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Characteristics of Ten Selected Ugandan Bio-Wastes Under Ultimate Analysis for Briquettes Production

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Abstract: Ten Ugandan bio-waste agricultural residues were characterized under the ultimate analysis to determine their elemental constitution. The Eltra CHS-580 (Thermo-graphical Analyzer) was employed for determination of carbon, hydrogen and sulphur; while nitrogen the method of protein analysis was used. The atomic absorption spectroscopy technique (NEN6465 Dutch Standard) was employed for Calcium, sodium, potassium, and silicon and the colorimetric method was used for phosphorous. The moisture and ash content were determined using the Eltra Thermostep – Thermographic analyzer. The focus was to determine whether the eleven characteristics (content by percentage of carbon, hydrogen, oxygen, nitrogen, phosphorous, calcium, potassium, sodium, silicon, ash and moisture) in the ten selected Ugandan bio-wastes had a relationship among them to project a high Carbon (c2) value for the biowaste briquette production. The contribution and difference between a fuel's fixed carbon under proximate analysis and its constituent elemental carbon under ultimate analysis is presented and explained in the context of the ten bio-residues data. Using stata, the biowaste ultimate analysis property values were regressed as independent variables against the carbon content c2. Statistical analysis showed hydrogen, oxygen, nitrogen, and sulphur and ash content constitution to be very significant at 95% confidence level in the bootstrapping-quantile regression model. A regression model equation was established from the analysis and in agreement with established scientific literature. The Kruskal-Wallis equality-of-populations rank test was employed to select bio-wastes residues with high carbon content for briquettes production. sunflower seed cake (sf), palm nut trash (pm), saw-dust (sd), ground-nut husks (gh), Cotton seed cake (cs), Cotton de-coated seed trash (cd), Maize cob trash (mc), Coffee husks (ch) were selected. Millet husks (mh) and rice husks (rh) were rejected owing to poor briquette fuel characteristics (low carbon value, high volatile matter and ash content) to harness for metallurgical application like reduction of iron ore.

Keywords: Characteristics, Bio-wastes, Ultimate analysis, Briquettes, Uganda

1. Introduction

Agricultural residues can be a sustainable energy supply, matching cycle crop production in any country (Ho, et al., 2014). Sustainability in crop production in Uganda, means shifting from subsistence agriculture to commercial farming which is not easy. There is lack of policy implementation initiatives on the part of government. The problems of land ownership, communities gleaning over protectionist rights over ancestral land, are aspects not helping the shift of subsistence farming character to high yield and technologically based farming methods (Ahaibwe, et al., 2013). Yet, population growth is taking place against land that is not increasing. The briquette industry requires a sustainable supply of bio-residues for it to engage in the country's economy. Urbanization is slowly absorbing the population that once used to depend on subsistence agriculture. Land acquisition by cooperate bodies should be replacing individual home consumption farming into extensive commercial agriculture (Ministry of Agriculture Animal Industry and Fisheries -MAAF, 2010). This should generate more agricultural waste or residues (Muwanga-Zake, 2009). Targeting these bio-wastes for the briquette industry is a good outcome for the Ugandan economy (Ferguson, 2012). Competition for the bio-residues utilization exists too; this being between animal feed (Rogers, et al., 2002) processors and those in the briquette industry for energy. Not all agricultural residues are animal feed targeted. Those outside the competition domain can be tapped for energy supply.

High energy briquettes are made from bio-wastes that are rich in carbon content: Fixed carbon or elemental carbon content. Fixed carbon is the pure carbon uncombined in the biomass fuel; hallmark of organic combustion (Sarkar, 2009). Elemental carbon is total carbon stock in the biomass: pure carbon in the biomass plus the combined carbon in the hydrocarbons, carbonates, and carbides that form the biomass constitution. Biomass constitution largely depends on local origin which affects mineralogical variability (Sánchez, et al., 2011; Vassilev, et al., 2012). Elemental carbon may dissociate from the compounds of belonging and escape as volatile matter in the form of carbon dioxide, methane and higher hydrocarbons. In this way it does not partake in combustion kinetics. Pyrolysis and torrefaction enrich the bio-waste fixed carbon value while limiting the effects of volatiles and ash constitution in biomass fuel (Basu, 2013). Sarkar, observes, the ultimate analysis is carried out to determine the chemical composition of the fuel; good for bio-waste combustion calculations and flue gas constitution. Ten bio-waste types: coffee husks, ground nut shells, millet husks, maize cob waste, saw-dust, rice husks, cotton seed cake, palm nut trash, cotton de-coated ash and sunflower seed cake were analyzed using the Eltra CHS-580 Thermographic analyser to determine their carbon, hydrogen and sulphur elemental constitution. Nitrogen was determined using the method for protein analysis (Association of Official Analytical Chemists, AOAC; 1990); Calcium (Ca), sodium (Na), potassium (K), were determined using atomic absorption spectroscopy technique (NEN6465 Dutch Standard) while silicon (Si) and phosphorous (P) were determined using colorimetric method. Oxygen was

