

THERMAL DECOMPOSITION OF LAFIA OBI BITUMINOUS COAL DURING GASIFICATION

1. INTRODUCTION

Derivation of energy from coal as an alternative energy source is mostly through thermal decomposition as this is predominantly the major way coal can be converted to gaseous and liquid fuels to derive energy from it. Coal is a readily combustible compound consisting more than 70% by volume and 50% by weight of carbonaceous material. It is for these reasons that a lot of attention has been drawn in recent past on coal as an alternative source of energy for power production and for heating purposes.

Lafia-obi bituminous coal is found in the Middle Benue Trough (MBT) of Nigeria and there is sufficient literature to justify its use as fuel for gasification.

The thermal decomposition of coal can be carried out using different thermo-analytical methods such as thermogravimetry (TG), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and gasification. These methods have become invaluable in the study of thermal decomposition and other thermal behaviours of many solid fuels.

There is quantitative and qualitative work on the suitability of Lafia-obi coal for power generation and other metallurgical purposes but little on the thermal decomposition of Lafia-obi coal during gasification. This work therefore looks at the combustion characteristics and thermal behaviour of Lafia-Obi bituminous coal during gasification process.

2. LITERATURE REVIEW

Baker (2012) wrote on the components and operations of fixed bed gasifier. He also looked at the factors influencing the efficiency of fixed bed biomass gasifier systems. In the reactor, biomass is heated by combustion. Four chemical processes can be distinguished, namely drying, pyrolysis, /carbonization, oxidation and reduction reactions. Combustion occurs in the oxidation zone. Introduced air in the oxidation zone consists beside oxygen and water vapour, inert gases such as nitrogen and argon. These inert gases are considered to be non-reactive with fuel constituent and play no role in the reaction. The oxidation takes place at the temperature of 700-2000°C. Heterogeneous reactions take place between oxygen in the air and solid carbonized fuel (charcoal), producing carbon monoxide, hydrogen and methane.

Barbara *et al.* (2021) reviewed the thermal cracking, hydrocracking and slurry phase hydroconversion kinetic parameters in lumped models for upgrading heavy oils. They made valuable suggestions such as the need for more models to be developed for much more efficient conversions.

Davis and Brown (2017) studied the thermal decomposition of a bituminous coal and laid particular emphasis on the heat flux to the coal particles. Individual spheres of coal were suspended from a recording balance in a stream of hot nitrogen. To begin with, the weight record showed a constant rate of loss and in the final part the rate of weight loss decreased with time. The initial constant rate of weight loss was found to be directly proportional to the heat flux and was zero at about 400° C.

Inesa *et al.* (2018) did a Kinetic Study of Thermal Decomposition and Co-Combustion of Straw Pellets with Coal. The main goal of their study is to assure a more effective use of CO₂ neutral fuel (wheat straw) for cleaner energy production with reduced greenhouse carbon emissions by partially replacing a fossil fuel (crashed coal) with a renewable one. The work combined

experimental study and mathematical modelling of the processes developing during the co-combustion of straw pellets and crashed coal, aimed at assessment of the influence of the elemental composition and heating values of the mixture components on the main gasification/combustion characteristics, heat output from the device and on the composition of the flue gas products. The experimental study of the development of main gasification/combustion characteristics involves a complex DTG and DTA analysis of straw pellets and crashed coal and an estimation of the main steps of their thermal decomposition, combustion of volatiles, char formation and burnout, thus providing a complex kinetic study of the mixture weight loss rates and of the formation of combustible volatiles (CO, H₂) at different stages of thermal decomposition of the solid fuel mixtures. A mathematical model for the combustion of volatiles (CO, H₂) downstream the combustor has been built using the MATLAB package, with an account of the CO:H₂ molar ratio variations at the inlet of the combustor and the development of exothermic reactions for the H₂ and CO combustion dependent on the changes in straw mass load in the mixture of solid fuels.

