Combustion Kinetics of Shankodi-Jangwa Coal

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ABSTRACT: *The lack of comprehensive data on the fuel properties of newly discovered coal deposits in Nigeria has hampered the prospective utilisation for power generation. Consequently, this study is aimed at characterising the physicochemical and thermokinetic properties of Shankodi-Jangwa (SKJ) coal recently discovered in Nassarawa state, Nigeria. The results indicate that SKJ comprises 40.50% fixed carbon, 43.34% volatile matter, and 2.36% sulphur with a higher heating value (HHV) of 27.37 MJ kg^{-1}. Based on this HHV, SKJ was classified as high-volatile B bituminous coal. Thermal analysis of SKJ under oxidative thermogravimetry (TG) at multiple heating rates revealed that SKJ is highly reactive and thermally degradable below 1000°C. Kinetic analysis using the Flynn-Wall-Ozawa model for conversions α = 0.05–0.90 revealed the activation energy to range from E_a = 113–259 kJ mol^{-1}, with the frequency factor ranging from A = 2.9 × 10^{13}–1.5 × 10^{23} min^{-1} and a range in R^2 = 0.8536–0.9997; the average values of these ranges are E_a = 184 kJ mol^{-1}, A = 9.2 × 10^{23} min^{-1} and R^2 = 0.9420, respectively. The study highlighted fuel property data vital for modelling and designing future SKJ coal power generation.*

Keywords: Combustion, thermal, kinetics, Shankodi-Jangwa, coal, Nigeria

1.   INTRODUCTION

Coal utilisation for electricity generation currently accounts for 40% of global power consumption. According to the International Energy Agency (IEA), the global annual demand for coal currently exceeds 2.6% of global energy usage and will account for 14.5% of the global energy mix by 2035. This will be evident in developing countries with large coal reserves beset by socioeconomic and energy poverty.[1] Since energy is crucial to poverty alleviation, developing countries require access to cheap and sustained energy supply to spur socioeconomic growth and sustainable development.

Nigeria has one of the largest coal reserves in Africa, estimated at 2.75 billion metric tonnes and containing large unexploited deposits.[2] The recent discoveries of large coal deposits in Garin Maiganga (GMG), Afuze (AFZ) and Shankodi-Jangwa (SKJ) have reignited the prospects of coal power generation in Nigeria.[3,4] However, the lack of comprehensive scientific data on coal properties and other sociotechnical factors have hampered utilisation. Furthermore, current research on Nigerian coals is mainly focused on rheological,[3,5] petrographic,[6–8] mineralogical,[9–10] geological and geochemical[11–13] properties, although some research groups have investigated coal conversion[14,15] and hydrocarbon potential.[16,17]

Consequently, there is inadequate empirical data on the physicochemical and thermokinetic properties of Nigerian coals vital for classification (ranking) and assessing their suitability for utilisation. Because the vast majority of coal-fired power plants utilise pulverised coal combustion (PCC) technologies for power generation, it is imperative to investigate the combustion kinetics of Nigerian coals. Therefore, this study is aimed at investigating the physicochemical properties of SKJ coal in addition to its thermokinetic properties under oxidative (combustion) conditions. Thermal degradation kinetics will be examined based on the Flynn-Wall-Ozawa model.

2.   EXPERIMENTAL

2.1   Materials and Methods

The coal sample was acquired from SKJ village in Nassarawa state, Nigeria. The sample was pulverised and sifted to obtain particles below 250 μm. Next, the pulverised coal was characterised by ultimate, proximate and bomb calorimetric analyses. Thermal decomposition behaviour was investigated in the Perkin Elmer TGA 4000 Thermogravimetric (TG) analyser by heating 8–10 mg of sample in an

alumina crucible from 35°C–1000°C at β = 10, 20, 30°C min^{-1} under an ultra-pure oxygen (O_2) purge gas flow rate of 20 ml min^{-1}. Subsequently, the resulting thermograms were analysed using the Pyris 6 TGA software to determine oxidative temperature profiles of SKJ. Next, the parameters of activation energy, E_a, and frequency factor, A, were deduced using the Flynn-Wall-Ozawa kinetic model for conversion α = 0.05 to 0.90.

