency of the coal inherent vitrinite and hence increase of the cake-ability of the coal. Decrease in ash contents has been reported to cause an increase in caking indices of Indian high ash coals. The reduction of the ash content of the Indian Bhojudih coal from 21 % to 15 % caused an increase in FSI from 2.5 to 3.33 [15].

3.2.2. Rheological/Thermoplastic Properties of the Binary Blend

Thermoplastic properties are dependent on petrographic maceral composition of a coking coal. For example, liptinite macerals exhibit very high fluidities, while inertinite macerals do not. Vitrinites are intermediate between these two groups. Thermoplastic properties are desirable for coke making and liquefaction, but they are undesirable for combustion and gasification because a combustor or gasifier can be choked by the resulting fused mass [16]. Based on the above assertion, the low and no or little fluidity of SKJ and other coal samples respectively is in conformity to their maceral group variation and level. Plasticity range at °C and maximum fluidity in dial division per minute are key factors used to determine coal or blend to be used for coke production of good strength [17]. In blend option with non-coking coal, the coke quality can be increased through pre-carbonization techniques like coal charge briquetting, stamping, pre-heating and drying to obtain maximum bulk density Obaro [18]. Arslan and Kemal [19] also posited that blends for metallurgical coke production is that the coals must complement each other. The blend should be characterized by volatile matter between 24–26 % (daf), a mean vitrinite reflectance of 1.2 % and maximum fluidity between 200 – 1000 DDPM. Also, the fluidity of the coals must affect the fluidity of the blends in a positive manner and widen the plastic range. In compliance to this position, the coal charge samples of this work which have low and little fluid levels were pre-heated, blended with bitumen and briquetted to improve the coke quality. During the blending process at elevated temperature (about 150 °C), it was observed that strong physical interaction occurred between the coal and bitumen particles (i.e. carbon and inert) as a result of bond formation that could either be isotropic or anisotropic (of which can be confirmed by optical microscopy in further study), producing black polished partially caked blend. Heavy evolution of volatiles was also noticed that just escaped helpless into the atmosphere. In comparison tendency, blending of the components at room temperature was carried out, and no physical interaction was noticed. The addition of the bitumen to this coal samples has indeed augmented and improved the Gieseler fluid properties of the weakly coking coals to cokeable grade for coke making, particularly the LMZ and SKJ coals which have appreciable fluidity of 76 and 390 dial divisions per minute respective (Figure 5). A cokeable blend that can produce coke of metallurgical grade is required to exhibit Gieseler maximum fluidity of greater than 300 DDPM [20]. The bitumen also upgraded the low grade coals such as CHK, AFZ and GMG for smokeless fuel production.

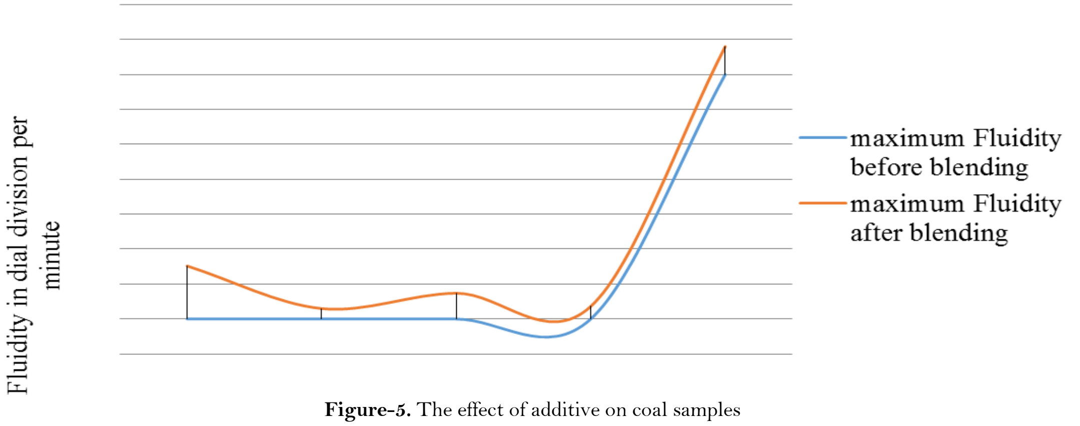

Figure-5. The effect of additive on coal samples

It was observed that the maximum fluidities of binary blend samples were found not to increase linearly with the carbon content of the coals (since coal quality depends on the carbon content as posited by many researchers), rather the fluidity differs between carbon content of individual coal blend, which may be due to variation of characteristic parameters of the coal deposits: SKJ coal has and intermediate carbon content value of 82.51 % [21] with the highest fluidity. However, percent dilatation of LMZ (8.5 %) and SKJ (20.5 %) coal sample strongly suggest that it generally increases as the coefficient index or G-value increases (LMZ = 0.92 and SKJ = 0.99), which is in agreement with Adeleke, et al. [22]. It also observed that only SKJ coal has a large temperature range, suggesting that it cokeable and may accommodate a wide range of coals whose temperature range overlap for coking technology to produce coke.

4. CONCLUSION

The characteristic low thermoplastic properties (low tar yield) of the coals indicate their low caking tendency, and so they are adjudged to be ideal for coal-fired electric power generation plant.

The physico-chemical analyses of these coal samples indicate that only SKJ coal has appreciable agglomerating potential (coking power of C, crucible number of 3 and coke yield 82.6 0 %). These parameters revealed that SKJ has coking potential and it is of weakly-coking in which reasonable quantity of it can go into blend formulation with even coking coal of high fluidity to produce industrial coke.

