DETERMINATION OF CALORIFIC VALUES OF SOME NIGERIAN BIO-MASS SOLID MATERIALS

by

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ABSTRACT

Nigerian biomass for thermal energy generation can be classified into field wastes, such as straw and corn cob; processing by products, such as rice husk, cocoa pods and palm kernel husk; and products from the lumber industry, such as saw dust, fire wood and wood shavings. These materials are produced in sufficiently large quantities within the country to warrant a thorough study on their potential utilization as renewable energy sources.

This paper deals with the experimental determination of the calorific values of some Nigerian solid fuel materials such as rice husk, corn cob, corn grain, corn stover, saw dust, wood shavings, palm kernel husk and coal. Mixtures of these materials (1:1) were also investigated. Calorific values were determined by standard methods using the adiabatic bomb calorimeter and ultimate analysis of the biomass. The results showed that gross calorific values ranged from 19,642 KJ/kg for palm kernel husk to 13,643 KJ/kg for rice husk which compared favourably with Nigeria's sub-bituminous coal with across calorific value of 28,466 KJ/kg. Calorific values were found to be inversely dependent on moisture content of the biomass, which is significant in determining energy availability from biomass.

INTRODUCTION AND LITERATURE REVIEW

The depletion of our non- renewable petroleum energy resources has caused increased interest in renewable biomass energy resources. Crop residues, wood residues, biomass from processing industries, all have possibilities for reducing our dependence on fossil fuels. The process of mechanisation and in particular of technological advancement is a continuous one and so the efficient conversion of biomass materials to useable heat energy requires a different technology than that developed for petroleum products for the following reasons;

1. Usually the biomass material is not free-flowing and is often not as uniform as discrete particles thus complex handling and feeding equipments are required.
2. The material contains a high proportion of volatile components such as sulphur, which vaporizes rapidly and can cause smoke.
3. Many biomass materials contain silica and the ash may fuse into an adherent slag to form tar at temperatures above 800^0C.
4. The materials often contain a high amount of moisture at harvest and require natural or artificial drying before use as fuel.

Various solid fuel materials are encountered on the farm, processing industries, mining plants and in the lumber industries. The quality of these fuels is determined by the elements that make up its composition, namely, carbon (C^W), hydrogen (H^W) and volatile combustible sulphur (S^W). The procedures for determining these constituents have been standardized (BS 1016 Part 6, 1977). The higher the percentage of these elements in the biomass, the larger is the amount of heat generated upon complete combustion.

Several workers have derived empirical relationships for the calculation of the calorific value of solid fuels whose ultimate analysis is known. Such relationships are

based on the assumption that each element makes the same contribution to the calorific value as it would make if it were present in a mixture and not in chemical combination with other elements. For this purpose, the percentages of each component in the fuel is multiplied by the known calorific value of the component and the results summed together. For example, the well known Dulong formula assumes that the oxygen present combines with hydrogen as water and hence reduces the amount of combustible hydrogen, thus for low oxygen content materials.

$$L.C.V. = 338.2C + 1440H + 93S \quad (1)$$

where L.C.V. = lower calorific value KJ/kg and C,H,O,S are the respective percentages of the elements on a dry basis.

When the oxygen content is high (>10%), a more precise expression is used;

$$L.C.V.=338.2C+1442.8(H-O/8)+94.2S. \quad (2)$$

However, volatile combustible sulphur is an undesirable and even harmful component of fuels because on combustion it yields the product sulphur dioxide (SO_2), a gas of unpleasant suffocating odor which in the presence of moisture forms sulphuric acid (H_2SO4) which destroys the metallic parts of heat generator furnaces. In addition with a large content of sulphur in the fuel (3 - 4%), the sulphurous gases often communicate an odor to the material being dried especially at high moisture content.

Paddy husk, rice bran and broken rice kernels are the main by-products of the rice milling industry and the yields are 20 - 24%, 5 - 7% and 3 - 5% respectively of the total paddy milled. The average straw-to-grain ratios for wheat, barley and oats are 0.88, 0.81 and 0.94 respectively[2]. Also the mass ratio of corn cob to grain is about 0.186 at 10% moisture contents. Thus the effective utilization for industrial farmstead and feed purposes of the biomass can yield substantial financial returns to the rice industry and other production enterprises. Rice husk, for example has a number of alternative use such as absorbents, bedding material, building material component, carbon source cellulose pulp, filter material, fuels, insulation and packing material. However its relatively high calorific value of 12,186 to 15072 KJ/kg, which is over one third of that for bituminous coal, makes its use as fuel particularly attractive. Singh et al developed a rice husk fired furnace for generation of heated air. The composition of rice husk, corn cob and Nigerian coal are shown in Table 1.