2.2   Kinetic Model Theory

The thermal decomposition of SKJ coal under combustion (oxidative) conditions can be represented by the general equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α represents the degree of conversion, t represents time, k(T) is the rate constant dependent on temperature, T is absolute temperature, and $f(\alpha)$ is the function of the reaction mechanism occurring during thermal degradation of the material. Consequently, the degree of conversion, α, can be expressed as:[18,19]

$$\alpha = \frac{m_i - m_t}{m_i - m_\infty} \tag{2}$$

where m_i represents the initial sample mass, m_t is the sample mass at time t, and m_∞ is the final sample mass at the end of the reaction. According to the Arrhenius equation, the temperature dependent rate constant, k(T), can be defined as:

$$k(T) = A\exp\left(\frac{E_a}{RT}\right) \tag{3}$$

where A is the frequency factor (min^{-1}), E_a is activation energy (kJ mol^{-1}), R is the universal gas constant (J mol^{-1} K^{-1}) and T is absolute temperature (K), respectively. Consequently, the rate of sample degradation and the effect of the rate-dependent constant on the mechanism of reaction can be obtained by substituting Equation 3 into Equation 1 as given by:

$$\frac{d\alpha}{dt} = A\exp\left(\frac{E_a}{RT}\right)f(\alpha) \tag{4}$$

By considering and introducing the effect of the heating rate, β, defined as:

$$\beta = \frac{dT}{dt} \tag{5}$$

The thermal degradation of SKJ coal sample can be represented by the equation:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{6}$$

After separation of the variables, Equation 6 can be expressed as:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) dt \tag{7}$$

By integrating Equation 7, the conversion function, $g(\alpha)$, which describes the thermokinetic decomposition of the SKJ coal at a specific heating rate, can be expressed as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dt \tag{8}$$

This is the fundamental equation for analysing the parameters of decomposition kinetics; activation energy, E_a, and the frequency factor of materials, A. By introducing the Doyle's approximation,[20] the solution to Equation 8 can be deduced, thereby presenting the basis for the isoconversional Flynn-Wall-Ozawa kinetic model given by:

$$\ln(\beta) = \ln\left(\frac{AE_a}{Rg_\alpha}\right) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \tag{9}$$

Hence, the kinetic parameters E_a and A can be deduced by plotting $In\ (\beta)$ against $(1/T)$. The E_a can be calculated from the slope $-1.052\ E_a/R$ (where $R = 8.314$ J mol^{-1} K^{-1}), while A can be calculated from the intercept $In\ [AR/E_a]$.

3.   RESULTS AND DISCUSSION

3.1   Physicochemical Fuel Properties

Table 1 presents the physicochemical properties of SKJ coal in dry basis (db). For comparison, the results of this study have been compared with values for SKJ coal reported by Ryemshak and Jauro.[3]

Table 1:   Physicochemical fuel properties of SKJ coal in wt% dry basis.

Sample name	Element symbol	This study wt% dry basis (db)	Ryemsak and Jauro wt% dry basis (db)
Carbon	C	75.21	82.51
Hydrogen	H	6.60	4.52
Nitrogen	N	1.49	1.31
Sulphur	S	2.36	1.63
Oxygen	O	14.36	10.03
Atomic hydrogen-carbon ratio	H/C	0.09	0.05
Atomic oxygen-carbon ratio	O/C	0.19	0.12
Higher heating value (MJ kg^{-1})	HHV	27.37	27.22
Moisture	M	5.05	1.33
Volatiles	VM	43.34	30.09
Ash	A	16.15	17.37
Fixed carbon	FC	40.50	52.26

As can be observed in Table 1, the results of SKJ do not contrast markedly from the reported values in literature. However, the observed difference in elemental composition is due to other researchers employing Seyler's formula[21] as opposed to using a more precise elemental analyser. The results also demonstrate that SKJ coal contains sufficient constituent elements for thermochemical conversion.

The fixed carbon content is used in conjunction with the calorific value when assigning a coal ranking.[22] The high percentage of fixed carbon, 40.50%, may place the coal in the high volatile bituminous B rank, with high potential for coke formation. However, the high compositions of *N*, *S*, and *A* potentially present challenges due to the likelihood of producing NOx and SOx gaseous emissions, as well as the possibility of undergoing agglomeration during conversion. Consequently, power generation from SKJ may require clean coal technologies (CCT) integrated with carbon capture and storage (CCS).

The higher heating value (HHV) is the most important property for the classification (rank) and assessment of the potential of coals.[21] The HHV for SKJ coal is 27.37 MJ kg^{-1}, which is slightly higher than the value of 27.22 MJ kg^{-1} that has been reported in literature[3,23] but lower than other Nigerian coals such as Lafia-Obi (30.30 MJ kg^{-1}), Enugu (32.90 MJ kg^{-1}) and Okaba (29.70 MJ kg^{-1}). [24] In addition, based on HHV and VM,[21] SKJ can be classified as high-volatile B bituminous agglomerating coal.