Jie *et al.* (2006) studied the thermal decomposition behaviour of lignite by pyrolysis. An in situ pyrolysis reactor combined with the Fourier transformation infrared spectrometer (PFTIR) technique was employed to study the coal structure and its thermal decomposition behaviors. The interface of pyroprobe with FTIR was designed delicately to ensure the path of the laser beam in FTIR was just 3 mm above the coal sample, so any detection information of products from coal pyrolysis would be acquired previous to the secondary reaction. The PFTIR technique can be adopted to determine the activation energy of coal pyrolysis. Lignite coal was used to evaluate this new method. The thermal decomposition behaviors of functional groups from lignite pyrolysis coincide with the first-order reaction.

Junhul *et al.* (2017) studied the effect of heating rate on thermal cracking characteristics and kinetics of Xinjiang oil sand bitumen by TG-FTIR. They concluded that the rate of heating is almost always directly proportional to thermal decomposition of the bitumen.

Kuhe (2012) investigated experimentally biomass gasification in a closed top throatless downdraft gasifier using coconut shells as fuel. The fuel properties of coconut shells and its gasification feasibility were investigated. The distinctive feature of the gasifier is that it can operate successfully on coconut shell with producer gas lower heating value of 5.95mJ/m³ and negligible clinker formation. The gasifier performed best at an equivalent ratio of 0.332 and was determined at an air flow rate of 0.00092m³/s and coconut shell consumption rate of 0.000557kg/s. From the results obtained, coconut shells were successfully used as feedstock in the gasifier which can be used as a clean fuel for rural communities in Nigeria.

Ksenia et al. (2017) studied the thermal decomposition and oxidation of coal processing waste. To assist the studies, a series of mathematical models of coal carbonization were developed. Models of the physical properties (e.g. specific heat, density, porosity and thermal conductivity) of coal during decomposition to coke were constructed in terms of the changes in the chemical composition and structure. These models of physical properties were then used to develop further models. Although the models may find more general application in studies of coal-based processes. This Paper describes the model of the chemical changes during thermal decomposition. To have sufficient generality for the applications envisaged, the model describes the kinetics of the release of the main volatile matter constituents, thereby permitting the changes in the mass and composition of the solid residue to be estimated by element balances. Correlations for the parameters of the model are derived so that predictions of volatiles evolution can be made from the coal ultimate analysis and volatile matter and the heating profile.

Littlewood and Mühlen (2017) investigated coal gasification reactions and concluded that it encompasses a series of reaction steps that convert coal containing carbon, hydrogen, and oxygen, as well as impurities such as nitrogen and sulphur into synthesis gas and other forms of hydrocarbons. This is accomplished by introducing a gasifying agent, which can be oxygen, carbon dioxide, steam, air, and/or a mixture of two or more, or all of the above into a reactor vessel containing coal feedstock where the temperature, pressure and flow pattern are controlled.

Lyrshchikov *et al.* (2016) researched the thermal decomposition of coal and coal-enriched wastes. The thermokinetic parameters of the thermal decomposition of coal and its processing wastes (filter cake) used in the preparation of coal–water and organic coal–water fuels were determined experimentally by thermogravimetry in an inert atmosphere. The dependence of the thermokinetic parameters of decomposition on the coal’s metamorphic stage was established; the activation energy of decomposition varies from 39.1 kJ/mol (lignite) to 109.4 kJ/mol (anthracite). There is practically no difference between coal and its processing wastes in the thermokinetic parameters of thermal decomposition. The results provide the starting point for an experimental database that may be used in modeling the ignition and combustion of coal and its derivatives: coal–water and organic coal–water fuels.

Mehran *et al.* (2015) made a kinetic study and thermal decomposition behaviour of lignite coal. A thermogravimetric analyzer was employed to investigate the thermal behavior and extract the kinetic parameters of Canadian lignite coal. The pyrolysis experiments were conducted in temperatures ranging from 298K to 1173K under inert atmosphere utilizing six different heating rates of 1, 6, 9, 12, 15, and 18Kmin⁻¹, respectively. There are different techniques for analyzing the kinetics of solid-state reactions that can generally be classified into two categories: model fitting and model-free methods. Historically, model-fitting methods are broadly used in solid state kinetics and show an excellent fit to the experimental data but produce uncertain kinetic parameters especially for nonisothermal conditions. In this work, different model-free techniques such as the Kissinger method and the isoconversional methods of Ozawa, Kissinger-Akahira Sunose, and Friedman are employed and compared in order to analyze nonisothermal kinetic data and investigate thermal behavior of a lignite coal. Experimental results showed that the activation energy values obtained by the isoconversional methods were in good agreement, but Friedman method was considered to be the best among the model-free methods to evaluate kinetic parameters for solid-state reactions. These results can provide useful information to predict kinetic model of coal pyrolysis and optimization of the process conditions.