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determined by difference from the constitution of carbon, hydrogen, sulphur, nitrogen and ash. The moisture and ash content were determined employing the Eltra Thermostep – Thermographic analyzer. The results data were treated to a statistical analysis.

2. Methodology

2.1 Sampling Procedure

The gross samples for this study were ten (10) agricultural bio-waste residue types, each in five replicates and collected from across the country. The random samples had clear labels to identify each replicate in the category.

Laboratory test samples were drawn from the gross samples collected from the field.

2.2 Experimental Procedures

2.2.1 Determination of Carbon, Hydrogen and Sulphur

The Eltra GmbH CHS-580 (2013) thermo-graphic analyzer was used. Pure oxygen (99.99%) adjusted at 4 bars from a cylinder was fed into the crucible environment of the equipment. The equipment furnace was turned on, letting the heating chamber temperature rise to 1350°C.Under the equipment software program, a calibration test was run using the ambient air around the test crucible environment. The samples were homogenized and weighed to \leq 200mg, using an ETRA84 precision weighing scale. They were loaded into the crucibles and conveyed into the heated chamber for the software to register their weights. The samples were then heated and fully oxidized from carbon, hydrogen and sulphur to carbon dioxide (CO₂), moisture (H₂O) and sulphur dioxide (SO₂) gas mixture. The gas mixture was sucked through a dust trap to remove any dust particles and conveyed to three infrared cells. Signals were then emitted from the infrared cells which were selective to correspond to CO₂, H₂O and SO₂ concentrations in the gas mixture. The signals were electronically linearized and integrated, divided by the sample weights and digitally displayed as % C, % H, and % S. A record for the results data was made.

2.2.2 Determination of Nitrogen

Nitrogen was determined using the Micro-Kjeldahl method (AOAC, Official Methods of Analysis, methods of Analysis, method 978.04). About 200g of finely ground sample were accurately weighted and quantitatively transferred into a digestion tube. To each tube, 2 kjeltabs (each tab contained: 7g of anhydrous potassium sulphate and 5mg of selenium powder) were added and 5ml of concentrated sulphuric acid. The samples were digested on a block digester (Gerhardt kjeldatherm) at 360 degrees for approximately 1hr and 30min. After digestion, the tubes were cooled to room temperature. The samples were then distilled using kjeltec distillation apparatus. The digestion tubes were placed in position of the steam distillation unit (2200 kjeltec Auto distillation FOSS TECATOR) and the distillate collected in Erlenmeyer flask containing 25ml of boric acid solution (4%) and mixed indicator (bromo creasol green and methyl red). Sodium hydroxide (40%) which was used to neutralize the excess acid and to release ammonium sulphate, was added automatically by the distillation unit. The collected distillate was titrated using 0.1N HCL (using automatic

titrator; Digtrate) with an end point titration of pH 4.7. The blank titrate was determined using a blank solution of boric acid and mixed indicator. The bio-waste nitrogen constituent was then calculated from equation (1) whose record was then generated.

% nitrogen= [(sample titer-blank titer)* normality of HCL*14*100]/ sample weight (g)*100 (1)

2.2.3 Determination of Calcium (Ca), Sodium (Na), and Potassium (K)

The biomass samples were first decomposed to determine the composition of Calcium (Ca), Sodium (Na), and Potassium (K). They were treated the same way as in the destruction of plants during analysis using atomic absorption spectroscopy technique (NEN6465 Dutch Standard). The apparatus consisted of a destruction-bloc with destruction tubes made of borosilicate glass and Nichiryo pipet model 3100 with removable tips. The reagents all had a low metal content and included: nitric acid, 65% HNO₃, Hydrogen peroxide, 30% H₂O₂ and pumice . The glass ware included a measuring cylinder, 50ml, and funnels of 6cm and volumetric flasks of 250ml. They were all rinsed with 1+1 HNO₃ before use.