In order to effectively use bio-mass solid materials as fuels, their calorific heating values have to be known. The objective of this work therefore was to experimentally determine the gross calorific values of Nigerian solid fuel materials. With such information, it would then be feasible to determine their potential contribution to the national energy requirements for grain drying, power and electricity generation and other thermal applications.

2. MATERIALS AND METHODS

The materials tested in this work ranged from agricultural wastes to fossil fuels and by-products from processing industries. These were rice husk, corn grain, corn cob, corn stover, wood shavings (hard and soft wood), saw dust, coal and palm kernnel husk. Here corn stover is taken to include stalks, leaves and husk while palm kernnel husk is the hard protective cover of the palm kernnel seed. These materials were tested up to a moisture content of 13.2 per cent wet basis (wb) and duplicate samples were used for each experimental condition. In addition some of the materials were mixed in the ratio of 1:1, in order to ascertain if any significant differences could be recorded between the pure samples and the mixtures.

Table 1: Composition of Biomass Materials for per 100 Kg

Material		Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur	Moisture	Ash
Rice Husk[4]	Weight (Kg)	39.26	4.99	32.70	1.99	0.10	3.56	17.40
	Molecular Weight	12	2	32	28	32	18	–
	Mole	3.27	2.49	1.02	0.071	0.003	0.198	–
Corn Cob[5]	Weight (Kg)	38.0	4.8	34.9	0.5	0.4	1.6	20
	Molecular Weight	12	2	32	28	32	18	
	Mole	3.17	2.4	1.09	0.018	0.013	0.09	
Coal *	Weight (Kg)	65.45	4.75	10.8	1.6	0.95	–	–
	Molecular Weight	12	2	32	28	32	–	–
	Mole	5.45	2.388	0.33	0.057	0.029	–	–

*Nigerian Coal Corporation

Generally, two broad methods are used in the experimental determination of calorific value of solid fuels. These are (1) calorimetric methods, subdivided into the adiabatic calorimeter, isothermal calorimeter and static calorimeter and (2) analytical methods based on the ultimate analysis of the fuels. When isothermal and static calorimeter are used, additional corrections are made to compensate for the heat loss to the water jacket surrounding the sample cell. These corrections can be obtained from the Regnault - Pfaundler technique as contained in the British Standard BS 1016 Part 5 of 1977[6]. In this work, the adiabatic bomb calorimeter was used.

2.1 Bomb Calorimeter Determination
(a) Brief description of equipment

In this work, we used the adiabatic bomb calorimeter model OSK 100A designed for precise determination of calorific value of solid materials. The principle of the method depends on the complete combustion of a known weight of the sample in oxygen at specified conditions in a bomb calorimeter in which there is virtually no heat loss exchanges. The equipment consists essentially of a gas- tight steel bomb which is immersed in a convection water jacket. This jacket is then placed inside an intermediate vessel which was in turn centrally located inside an outer jacket. The inner and outer water jackets are equipped with stirrers driven by the same motor. The bomb contains a receptacles in which the samples are placed and receptacle for the introduction of oxygen and application of heat for ignition. The sectional view of the adiabatic bomb calorimeter is shown in Fig. 1.

(b) Preparation of sample and Experimental Procedure.
The experimental conditions were as shown in Table 2. The materials to be tested were crushed and sieved through a screen with 0.2 mm perforations. The known masses of the sieved samples, usually 1 gm, were weighed with an

electronic balance sensitive to 1 mg and wrapped with a thin rice paper of known heat capacity, after which the rolled racer was tied with the ignition wire connected to the electrodes.

The moisture content of the samples under test was determined by oven methods at 100°C. Determination of calorific value on a dry weight basis was done by drying the samples to constant weight. They were then ground and sieved for the test as described above. For each sampled test condition, duplicate determinations were made.

After the samples were placed in the bomb, oxygen was admitted through a reducing value until the pressure was 25 to 30 bar. The bomb was lowered into the inner vessel containing a known quantity of water and water was introduced into the outer jacket from an overhead inlet until it overflowed. The stirrers were then started to stabilise the water temperature in the two vessels. This was taken as the temperature before ignition. The ignition button was then pressed and the heat generated within the bomb was quickly conducted to increase the temperature of water in the inner vessel. Temperatures were read with certified Beckman thermometers at 1 minute intervals until steady state was attained and the readings were taken for a further 3 minutes. The steady temperature was taken as the maximum temperature from which the temperature rise for the sample under test was obtained. The Beckman thermometers were graduated 0.001°C. scale divisions and encorporate a Lup having a scale of 0.001°C. They were equipped with a viewer which has a magnification of X5 for reading temperatures to the desired accuracy and correction factors were provide with the equipment.