Maria *et al.* (2017) studied the thermal cracking of coal residue: kinetics of asphaltene decomposition. An asphaltenic residue from a synthetic crude obtained by coal liquefaction was processed by thermal cracking. The kinetics of formation of oil + gas and coke (toluene-insoluble) from conversion of the asphaltenic fraction were determined. A three-lump model is proposed which considers parallel reactions for oil + gas and coke formation. Conversion data fitted second-order kinetics throughout for asphaltene conversion and oil + gas and coke formation. Delplot analysis indicated that under the most severe experimental conditions, asphaltenes and oils participated in secondary coke-forming reactions which are not included in the model. The activation energies ranged from 63.94 to 86.13 kJ mol⁻¹, the highest being that for asphaltene conversion. The highest asphaltene conversion, 55.9 wt%, was obtained at 475°C and 40 min reaction time. At short reaction times, the asphaltenic fraction converted to coke (~30 wt%) was much less than that converted to oil (~70 wt%) at the four temperatures used, whereas at long reaction times this trend was reversed, especially at 475°C. Structural analysis showed lower aromaticity and higher H/C and N/C ratios in the oil from the products than from the feed.

Popoola and Asere (2013) conducted a research on the combustion characteristics of Lafia-obi coal in fluidized Bed combustor. They used appropriate American Society for Testing and materials (ASTM) standards to obtain proximate and ultimate Analysis of samples of Lafia-obi coal. They reported that data obtained from combustion Lafia-obi coal is useful in application where energy generator is critical.

Seeker *et al.* (1981) studied the thermal decomposition of pulverized coal. The physical, thermal and chemical behaviour of pulverized coal particles during thermal decomposition were examined for five coal types. Particles were injected axially into a lean (35% excess air) and analysed. Devolatilisation occurred between 10 to 75 msec and large soot particles were formed.

Wanzl (1988) studied the chemical reactions in thermal decomposition of coal. The results of an extended experimental program on coal pyrolysis and hydrolysis in different equipment were analysed and the present knowledge about the modeling of coal pyrolysis reactions is reviewed. The limits of the applicability of the model of independent parallel decomposition reactions were discussed in terms of the coaction of primary and secondary reactions and the influence of process parameters like pressure and type of gas atmosphere, heating rate, and residence time.

Wei *et al.* (2019) looked at thermal Decomposition Model and Its Reaction Kinetic Parameters for Coal Smoldering with the Use of TG Tests in Oxygen-depleted Air. Smoldering of coal is a considerable source of danger in coal mines because it can lead to a gas explosion, which can cause heavy casualties. Their work investigated the apparent smoldering reaction model of coal and its kinetic parameters, which are needed to study smoldering fire in a closed fire area of a coal mine. A series of thermogravimetric tests at different oxygen concentrations were performed, and the change in the pyrolysis and oxidation reaction with the oxygen concentration was analyzed. It is concluded that the apparent reaction model of smoldering coal should include a three-step pyrolysis reaction (i.e., drying, depolymerization, and polycondensation) and a five-step oxidation reaction (i.e., oxidation of coal, semi-coke, and three types of char). A generic algorithm was used to identify the optimal kinetic parameters of the smoldering reaction. It is determined that in atmospheres with different oxygen concentrations, coal has different kinetic parameters. When studying smoldering fire in a closed fire area of a coal mine, it is suggested to adopt the kinetic parameters of the smoldering reaction in a 1% oxygen concentration atmosphere.

Williams and Larson (1996) undertook a study to establish the impact of fuel properties on gasification. They used Wyodak coal and cellulose to conduct the study. A Pyrolysis experiment was conducted. Nearly complete de-volatilisation of cellulose was found to occur below 500°C.

