

Review

Application of cassava harvest residues (*Manihot esculenta* Crantz) in biochemical and thermochemical conversion process for bioenergy purposes: A literature review

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Bioenergy production from biomass and agricultural wastes has gained significant interest due to rising fossil fuel prices and their decrease in air pollutant emissions. This review paper evaluates the state-of-art for the several applications from cassava harvest residues and their use in bioenergy industry, using different thermochemical and biochemical processes. Regarding the great available literature for this biomass, several pretreatment techniques, including mechanical, chemical, biological, thermal, ultrasonic and wet explosion were observed. The use of cassava harvest residues for the biochemical pretreatments, for example, hydrolysis, fermentation and thermochemical processes, such as direct combustion, gasification, pyrolysis, fast pyrolysis and oxy-fuel combustion was also discussed. Therefore, studies are necessary in order to understand that the use of cassava residues in thermal processes can increase the viability of this feedstock for biofuels production and/or in power co-firing units. After extensive study, it was observed that informations are still lacking about the use of cassava harvest residues in other conversion processes, thus, new studies to discover more on the use of this biomass, in order to extend their application in the bioenergy market is encouraged.

Key words: Biomass, cassava, harvest, processes, residues, biochemical, thermochemical.

INTRODUCTION

The main issues faced by many developed and developing countries around world are actually the future energetic security and inadequate use of natural

resources (Naqvi et al., 2018; Ferreira-Leitão et al., 2010). The geopolitical, environmental and economic scenario requires the urgent development of renewable

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energy resources and, in particular, bioenergy, for example, biomasses (Welfle, 2017).

Biomasses are found abundantly in nature and can be conveniently generated in most non-urban configurations (Ozturk et al., 2017). Generally they are classified into two types: natural materials and derivatives (Toklu et al., 2010). Biomass resources are subdivided into some categories: agricultural production wastes, energy crops, agriculture processing, urban organic, urban pruning-woods and woods mill (Nansaior et al., 2013; Main-Knorn et al., 2013). Conversion of biomass into energy is an alternative that will mitigate negative socioenvironmental impacts, such as rural unemployment and global warming (Mckendry, 2002; Okudoh et al., 2014; Ozturk et al., 2017; Long et al., 2013). Bioenergy from biomass is a clean technology, safe and renewable resource, and is considered as a potential alternative to partially replace fossil fuels, which will decrease in the future (Ali et al., 2017).

Agroindustrial wastes derived from the crop harvest and food processing are examples of renewable resources and can be used as feedstock for generating bioenergy (Simangunsong et al., 2017; Pereira and Costa, 2017). In 2011, Food and Agriculture Organization (FAO) estimated in their annual report that approximately one-third of all food produced for human consumption worldwide is discarded, representing about 1.3 billion metric tons of wastes per year (Kreuger et al., 2011). Despite the large amount of agricultural wastes generated worldwide, their use as biofuel is still irrelevant, mainly due to limited information on its thermochemical characteristics (Ion et al., 2013).

The traditional use of lignocellulosic biomass was by many years limited to burning for cooking and heating, which lead to significant negative environmental impacts such as land degradation and desertification (Lynd et al., 2015). By means of thermochemical and/or biochemical conversion routes, the lignocellulosic biomass can be converted into energy or bioenergy transporters. Thermochemical conversion uses thermal and chemical processes for producing energy products from biomass, including combustion, pyrolysis, oxy-fuel combustion, gasification and liquefaction (Goyal et al., 2008; Cruz and Crnkovic, 2016; Cai et al., 2017).

The bioenergy production from biomass or agricultural wastes has gained significant interest also due to rising fossil fuel prices (Pereira and Costa, 2017). Several studies have determined the physicochemical characteristics of crop residues, such as corn cobs and straws, rice and coffee husks, pine sawdust, olive and *tucumã* seeds, sugarcane bagasse among others (Graham et al., 2007; Donaldson et al., 2001; Berndes et al., 2003; Ezui et al., 2015; Cruz et al., 2017; Veiga et al., 2016). However, detailed information on the use of cassava harvest residues for the different energetic applications is still missing.