The following procedure was employed: 1.250g of dried sample (24hours at 103° C) was transferred to the destruction tube and 25ml HNO₃ was added with three boiling chips with a funnel placed on top of the destruction tube. The tube was heated: To 100° C and maintained for one hour.

- To 125°C and maintained for 15 minutes
- To 150°C and maintained for 15 minutes
- To 175°C and maintained for 15 minutes
- To 200°C and if it was necessary in the cases where no volume was left, 5 ml HNO₃ was added

The material was concentrated to 5ml by adding after cooling, 1 ml 30% H_2O_2 and destruct for 10 minutes, 1x. 3 ml 30% H_2O_2 further added and destruct for 10 minutes. 25 ml of water added while mixing and heated till boiling started. The sample thus treated was transferred to a 250 ml

volumetric flask and filled up to the mark while mixing was taking place. It was allowed to settle during the next 15 hours after which the absorbance of the supernatant was measured. After 7 hours the two blank tests were carried out. A record of the results was made.

2.2.4 Determination of Ash content

The the Eltra Thermostep – Thermographic analyzer was employed. Homogenized and weighed (800-1100 mg) dry samples were loaded in the crucibles of the equipment. Nitrogen gas at 4bars was pumped into the equipment from the cylinder. A calibration test was first run by the equipment software program. At 750° C, the N₂ gas was pumped out of the equipment. The samples crucible lids were opened. Pure oxygen 99.99% from the cylinder was pumped in the samples atmosphere, replacing the N₂ gas. The incoming oxygen oxidized all the fixed carbon in the samples and the software program automatically weighed the remaining char and registered it within to less than 0.001mg and then stopped. The software program allowed a backward s check of the experiment and produced automatically the

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spreadsheet of the test results as percentages moisture and ash content of the test biomass residues samples.

3. Results

The regression model produced from statistical analysis (Tables A1) for ultimate analysis was not reliable. Sufficient statistical significance was lacking with carbon because the data were not normally distributed.

Table A1: Regression model	for ultimate analysis variables
, regress c2 h2 o2 n2 s2	ca2 na2 k2 p2 si2 a2 m2

Source	SS	df	Μ	MS		Number of obs = 50			
Model	1661.4722	11	151.042927			F(10, 39) = .			
Residual	1.3158e-	38	3.462	6e-12		R- squared= 1.0000			
Total	1661.4722	49	33.90)7596	A	Adj R-squared $= 1.0000$			
		R	oot MS	SE = 1	.8e-	-06			
c2	Coef.	Std.	Err.	t		P> t 	[95%	Conf.	
h2	-1.000001	7.39	9e-07	-1.4e+	-06	0.000	-	-	
o2	-1	1.05	5e-07	-9.6e+	-06	0.000	-1	-	
n2	-1	2.47	7e-07	-4.1e+	-06	0.000	-	-	
s2	9999959	1.86	5e-06	-5.4e+	-05	0.000	-	-	
ca2	-1.42e-07	1.73	3e-06	-0.0	8	0.935	-3.65e-	3.37e-06	
na2	-6.18e-07	3.86	5e-06	-0.1	6	0.874	-8.44e-	7.20e-06	
k2	-1.34e-07	3.89	9e-07	-0.3	5	0.732	-9.22e-	6.54e-07	
p2	5.54e-07	1.35	5e-06	0.4	1	0.685	-2.19e-	3.29e-06	
si2	4.33e-08	4.75	5e-08	0.93	1	0.368	-5.28e-	1.39e-07	
a2	-1.000009	.000	0172	-5.8e+	-04	0.000	-	-	
m2	-1.34e-07	1.45	5e-07	-0.9	3	0.359	-4.27e-	1.59e-07	
_cons	100	9.58	Be-06	1.0e+	07	0.000	99.99999	100	