Only about 40% of coal was de-volatilised and only after heating to close to 900°C. The slower weight loss with coal reflects its inherently lower thermochemical reactivity and much higher fraction of weight remaining even after heating to 900°C reflects the much lower content of volatile components in coals compared to cellulose.

Wu and Chein (2015) modeled biomass gasifier with preheated air at high temperature. Effects of reaction temperature, moisture content, and preheated air temperature on biomass gasification performance such as syngas composition, cold gas and second law efficiencies, and caloric value, were studied based on a thermodynamic equilibrium model. The results indicated that the contents of the combustible species (H₂, CO, and CH₄) in the product syngas control the gasification performance. Low amounts of combustible species were reported for the conditions of high reaction temperature, high moisture content, and low preheated air temperature. Using H₂ content as a reference, there appears an optimum reaction temperature. With biomass moisture content exceeding a certain amount, reduction in combustible species was found. Although the gasification performance can be enhanced by using preheated air.

Yuji and Masayuki (2006) analysed the thermal decomposition behaviour of coals using high temperature infrared spectrophotometer system. Thermal decomposition behaviors of coals were measured by high temperature infrared (IR) spectrophotometer system. It is important to know the thermal decomposition process of coals in order to understand their chemical properties during coking reaction. The coal samples were heated from 50°C up to 600°C in an N₂ ambience, and IR spectra were measured in transmission mode every 10°C. The changes of IR spectra as sample heating were well obtained. Especially, high temperature region over 400°C, a peak intensity based on aliphatic C-H bond was decreased. While a peak intensity based on aromatic C-H bond was stable below 600°C. At least, two types of hydroxyl groups were obtained in coal samples. One type is dehydrated below 400°C, another type is stable in high temperature region over 400°C. Additionally, dehydrate behavior of kaolin which is mineral matter in coal was well

obtained. Dehydrate temperature of kaolin is used for good monitor of sample temperature. The high temperature IR system can measure functional groups during high temperature region, and useful for analysis of thermal decomposition behavior of coals.

Zhang et al. (2020) had some study on In Situ catalytic cracking of coal tar by plasma preparation of the pyrolysis coke catalyst. A two-stage pyrolysis fixed bed was used, and the vapor-modified pyrolysis coke was used as a carrier. A ZHPC catalyst was prepared by plasma calcination. Gas-phase tar produced by the pyrolysis of raw coal was subjected to in situ catalytic cracking to improve tar and gas yield. The effects of plasma calcination power, calcination time, and ZnO loading on in situ cracked products were studied. The prepared catalyst was characterized by X-ray electron spectroscopy, X-ray diffraction, Brunauer–Emmett–Teller, and scanning electron microscopy. The results showed that (1) compared with traditional catalysts, the catalyst prepared by plasma has better performance; (2) the optimal calcination time of the ZHPC catalyst is 5 min, calcination power is 60 W, and ZnO loading is 10%; (3) compared with raw coal pyrolysis, the optimal ZHPC catalyst on in situ catalytic cracking tar, gas yield increased by 66.16%; the cracking rate of tar increased by 54.46%, and the content of light components increased to 60.7%; (4) in situ catalytic cracking of tar with the optimal PC, the light tar has been greatly improved, in which the light oil, phenol oil, naphthalene oil, and wash oil have increased by 93.04, 126.31, 257.28, and 108.08%, respectively. The anthracene oil and asphalt have decreased by 26.98 and 58.71%; the tar cracking rate has increased.

Zubstov (2011) conducted an experiment with air pre-heated to 1000°C when gasifying skyline coal. The resulting producer gas was found to have a heating value of about 1400kcal/m³ (5857.6kJ/m³). Without the pre-heated air, only 850kcal/m³ (3556.4kJ/m³) could be achieved. When ambient temperature air was used, the resulting low combustion temperature would prevent the reactions from reaching completion resulting in low heating value gases and low conversion efficiency. It was concluded that gasification temperature does not only affects the

product yield but also governs the process energy input. High gasification temperatures produce a gas mixture rich in H₂ and CO with small amounts of CH₄ and higher hydrocarbons.

3. MATERIALS AND METHODS

Coal samples used in this work were sourced from Lafia-Obi local government area of Nassarawa state Nigeria. The coal samples were crushed manually and sieved to particle size of about 2cm, charged to the gasifier and heated up in an updraft gasifier to a temperature of 900°C in air flow rate of 62 L/min.



