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Compositional analysis of lignocellulosic materials: Evaluation of an economically viable method suitable for woody and non-woody biomass

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ABSTRACT: The determination of the composition of lignocellulosic substrate is a crucial step in order to determine the overall efficiency of the processes designed to convert lignocelluloses to ethanol. Standard methods as gravimetric, chromatography, and spectroscopic are routinely explored in the scientific literature. This paper details our investigations in the application of economically viable gravimetric methods particularly suitable for developing countries. The methods were proven to be reproducible and representative for the analysis of biomass as sugarcane bagasse, siam weed, shea tree sawdust.

Keywords: Gravimetry, lignocelluloses, biomass, extraction, analysis

I. INTRODUCTION

The overall efficiency of processes designed to convert lignocellulosic biomass to ethanol lies on determining the compositions of such material. Lignocelluloses mainly consist of cellulose, hemicelluloses, and lignin which are bonded together by covalent bonding, various intermolecular bridges, and van der Waals' forces forming a complex structure, making it resistant to enzymatic hydrolysis and insoluble in water [1]. Lignocelluloses continue to be investigated as a source of fermentable sugars for biofuel (ethanol) production because of their high availability [2]. Lignocellulosic biomass includes all plants and plant derived materials, including agricultural crops and trees, wood and wood residues, municipal residues, and other residue materials [3]. The Cellulose (40–55% of total feedstock dry matter) is a glucose polymer linked by β-1,4 glycosidic bonds with the degree of polymerization from 10,000 in native wood to 1,000 in bleached kraft pulps. The basic building block of this linear polymer is cellobiose, a glucose-glucose dimer. Cellulose has a strong tendency to form intra-and inter-molecular hydrogen bonds by the hydroxyl groups on the linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure and give cellulose a multitude of partially crystalline fiber structures and morphologies. Hydrolysis of cellulose results in individual glucose monomer. This process is also known as saccharification. Its density and complexity resist hydrolysis without preliminary chemical or mechanical degradation or swelling. In nature, cellulose is usually associated with other polysaccharides such as hemicellulose (xylan)/or lignin. It is the skeletal basis of plant cell walls [4]. It contains both crystalline (70%) and non-crystalline or amorphous (30%) structure. Hemicellulose (24–40% of total feedstock dry matter) is a short, highly branched polymer of five carbon (C_5) and six carbon(C_6) sugars. Specifically hemicellulose contain xylose (xylose has acidic group glucuronic acid which makes it more resistant to enzymatic hydrolysis) and arabinose (C_5) and galactose, glucose, and mannose (C_6). It is more readily hydrolyzed compared to cellulose because of the branched amorphous structure. A major product of hemicelluloses hydrolysis is the C_5 sugar. The monosaccharides released upon hemicellulose hydrolysis include a large fraction of pentoses [5]. Lignin is a highly cross-linked phenyl propylene polymer and the largest non-carbohydrate fraction of lignocellulose. It's the third major component of lignocellulosic biomass. In wood biomass it makes up 25–36% depending on the type of wood. It plays an important role in cell wall structure as a permanent bonding agent among plant cells. Unlike cellulose, lignin cannot be depolymerised to its original monomers. Lignin and hemicellulose form a sheath that surrounds the cellulosic portion of the biomass. Lignin protects lignocellulose against insect attack. This complexity has made it as resistant to detailed chemical

characterization as it is to microbial degradation, which greatly impedes the understanding of its effects. Cellulose, hemicelluloses, lignin and the other components are ordered in varying composition in the different parts of the fibre wall depending on the species of biomass. Extractives include non-structural components that are non-chemically bound components of biomass such as sucrose, nitrate/nitrite, protein, ash, chlorophyll, waxes. The extractives are removed because they potentially interfere with downstream analysis of biomass sample. Gravimetric analysis describes a set of methods for the quantitative determination of a sample or material based on the mass of a solid. Mostly, collected dried solids are weighed with an analytical balance. When carefully followed especially during weighing, gravimetric method can provide precise analysis. It provides very little room for instrumental error. It does not require expensive equipment. Determination of the composition of lignocellulosic substrates using gravimetric analysis exists in scientific literature. These included the monoethanolamine method [6], the trifluoroacetic acid method [7], concentrated sulphuric acid method [8]. Acid and neutral detergent method [9]. These methods are directly applicable to specific lignocelluloses, and the sources of the materials [2]. Therefore, the present study aims at a simple, economically viable, and readily available procedures devoid of very sophisticated equipment for lignocellulosics compositional analysis. Estimations of extractives, cellulose, hemicellulose, lignin, and ash can potentially be performed by gravimetric determination.