The calorific value (KJ/kg) of the samples under test is calculated from the temperature rise of the VI in the calorimeter vessel and the mean effective heat capacity of the system. Allowances are made for the heat released by the ignition wire and where appropriate, for heat 10, from the calorimeter to the outer jacket. The equation used for their calculation is as follows.

Calorific Values (KJ/kg) =

$$\frac{((Ee + W_1)\, TR - C)}{s} \times 4.1868 \quad (3)$$

where We = water equivalent of the calorimeter (581 g).

W_1 = Quantity of water in the inner vessel, g

TR = temperature rise, °C.

C = correction factor for rice paper and ignition wire (154 cal)

S = weight of sample, g.

The calorific values obtained from eqtn. (3) are the gross values at constant volume, and this is defined as the number of heat units measured as being liberated when unit mass of solid fuels is burned in oxygen in a bomb under standard conditions. Since most fuels contain hydrogen, some steam will be formed during the subsequent cooling process and the last heat used to vaporise the water is not usually available as heat source. Thus Payne[7] recommended only 93 per cent bomb calorimeter values should be considered as useful energy for thermal processes such as grain drying.

3. EXPERIMENTAL RESULTS AND DISCUSSION.

Following the procedures outlined earlier, the gross calorific values of the materials tested were obtained. Table 3 shows the results for samples
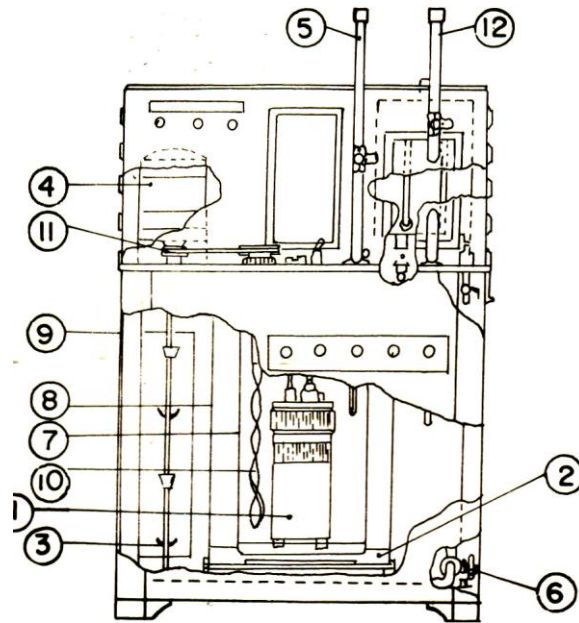
1. BOM B
2. TRIANGLE SUPPORT
3. STIRRER FOR OUTER JACKET
4. MOTOR FOR STIRRER
5 BECKMANS THERMOMETER
6. OUTER   JACKET
7. INNER VESSEL
8. INTERMEDIATE VESSEL
9. OUTER JACKET
10. STIRRER FOR INNER VESSEL
11. DRIVING   PULLE Y
12. BECKMANS TERMOMETER

Fig. I SECTIONAL VIEW OF EXPERIMENTAL EQUIPMENT

TABLE 2: THE EXPERIMENTAL CONDITIONS

S/NO.	Material	No. of Samples tested	Max. Moisture Content % wb	Room Temp. °c	Oxygen Pressure	Quantity of water (W1)gm	Temperature rise, °c
1	Rice husk	8	8.50	27	27	1750	1.464 ±: 0.019
2	Com cob	8	9.23	29	27	1800	1. 787 ±: 0.019
3	Com grain	4	12.00	28	29	1900	2.196 ±: 0.024
4	Com stover	4	13.20	28	29	1650	1. 787±: 0.021
5	Wood shaving (hard wood)	3	9:45	29	27	1650	1. 978 ±: 0.018
6	Wood shaving (soft wood)	8	7.50	27	27	1600	1. 907 ±: 0.022
7	Saw dust	8	9.5	27	27	1600	1. 983 ±: 0.023
8	Palm kernel husk	8	8.8	29	27	1900	1. 983 ±: 0.049
9	Rice husk +com cob	4	Bone dry	28	29	1800	1. 373 ±: 0.017
10	Com cob +shaving (soft)	4	"	28	29	1750	1. 767±: 0.015
11	Rice husk + shaving (hard)	4	"	28	29	1750	1.619 ±: 0.027
12	Coal (Sub-bitumious)	2	"	28	29	1900	2.802 ± 0.032

Table 3: Gross Calorific Value of Fuel Materials Tested

Specimen	Bomb calorimeter	Calorific Value, KJ/kg Literature	
Rice husk	13,643	12297	... ref. [4]
Palm Kernel husk husk	19,642	-	
Com Grain	22,165	21220	...ref. [8]
Corn cob	17,163	18518	...ref. [8]
Com Stover	16,045	1650C	...ref. [9]
Saw dust	17,463		-
Wood shaving (hard wood)	17 ,831		-
Wood shaving (soft wood)	16,769		-
Wheat straw		18769	... Ref. [10]
Peanut shell		20400	ref. [10]
Coal	28,466	28503	...*
Rice husk + Corn cob (1:1)	13,042		-
Corn Cob + Wood shaving (1 : 1) (soft)	16,600	-	
Rice husk + wood shavings (hard) (1:1)	15,155	-	

*Nigerian Coal Corporation, (1981)

dried to constant weight, which include the bomb calorimeter values, and values obtained from literature. The differences in the values are of the order of 10 per cent or less which are in the domain of experimental errors. This gives some reasonable confidence on the accuracy of our experimental results especially when such comparisons have not taken into consideration any production, varietal or environ- mental factors that might alter the relative composition of the biomass materials. The differences in values between duplicate samples were of the order of 300 KJ/kg which gave acceptable repeatability. Also the results showed that mixtures of samples (1:1 ratio) had calorific values that were somewhere between the values for the individual components. This seems to indicate that there is no apparent advantage in mixing the samples.

The temperature history of a sample of wood shavings under test is shown in Fig. 2. This graph exhibits an assymptotic steady-state temperature which was achieved within 15 minutes in all experiments of the different materials investigated. Such a temperature - time graph can be used to obtain an approximate calorific value of the specimen by considering the thermodynamics of the process, that is;
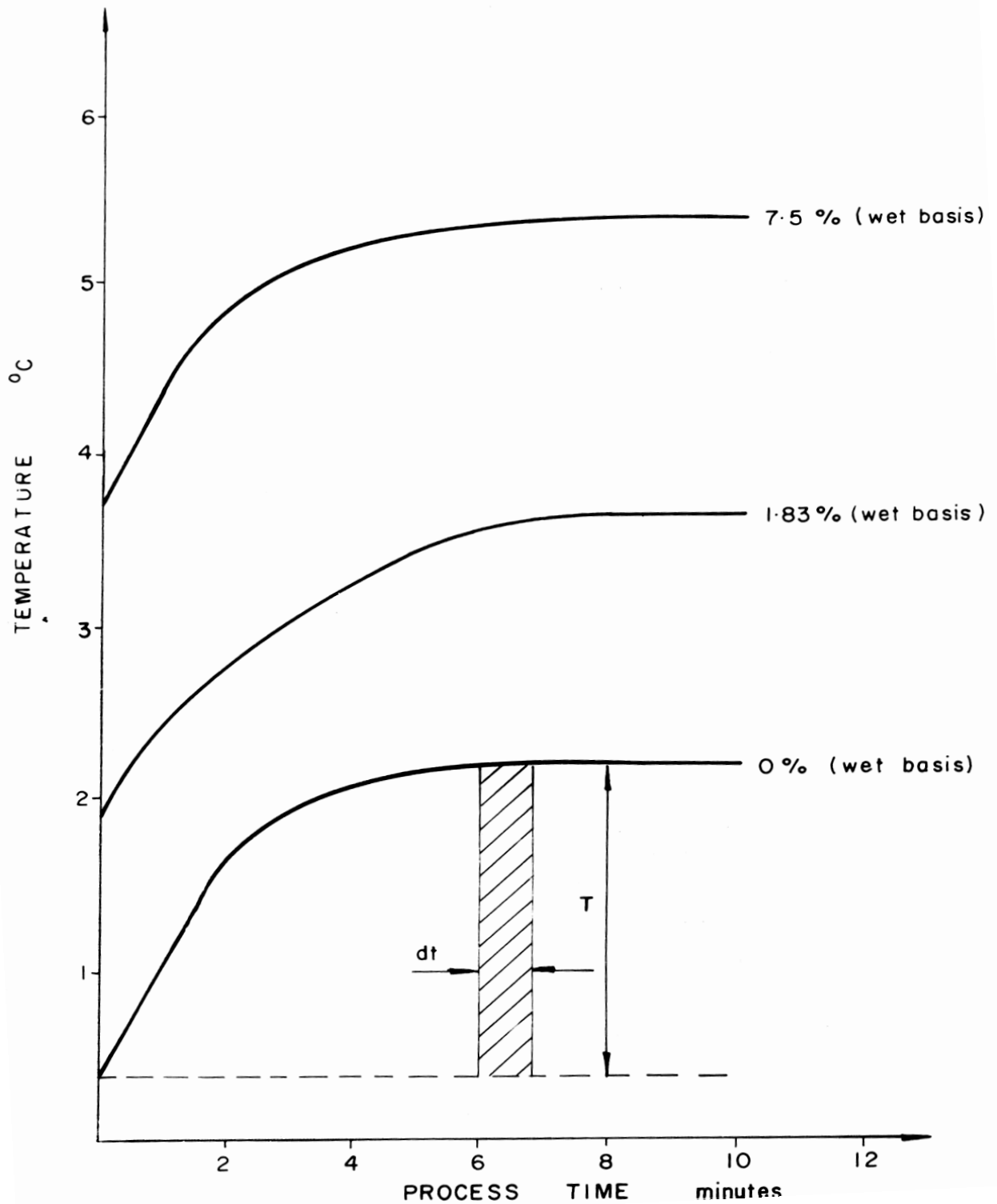
FIG 2: TEMPERATURE HISTORY OF A SAMPLE OF WOOD SHAVINGS (soft wood)

$$Heat\ released = K \int_0^t T dt \qquad (4)$$

where the integral is the area under the curve and K, is a product dependent constant. Equation (4) is sensitive to moisture content and once the value of K has been determined for a given material, its time-temperature plot when integrated will provide the heating value at any moisture content.

The change in temperature with time for the different materials is plotted in Fig. 3. The curves exhibit the characteristics of a spontaneous combustion process in which a rapid temperature increase is followed by a relatively slower decrease due to thermal inertia. They also showed that coal, which had the highest calorific value of all materials tested, experienced the highest temperature increase. The relative delay in attainment of maximum temperature change displayed by corn kernel may have been due to the relatively high moisture content of 11.8 per cent (w.b.).

An analysis of the results showed that the calorific value decreased as moisture content of the specimen increased as shown in Fig.4. 'This is because the presence of moisture in the fuel reduces its specific content of combustible elements and thus the smaller the proportion of dry matter content to provide the required energy. Besides, a part of heat generated during ombustion is spent on achieving a phase change of the contained moisture, thus leading to a decrease in available energy. The curves shown in Fig. 4 are linear within the experimental conditions and can be expressed by an equation of the form
G.C.V. = a - bM   (5)

where G.C.V. is the gross calorific value, KJ/kg; M is the moisture content of specimen in per cent (w.b.). The values of the constant in equation (5) and correlation
coefficients for the materials tested are shown in table 4 working with corn biomass. Loewer et al[11] also found a linear relationship between calorific value and moisture content with negative slopes similar to those shown in Fig 4.

The energy availability shown in table 3 were based on a dry matter basis. However, when biomass is gasified, part of the energy must be used in removing the moisture contained in the material. The latent heat of vaporization for water is approximately 2.46 MJ/kg. Thus for each kilogram of moisture in the biomass, 2.46 MJ of energy will be used for vaporization rather than as a source of energy for say, grain drying.
The moisture content of each biomass materials must be known if the net energy available for drying is to be computed.

To determine the net energy, the dry matter content of the biomass is multiplied by the gross calorific value to obtain the gross energy content. However, the moisture contained in the material need to undergo a phase change from liquid to vapour, when the material is burned. This has the effect of reducing the energy output of a given moist biomass. Thus the energy potential of a biomass material will be given as

$$EP = (\frac{100 - M}{100})\ GCV - \frac{M}{100}\ hfg$$

Where
EP = energy available per unit
    M = Per cent moisture content of biomass
    GCV = gross calorific vale per unit of biomass, dry basis
    h_{fg} heat of vaporization of water

The significance of equation (6) is that the higher the moisture content of a given weight of biomass, the less the proportion of dry matter to provide energy. Also the greater the moisture content, the greater the total energy required to vaporize moisture thus leaving less energy available. This means that the field moisture content will be an important consideration, if the biomass component is to be utilized directly at the time of harvest. According to Gerzho1[5], the presence of a considerable amount of moisture in the products of combustion retards the reaction of combustion reduces   the
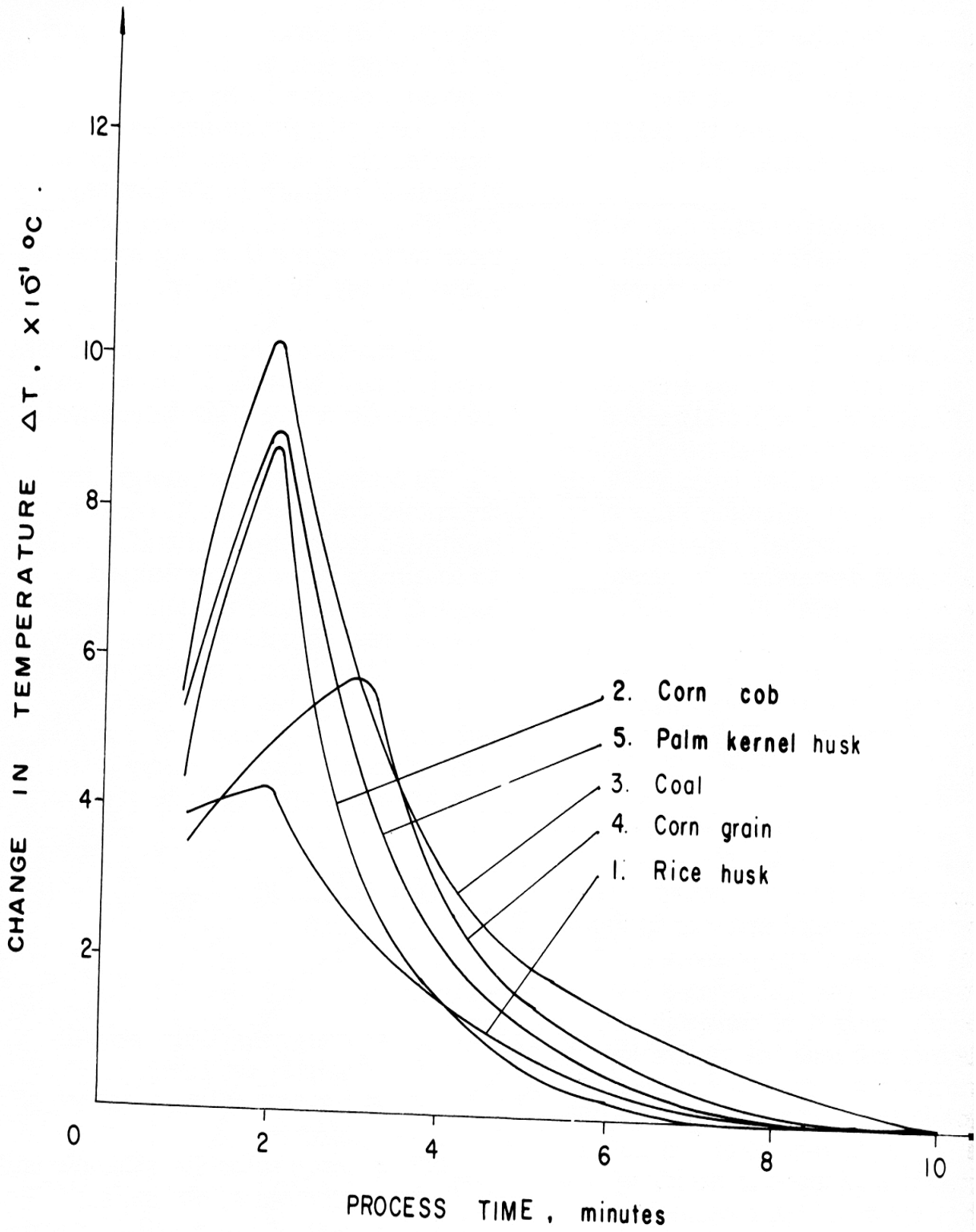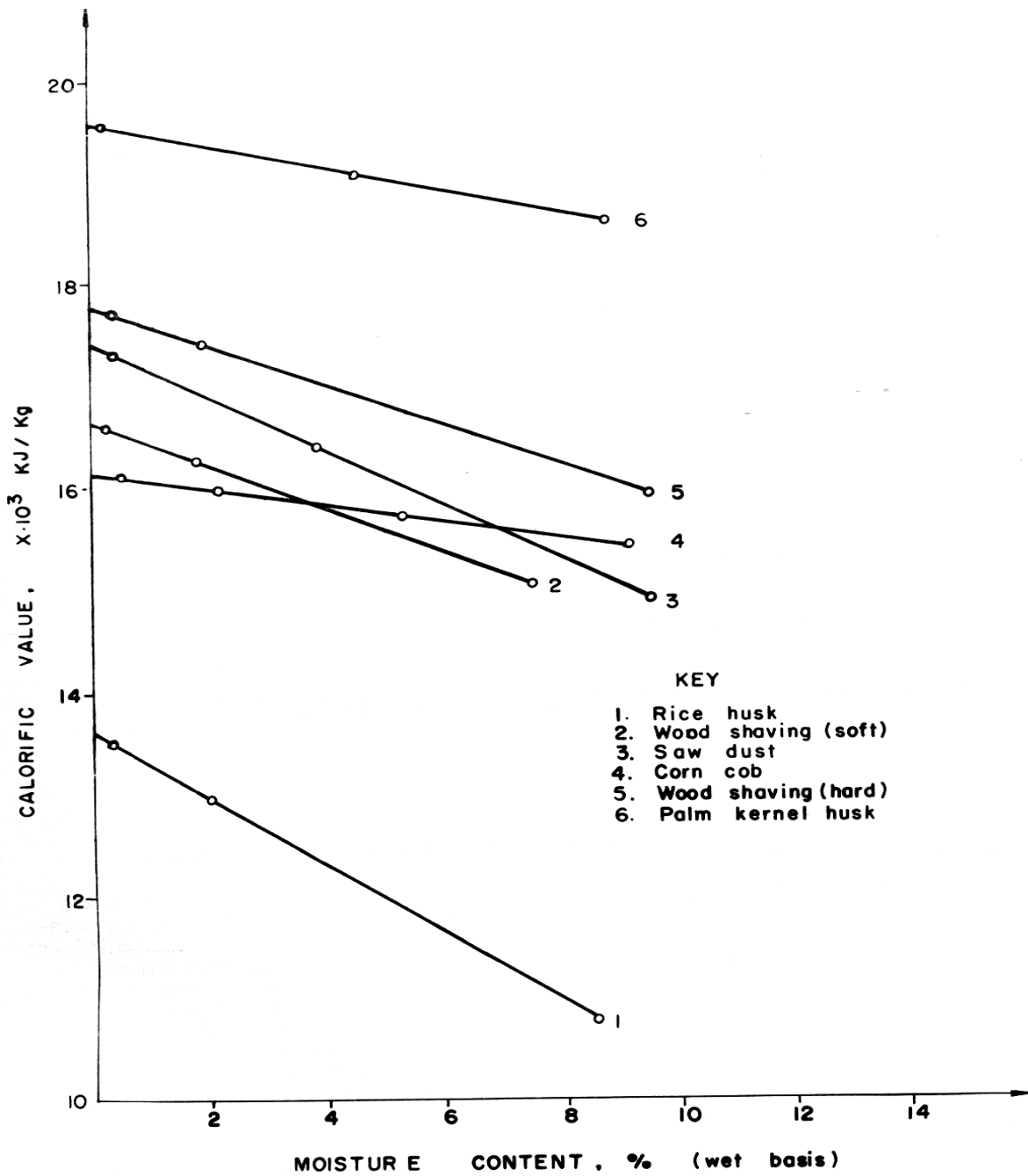
Fig. 3: CONTINUOUS TEMPERATURE CHANGE WITH TIME

Fig 4. VARIAITION OF CALORIFIC VALUE WITH MOISTURE CNTENT

TABLE 4: REGRESSION COEFFICIENTS FOR DEPENDENCE OF CALORIFIC VALUE ON MOISTURE CONTENT

Material	a	b	R
Rice husk	13643	351.67	0.98
Saw dust	17463	264.12	0.94
Hood shaving (hard)	17831	186.52	0.91
Hood shaving (soft)	16769	206.79	0.93
Com cob	17163	77.55	0.96
Palm kernel husk	19642	176.00	0.89

temperature in the furnance and therefore adversely affects the conditions of combustion of the fuel as a result smoke and even soot may appear in the exhaust. stream. When the fuel moisture content exceeds 12 to 14 percent (w.b.) it may be difficult to obtain desired thermal efficiency, furnance capacity or even ignition.

Drying corn from 25 percent to 12 per cent (w.b.) would require removal of 119.3 kg water per cubic meter of grain (28.4 bushels). Using the data of Loewer et al[11], the production of corn cob from 1 m³ of grain is approximately 142.15 kg. Since the gross calorific value of corn cob is about 17 .16 MJ /kg, dry cobs from 1 m` of shelled com will normally dry about 3.2 m³ (90 bushels) of shelled corn on the basis of our results. It is thus clear that the high calorific values of Nigerian solid fuel materials make them excellent candidates as alternative energy sources to conventional ones like gas, liquid petroleum
and electricity, for thermal energy generation.

Obviously, the development of crop dryers that are fired with solid fuel materials will enhance effective utilization of Nigerian biomass. Smith et al[12] reported efficiencies as high as 79 per cent for a water heater that burned wood chips. Ezeike[13] developed a solid fuel fired dryer

in which the combustion of firewood and coal produced heated air at about 60^0c for drying a deep bed of com and thin layers of cassava pellets. Thermal efficiencies of about 71 per cent were obtained. Singh et al[14] reported a thermal efficiency as high as 80 per cent for a rice husk fired furnance. Also the thermal efficiency of an indirect fired wood f'urnance designed by Rice and Brown[14] was 50 to 73 per cent.

CONCLUSION

The gross calorific values of some Nigerian solid fuel materials such as rice husk, corn cob, corn stover, corn grain, saw dust, wood shavings, palm kernel husk and coal, have been determined experimentally with the adiabatic bomb calorimeter. The values ranged from about 13 megajoules per kilogram for rice husk to 28 megajoules for coal. The values obtained were found to be sufficiently accurate to be used in an engineering thermal analysis.

Available energy from biomass was shown to be inversely dependent on moisture content. This result is significant if the biomass is to be used directly at harvest. Considering the quantity available and high calorific values of the solid fuel materials tested, Nigerian biomass could be a dependable alternate source for thermal energy generation for grain and other processing operations.

REFERENCES

1. Ramalingam, M and Ibrahim, N. (1979). Modernisation of rice milling industry in India. Indian J. of Agric Engr. P. 15

2. Wood, R.S (1974). Straw production and disposal in oxfordshire. In Report of Straw Utilization Conference, 1971 Ed. A.R. Staniforth OXford.

3. Morey, R.V. and Thimsen, D.P. (1980) Conbustion of crop residues to dry corn. Agricultural Energy Vol. 1: 142-47.

4. Singh, R.: Maheshwari, R.C. and Ojha. T.P. (1980). Development of a Husk Fired Furnance. J Agric. Eng'g Res. 25: 109 - 120.

5. Gerzhol, A.P. and Samochetor, V.F. (1958). Grain drying and grain dryers. Khleboizdat publishing Co. Moscow. Reproduced by the National Technical Information Service, Spring Field VA, 22151.

6. Francis, W. and Peters, M.C. (1980). Fuels and Fuel Technology, Pergamon Press, Oxford, New York.

7. Payne, F. (1978) Potential of biomass conversion processes for grain drying in Kentucky. Kentucky department of energy cooperative extension publication AEES - 4.

8. Crampton, E.W. and Harris, L.E. (1969). Applied animal nutrition 2nd Ed. W.H. Freeman and Company, San Ft-anc i.sco , Ca.

9. Kajewski, A.H.; Marley, S.J. and Buchele, W.F. (1977) Drying corn with a crop residue fired furnace ASAE paper No. 77 - 3525. St. Joseph MI 49085.

10. Sumner. H.R.; Sumner, P.E.; Harmnond, v.c., Monroe, G.E. (1983). Indirect-fired biomass furnace test and bomb Calorimeter determinations. Trans. ASAE 26(1), pp. 238 - 241.

11. Loewer, O.J.; Black, R.J.; Brook, R.C.; Ross, I.J. and Payne, F. (1980) Economic potentials of on-farm biomass gasification for corn drying ASAE paper No. 80 - 8508. St Joseph MI. 49085.

12. Smith, N.; Riley, J.G.; Christensen, T.E .. (1980). Automatically controlled wood chip furnaces for residential use. Agricultural Energy 1: 357 - 62.

13. Ezeike, G.O.I. (1981) Development and testing of a solid fuel fired dryer. Proceedings, Nigerian Society of agricultural Engineers (NSAE) University of Ife, Ile-Ife, Nigeria.

14. Rice, C.E. and Brown, R.H. (1979). Solar heat for broiler production from a biomass burner system. ASAE. paper SER 79 - 039. ASAE St. Joseph. MI 49085.