Plate 1. Sized Lafia-Obi bituminous Coal.

3.1 Thermal Decomposition of Lafia-Obi bituminous coal during Gasification

Reaction kinetics of the coal thermal decomposition is a complex phenomenon as it involves a series of heterogeneous reactions of different components of the coal sample. Thermal decomposition of the coal starts from the drying zone of the gasifier to the pyrolysis zone, reduction zone through to the combustion zone. The first step, during which the coal is heated and rapidly loses hydrocarbons, tars and other volatiles, is referred to as pyrolysis or devolatilisation. This is the fastest of the three stages and does not play a major role in determining the overall kinetics of the gasification system. It does, however, affect the amount of char produced and the structural properties of this char. Therefore, it has a strong influence on the levels of conversion achievable in the gasifier. The releases of volatiles from coal can be represented by the following equation;

$$C_{m01} H_{m02} O_{m03} N_{m04} S_{m05} ASH_{m06} MOis_{m07} \rightarrow C_{m11} H_{m12} O_{m13} N_{m14} S_{m15} MOis_{m16} +$$

$$C_{m17} ASH_{m18} \quad (1)$$

Where C, H, O, N and S represent carbon, hydrogen, oxygen, nitrogen and sulphur respectively which are the major constituents of coal. Ash represent ash content while *MOis* represent the unbound water/water vapor contained in the particle.

The combustion of the released volatiles also produces much of the heat required for subsequent conversion of the char and this is the second step of the gasification process. In the third step, the resultant char undergoes heterogeneous reactions with the various gaseous species present in the gasifier. This stage produces a gas that is typically rich in CO and H₂. The reaction of char with O₂, present in the gasifier also provides the much-needed heat for the endothermic char-CO₂ and Char-H₂O reactions that continue after the O₂ has been consumed.



Plate 2. Ignition of coal in hearth zone of the updraft gasifier.

Hydrogen in the fuel reacts with oxygen in the air blast, producing steam. The combustion is described by the following chemical equations:





The gas forming reaction that takes place in the reduction zone of the gasifier are as follows:

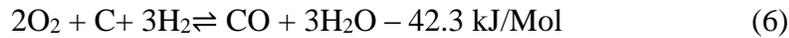
Boudouard reaction



Water gas reaction



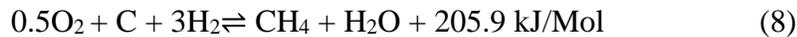
Water shift reaction



Methane production reaction



Methane production reaction



Equations 4 and 5 are the main reactions taking place in the reduction zone and they are endothermic, this results in temperature decreasing during these reactions. The hot gases and coal char coming from the oxidation zone provide the energy required for the reduction chemical reactions to take place. As these reactions proceed the temperature inside the reactor reduces progressively until it is as low as 700°C. This implies that the extent of reduction reactions depends on the amount of energy entering the reduction zone and on the heat losses from the reactor. Carbonisation is the thermal decomposition of coal fuels in the presence of 26-30% of Oxygen at temperature ranging from 450°C to 600°C. The Coal thermal decomposition can be represented by the equation:

$$\frac{d\alpha}{dt} = K(1 - \alpha)^n \quad (9)$$

Where α is the fraction of coal decomposed and is defined as

$$\alpha = \frac{w_0 - w_t}{w_0 - w_\alpha} \quad (10)$$

Where

w_0 = initial weight loss

w_α = weight after complete decomposition

w_t = weight loss after time t

From equation 9, K is the specific rate constant, n is the reaction order. K is dependent on temperature and is represented by the *Arrhenius* equation;

$$K = Ae^{\frac{-E_a}{RT}} \quad (11)$$

Where A= Arrhenius constant or collision frequency or collision factor. E_a is the activation energy of the reaction.

R is the gas constant = 8.314 kJ/kmol. K

T= absolute temperature.