The pyrolysis of tar sand at about 250 °C, employed as a processing technique has a high yield of 66.66 % bitumen, which can be adopted on commercial scale in term of coke and briquette production. The sieve size of 1.0 mm diameter can filter out satisfactory pure bitumen. And also, facility for trapping the volatiles can be installed for recovery of useful chemicals.

REFERENCES

[1] M. G. Alonso, A. G. Borrego, D. Alvarez, and R. Menendez, "Pyrolysis behaviour of pulverized coals at different temperatures," *Journal of Fuels*, vol. 78, pp. 1501–1513, 1999.

[2] M. J. Fabianska, L. Lewinska-Preis, and R. Galimska-Stypa, "Changes in organic matter of selected miocene lignites and embedded sediments caused by microbial desulphurization," *Journal of Fuels*, vol. 94, pp. 586 – 595, 2012.

[3] Integrated Synthetic Fuel Incorporated [ISFI], "Pyrolysis." Available http://www.isfuel.com/18.html [Accessed October 24, 2015], 2009.

[4] T. K. Gale, C. H. Bartholomew, and T. H. Fletcher, "Decrease in the swelling and porosity of bituminous coals during devolatilization at high heating rates," *Journal of Combustion and Flame*, vol. 100, pp. 94 – 100, 1995.

[5] A. Jauro, "Characterization of benue trough coal extracts," Unpublished Ph. D Thesis, Abubakar Tafawa Balewa University, Bauchi, 2007.

[6] C. Y. Cha, M. Duc, and C. J. Hogan, "Pyrolysis method with production oil recycling." Available Pyrolysismethodwithproductoilrecycling-westernresearch [Accessed February 27, 2015], 1991.

[7] C. A. Lechner, M. E. Findley, and A. I. Liapis, "Kinetics of the pyrolysis of utah tar sands," *Canadian Journal of Chemical Engineering*, vol. 65, pp. 487–493, 2009.

[8] A. G. Mamman, "Analysis of liquefaction and carbonization products of Nigeria's sub-bituminous coals," Unpublished M.Sc. Thesis, Abubakar Tafawa Balewa University, Bauchi, 2000.

[9] CoalTech – Consultancy in Coal Utilization Technology, "Plastic properties." Available Hp%20Sys/Documents/DOWNLOADS/Plastic%20Properties.htm [Accessed June15, 2012], 2007.

[10] American Society for Testing and Materials, *Annual book of ASTM standard; petroleum products, lubricants and fossil fuels* vol. 05. Easton, MD, U.S.A: American Society for Testing and Materials, 1990.

[11] Bureau of Indian Standards, *Indian standard (IS - 1353) methods of test for coal carbonization - caking index, swelling number and gray-king assay*. New Delhi, India: Printrade, 1993.

[12] M. A. Diez, R. Avarez, and C. Barriocanal, "Coal for metallurgical coke production: Prediction of coke quality and future requirement for coke making," *International Journal of Coal and Geology*, vol. 50, pp. 389 – 412, 2002.

[13] R. A. Meyers, *Encyclopedia of physical science and technology*, 3rd ed. vol. 3. London: Academic Press, 2001.

[14] National Metallurgical Development Centre (NMDC), *Data bank of raw materials for the metallurgical industry*. Kaduna, Nigeria: AB Enterprises Limited, 2008.

[15] L. Parthasarathy, R. P. Sharma, and N. B. Gash, "Coal selection and preparation steps towards improving coke quality in sail," in *Proceedings of 2nd International Cokemaking Congress*, London, 1992, pp. 152 – 171.

[16] A. W. Scaroni, "Coal utilization – encyclopaedia Britannica." Available http://www.britannica.com/EBchecked/topic/122944/coal-utilization [Accessed April 6, 2015], 2015.

[17] M. Castro-Diaz, S. M. Kokonya, C. Barriocanal, and C. E. Snape, "Introducing biomass in coking blends without impairing fluidity and coke strength," in *Proceedings of 2013 International Conference on Coal Science and Technology ICCS&T*, State College, USA, 2013, pp. 1208 – 1218.

[18] D. M. Obaro, *Maximum utilization of Nigerian non-coking coals in the blend for the production of high quality metallurgical coke.* Lagos, Nigeria: UNDP (United Nations Development Programme)/TOKTEN (Transfer of Knowledge through Expatriate Nationals Programme) Consultant, 1997.

[19] V. Arslan and M. Kemal, "The effects of inert matters and low volatile coal addition on the plasticity of high volatile Zonguldak coals," *Journal of the South African Institute of Mining and Metallurgy*, vol. 106, pp. 199 – 204, 2006.

[20] A. O. Adeleke, R. S. Makan, and S. A. Ibitoye, "An evaluation of the coking characteristics of polish coking coals for coke making with the non-coking Nigerian coals," *Journal of Petroleum and Coal*, vol. 49, pp. 1-6, 2007.

[21] S. A. Ryemshak and A. Jauro, "Proximate analysis, rheological properties and technological application of some Nigerian coals," *International Journal of Industrial Chemistry*, vol. 4, pp. 1-7, 2013.

[22] A. A. Adeleke, R. S. Makan, S. Ryemshak, and K. M. Oluwasegun, "An evaluation of the significance of some laboratory coking tests in predicting the cokeability of coals," *Pacific Journal of Science and Technology*, vol. 13, pp. 97 – 104, 2012.

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