The elemental constitution c2 from ultimate analysis regressed well and with sufficient statistical significance at 95% confidence interval with hydrogen, oxygen, nitrogen, sulphur and ash content. The other elements do not show statistical significance with the carbon content. These observations were agreeable with other literature (Friedl, et al., 2005). Due to lack of normal distribution in the datasets, non-parametric statistical analysis methods were employed for analysis. The datasets sample size n=9 were insufficient for reliability analysis. Quantile regression (Table A2) method was employed to determine the relationship between bio-waste eleven variables. Bootstrapping (Table A3) with quantile regression that can produce replications to compensate for the small sample size was employed to generate stable and more reliable regression results. The optimal regression model was generated employing bootstrapping-quantile regression on the most significant variables to obtain the model equation (2).

 Table A2: Quantile regression model for ultimate analysis

variables				
. greg c2 h2 o2 n2 s2 ca2 na2 k2 p2 si2 a2 m2, quantile (50)				
note: weighted least squares perfect fit				
Iteration 1: sum of abs. weighted deviations = .00008189				
Iteration 2: sum of abs. weighted deviations = .00007055				
Iteration 3: sum of abs. weighted deviations = .00006891				
Iteration 4: sum of abs. weighted deviations = .00006849				
Iteration 5: sum of abs. weighted deviations = .00006686				
Iteration 6: sum of abs. weighted deviations = .00006672				
Iteration 7: sum of abs. weighted deviations = .00006593				
Iteration 8: sum of abs. weighted deviations = .00006522				
Iteration 9: sum of abs. weighted deviations = .00006509				
Iteration 10: sum of abs. weighted deviations = .00006507				
Iteration 11: sum of abs. weighted deviations = .00006497				

T										
Iteration 12: sum of abs. weighted deviations = .00006492										
Iteratio	Iteration 13: sum of abs. weighted deviations = .00006492									
Mediar	regression l	Number of	obs = 50	0						
Raw su	Raw sum of deviations 212.1 (about 40.5)									
Min su	Min sum of deviations .0000649 Pseudo $R2 = 1.0000$									
c2	c2 Coef. Std. Err. t P> t [95% Conf. Interval]									
h2	-1.000001	3.64e-06		0.000	000009	999994				
o2	-1	5.19e-07		0.000	-1.000001	99999992				
n2	-1.000001	1.22e-06		0.000	-1.000003	9999981				
s2	9999934	9.24e-06		0.000	-1.000012	9999747				
ca2	-3.95e-06	8.45e-06	-0.47	0.642	0000211	.0000131				
na2	5.71e-07	.0000192	0.03	0.976	0000382	.0000394				
k2	1.36e-07	1.93e-06	0.07	0.944	-3.77e-06	4.05e-06				
p2	-1.23e-07	6.46e-06	-0.02	0.985	0000132	.000013				
si2	8.11e-08	2.28e-07	0.36	0.724	-3.80e-07	5.42e-07				
a2	-1	.000085		0.000	-1.000172	9998282				
m2	-2.07e-07	6.26e-07	-0.33	0.743	-1.47e-06	1.06e-06				
_cons	100	.0000473		0.000	99.99993	100.0001				

 Table A3: Bootstrapping regression model for replications on limited bio-waste sample size

