

**Article title:** Elemental and Thermogravimetric Analysis of Plastic-Paper Composites as Refuse-derived Fuels for Energy Generation.

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# Elemental and Thermogravimetric Analysis of Plastic-Paper Composites as Refuse-derived Fuels for Energy Generation.

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#### Abstract.

Waste generation in Nigerian cities continue to rise with increasing population. Where and how to effectively and efficiently channel these wastes remains a serious challenge for the nation. In this study, plastic and paper waste samples were collected - as received, dried and sorted manually into sub-fractions, pulverized and homogenized in prescribed mixing ratio by weight, and compacted into briquettes. The elemental analysis to determine the carbon (C), hydrogen (H), nitrogen (N), sulphur (S), and oxygen (O) content of the samples was carried out in accordance with ASTM D3176-15 standard using an element analyzer. While, thermogravimetric tests were performed on the samples in a thermal analyser according to IUPAC procedure. The results revealed that; plastic -paper composite samples in the group exhibited a lower elemental carbon and hydrogen than the pure (PL100) plastic benchmark; the tested composite samples displayed a comparably higher presence of elemental oxygen, with exception of the composite sample with 25wt%. of paper; it was evident that plastic-paper composite samples with 25 wt%., 50wt%., and 75wt%. of paper exhibited 0.08 %, 0.04 %, and trace % increase in sulphur content, while for sample with 100wt%. of paper showed a decrease in elemental sulphur by 0.04wt%. Based on the peak temperature at the maximum weight loss rate indicating sample combustibility, samples PL100 with DTG peak temperatures (417.08-474.62°C), PL50+PA50 (383.27- 441.47°C) and PL75+PA25 (373.70- 426.41°C) are more combustible than samples PL5+PA95 (322.52+ 402.05°C) and PA100 (367.48°C), and would be recommended for use as refuse-derived fuel for on account of their energy recovery potentials.

**Keywords:** Plastic- paper composites, elemental analysis, thermogravimetric analysis, peak temperature.

#### 1. Introduction.

There is no doubt in the fact that global reserves of traditional sources of energy derived from fossil fuels are fast depleting, notwithstanding the attendant challenges associated with the earth's rising temperature, pollution, deforestation, and desertification arising from; fossil fuel combustion and plunder of the nation's forest resources, influenced by the economic pressure to meet the demand of the teeming human population. In most cities in the developing world, several tons of municipal solid waste are left uncollected on the streets each day, interfering with the free flow of drainage, creating a feeding ground for pests that spread diseases and creating enormous health and infrastructural problems (Ferronato, and Torretta, 2019). The degradation of the environment caused by inefficient disposal of waste can pollute and contaminate the environment, endangering the life of flora and fauna alike (Gangola, et al., 2018). In order to reduce landfill, some countries have successfully implemented new strategies, focusing in waste to energy, using incineration and advanced thermal treatment where these researchers are providing treatment unit for the flue gas to reduce dioxins released to the environment (Makarichi, et al., 2018).

The plastic deluge world-over, has generated huge public concern, and the vast majority of the impact of plastic pollution are invisible. By 2025, there will be an estimated 250 million tonnes of plastic in the oceans, citing previous studies. It has been projected that by 2040, almost 700 million tonnes of plastic waste would be generated, and by 2050 the weight of plastic will likely far exceed the weight of all fish in every ocean on Earth. Hence, the world's plastic pollution challenge was adjudged to constitute a 'planetary emergency' that is equal to climate change and biodiversity loss, and the global community has been urged to commit to evolving a UN treaty to commit to legally binding targets to combat plastic waste (EIA,2022).

In Abuja-Nigeria, waste bulks mainly consist of plastics, paper, glass, metal and other recyclable components (refer to table1). The degradable portions of the waste consist of food waste and yard waste. Waste generation is high due to the economic status and population density of the residents of the Federal Capital city. Studies have also reported a positive correlation between income level and waste generation quantities (Ayuba, et.al. 2013). However, with the high dependency of many countries on modern technology and packaged food products, this has caused suburbs and rural areas to have high waste generation rates. To remedy this situation on the journey towards a global circular economy, plastic waste reduction, re-use and recycling is being advocated when there are no other alternatives for re-use, remanufactured or repair.