The study detailed our investigations using gravimetric method for the compositional analysis of lignocellulosic biomass with evaluations on sugar cane bagasse, siam weed, and shea tree sawdust [3,10-12].

II. MATERIALS AND METHODS

Chemicals, reagents, and raw biomass materials: All chemicals and reagents used in this study were of analytical grade and commercially available. Raw biomass materials were sugar cane bagasse, siam weed, and shea tree sawdust.

Preparations of raw biomass: Sugar cane (*Saccharum officinarum*) was purchased from an open market in late November, 2012 from Zaria Town (11^{o}04'N 7^{o}24'E), Kaduna State, Northern Nigeria. The juice was extracted from the sugar cane stalks (local name as Ireke) at a local mill in Ota (6^{o}40'N 3^{o}14'E), Ogun state, Nigeria. The biomass without the juice was air-dried in an open space (average temperature of 35±2 ^{o}C) for three days (8 h per day). The stem of the siam weed (*Chromolaena odorata*, local name as ewe Akintola or ewe Awolowo) was harvested from a nearby fallow land (bush) in Ota, Ogun State, South West, Nigeria [12]. After it was harvested, it was sun dried for days. The sample size was reduced to about 2 cm in length for effective milling. Size reduction was carried out on both sugarcane bagasse and siam weed by knifing and milling. The Shea tree (local name as Igi Ori), *Vitellaria paradoxa*, was harvested from the forest around Idanre (6^{o}51'N 5^{o}06'E), south west, Nigeria in early April 2010. The logs were reduced to different sizes at the central processing unit of the local sawmill (Ilepa, Ifo, Nigeria; 6^{o}49'N 3^{o}12'E) [10]. The residues after this milling were used for the compositional analysis. A portion of the materials was screened into different sizes using a sieve shaker. While the remaining portion was labeled as unscreened. Fig. 1 shows the biomass materials before and after size reduction.

Compositional analysis of the raw lignocellulosic materials: Each of the biomass materials was subjected to compositional analysis using the gravimetric method. Materials used in this study were all unscreened. The schematic representation of the step-by-step compositional analysis is as shown in Fig. 2.

Extractives: 2.5 g of dried raw biomass was loaded into the cellulose thimble. With the Soxhlet extractor set up, 150 mL of acetone was used as solvent for extraction. Residence times for the boiling and rising stages was carefully adjusted to 70 ^{o}C and 25 min respectively on the heating mantle for a 4 h run period. After extraction, the sample was air dried at room temperature for few minutes. Constant weight of the extracted material was achieved in a convection oven at 105 ^{o}C. The %(w/w) of the extractives content was evaluated as the difference in weight between the raw extractive-laden biomass and extractive-free biomass [13-15].

Hemicellulose: 1 g of extracted dried biomass was transferred into a 250 mL Erlenmeyer flask. 150 mL of 500 mol/m^3 NaOH was added. The mixture was boiled for 3.5 h with distilled water. It was filtered after cooling through vacuum filtration and washed until neutral pH. The residue was dried to a constant weight at 105 ^{o}C in a convection oven. The difference between the sample weight before and after this treatment is the hemicellulose content (%w/w) of dry biomass [10, 13-15].

Lignin: 0.3 g of dried extracted raw biomass was weighed in glass test tubes and 3 mL of 72% H_2SO_4 was added. The sample was kept at room temperature for 2 h with carefully shaking at 30 min intervals to allow for complete hydrolysis. After the initial hydrolysis, 84 mL of distilled water was added. The second step of hydrolysis was made to occur in an autoclave for 1 h at 121 °C. The slurry was then cooled at room temperature. Hydrolyzates were filtered through vaccum using a filtering crucible. The acid insoluble lignin was determined by drying the residues at 105 ^{o}C and accounting for ash by incinerating the hydrolyzed samples at 575 ^{o}C in a muffle furnace. The acid soluble lignin fraction was determined by measuring the absorbance of the acid hydrolyzed samples at 320 nm. The lignin content was calculated as the summation of acid insoluble lignin and acid soluble lignin [16].

Cellulose: The cellulose content (%w/w) was calculated by difference, assuming that extractives, hemicellulose, lignin, ash, and cellulose are the only components of the entire biomass [13-15].