bsqreg c2 h2 o2 n2 s2 ca2 na2 k2 p2 si2 a2 m2, quantile (50 reps(30)										
(fitting base model)										
(boo	tstrapping .)							
Med	lian regress	sion, boot	strap(30)	SEs N	umber of	obs =	50			
Raw sum of deviations 212.1 (about 40.5)										
Min sum of deviations .0000649 Pseudo $R2 = 1.0000$										
c2	Coef.	Std. Err. t P> t [95% Conf. Interval]								
h2	-1.000001	1 2.13e-0)6 -4.7e-	+05 0.0	00 -1.00	0006	99999	71		
o2	-1	3.57e-0)7 -2.8e-	+06 0.0	00 -1.00	0001	99999	96		
n2	-1.000001	1 1.03e-0)6 -9.7e-	+05 0.0	00 -1.00	0003	99999	85		
s2	9999934	4 3.95e-0)6 -2.5e-	+05 0.0	00 -1.00	0001	99998	54		
ca2	-3.95e-06	3.69e-0	6 -1.07	0.2	91000	0114	3.52e-0	6		
na2	5.71e-07	.00002	81 0.02	0.9	84000	0563	.000057	/5		
k2	1.36e-07	7.13e-0	0.19	0.8	50 -1.31	e-06	1.58e-0	6		
p2	-1.23e-07	3.09e-0	6 -0.04	0.9	69 -6.37	e-06	6.12e-0	6		
si2	8.11e-08	8.63e-0	0.94	0.3	54 -9.37	e-08	2.56e-0	7		
a2	-1	.00004	08 -2.5e-	+04 0.0	00 -1.00	0083	99991	78		
m2	-2.07e-07	2.77e-0	07 -0.75	0.4	60 -7.67	e-07	3.54e-0	7		
cons	100	.00002	95 3.4e+	06 0.0	00 99.99	996	100.000)1		
reps	(500) ng base mo	del)		- K2 p2	512 42 11	<u>, q</u>		(50)		
(000	tstrapping									
	•••	• • •					<i></i>			
Ned	lian regress	sion, boot	strap(500	<u>) SES r</u>	umber of	t obs	= 50			
Raw	sum of dev	/lations 21	2.1 (abou	$\frac{t}{1}$ 40.5)	1 1 0000	<u>,</u>				
	Sum of dev	fations .00	000649 PS		2 = 1.0000) f T.	+			
C2 h2	1.000001	510. Err.	ι 5.60±05	r > u	1 00000	$\frac{1}{5}$				
n2 02	1	1.79e-00	-3.00 ± 0.06	0.000	1.00000	1 00	00007	1		
$\frac{02}{n^2}$	1 000001	2.72e-07	1.70 ± 00	0.000	1.00000	$\frac{1}{2}$	000001	1		
n2 62	0000034	3 580 06	280+05	0.000	1 00000	1 00	00862	1		
82 092	3 050 06	3.500-00	1.00	0.000	-1.00000	$\frac{1}{2}$ $\frac{77}{2}$	2002	1		
caz	5 71e-07	0000275	0.02	0.285	000011.	1 000	20562	1		
11a2 k2	1.36e-07	$6.49e_07$	0.02	0.904	000033	5 1 1/	5e-06	1		
n2	-1 23e-07	2.46e-06	-0.05	0.960	-5 10e-06	5 4 8	5e-06	1		
r- si2	8 11e-08	8 67e-08	0.94	0.355	-9 43e-08	2 5	6e-07	1		
a2	-1	0000389	-2.6e+04	0.000	-1.00007	9 . 90	99215	1		
m2	-2.07e-07	2.45e-07	-0.84	0.404	-7.03e-07	2.90	De-07	1		
cons	$\begin{array}{c} \text{cons}100 \\ \text{cons}100 \\ \end{array} \begin{array}{c} 0.000237 \\ \text{4.2e+06} \\ 0.000 \\ 99.99998 \\ 100 \\ 0001 \\ \end{array}$									
- 0110	consilio .0000237 4.2e+00 0.000 99.99998 100.0001									

A regression model equation relating carbon content with hydrogen, oxygen, nitrogen, sulphur and ash percentage content was generated:

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 $C\% = 99.999999 - .9999949 *S - 1*N_2 - .9999993*H_2 - 1*O_2 - .999999*ash(2)$

Where C% is elemental carbon content from the ultimate analysis of the bio-waste; S = % sulphur content; $N_2 = \%$ nitrogen; $H_2 = \%$ hydrogen; $O_2 = \%$ oxygen; and ash = the % ash content.

Table B: Bootstrapping-quantile regression model for determination of elemental carbon from the ultimate analysis bears $a^2 b^2 a^2 n^2 a^2 a^2$, guartile (50) rang(20)

. bsqr	bsqreg c2 h2 o2 h2 s2 a2 , quantile (50) reps(30)									
(fitting	g base mod	el)								
(boots	trapping)							
Media	Median regression, bootstrap(30) SEs Number of obs = 50									
Raw s	Raw sum of deviations 212.1 (about 40.5)									
Min s	Min sum of deviations .0000679 Pseudo $R2 = 1.0000$									
c2	Coef.	Std. Err.	t	P> t 	[95% Con	f. Interval]				
h2	99999993	1.31e-06	-7.6e+05	0.000	-1.000002	9999966				
o2	-1	1.73e-07	-5.8e+06	0.000	-1	9999997				
n2	-1	4.79e-07	-2.1e+06	0.000	-1.000001	99999991				
s2	99999949	2.23e-06	-4.5e+05	0.000	99999994	9999904				
a2	99999	.0000295	-3.4e+04	0.000	-1.000049	9999306				
cons	99.99999	.0000162	6.2e+06	0.000	99.99996	100				