Cassava is a perennial plant of the genus *Manihot*

esculenta Crantz. The main producer countries of cassava in the world are Nigerian, Brazil, Thailand and Ghana, in that order (Suttibak et al., 2012). Cassava is a shrub cultivated extensively as an annual crop in tropical and subtropical regions, and their root is an edible starchy tube (Edhirej et al., 2017). Their residues are available in the fields after harvest (Zhang et al., 2003). The roots are collected and transported, while some stems are used for crop replating and most of the green mass is left in soil, which decompose and some nutrients return to the soil (Isahak et al., 2012; Sorapipatana and Yoosin, 2011; Liu et al., 2013; Sánchez et al., 2017).

It was noted that few papers discussed the use of cassava residues by thermochemical processes as energy source. Pattiya (2011) characterized the cassava wastes used as fuel in Thailand and classified the stalks and seed stem as residues, characterizing them physically and chemically. Wei et al. (2015) discussed the possibility of extracting starch from cassava branches for producing ethanol and also evaluated aspects such as the production origin region. Veiga et al. (2016) sought to quantify and characterize cassava harvest residues by thermogravimetric analysis in oxidizing and inert atmospheres for studying the residues behavior as biofuel.

Due to several factors earlier reported, this review paper is justified for allowing compilation of works that demonstrate the importance of the characterization from cassava harvest residues and the use in bioenergy industry. Regarding the available literature, it was observed that several pretreatment techniques, including mechanical, chemical, biological, thermal, ultrasonic and wet explosion can be employed for this biomass. The use of cassava harvest residues for thermochemical processes was also discussed (direct combustion, gasification, pyrolysis, fast pyrolysis and oxy-fuel combustion).

CHARACTERISTICS OF THE CASSAVA

What is cassava?

Cassava (*Manihot esculenta* Crantz) is a tubercle, 5 to 10 cm in diameter and 15 to 35 cm in length (Figure 1). It is cultivated in almost all tropical countries and grows in degraded soils, where no other crop can grow (Kuiper, 2007). Furthermore, cassava can be harvested anytime between 8 and 24 months after planting (DAFF, 2010; Okudoh et al., 2014). Regarding cassava starch, this has several industrial applications and creates a huge global business. The raw material is manioc roots. The starch content in the cassava roots varies from 20 to 32% and depends of the region, climate, soil type and crop, while water content in the cassava roots is about 60% (Chavalparit and Ongwandee, 2009; Kristensen et al., 2013).



Figure 1. Cassava tubers. **(A)** Root with stems attached. **(B)** Root without stems attached
Source: Okudoh et al. (2014).

Dry cassava pulp, a residue from starch production, contains around 50% of this polysaccharide and 43% insoluble dietary fiber (dry weight basis). Such pulp when discarded in inappropriate places causes damage to the environment and diseases proliferation in humans transmitted by animals (Tan et al., 2017). Authors reported recovering of the starch via sonication or enzymatic hydrolysis of their fibrous content, using a multi-enzyme mixture of cellulase and pectinase (Agyepong and Barimah, 2017). The pulp, also called cassava fibrous wastes or bagasse, contains between 30 and 50% starch content (dry weight basis) and cellulose and hemicellulose levels of 24.99 and 6.67% (w/w), respectively (Sriroth et al., 2000). After the removal of the tuberous roots, the cassava crop residues and plant shoots are estimated from 144 to 257%. Use of cassava stems, leaves as forage or addition of roots wastes to prepare feed flour is justified, due to their nutritional value and high forage yield per hectare (Bose and Martins Filho, 1984). Several steps are involved in cassava roots processing to obtain industrial products, such as starch and cassava flour (*tapioca*): peeling and washing, grating, pressing, disintegration, sifting, drying, milling and screening (Tan et al., 2017).

Cassava composition

Tubercle of cassava is organically rich in starch and carbohydrates, also containing small amounts of protein, vitamins and minerals (Lancaster et al., 1982). The protein contents of the *in natura* and dry cassava are 1 and 1.41%, respectively (Table 1). Soccol (1996) reported that *in natura* cassava tubers has moisture 65%; 0.9% of ash and 0.03% of phosphorus (P).

The main composition of cassava is starch and

carbohydrates, proteins, vitamins and minerals trace (Lancaster et al., 1988). The carbohydrate contents of the *in natura* cassava are estimated at 35% (Kuiper et al., 2007). Montagnac et al. (2009) assumed the carbohydrate content of the whole cassava root, and peeled roots as 37.9, 31 and 28.8%, respectively. It also contains significant amounts of calcium (Ca), phosphorus (P), zinc (Zn), magnesium (Mg), copper (Cu), iron (Fe), manganese (Mn), potassium (K) and vitamins, such as vitamins C, folates, thiamine, pyridoxine (B6 vitamin), ribofin and pantothenic acid. Another important feature of this biomass is their high oxygen content, which can be higher than 35%, approximately ten times higher than in high-grade coal, which is below 4% (Demirel, 2014).

Torquato et al. (2017) used thermogravimetric analysis (TG) to perform the proximate analysis for several biomass samples. This method describes the determination of moisture, fixed carbon, volatile materials and ash. Veiga et al. (2016) also used thermogravimetric analysis for samples from three cassava plant parts, that is seed stem, coarse and fine stems.

Veiga et al. (2016) presented results of elemental analysis for the different crops and cassava varieties and observed that few variations were found between the different plant parts, except for nitrogen (N), which presented highest amounts, that is 1.7% for thin stems and 0.27% for thick stems. In other cassava varieties (IAC 14 and IAC 90) the N concentration ranged between 0.55 and 0.80%, respectively. It was observed that knowledge of the N content is necessary for estimating the nitrogen oxide (NO) formation through the NO-fuel mechanism in wastes combustion processes (Pattiyia et al., 2011).

Veiga et al. (2016) presented in their study the amount of cellulose, hemicellulose and lignin of parts from cassava harvest residues, as shown in Table 2. It was

Table 1. Physical-chemical properties of cassava tubers (100 g).

Composition	Units	Fresh weight	Dry weight	References
Calories	cal	135	335	Okudoh et al. (2014)
Peel	%	10 – 20	n. a.	Lancaster et al. (1982)
Cork layer	%	0.5 – 2.0	n. a.	Kuiper et al. (2007)
Edible portion	%	80 – 90	n. a.	Soccol (1996)
Moisture	%	62 – 66	15 - 19	Lancaster et al. (1982)
Total solids (TS)	%	38	81	Lancaster et al. (1982)
Volatile solids (VS)	%	99	98	Lancaster et al. (1982)
Protein	g	1	1	Lancaster et al. (1982)
Total nitrogen	%	0.22	0.46	Lancaster et al. (1982)
Lipid	g	0.20	0.50	Lancaster et al. (1982)
Starch	g	18 – 32	81	Lancaster et al. (1982)
Fibre	g	1.10	1.20	Lancaster et al. (1982)
Carbohydrate	%	35	n. a.	Kuiper et al. (2007)
Total carbon (TC)	%	19	40	Soccol (1996)
Ash	g	0.9 – 1	2	Lancaster et al. (1982)
Calcium	mg	26	96	Lancaster et al. (1982)
Phosphorus	mg	32	81	Lancaster et al. (1982)
Iron	mg	1	8	Lancaster et al. (1982)
Sodium	mg	2	n. a.	Lancaster et al. (1982)
Potassium	mg	394	n. a.	Lancaster et al. (1982)
B2 Vitamin	mg	0.04	0.06	USDA (2003)
C Vitamin	mg	34	0.00	USDA (2003)
Niacin	mg	0.60	0.80	Lancaster et al. (1982)
Cyanide	%	n. a.	2	Lancaster et al. (1982)

n. a. not available.

Table 2. Amount of cellulose, hemicellulose and lignin of parts from cassava residues (Veiga et al., 2016).

Cassava parts	Cellulose	Hemicellulose	Lignin
Seed stem	39.93	11.73	17.87
Thin stalk	37.67	11.77	22.60
Thick stalk	40.73	12.14	20.05

observed that cellulose amount ranged from 37 to 41%; hemicellulose between 11 and 12% and lignin from 17 to 23%, indicating its has lignocellulosic material characteristic.

Table 3 presents the chemical composition of cassava wastes and comparison with other biomasses commonly used for biofuel, such as sugarcane bagasse, rice straw, yard waste, switch grass, wheat straw and eucalyptus. In general, cassava garbage characteristics resemble most other biomasses, considering elemental analysis (Veiga et al., 2016).

Cassava cultivation

Cassava belongs to the family Euphorbiaceae. This crop

grows on infertile land with minimal need of chemical products, such as fertilizers, herbicides and insecticides; making it one of the cheapest and most sustainable agro-based feedstocks. Cassava is cultivated primarily in tropical climate, with approximately 70% of their production occurring in subtropical and tropical regions. It is mainly cultivated by small-scale farmers in Africa, Latin America and Asia (Zhang et al., 2016). Cassava is replanted, using the cut stem in their harvest. The stems are cut, ranging from 20 to 25 cm long and planted in a slanting or angular position of 45°, burying them in the soil with one-third of their stems above the surface, ensuring that lateral buds point towards the sun direction, ensuring that the same germinates (Edhirej et al., 2017). Conventionally, it is recommended that the stems are

Table 3. Chemical composition of cassava wastes to comparison with other typical biomasses.

Elemental composition% (dry basis)	Cassava waste ¹	Sugarcane bagasse ²	Rice straw ³	Yard waste ³	Switch-grass ³	Wheat straw ⁴	Eucalyptus ⁴
C	44.12	40.34	38.24	41.54	46.68	44.92	50.15
H	6.44	5.66	5.20	4.79	5.82	5.46	7.45
O	48.62	47.91	36.26	31.91	37.38	41.77	39.64
N	0.81	0.58	0.87	0.85	0.77	0.44	0.50
S	<0.2	0.17	0.18	0.24	0.19	0.16	0.02
Cl	<0.3	0.26	0.58	0.30	0.19	0.23	0.55

¹Veiga et al. (2016); ²Bizzo et al. (2014); ³Jenkins et al. (1998); ⁴Cuiping et al. (2004).

planted at a spacing of 1 × 1 m on the crest of ridges or mounds, which will give a plant population of 10,000 stands ha⁻¹ (Agyepong and Barimah, 2017).

MAIN TECHNIQUES OF PRETREATMENTS FOR THE CASSAVA BIOMASS - AN OVERVIEW

Agricultural biomasses (focus of this review paper) present physical-chemical properties that can be considered for thermal engineering applications, such as: density, fluxability, grindability, moisture sorption, ash and volatile materials content, thermal properties and energy content. Therefore, it is necessary for choosing the correctly pretreatment techniques (Cai et al., 2017). Generally, technologies of pretreatment are subdivided into three major groups, that is thermal, chemical and biological. Although each method presents some advantages, one specific method cannot be applied for all biomasses type. Fundamental understanding of various technologies of pretreatment, different biomass composition, the relationship between feedstock composition and pretreatment methods, can match significantly the best pretreatment method or combinations of this for a specific feedstock. Biomass pretreatment for the reduction of their recalcitrance is a necessary step for bioethanol production (Himmel, 2007). Therefore, the main components of the cassava (bark, stem and leaves) need to be pretreated to unlock their cellulose and hemicellulose contents, which compose more than 50% of their dry weight (Aripin et al., 2013; Nanssou et al., 2016).

Mechanical pretreatment

Mechanical pretreatment used in some biomasses is essential to improve particle distribution and densification, enzymatic accessibility and bioconversion affectivity (Peltola et al., 2004). According to Barakat et al. (2014), such pretreatment also increases porosity and bulk density, improves flow properties and generates new surface areas, without the production of toxic side

streams. These pretreatments involve the physical dispersion of substrate components, reducing particle size and increasing the available surface area (Liau et al., 2011). For the cassava biomass, this reduction in particles size facilitates a faster moisture adsorption and makes nutrients readily available to the microorganisms that are responsible for anaerobic fermentation and therefore, leads to better methane gas production (Salomoni et al., 2011). The mechanical breakdown that usually occurs in the cassava cell walls can be monitored by increasing the oxygen-soluble chemical (COD) content of the substrate.

The mechanical methods need an initial energy to disrupt noncovalent forces between the cassava cells (Muñoz et al., 2006). Chemical modifications of the organic matrix rarely are observed, and when these occur, they are not significant (Barakat et al., 2014). Peltola et al. (2004) observed an increase of approximately 60% in soluble COD content by using mechanical pretreatment for samples of municipal solid wastes (MSW). However, more researches need to be carried out, focusing on the efficiency of this pretreatment for cassava residues, as well as the particle size effect of this biomass for methane production via anaerobic fermentation processes. In addition, this mechanical method has been applied to maintain the integrity of plant enzymes and improve the digestion of energy crops. For cassava biomass, the main problem in the use of this method is the energy required for their milling, which can compensate the gains obtained in biogas production (Buaban et al., 2010). As can be seen, there are some advantages and disadvantages for this pretreatment technique. For example, using an agitated ball mills, a solubilization among 10 and 30% and an increase from 10 to 20% in the biogas production can be obtained (Buaban et al., 2010; Liao et al., 2011). On the other hand, main disadvantages for using this technique are the capital and operational costs (Salomoni et al., 2011).

Chemical pretreatment

Chemical pretreatments such as acid, alkaline or ozone

can be used, which enable a solubilization from 30 to 60% for the insoluble substrates (Silverstein et al., 2007). Ozone treatment produced a 41% increase in biogas production, while alkaline treatment produced 25 to 100% increase in biogas yields, as well as in methane production (Edhirej et al., 2017). The main disadvantage of chemical treatment lies with the cost for acquiring the chemicals. Ozone treatment is highly economical in a commercial scale (Mosier et al., 2005). Zhang et al. (2011) used this method for cassava treatment and reported methane yields of 259.46 ml g⁻¹ of volatile materials destroyed.

Hydroxides of sodium (NaOH), potassium (KOH), calcium (Ca(OH)₂) and ammonium (NH₄OH) are the alkali pretreatments used more for bioethanol production (Rabelo, 2010; Rezende et al., 2011; Cruz et al., 2017). The Ca(OH)₂ used in this process can be recovered using lime kiln technology (Cai et al., 2017). This method is also known for causing chemical swelling in the cellulose fibrous (Mosier et al., 2005; Cruz et al., 2017), in which occurs saponification reactions and salvation, leading to the disruption of the cross-links between hemicellulose and other components; hence, increasing the biomass porosity (Sun and Cheng, 2002; Cruz et al., 2017). More specifically, cross bonds between ester, lignin and xylan are disrupted, producing the delignification process. Comparatively, alkaline pretreatments are performed at lower temperatures, approximately 60°C and do not require complex reactors that are appealing to be employed on farms (McIntosh and Vancov, 2010).

Acid pretreatment, in particular, using sulfuric acid (H₂SO₄) is the most employed chemical pretreatment for lignocellulosic biomass, where polysaccharides (mainly hemicellulose) are hydrolyzed to monosaccharides, leading to higher accessibility of cellulose to enzyme hydrolysis (Rabelo, 2010; Rezende et al., 2011; Cruz et al., 2017). Acid pretreatment can be performed either under low acid concentration and high temperature or under higher acid concentration and lower temperature (Taherzadeh and Karimi, 2008). According to Xu et al. (2007), soybean straw samples were soaked in ammonia liquor (10% NH₄OH) for 24 h at room temperature, and it was observed that their hemicellulose and lignin contents decreased by 41.45 and 30.16%, respectively. Generally, to use concentrated acid is more economical, when the process is performed at low temperatures (Girio et al., 2010; Mood et al., 2013).

Zhang et al. (2011) investigated cassava residues pretreatment by thermally diluted sulfuric acid hydrolysis by means of statistically designed experiments. Results obtained indicated that the hydrolysis, using dilute sulfuric acid, is adequate to predict the ideal pretreatment condition, which showed to be effective for cassava wastes pretreatment, increasing the methane yield. Martín et al. (2017) carried out the chemical characterization of cassava stems from different origins

(South China 205-SC205, Xinxuan 048-XX048 and South China 5-SC5), where cassava stems were submitted for saccharification, including starch hydrolysis, pretreatment with sulfuric acid or 1-ethyl-3-methylimidazolium acetate and enzymatic hydrolysis of cellulose. Pretreatment with OAc resulted in 20% higher glucan conversion than pretreatment with acid.

The use of these chemical pretreatments also presents some advantages and disadvantages. For instance, with the alkaline method solubilization ranging from 30 to 60% can be obtained (Taherzadeh and Karimi, 2008), although the increase of non-biodegradability materials is the main disadvantage for using this technique. Ozone technology can improve the solubilization at 30%, but this pretreatment cause destruction of cell structure (Mshandete et al., 2008).

Biochemical pretreatment

Among pretreatments different for the biomasses discussed in this review paper, biochemical pretreatments present advantages, such as simplicity in experimental operation and low capital investment, which makes them more attractive (Mshandete et al., 2005; Chen et al., 2010). Biochemical pretreatments commonly use microorganisms, such as brown, white and soft rot fungi for lignin degradation and hemicellulose from lignocellulosic biomasses (Sindhu et al., 2016). Second, Sindhu et al. (2016) biochemical pretreatments, using white rot fungi that are able to degrade lignin, seems very promising, because less energy is consumed and the environment is not damaged. Currently, studies are being performed for detecting alterations in the structure, chemistry composition and enzymatic hydrolysis of lignocellulosic biomass after biological pretreatment (Chen et al., 2010). