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Physico-chemical characterization of forest and agricultural residues for energy conversion processes

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Abstract:

Agricultural and forest residues could become potential sources of energy in various countries. However, incomplete understanding regarding physico-chemical properties of these residues presents the main challenges for energy conversion processes. This study presented a complete and comprehensive database of characteristics and compositions of a wide range of agricultural and forest residues. Physical characteristics (moisture, bulk density, calorific value, volatile matter, fixed-carbon content, and ash content), elemental compositions (C, H, N, O, and S), as well as lignocellulosic compositions (cellulose, hemicellulose, and lignin) of ten biomass residues were analyzed. The major impacts of the variability in biomass compositions to biochemical and thermochemical processes were also discussed.

Keywords. Biomass properties, proximate analysis, ultimate analysis, biochemical analysis.

1. INTRODUCTION

In the context of sustainable development, various countries are trying to rebalance their energy mix, responding to their energy security and environmental concerns.[1] This could be achieved by deploying a range of biomass conversion technologies and approaches suitable for each country's context.[2] Biomass feedstocks are plenty available in developing countries, especially agricultural and forestry residues.[3] In spite of resources capabilities, there is a huge untapped potential of these sources due to a lack of knowledge on the properties of these feedstocks. The two most common pathways for transforming biomass to energy are biochemical and thermochemical conversion technologies.[4] The biochemical conversion includes technologies using microbial processes to convert biodegradable wastes, such as fermentation or aerobic digestion. Biomass can be turned into different products, such as hydrogen, biogas, ethanol, acetone, butanol, organic acids, etc. by selecting different microorganisms in the process.[5] This pathway is much slower than thermochemical conversion, but it does not require much external energy. Thermochemical conversion can be defined as the controlled heating or oxidation of feedstocks to produce energy products. This pathway covers a range of technologies including pyrolysis, gasification, and combustion which can provide heat, electricity, gaseous, or liquid fuels.[5] It is crucial to select the most economical process to convert the collected biomass into fuels, energy, or chemical products. This can only be done by having extensive knowledge of the physico-chemical properties of the biomass feedstock, as they have a significant impact on each of the processing steps during conversion processes.[6] Differences between biomass feedstocks and conversion technologies offer both opportunities and challenges. For instance, a commercial gasification model using exclusively wood chips cannot directly be transferred to other places that have different types of biomass resources.[7]

As demand for biomass feedstocks increases, characteristics of new resources must be investigated to ensure a good choice of the technologies, or to suggest a change in conversion process parameters of existing systems. The physical and chemical properties of biomass have direct and indirect impacts on conversion performance. The mismatch of biomass feedstock to a certain energy conversion technology could also be mitigated through the selection of pre-treatment processes, or by blending different types of biomass to diminish detrimental effects, if the characteristics of the feedstock are known. Three common analysis techniques for describing biomass characteristics are biochemical, proximate, and ultimate analysis. Biochemical analysis refers to the relative abundance of various biopolymers, such as hemicellulose, cellulose, and lignin in the biomass.[8] The proximate analysis intends to characterize biomass based on relative proportions of volatile matter, ash content, and fixed carbon.[9] Ultimate analysis refers to the relative abundance of individual elements, such as C, H, O, N, and S.[10] These techniques are inter-related, but information extracted from analysis results can be used much differently. While biochemical conversion processes focus on characterizing biomass in a biochemical paradigm, proximate and ultimate analyses are more appropriate for thermochemical conversion processes. Thus, the presentation of important biomass characteristics in the context of proximate or ultimate analysis, as well as biochemical analysis gives valuable information for engineers and developers to conceptualize, build or choose appropriate technologies. Besides, the intrinsic nature of biomass, moisture content and bulk density are also of importance when evaluating the potential use of biomass for energy purposes. Even moisture content can be considered part of the standard proximate analysis procedure, it can also be evaluated by itself. For instance, moisture content of the feedstock not only directly impacts the efficiency of the conversion process but also indirectly impacts the pre-treatment of the material, such as drying or grinding processes.[11] Similarly, low bulk density also causes issues, such as increases in transportation and handling costs, or difficulties in feeding and handling systems.[12]

Biomass feedstocks vary significantly in their compositions. This fact is observed clearly when considering diverse bioenergy feedstocks. Various types of biomass solid wastes have been proved to be potential for energy production, including agricultural and forest residues.[13] Several feedstocks in this category have been characterized.[14] In general, agricultural residues, in addition to having higher ash content, exhibit more variabilities in their compositions than forest residues.[15] However, data regarding the properties of agricultural residues are still fragmented and incomplete. Characteristics of raw materials are usually only introduced in one of three ways, either proximate, ultimate, or biochemical analysis. Moreover, the characteristics of these biomass feedstocks are influenced not only by their intrinsic nature but also by the upstream processes and the storage conditions. Therefore, the properties of one biomass residue cannot be extrapolated to other types. This requires complete and accurate data on the characteristics of biomass residues, based on all the analysis techniques mentioned above.

This study presented a complete characterization of ten biomass types for their use as feedstock for energy production, namely bamboo chip, cassava pulp, corn stalk, corn cob, rice husk, rice straw, sugarcane bagasse, rubberwood chip, coir fiber, and sawdust. These residues, abundantly and easily found in Vietnam and other developing countries, represent main sources of environmental pollution from agricultural and forest activities. The major impacts of the variability in biomass compositions on biochemical and thermal conversion processes were also discussed.

2. MATERIALS AND METHODS

2.1. Collection and pre-treatment of biomass feedstocks

Ten types of residues, namely: bamboo chip, cassava pulp, corn stalk, corn cob, rice husk, rice straw, sugarcane bagasse, rubberwood chip, coir fiber, and sawdust were collected in processing factories in different regions of Vietnam (figure 1). The moisture content (M) of these samples was firstly determined according to the ASTM E1756-08 standard. The samples were then cleaned with distilled water to remove dust and impurities, and dried in the Memmert Oven (Model 800) at 105 °C for 24 hours to remove their moisture content. Bulk density was determined according to the ASTM E873 – 82 standard. Next, biomass feedstocks were ground and sieved to get homogeneous particles below 0.5 mm in diameter. The biomass samples were then stored in air-tight boxes at room temperature for further analysis.

2.2. Characterization of biomass feedstocks

Proximate analysis, i.e. volatile matter (V), fixed carbon (FC) and ash (A), ultimate analysis, i.e. Carbon (C), Hydrogen (H), Nitrogen (N), Sulfur (S) and Oxygen (O), biochemical analysis, i.e. cellulose, hemicellulose, and lignin, and higher heating value (HHV) were conducted to characterize biomass feedstocks. The VM and A contents were determined following the ASTM D 3175-07 and ASTM D 3174-04 standards, respectively. The FC was calculated by the formula: FC (% wt.) = 100 – V – A. The HHV was evaluated using the Parr 6200 Calorimeter, following the procedure described in the NREL protocol. The C, H, N, O, S contents were determined using the PerkinElmer 2400 Series II Elemental Analyser. The cellulose, hemicellulose and lignin contents were determined following the Forage Fiber Analysis method.[16]


Bamboo chip
Cassava pulp
Corn stalk
Corn cob
Rice husk
Rice straw
Bagasse
Rubberwood chip
Coir fiber
Saw dust

Figure 1: Selected forest and agricultural residues

3. RESULTS AND DISCUSSION

3.1. Moisture content and bulk density

The moisture content in biomass varies depending on the type, growing conditions, and harvesting time. Regarding biomass feedstock, the moisture greatly depends on storage conditions and upstream processing treatments. The moisture content of these biomass samples was found in the range of 9.53 (for rice husk) and 66.16 % (for corn stalk) (table 1). The high moisture of some feedstocks may strongly affect thermochemical processes. It reduces the temperature in the system, thus resulting in the incomplete conversion of biomass feedstock and/or other operational problems. Moisture above 10 % is usually not preferred in the thermochemical conversion process.[9,17,18] Meanwhile, although biochemical processes have a higher tolerance on this aspect, moisture content above 20 % is usually not preferred.[19] Therefore, corn stalk, bamboo, sawdust, and wood chips are highly recommended to be dried before using feedstocks for any thermochemical conversion process.

The bulk density of agricultural residues are generally lower than forest residues (table 1). Rice straw and sugarcane bagasse had the lowest bulk density, approximately 80 kg m^{-3}. Meanwhile, rubber wood chip had the highest bulk density (470.8 kg m^{-3}), followed by sawdust (380.9 kg m^{-3}). Low bulk density is known to cause difficulties in the storage and transportation, as well as the loading of the biomass to the system. This also causes difficulties during the energy conversion processes. As an example, gasification of rice straw in their natural form is not recommended, as the gap between particles can lower temperature in the gasification zone, resulting in a low syngas quality. Therefore, pretreatment techniques such as pelletization or densification of rice straw and sugarcane bagasse are highly recommended.

3.2. Proximate analysis

Volatile matter, ash content, and fixed carbon content are important components for the characterization of fuel materials. Higher heating value is also an important parameter for the conception of a thermochemical conversion system. table 1 presents the proximate analysis results of biomass feedstocks.

Biomass having high volatile matter and low ash content is generally promising feedstock for biofuel production. The volatile matter of these biomass samples was found in the range of 66.17 (for rice husk) and 85.12% (for cassava pulp). This could be advantageous for thermochemical processes: during the decomposition stage, volatile is transformed to the form of gas instantaneously, releasing an important amount of chemical energy in a very short time via direct or indirect combustion.

Table 1: Proximate analysis of biomass feedstocks

Sample	M (%wt)	BD (kgm^{-3})	Proximate analysis (% wt, db)			HHV (MJkg^{-1}, db.)
			V	A	FC	
Bamboo	44.51	290.5	76.61	1.71	21.68	15.47
Cassava pulp	15.13	299.1	85.12	1.12	13.76	17.51
Corn stalk	66.16	119.1	74.31	7.11	18.58	15.02
Corn cob	10.01	155.3	80.01	1.92	18.07	16.67
Rice husk	9.53	117.9	66.17	16.21	17.62	13.68
Rice straw	10.01	80.1	71.02	13.51	15.47	14.27
Sugarcane bagasse	10.21	82.1	74.98	7.91	17.11	15.76
Rubber wood	32.19	470.8	80.21	1.91	17.88	16.77
Coir fiber	12.29	111.1	68.12	3.45	28.43	13.91
Sawdust	33.91	380.9	77.65	3.81	18.54	15.93

M: Moisture content, BD: Bulk density, V: Volatile matter, A: Ash content, FC: Fixed-carbon content, db.: dry basis.

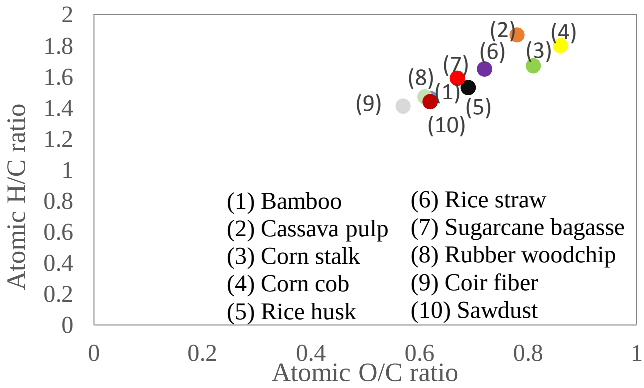

Figure 2: Van Krevelen Diagram of ten biomass types

Ash is the incombustible solid mineral matter present in the biomass, which mainly contains oxides. The ash content of biomass samples ranged from 1.12 (for cassava pulp) to 16.21% (for rice husk), suggesting a significant difference between the mineral contents in biomass. A more important amount of slag might also be generated due to the melting of ash during thermochemical conversion processes, blocking the hydrodynamics and the gas generation.[20] This problem can become serious over time and may damage the whole system. Meanwhile, in biological processes, such as microbial fermentation or anaerobic digestion, are typically much more dependent on biomass carbohydrate content and less susceptible to ash contents. Therefore, biological conversion processes seem to be a better choice when using herbaceous crops that typically have high ash contents compared to thermochemical conversion processes.

Heating value is a measurement of the amount of heat released by a specific quantity during the combustion process. The higher heating value of biomass samples ranges from 13.68 to 17.51 MJkg^{-1}, a bit lower than woody biomass[21] and comparable to half of the coal generally.[22] This heating value of rice husk could be an input in the calculation of heat balance and simulations, therefore help determine the capacity and dimensions of the energy conversion systems. Therefore, considering the proximate analysis, rice husk and rice straw are less favorable for thermochemical conversion processes due to their high ash content.

3.3. Ultimate analysis

The ultimate analysis results are shown in table 2. The different biomass samples possessed slightly different contents of C, H, and O, which would impact the composition of the energy product. Only very small amounts of N and S were trapped in plants during the growth, marking the low risk of NOx and/or SOx emissions from selected biomass feedstocks.

Table 2: Ultimate analysis of biomass feedstocks

Biomass	Ultimate analysis (% wt, daf)				
	C	H	O	N	S
Bamboo	51.11	6.22	42.52	0.09	0.06
Cassava pulp	45.53	7.11	47.29	0.03	0.04
Corn stalk	45.05	6.27	48.56	0.01	0.11
Corn cob	43.61	6.55	49.74	0.01	0.09
Rice husk	48.89	6.22	44.72	0.09	0.08
Rice straw	47.56	6.55	45.72	0.01	0.16
Sugarcane bagasse	49.3	6.55	43.88	0.02	0.25
Rubberwood chip	51.44	6.32	41.99	0.17	0.08
Coir fiber	53.11	6.22	40.55	0.01	0.11
Sawdust	51.11	6.13	42.52	0.19	0.05

C: Carbon content, H: Hydrogen content, O: oxygen content, N: Nitrogen content, daf: dry-ash-free basis.

A Van Krevelen that correlates Hydrogen to Oxygen content (figure 2), all compared to Carbon content in biomass with refers to the ultimate analysis, was also established. The atomic H/C ratio of biomass samples ranged from 1.41 to 1.87. This result is in coherence with previous studies[23] observed that the atomic H/C ratios of 5 different kinds of wood ranged from 1.57 to 1.67. Coir fiber, sawdust and rubber woodchip were found in the most-left side of the diagram, suggesting their highest intrinsic energy content. Generally, herbaceous residues have a lower atomic H/C ratio compared to woody residues, and consequently, it would produce a higher yield of char and a lower yield of tar during thermal conversion processes.[23] Upgrading gaseous pyrolysis and gasification products to liquid fuels also requires a specific H/C stoichiometry.[24] Biomass usually provides a low H/C ratio compared to that required in typical bio-fuels, therefore knowing the ultimate analysis of samples could help calculate the amount of supplemental H_2 in the form of steam or H_2 in the upgrading process. [25]

3.4. Biochemical analysis

Lignocellulosic biomass is composed of three major components, which are cellulose, hemicellulose, and lignin, besides the extractives and minerals.[26] Results of the three main compositions of biomass feedstocks are presented in table 3.

Hemicellulose consists of a few types of sugar unit and sometimes referred to sugars they contain. This component is associated with cellulose and contribute to the structural component of the plant.[27] Corn cob showed the highest content of hemicellulose (37.33 %), followed by the sugarcane bagasse (30.11 %). Meanwhile, coir fiber showed a very low hemicellulose content (0.99 %).

Table 3: Lignocellulosic compositions of biomass feedstocks (% weight, as received)

Sample	Hemicellulose	Cellulose	Lignin
Bamboo	14.11	47.01	22.12
Cassava pulp	21.11	13.99	2.35
Corn stalk	23.11	27.01	3.55
Corn cob	37.33	34.12	6.14
Rice husk	9.99	47.88	19.11
Rice straw	22.99	41.91	4.98
Sugarcane bagasse	30.11	40.15	22.89
Rubberwood chip	12.12	49.53	20.17
Coir fiber	0.99	42.11	33.44
Sawdust	11.56	40.11	24.15

Cellulose is a major part of polysaccharides with a higher degree of polymerization compared to that of hemicelluloses.[28] Several types of cellulose exist in plants, such as crystalline and non-crystalline, or accessible and non-accessible which is referred to the capability to interact with water or microorganism. Rubberwood chip, bamboo, and rice husk showed the highest cellulose contents (47-49 %), while cassava pulp showed a very low one (13.99 %).

Lignins are highly cross-linked molecular complex with an amorphous structure and act as a binder between individual cells and between the fibrils that form the cell wall.[28] The high lignin in the biomass residues can increase the hardness of the compacted biomass product due to its function as glue (binder). Bamboo, sawdust, coir fiber, and sugarcane bagasse showed a high content of lignin (> 20 %), while herbaceous residues such as cassava pulp, rice straw, and corn stalk showed a much lower lignin content (< 5 %), indicating a high amount of loosely bound fibers.

Cellulose and lignin contents greatly affect the yields of thermochemical conversion products. The biochemical components that constitute the plant have different thermal stability levels: while hemicellulose is decomposed between 423 and 623K, cellulose and lignin are decomposed at higher temperature ranges: between 548 - 623K; and 523 -773K, respectively.[29] Therefore, biomass with higher hemicellulose content is easier for thermal decomposition, with more smoke released. In contrarily, biomass with higher lignin content also has a higher tar yield and produces more stable components in tar due to its molecular structure. Bridgwater *et al.* highlighted that a concentrated lignin (about 50 % lignin and 50 % cellulose) slightly reduced the amount of a typical bio-oil, while a purified lignin material produced a much lower amount of a different kind of bio-oil.[30] Meanwhile, for the biochemical conversion pathway, biomass with a higher cellulose content can be easier to be converted into simple sugars and fermented into alcohols. The work of Demirbas has highlighted the benefits of using cellulosic biomass resources such as forest materials, agricultural residues and urban wastes for the bioethanol.[31] Contrarily, lignin may play a negative impact in the biochemical process for producing biofuels produced from anaerobic digestion.[32] The conversion of lignocellulose to free sugars using biochemical processes is hindered by the presence of lignin because it acts as a physical barrier to enzymes, and because enzymes reversibly bind to lignin, resulting in the inefficient use of the polysaccharide-degrading enzymes. Therefore, coir fiber and woody residues are not preferred for biochemical processes. Regarding bio-oil produced from pyrolysis, a study of Klemetsrud *et al.* stated that the impact of lignin content changed with the pyrolysis temperature.[33] At a pyrolysis temperature of 500 °C, an increase in lignin content from 17 to 22 % decreased the relative bio-oil yield from 73 to 65 %, but at 600 °C, there was neither a decrease in the yield of bio-oil nor an increase in the char yield.

4. CONCLUSION

A complete and comprehensive database of physico-chemical properties of ten forest and agricultural residues were reported in this study. Characterization results highlighted the variability in the nature of biomass. These identified characteristics could be a good indication for the preparation of the feedstock, the choice of energy conversion technologies, and also the prediction of the product's quality. For instance, drying of corn stalk, bamboo, sawdust, and wood chips are necessary before any conversion processes. Pelletization or densification of rice straw and sugarcane bagasse are also highly recommended for thermal conversion processes. High-ash-content biomass such as rice husk and rice straw are less favorable for thermochemical conversion processes, while coir fiber and woody residues are not preferred for biochemical processes due to their high lignin-content. Results could give valuable information for the development of biochemical and thermo-chemical conversion processes, as well as different usage strategies of these feedstocks.

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