District Names							
Waste type (%)	Garki	Wuse	Maitama	Asokoro	Gwarimpa	Apo	
Paper	13	12	13	13.6	6.9	10.1	
Metal	5.6	3.3	5.30	6.7	5.4	4.9	
Glass	5.5	4.4	5.32	4.1	4.1	-	
Plastic	16.2	17.3	20	15.1	21.3	18.7	
Food remnants	52	54.3	54.80	53	61.2	65.3	
Textile	2.2	4.7	0.10	3.1	-	-	
Rubber	3.4	1.5	0.19	0.7	-	0.9	
Others	1.8	2.4	0.60	2.8	1.1		
Person/household	8	8	6	6	13	6	

Table 1: Household waste composition for different districts in Abuja

Source: FMEnv (2004)

Hence, rather than losing the value of plastics and waste paper to landfills, their potential as a replacement for fossil fuels, using non-recyclable materials to generate refuse -derived fuel (RDF) is generally encouraged as the most sustainable option for the huge amount of waste generated and managed each year (Wakelin, 2014). Briquettes produced from RDFs are used domestically and industrially for heat and power generation. Combustion of the produced briquette fuel is an alternative thermal treatment method available for waste management and the knowledge of the combustion behaviors of the waste fuel is critical in order to control the process and minimize the environmental impacts. Its application has the potential of reducing the mass and volume of wastes, while simultaneously allowing energy recovery. Towards this end, the study of the combustion behavior of plastic -paper composites derived from municipal solid waste (MSW) generated in urban Nigeria - via elemental and thermogravimetric analysis, is being undertaken as the main trust of this research paper, to evaluate its candidacy for RDF production as a measure to reduce plastic pollution, and use resources more sustainably.

# 2. Materials and Method

# 2.1 Sample collection and preparation

Samples were collected manually from a static lot using sampling scoop from four (4) different points within 1 km radius in Maitama District of the Federal Capital Territory, Abuja, Nigeria. For each location, samples were taken from the top, middle and bottom of the material alternately. The samples as-received had high moisture content, and were sun pre-dried in compliance with BS EN 15442:2011 test specification (BSI, 2011), to avoid problems of decomposition by micro-organisms. Subsequently, the samples were sorted manually by hand into sub-fractions, such as;

plastics, textile, wood, and paper in line with BS EN 15440:2011test procedure (BSI, 2011). Refer to plates 1, 2, 3, and 4 respectively for plastic and paper samples.



#### 2.2 Preparation of plastic-paper composites

The samples of the solid waste materials were pulverized (0.2mm) and mixed / homogenized in the prescribed mixing ratio by weight in proportions presented in table 1 below:

Table 1: Plastic- paper composite samples used.

Samples	Percentage by Weight
PA 100	Paper 100% by weight.
PL 25 + PA 75	Plastic 25% by weight and Paper 75% by weight
PL 50 + PA 50	Plastic 50% by weight and Paper 50% by weight
PL 75 + PA 25	Plastic 75% by weight and Paper 25% by weight
PL 100	Plastic 100% by weight

# 2.3 Production of RDF Briquette

The briquettes were formed in a cylindrical mould with an inner diameter of 14.0 mm, a height of 95.0 mm and a rod with 80.0 mm outer diameter placed in the center to create a hole in the middle of the briquette. The hole helps to increase porosity and oxygen supply, thereby improving briquette combustion. The mould was filled with the RDF mixtures and densified under constant operating conditions (i.e. temperature of 36 - 37 °C, pressure range of 40 kPa) with a manually operated 5-tonne air hydraulic piston pressure, Budenberg Steel Tube, 200 kN Capacity Compressive Strength Testing Machine (refer to plate 5). Thirty-five (35) briquettes were produced from each sample and their initial densities were measured immediately after ejection from the mould. The resultant briquettes shown in plates 6, and 7 were placed on a flat surface and left to air dry in a closed room with adequate air ventilation for 35 days before testing the properties.



Plate 5. Compressive strength testing machine



- 2.4 Material characterization
- i. Ultimate analysis of the test samples.

The ultimate analysis to determine the carbon (C), hydrogen (H), nitrogen (N), sulphur (S), and oxygen (O) content of the samples was performed in accordance with ASTM D3176-15 (ASTM, 2015) standard using an element analyzer (model 2400 CHNS/O Series II Perkin Elmer) at the Geoscience laboratory, Kaduna, Kaduna State. For the determination of the aforementioned elements, the standard BS EN 15407:2011 and BS EN 15408:2011 tests protocols were adopted and used (BSI, 2011). All determined values in both proximate and ultimate analyses are reported in this paper as dry basis (d.b.).

ii. Thermogravimetric analysis of test samples.

Combustion tests were performed in a thermal analyser. The instrument was regularly calibrated according to IUPAC procedure (Gmelin,1995). Temperature measurement is granted within 0.1% and heat flow within 2%. Thermogravimetric analysis (TGA) was conducted in oxygen atmosphere (20 mL/min) with the aid of thermogravimetric simultaneous thermal analyser (STA) 6000 TGA (Perkin Elmer), a powerful analytical technique for evaluating decomposition profile of solid samples. This technique allows acquisition of data relating the weight of sample and

decomposition rate with respect to temperature, time or both under a controlled environment. The decomposition profile was evaluated from ambient temperature to 850 °C at 10 °C/min three heating rates. Sample size of approximately 10.0 mg (particle size of 0.2 mm) was used. The experiment was performed twice for reproducibility (Fan, et al. 2008). The sample weight loss and derivative weight loss with respect to temperature were recorded simultaneously during the tests and used for the production of the thermogravimetry (TG), Derivative thermogravimetry (DTG) combustion curves respectively (Bayerns, et al., 2010b).

#### 3. Results and Discussion

i. Elemental analysis of plastic and paper composites.

Ultimate analysis can be defined as the total elemental analysis to determine the percentage of elements, mainly, carbon, hydrogen, oxygen, nitrogen, sulphur and present. The oxygen value is calculated by subtracting the other components, including ash and moisture, from 100%. This analysis is used to characterize the chemical composition of the organic fraction of the waste; which in turn is useful in assessing the stability of the waste as a fuel and predicting emissions from combustion. The results of the ultimate analysis of the RDF samples of plastics, paper and plastic-paper composites are presented in table 2 and figure 1 respectively.

RDF Sample	Carbon	Hydrogen (%)	Oxygen (%)	Sulphur	Nitrogen (%)
	(%)			(%)	
PL 100	47.41	5.56	28.61	0.14	0.73
PA 100	27.56	3.50	36.07	0.10	1.09





Table 2: Ultimate analysis of plastic and paper samples

Figure 1: Elemental composition of plastic and paper sample blends.

Elemental analysis of plastic-paper composites. It could be seen from figure 1 that plastic samples with PL75 +PA25 (25% wt. paper), PL50 +PA50 (50 % wt. paper), PL25 +PA75(75% wt. paper), and PA100 (100% wt. of paper) exhibited 5.53%, 8.86%,14.06%, and 19.85% lower content of elemental carbon than in PL100 (0 % wt. of paper). It is evident that plastic material exhibits the highest carbon and hydrogen content of the samples in the group.

Plastics are polymers. Polymers have a longer carbon chain, and hence; a large carbon and energy content, which makes plastic waste interesting for energy recovery by incineration, or for fuel production via gasification. But also, material and feedstock recycling (via pyrolysis, hydrocracking, or gasification) of plastics are very much desired options which aim at the substitution of fossil petrochemicals as feedstock for production. Energy recovery and mechanical recycling of plastic are currently the most common techniques and mechanical recycling is having a recycling rate of about 50% usually recommended for scrap reprocessing (Bayerns, et al. 2010b).

Similar trend was also observed for elemental hydrogen where; samples with 25% wt., 50%wt., 75%wt., and 100% wt. of paper in plastic samples demonstrated 0.6%, 0.92%, 1.48% and 2.06% reduction in elemental hydrogen. The elemental presence of hydrogen is also highest in plastic materials and decreases in the blended samples in the decreasing order of the proportion of paper in the sample mixture. It was also observed that elemental oxygen in the tested samples in the group present a 2.43% decrease for sample with 25%wt. of paper; a 1.4%, 5.38% and 7.46% increase in elemental oxygen was recorded for 50%wt., 75%wt., and 100% wt. of paper in plastic samples. Oxygen is increasingly used as an oxidant in delignification, oxygen alkali extraction, ozone bleaching, and chemical and energy recovery in paper production. Hence, the presence of elemental oxygen is indicative of the presence of oxygen molecules in the material from whence paper was produced (Anonymous,2022).

In the case of elemental sulphur, it was also evident from figure 1, that plastic samples with 25% wt., 50%wt., and 75%wt. of paper exhibited 0.08 %, 0.04 %, and 0% increase in sulphur content, while for sample with 100% wt. of paper show a decrease in elemental sulphur by 0.04% wt. The key component for recycling of paper and cardboard are the contained cellulose fibers: 57% of fibers used in the paper industry originate from recycled paper and cardboard (Worrell and Reuter, 2014) and about 38% of recovered paper originates from households (Baeyens, et al. 2010a). The evidence of sulphur in the tested specimens could be attributed to the use of

sulphide salts with excess of sulphur dioxide, and caustic soda with sodium sulfide to dissolve and stabilize recycled pulp after bleaching for paper production (Nicholas , et al. 2010).