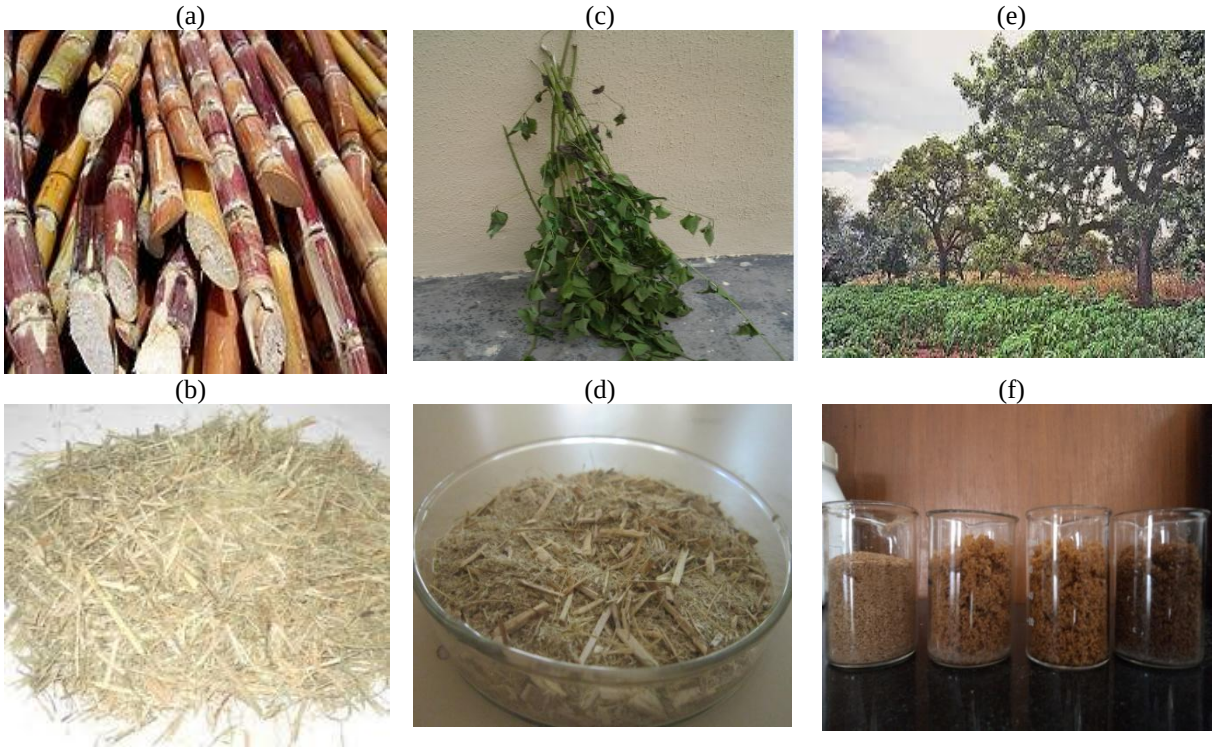

Fig. 1: Raw biomass before and after size reductions. Sugar cane (a); unscreened sugar cane bagasse (b). Siam weed including the leaves (c); unscreened sample of siam weed (d). Shea tree (e); screened shea tree sawdust (f).

III. RESULTS AND DISCUSSION

The basic compositions of the three lignocellulosic materials is as shown in Table 1. Each experiment was replicated twice; reported results indicate the average values of the replicated experiments. Studies have been reported for other varieties of sugarcane bagasse (Table 2)[18-22], and shea tree sawdust [10]. To the best of the authors knowledge, there is no comprehensive information for Nigeria sugarcane bagasse and siam weed varieties.

Results in this study are comparable to those available in the literature (Table 2). Biomass compositions vary according to whether woody or non-woody, geographical locations of materials, methods (procedures) developed for analysis, biomass variety, differences in solvents and the part of plants used in the compositional analysis. Shea tree composition falls within most reported values for woody biomass [23]. For example, Pettersen [24] reported lignin content for Douglar fir to be 32%(w/w) and for red pine lignin as 29%(w/w), total carbohydrate as 63%(w/w). Douglar fir total carbohydrate content was about 67%(w/w) [24]. Sugar cane bagasse total carbohydrate content was about 69%(w/w) which is comparable to most other reported values in the

literature (Table 2). Siam weed, an herbaceous plant, has a total carbohydrate content of about 70%(w/w) which is comparable to most herbaceous biomass values such as corn stover 61.7%(w/w), wheat straw 58%(w/w)[23].

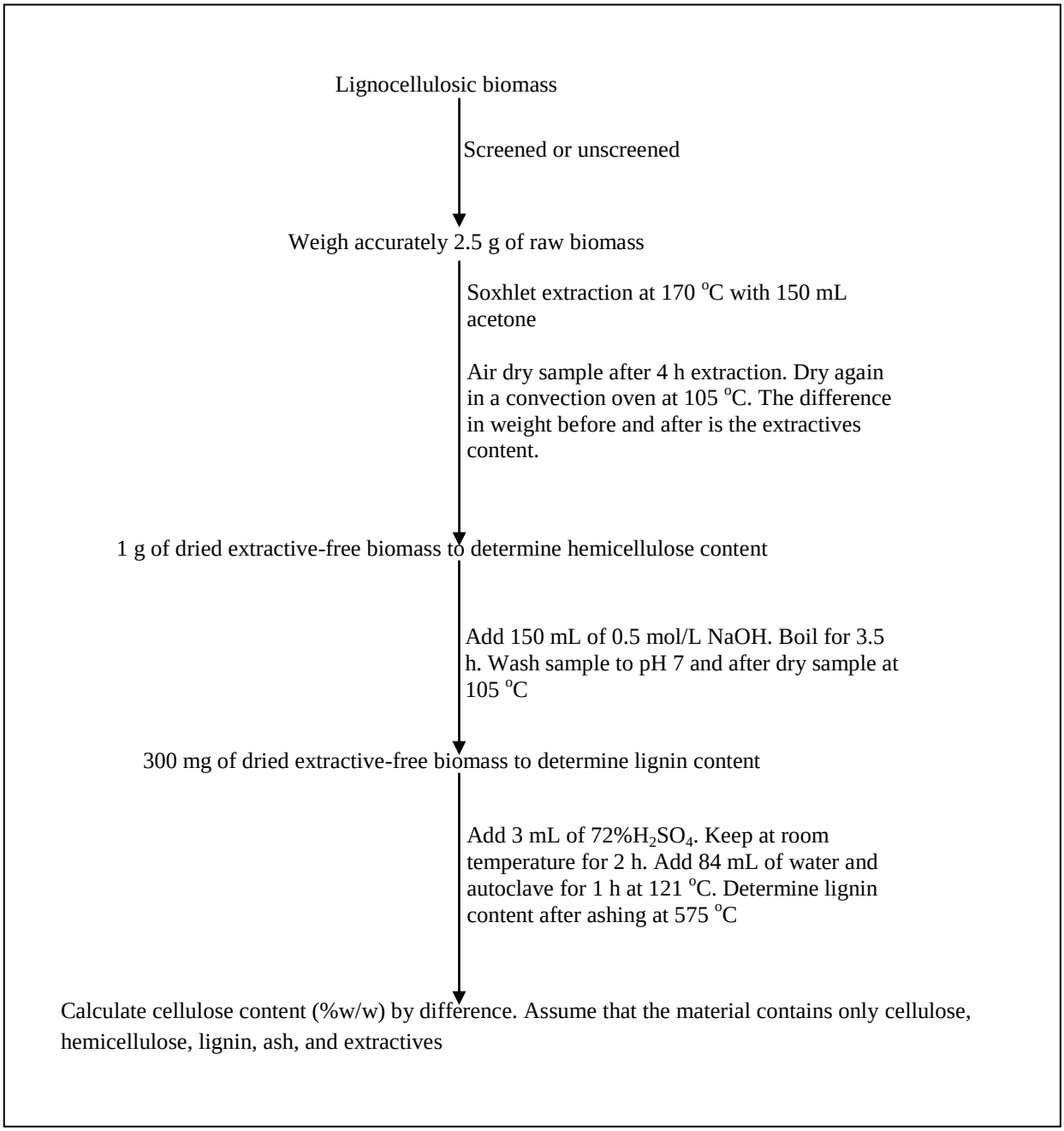

Fig. 2: Schematic representation of the compositional analysis of the lignocellulosic materials

Table 1: Compositional analysis of raw lignocelluloses of sugarcane bagasse, siam weed, and shea tree sawdust (%w/w)

	Sugarcane bagasse [18-22]	Siam weed[12]	Shea tree sawdust[10]
Extractives	2.14±0.6	4.8±0.9	1.9±1.7
Cellulose	35.28±1.2	40.2±2.3	45.9±9.2
Hemicellulose	33.28±0.8	29.9±0.7	20.3±11.5
Lignin	25.20±1.1	23.2±5.3	29.9±13.2
Ash	4.1±0.3	0.9±3.1	2.04±3.1

Table 2: Reported compositions (% dry weight) of sugarcane bagasse

Cellulose	Hemicellulose	Lignin	Ash	Extractives	References
37	28	21	-	-	[18]
39	26.2	24	-	-	[19]
26-47	19-33	14-23	1-5	-	[20]
43	31	11	6	9	[21]
49	16	27	8[a]	-	[22]

[a]addition of ash, extractives and proteins

IV. CONCLUSIONS

This study has highlighted a very simple procedure for compositional analysis of both woody and non-woody lignocellulosic biomass. Comparable results were obtained for the tested raw materials and those reported by scientific literature. The procedures proved to be economically viable for developing countries since sophisticated equipment, expensive and scarce chemicals are not required (chemicals for the entire compositional analysis are common and readily available on the shelf). By extension, the method can be utilized in most established economies of the world because of the reliability and cost-effectiveness of the whole process.

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