Combining equation (9) and (11) and taking a first order reaction;

We have that

$$\frac{d\alpha}{dz} = Ae^{\frac{-E_a}{RT}}(1-\alpha) \quad (12)$$

From equation (11),

$$\ln K = \ln Ae^{\left(\frac{-E_a}{RT}\right)} \quad (13)$$

$$\ln(K) = \frac{E}{R} \left(\frac{1}{T}\right) + \ln(A) \quad (14)$$

Which is similarly analogous to:

$$Y = mx + c$$

A plot of $\ln K$ against $\frac{1}{T}$ shows a straight line graph with slope $\frac{E_a}{R}$ and intercept of $\ln(A)$ for a

first order equation (9) can be modified by introducing the rate of heating as;

$$\frac{d\alpha}{dt} \cdot \frac{dT}{dt} = Ae - \left(\frac{E_a}{RT}\right)(1-\alpha) \quad (15) \text{ or}$$

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right)e - \left(\frac{E_a}{RT}\right)(1-\alpha) \quad (16)$$

Where $\beta = \text{Heating rate}$

Integrating and taking logarithm, we have

$$\ln[-\ln(1-\alpha)/T^2] = \ln \frac{AR}{\beta E} - \frac{E_a}{RT} \quad (17)$$

3.2 Heat Energy Balance

Heat Input:

The heat input into the gasifier is comprised of:

1. Calorific value of coal.
2. Enthalpy of water
3. Enthalpy of steam

The heat energy input comprises the higher heating value or gross calorific value of coal feed, enthalpy of air feed (from the centrifugal blower and the supporting fan) and the latent heat of moisture in air as shown in table 3.1.

Tale 3.1: Heat input to the gasifier

Heat Input	kJ/kg	Symbol
CV (Calorific Value) of coal	31657.5	A
Enthalpy of water vapour in air	41.6	B
Enthalpy of steam	694.5	C
Total	32393.6	(A+B + C)

Heat Output:

The heat output of the gasifier is comprised of:

1. Calorific value of dry producer gas obtained from the gas analyser.
2. Sensible heat of dry producer gas obtained from the gas analyser.
3. Enthalpy of water vapour in hot gas

The heat output includes the higher heating value or gross calorific value of producer gas, the sensible heat of producer gas and the enthalpy of water vapour in hot producer gas. Heat losses include the unrealised heat of combustion, endothermic heats of reaction and heat losses from the gasifier vessel to the environment through the wall.

Table 3.2: Heat output from the gasifier

Heat Output	kJ/kg	Symbol
CV of dry PG	23597.8	D
Sensible heat of dry Producer gas	3902.8	E
Enthalpy of H ₂ O vapour in hot gas	341.4	F
Total heat output	32393.6	(A+B+C)
Heat losses	4551.6	(A+B+C) - (D+E+F)

$$\text{Cold Gas efficiency} = \frac{\text{Potential Energy of Gas made} \times 100}{(\text{Total heat input} = \text{CV of coal} + \text{sensible heat of coal,air,steam})} \quad (18)$$

$$\text{Cold gas efficiency (CGE) of the gasifier: } \text{CGE} = \frac{D}{A+B+C} \times 100$$

$$\text{Cold gas efficiency} = 23597.8 \times 100 / 32393.6$$

$$= 73\%$$

$$\text{HGE} = \frac{(\text{PE of gas} + \text{sensible heat of gas} + \text{sensible heat of water vapour} + \text{PE of tar} + \text{PE of soot} + \text{sensible heat of tar} + \text{sensible heat of soot}) \times 100}{\text{Total heat input}} \quad (19)$$

Hot Gas efficiency (HGE) of the gasifier: $HGE = \frac{D + E + F}{A + B + C} \times 100$

Hot Gas efficiency = $27842 \times 100/32393.6$

= 86 %

Thermal Efficiency = $\frac{(\text{Potential energy of gas} + \text{enthalpy of steam produced}) \times 100}{\text{Total heat input}}$ (20)

Thermal efficiency (TE): $TE = \frac{D + F}{A + B + C} \times 100$

Thermal efficiency = $23939.2 \times 100/32393.6$

= 74%

CONCLUSION

The thermal decomposition of Lafia-Obi bituminous coal during gasification involves several reaction mechanisms as highlighted in this text and obeys the Arrhenius equation which combines decomposition parameters of temperature, pressure, activation energy and weight loss in linear progression.

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