The bio-wastes for briquette production were selected using the Kruskal-Walis –population- rank test (Tables C)

From Table C:

- Kruskal-Wallis equality-of-populations rank test of elemental carbon the order of highest –low rank is sf, pm, sd, gh, cs, cd, mc, ch, mh,rh
- Kruskal-Wallis equality-of-populations rank test of fixed carbon the order of highest –low rank is cs, gh, cd, ch, cf, mc, pm, rh, sd, mh
 - **Table C:** The Kruskal-Wallis equality-of-populations rank test bio-waste proximate-ultimate and ultimate analysis

. k	. kwallis c2, fc, vdp, ap by (sat)								
ŀ	Kruskal-Wallis equality-of-								
sat	Obs Rank Rank Rank Rank								
		Sum	Sum	Sum	Sum				
cd	5	122.00	183	72	185				
ch	5	79.50	150	142	144				
cs	5	139.00	222	118	78				
gh	5	145.50	217	97	149				
mc	5	108.50	135	196	34				
mh	5	59.00	21	47	210				
pm	5	204.00	105	173	58				
rh	5	18.00	71	15	240				
sd	5	186.50	35	240	74				
sf	5	213.00	136	175	103				

Figures 1(a)-(1), 2(a)-(1) and 3(a)-(1) show phenomena of lack of statistical dataset normal distribution. Figure 1(a)-(1) shows the histograms of individual bio-waste data against the normal distribution. Most of the data is either skewed positively or negatively. Figure B1-12 shows the Kernel density distribution of individual bio-waste while Figure 3(a)-(1) linear fits against scatter of individual spread for the normal distribution and outlier indication is depicted. Figures 4(a)-(1) shows the compensatory of quantile distribution lines of fit superimposed against linear fits for the bio-waste datasets.

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Figure 1(a)-(l): Results Data Normal Distribution percentage content : Carbon (c2), Hydrogen (h2), Oxygen (o2), Nitrogen (n2), Sulphur (s2), Sodium (na2), Calcium (ca2), Potassium (k2), Silicon (si2), Phosphorous (p2), Ash (ash2) and Moisture content (M2)



Figure 2(a)-(l): Results Data Kernel density and normal distribution for : Carbon (c2), Hydrogen (h2), Oxygen (o2), Nitrogen (n2), Sulphur (s2), Sodium (na2), Calcium (ca2), Potassium (k2), Silicon (si2), Phosphorous (p2), Ash (ash2) and Moisture content (M2)

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Figure 3 (a)-(l): Results Data line of fit and two-way scatter plots for : Carbon (c2), Hydrogen (h2), Oxygen (o2), Nitrogen (n2), Sulphur (s2), Sodium (na2), Calcium (ca2), Potassium (k2), Silicon (si2), Phosphorous (p2), Ash (ash2) and Moisture content (M2)

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Figure4 (a)-(l): Results Data two-way scatter plots, line of fit against quantile line of fit for : Carbon (c2), Hydrogen (h2), Oxygen (o2), Nitrogen (n2), Sulphur (s2), Sodium (na2), Calcium (ca2), Potassium (k2), Silicon (si2), Phosphorous (p2), Ash (ash2) and Moisture content (M2)

4. Discussion

The significance for the negative regression coefficients of equation (2) gives the impression that the exclusion of these elements in the bio-waste enriches the fuel. Its combustion in metallurgical application becomes more efficient. Biomass briquetting increases volumetric energy content due to compaction. It also improves the handling operations of the material on its looseness, volatility, bulk density, transport and storage. In metallurgical operations the carbon content of the biomass is very important. It is what provides the biowaste the fuel capacity for chemical reduction kinetics. Any process to increase on the bio-waste carbon content is good for the metallurgist. However biomass in its raw form is not so rich in carbon. The biomass constitutes other elements that can supplement the carbon fuel properties like hydrogen and sulphur (H₂ and S). Others are detrimental such as nitrogen, chlorine, Oxygen, potassium, calcium, silicon. The elemental matter of ultimate analysis is what constitutes the mineral matter of biomass. Plant growth relies on nineteen (19) most essential minerals (Xu, F., 2010) among which are: the acidic group nitrogen (N), phosphorous (P), sulphur (S), chlorine (Cl) and silicon(Si); the basic metals sodium (N), potassium (K), calcium (Ca) and magnesium (Mg) on top of the chief organic elements carbon (C), hydrogen (H₂) and oxygen (O₂). The mineral matter constitution in the biomass

is in the range of (0.1-1.5 %). These minerals are in the constitution of basic plant structures like proteins and acids and in control of osmotic pressure essential for micronutrient transfer in the biomass (Lee, *et al.*, 2014). The inorganic species in organic matter is linked to ash formation in biomass combustion; accounting for an ash content of (1-20%) on average.

When combustion takes place, the organic matter decomposes freeing the inorganic component to either form volatiles or ash (Olanders, *et al.*, 1995) .The most reactive like the alkalis and acids leave as volatile matter chlorides, hydroxides and oxides to react with SO₂, CO₂, CO and form $K_2 SO_4$, CaSO₄, CaSO₄, Ca₅ (PO₄)₃OH and Ca(OH)₂.

These ashes have a problem of not only fouling the furnaces but form slag and corrode furnace walls (Llorente, *et al.*, 2006). The thermo-chemistry of biomass is necessary to provide the reaction kinetics for a successful metal-ore reduction. Characterization of the biomass is essential to determine its elemental constitution. In this regard, it is possible to understand whether it can produce a good fuel with high or low carbon content.

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The observations from the Kruskal-Wallis equality-ofpopulations rank test for bio-waste ultimate analysis were as follows:

- (a) Raw sunflower seed cake fixed carbon value is less than the elemental carbon in the biomass. The rank sum category score was 136 at proximate analysis and 213 at the ultimate analysis. Comparing absolute values from experimental data: [c2 =47.420%] and [fc =15.400%] implied for 100g of sunflower seed cake 47.420 g was elemental carbon and 15.400g of 47.420g fixed carbon, clearly indicating much of the carbon in sunflower seed cake is combined carbon with other elements. The implication is to briquette sunflower seed cake it may require enriching or concentrating the free carbon through processes like torrefaction (Batidzirai, et al., 2013) and pyrolysis (Elyounssi, et al., 2010) before producing the briquettes. A likelihood of losing the carbon as in volatile matter is high. This confirmation is clearly observed in sunflower seed cake high volatile matter (78.673%) and ash (4.280%) content.
- (b) Raw palm nut trash behaved in similar manner like sunflower seed cake because the rank sum category score was 105 at proximate analysis and 204 at the ultimate analysis. Comparing absolute values from experimental data: [c2=50.220% and fc=15.009%] and palm nut high volatile matter rank sum score was 173 against vdp=81.118% and ash content at the rank sum of 58==1.494%.
- (c) Raw saw-dust fixed carbon value was by far less than the elemental carbon in the biomass. The rank sum category score was 35 at proximate analysis and 186 at the ultimate analysis. Comparing absolute values from experimental data: [c2= 43.780% and fc= 9.557%] and the volatile matter of vdp=85.790\% and ash content of 3.176% indicates a need to either torify or pyrolyse the bio-waste before briquetting. Most of the carbon content in the biomass is in the combined form and by Llorente's argument above; might escape as either volatile matter or ash.
- (d) Raw ground nut husks the rank sum category score was 217 at proximate analysis and 145 at the ultimate analysis. The absolute values from experimental data were fixed carbon 18.034% and the elemental carbon content was 42.720% while the volatile matter ground nut husks had a rank sum of 97 = 74.284% and ash content rank sum score 149==5.197%. The indication is ground nut husks has a lot of mineral matter and volatile content compared to other bio-residues in the study. The bio-residue is more in the both extremes of volatile matter and ash content compared to other bio-residues in the study. Its fixed carbon is well above the majority in the study category though. Ground nut husks on reducing the ash content concentration and volatiles could be the most favorable at producing the best high energy briquettes.
- (e) Raw cotton seed cake the rank sum category score was 222 at proximate analysis and 139 at the ultimate analysis. The absolute values from experimental data were fixed carbon 17.900% and the elemental carbon content was 41.060% while the volatile matter cotton seed cake had a rank sum of 118 ==75.314% and ash content rank sum 149==3.217%. The behavior of cotton seed cake is close to that of ground nut husks. However

it is highly competitive for animal feed processors because of its relatively sufficient protein and fibre content (Rogers, *et al.*, 2002).

Raw de-coated cottonseed had its rank sum category score as 183 at proximate analysis and 122 at the ultimate analysis. The absolute values from experimental data were fixed carbon 17.037% and the elemental carbon content was 40.560% while the volatile matter de-coated cottonseed had a rank sum of 72=72.050% and ash content rank sum 185==7.168%. The behavior of de-coated cottonseed is like cotton seed cake but it has almost double the amount of mineral matter (potassium 2.600%, silicon 10.114% and much oxygen content of 52.244% which are important in ash formation transformations (Skoglund N., 2014).

- (f) Raw maize cob trash rank sum category score was 133 at proximate analysis and 108.5 at the ultimate analysis. The absolute values from experimental data were fixed carbon 15.510% and the elemental carbon content was 40. 180% while the volatile matter maize cob trash had a rank sum of 196==80.037% and ash content rank sum 34==2.002%. Maize cob trash has very high volatility implying it easily catches fire and with its low ash content can produce briquettes with high carbon content in the same way as sunflower seed cake.
- (g) Raw coffee husks rank sum category score was 150 at proximate analysis and 79.5 at the ultimate analysis. The absolute values from experimental data were fixed carbon 15.943% and the elemental carbon content was 39.860% while the volatile matter coffee husks had a rank sum of 142==79.801% and ash content rank sum 144==4.929%. Coffee husks have very high volatile matter and ash content and this works against coffee husks total carbon content. The implication is coffee husks requires a lot of carbon enrichment by pyrolysis and or torrefaction before briquetting the bio-waste to get enriched fuel out of it.

Raw rice and millet husks were characterized with excessive ash content more than all other bio-residues in the study: rice husks ash content =25.057 % and millet husks =18.674%! Equally their volatile matter was high: rice husks =59.682% and millet husks =69.744%. Their mineral matter content the cause for their high ash content correspond to high phosphorous content: rice husks =0.657% and millet husks = 1.060% compared with maize cob trash = 0.051%, coffee husks =0.254%; potassium rice husks =2.00% and millet husks = 1.500%. Their low fixed carbon values: rice husks= 13.486 % and millet husks =8.798% together with the high level of volatility and excessive ash content, they require a lot of preparatory work to transform into high carbon briquettes. They are disqualified on this basis for briquettability.

5. Conclusion

Ultimate analysis for elemental composition on the study of the ten bio-residues from Uganda and the statistical tool of stata has produced results with which it has been possible to select bio-residues with best characteristics for high- fixed carbon briquette production. The Kruskal-Wallis equality-of-

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populations rank test for bio-waste proximate-ultimate analysis and the discussion show the following bio-residues qualified for briquetting to produce high carbon value briquettes: sunflower seed cake, palm nut trash, saw-dust, ground nut husks, cotton seed cake, de-coated cottonseed, maize cob trash and coffee husks rank. The reason for rice and millet husks disqualification from briquetting is also warranted. The low regression coefficients make it clear why the energy from bio-waste does not show much significance from the values of its raw form variables. This makes it clearer why other processes like torrefaction and or pyrolysis are needed in the briquettology science if high fixed carbon briquettes are to be produced. This is necessary because the environmental concerns due to global warming if they have to be addressed by energy conversion techniques to overcome fuel starved metallurgical demand for ore reduction and processing, then this seems the rational way to move. The ultimate analysis on biomass is also good for selecting design parameters for furnaces, control of slugging, fouling and corrosion. The data results on volatile matter and ash content was much in agreement with established literature, and lends credence and reliability on the data collection methods used for this study. Reduction of metallic ores needs fuels with high carbon content. This is good news for the prospective metallurgist in quest for efficient fuel alternatives for metallic ore reduction.

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