3.2   Thermogravimetric (TG) Analysis

Figure 1 presents the burning profile (oxidative thermal) of SKJ coal at different heating rates. The burning profile of coal is vital in assessing its reactivity, combustibility and suitability for combustion systems.[25] The plots clearly displayed the reverse S – weight loss curves typically observed for thermally decomposing carbonaceous materials under non-isothermal conditions.[26,27]
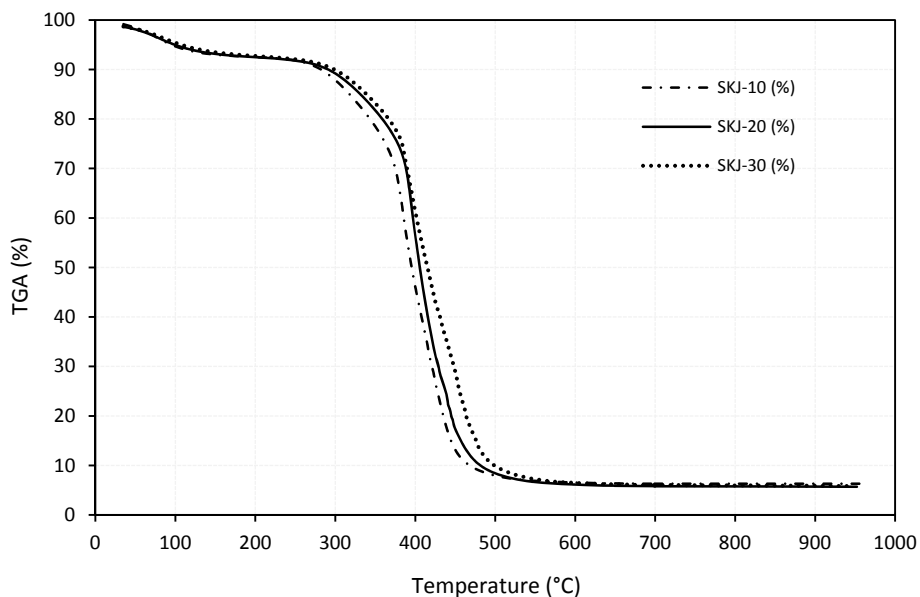

Figure 1:   TG plots for SKJ Coal at different heating rates.

The TG plots observably shifted to the right hand side (higher temperatures) due to the thermal-time lag which occurs during TGA at different heating rates. Consequently, the heat transfer and reaction time is limited at higher heating rates, causing the shift in TG curve and temperature profiles.[28] Hence, the results demonstrate that the change in heating rate influenced the weight loss of SKJ during oxidative conditions.

The DTG plots for SKJ combustion in Figure 2 revealed the typical endothermic peaks for the derivative weight loss of decomposing materials during TGA.[26,27]
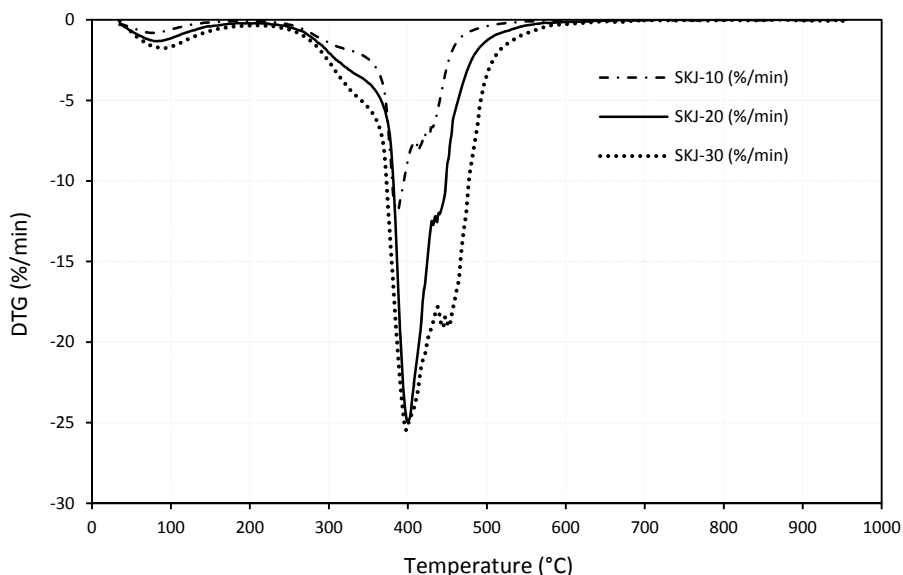

Figure 2:   DTG plots for SKJ coal at different heating rates.

Similarly, the effect of heating rate was also observed in the DTG plots for SKJ coal. This indicates that the varying heating rate resulted in an increase in the size and orientation of the DTG plots, which highlights the influence of temperature on SKJ coal degradation. Furthermore, the plots also revealed two endothermic peaks for the degradation of SKJ at 10 and 20°C min^{-1} as was also reported for other Nigerian coals.[25] However, the DTG plot at 30°C min^{-1} indicated two major peaks and one minor peak, which may indicate a higher rate of reactivity of SKJ.

The weight loss peaks for SKJ coal from 30°C–200°C can be ascribed to drying (loss of moisture and mineral hydrates) during thermal degradation.[29] The weight loss observed during the drying of SKJ coal ranged from 5.95%–6.65%, which is in good agreement with the determined moisture content (5.05%) for SKJ coal presented in Table 1. Moisture can significantly influence coal classification, processing and thermal efficiency during conversion.[21]

The weight loss observed for SKJ from 200°C–600°C can be attributed to the devolatilisation of organic matter. The weight loss observed during this stage ranged from 85.95%–86.34%, which suggests that weight loss may not be due only to devolatilisation (as the loss of volatile matter, VM, was only 43.34%) but also to the presence of other components in the coal composition.

The combustibility of SKJ was evaluated from the peak decomposition temperature, T_{max}, of the DTG plots. The T_{max} is the temperature at which maximum weight loss occurs and denotes the ease of ignition, reactivity and coal rank; a lower T_{max} indicates a higher rank and thus greater ease of burning or coal degradation.[25,29,30] The T_{max} for SKJ ranged from 387°C–400°C from 10°C–30°C min^{−1}, which is similar to values of 384–451°C reported for Indonesian coals.[31] However, Sonibare and co-workers reported T$_{max}$ values of 445°C–500°C for lignite and sub-bituminous Nigerian coals,[25] which confirms the higher bituminous rank of SKJ.

3.3   Combustion Kinetic Analysis

The FWO model was used to determine the activation energy, E_a, and frequency factor, A, of SKJ coal combustion. The E_a and A were obtained from the slope and intercept of the plot of *In (β)* against (1/T) at multiple heating rates. Figure 3 presents the kinetic plots for SKJ combustion for conversions $\alpha = 0.05$–0.90.
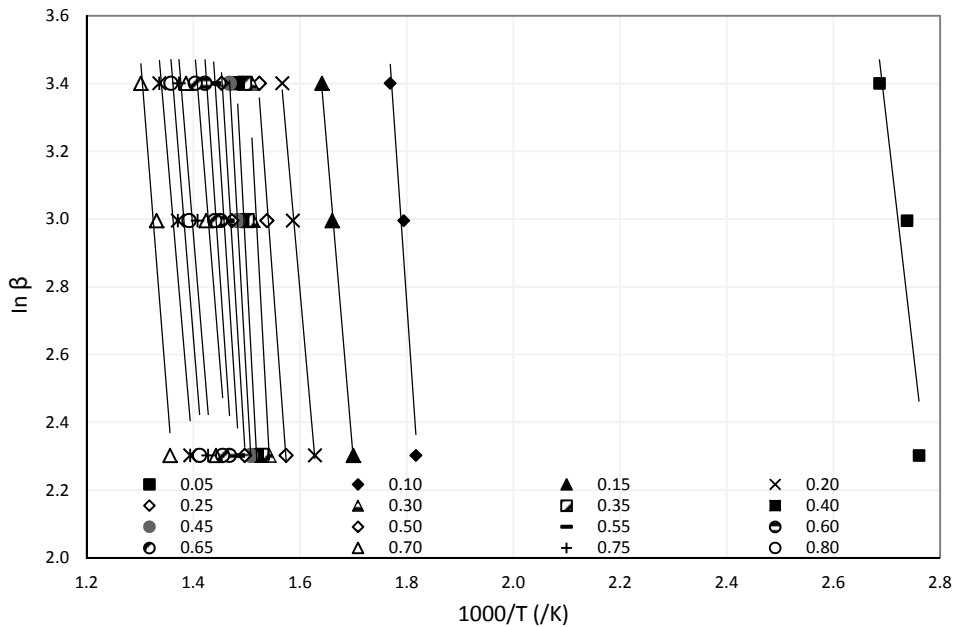

Figure 3: Kinetic plots for SKJ coal combustion.

The values for E_a and A for SKJ coal conversion are presented in Table 2. The E_a values ranged from 113.13–259.12 kJ mol^{−1}, while A ranged from 2.89×10^{13} to 1.49×10^{23} min^{−1} with correlation values of $R^2 = 0.8536$–0.9997.

Table 2: Kinetic parameters for SKJ coal combustion using FWO method.

(a)	R^2	E_a (kJ mol^{-1})	Frequency Factor, A (min^{-1})	A 10°C min^{-1} (min^{-1})	A 20°C min^{-1} (min^{-1})	A 30°C min^{-1} (min^{-1})
0.05	0.8660	113.13	3.28×10^{18}	3.28×10^{19}	6.55×10^{19}	9.83×10^{19}
0.10	0.9667	188.36	1.83×10^{20}	1.83×10^{21}	3.67×10^{21}	5.50×10^{21}
0.15	0.9978	154.52	9.68×10^{15}	9.68×10^{16}	1.94×10^{17}	2.90×10^{17}
0.20	0.9977	147.86	6.59×10^{14}	6.59×10^{15}	1.32×10^{16}	1.98×10^{16}
0.25	0.9904	177.01	7.52×10^{16}	7.52×10^{17}	1.50×10^{18}	2.25×10^{18}
0.30	0.9076	242.15	9.34×10^{21}	9.34×10^{22}	1.87×10^{23}	2.80×10^{23}
0.35	0.9428	259.12	1.49×10^{23}	1.49×10^{24}	2.98×10^{24}	4.47×10^{24}
0.40	0.9823	243.98	6.60×10^{21}	6.60×10^{22}	1.32×10^{23}	1.98×10^{23}
0.45	0.9997	229.96	3.58×10^{20}	3.58×10^{21}	7.16×10^{21}	1.07×10^{22}
0.50	0.9926	211.33	8.60×10^{18}	8.60×10^{19}	1.72×10^{20}	2.58×10^{20}
0.55	0.9499	200.52	8.94×10^{17}	8.94×10^{18}	1.79×10^{19}	2.68×10^{19}
0.60	0.9128	190.14	9.76×10^{16}	9.76×10^{17}	1.95×10^{18}	2.93×10^{18}
0.65	0.8536	162.30	5.01×10^{14}	5.01×10^{15}	1.00×10^{16}	1.50×10^{16}
0.70	0.8855	152.35	6.36×10^{13}	6.36×10^{14}	1.27×10^{15}	1.91×10^{15}
0.75	0.9099	158.64	1.47×10^{14}	1.47×10^{15}	2.93×10^{15}	4.40×10^{15}
0.80	0.9099	162.21	2.02×10^{14}	2.02×10^{15}	4.04×10^{15}	6.06×10^{15}
0.85	0.9291	153.11	2.89×10^{13}	2.89×10^{14}	5.77×10^{14}	8.66×10^{14}
0.90	0.9623	165.46	1.12×10^{14}	1.12×10^{15}	2.25×10^{15}	3.37×10^{15}
	0.9420	184.01	9.19×10^{21}	9.19×10^{22}	1.84×10^{23}	2.76×10^{23}

The average E_a, A and R^2 values were 184.01 kJ mol^{-1}, 9.19×10^{23} min^{-1} and 0.9420, respectively. These E_a and A values are significantly higher than those reported for the combustion of other Nigerian coals.[25] Sonibare and co-workers reported E_a values in the range of 68–90 kJ mol^{-1} and A values between 1.1×10^1–6.7×10^2 min^{-1} for lignite and sub-bituminous coals.[25] Evidently, this difference is due to the coal rank and reactivity, which differs when compared to the bituminous SKJ coal examined in this study.

4.   CONCLUSION

The study presented the physicochemical and thermokinetic decomposition properties of the newly discovered Shankodi-Jangwa (SKJ) coal. The results indicate that SKJ contains high contents of fixed carbon, volatile matter and sulphur. Based on its heating value and volatile matter, SKJ was classified as

high-volatile B bituminous agglomerating coal. Thermal analysis revealed the high reactivity, combustibility and thermally degradability of SKJ below 1000°C. The average decomposition was 94.05% for multi-heating rate combustion from 35°C–1000°C. The activation energy, E_a and frequency factor, A, were determined using FWO model kinetics. The average values of Ea, A and R^2 were 184.01 kJ mol^{-1}, 9.19 × 10^{23} min^{-1} and 0.9420, respectively. The results presented will be vital in the modelling and design of future combustion systems for SKJ coal.

5.   ACKNOWLEDGMENT

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