The presence of elemental nitrogen in the test samples was also observed from the results as; 25% wt., 50%wt., 75%wt., and 100% wt. of paper in plastic samples exhibited 0.13%, 0.17%, 0.28% and 0.36% increase in elemental nitrogen. The noticeable level of elemental nitrogen in the test samples is traceable to the prevalence of the use of nitrogen in dyes production for paper coloration. With its high concentration in the dye bathe and under nitrogen atmosphere, the dye diffuses and migrates more intensely into the fibre.

#### ii. Combustion characteristics of plastic-paper composites.

Generally, the combustion of fuels is an alternative thermal treatment method available for waste management. Its application has the potential of reducing the mass and volume of wastes, while simultaneously allowing energy recovery. However, toxic metal particles or vapours are generated when contaminated wastes and metals are burned. Therefore, the knowledge of the combustion behaviour of the waste fuel is critical in order to control the process and minimize the environmental impacts (Grammelis, 2009). In order to evaluate the potentials of the waste from the components of the municipal solid wastes under survey, the combustion characteristics of the samples from plastic- paper composites are presented in Figure 2 of TG and DTG, after drying.

Figure 2 presents the TGA curves corresponding to both plastic-paper composites at different ratios; 25% wt., 50%wt., 75%wt., 0% wt. and 100% wt. of paper in plastic samples each. The onset temperatures were 296.74 (94.12 %), 326.54 (97 %), 309.70 (93.66 %), 329.34 (90.39 %) and 309.13 (89.27 %) for 25% wt., 50%wt., 75%wt., 0% wt. and 100% wt. of paper in plastic samples respectively. At these stages, the temperatures corresponded to the removal of absorbed or unbounded water and volatile compounds from the samples. It can be seen from Table 2 that PL100, and PA 100 TGA curves presented the highest degradation temperature of  $309.13-562.10^{\circ}C$  and  $329.34-546.60^{\circ}C$ ; followed by PL75 + PA25 ( $309.70-483.50^{\circ}C$ ). The recorded mean value of samples with lowest degradation temperature are PL25 + PA75 ( $296.14-402.05^{\circ}C$ ), and PL50 + PL50 ( $326.54-463.40^{\circ}C$ ) samples. The thermal decomposition of PL50 + PL50, PL25 + PA75 and PL100 showed the presence of two major endothermic peaks except for PL25 + PA75 and PA100 as shown in Table 2.



Figure 2: TGA and DTG curves for: (a) PL25% +PA75%; (b) PL50% + PA50%; (c) PL75 + PA25%; (d) PL100%; and (e) PA100% at the same heating temperature and time.

Sample	% Wt. of Paper	Onset	Degradation temp.	TGA step	DTG peak	% organic
		temperature	range			matter
PL25 + PA75	25%	296.74 (94.12 %)	296.14-402.05	1	322.52,	5.03
					402.05	
PL50 + PA50	50%	326.54 (97.02 %)	326.54-463.40	2	383.27,	18.31
					441.47	
PL75 + PA25	75%	309.70 (93.66 %)	309.70-483.50	2	373.70,	22.98
					426.41	
PL100	0%	329.34 (90.39 %)	329.34-546.60	2	417.08,	6.15
					474.62	
PA100	100%	309.13 (89.27 %)	309.13-562.10	4	367.48	13.51

Table 2: Information from TGA and DTG analysis for both plastic and paper.

Thermogravimetric kinetics may be explored for insight into the reaction mechanisms of thermal (catalytic or non-catalytic) decomposition involved in the pyrolysis and combustion processes of different materials (Coats, and Redfern, 1963; Reyes-Labarta, and Marcilla, 2012; Marcilla, Gómez, and Reyes, 2001; Marcilla, et al., 2003a; Marcilla, et al., 2003b; Conesa, 2004; Reyes, 2001). In this case, it is used to determine the thermal stability of plastic -paper composite materials. Hence, by accurately monitoring the weight of a sample while heating at a constant rate, a sample's weight can be evaluated and attributed to a specific material response to a thermal stress (refer to figures 2a, b, c, and d.). In a desired temperature range, if a species is thermally stable, there will be no observed mass change. Negligible mass loss corresponds to little or no slope in the TGA trace. TGA also gives the upper use temperature of a material, and beyond this temperature the material will begin to degrade. The four stages of coal oxidation are water evaporation, oxygen chemisorption, significant decomposition reactions, and the stage dominated by direct burn-off reaction. Meanwhile, the mass loss led by water evaporation is much larger than the mass increase due to oxygen adsorption, thereby resulting in the observed decline in the TG curve (Chukwu, et al., 2016).

It could be seen from table 2 and figure 2 that the onset temperature of PL100  $(329.34 \,^{\circ}C)$  is the highest with an evidence of 6.15% organic matter in the polymeric material. While, sample PL25+PA75 (296.74  $^{\circ}C$ ) exhibited the lowest onset temperature amidst the presence of 5.03% organic matter. The onset temperature is the ignition temperature where mass loss reaches a rate of 1% per minute on the DTG profile in figure 2. Conversely, the PL100 sample presented the highest degradation temperature within the range 329.34-546.60°C at a TGA of 2 step processes. PL25+PA75 plastic composite recorded the lowest degradation temperature of 296.14-402.05°C under a single step TGA degradation process. The

thermal decomposition of PL50 + PL50, PL25 + PA75 and PL100 showed the presence of two major endothermic peaks, except for PL25 + PA75 and PA100. At these peak temperatures, the maximum weight loss rate was observed, and this indicative of effective sample combustibility.

The lower temperature that appeared in DTG curves represent the decomposition of hemicellulose material, while the higher temperature represents the burnout temperature where DTG profile reaches a 1% combustion rate at the tail-end of the profile, indicating the completion of sample oxidation. However, there was a significant interaction between characteristics between plastic and paper during the thermal decomposition. Studies have shown that polymeric materials usually melt before they decompose. Most polymers melt or degrade before 200 °C. However, there is a class of thermally stable polymers that are able to withstand temperatures of at least 300 °C in air and 500 °C in inert gases without structural changes or strength loss, which can be analyzed by TGA (Liu, and Yu, 2006; Marvel, 1972; Tao, 2009). In addition, studies have shown that organic matter (macerals) significantly influences combustion behavior, ignition, and flame stability (Falcon and Ham, 1988). The mass of the residue organic matter for the composite materials increased with the increase of the plastic content as presented in table 2 with the lowest content of plastic in the sample with the least percentage, and the result corroborated the findings of Ansah et al. (2016).

Given that thermal decomposition of unstable oxygenated complexes is a relatively slow process at temperatures between initial temperature and peak temperature, the amount of heat released increases with the temperature rise, which has been displayed by the DSC curves of all samples. Based on the peak temperature at the maximum weight loss rate, which indicates sample combustibility, sample PL100 with peak DSC temperatures (417.08- 474.62°C), PL50+PA50 (383.27- 441.47°C) and PL75+PA25 (373.70- 426.41°C) are more combustible than Samples PL25+PA95 (322.52+  $402.05^{\circ}$ C) and PA100 (367.48°C), as represented on the combustion thermograms.

# 4. Conclusion

The ultimate and thermogravimetric analysis of composites materials derived from MSW were successfully analyzed. The following could be inferred:

i. The plastic -paper composite samples in the group exhibited a lower elemental carbon and hydrogen than the PL100 plastic benchmark.

- ii. The tested composite samples displayed a comparably higher presence of elemental oxygen, with exception of the composite sample with 25%wt. of paper.
- iii. It was evident that plastic-paper composites samples with 25% wt., 50%wt., and 75%wt. of paper exhibited 0.08 %, 0.04 %, and 0% increase in sulphur content, while for sample with 100% wt. of paper show a decrease in elemental sulphur by 0.04% wt.
- iv. All plastic -paper samples in the group exhibited an incremental rise in elemental nitrogen.
- v. The onset temperatures were 296.74 (94.12 %), 326.54 (97 %), 309.70 (93.66 %), 329.34 (90.39 %) and 309.13 (89.27 %) for 25% wt., 50%wt., 75%wt., 0% wt. and 100% wt. of paper in plastic samples respectively. At these temperatures absorbed or unbounded water and volatile compounds are removed from the samples.
- vi. The PL100 sample presented the highest degradation temperature of 329.34-546.60°C followed by PL75 + PA25 (309.70-483.50°C).
- vii. Based on the peak temperature at the maximum weight loss rate, which is an evidence of combustibility, presents samples PL100 with peak DSC temperatures (417.08- 474.62°C), PL50+PA50 (383.27- 441.47°C) and PL75+PA25 (373.70- 426.41°C) as more combustible than samples PL25+PA95 (322.52+ 402.05°C) and PA100 (367.48°C), represented on the combustion thermograms.

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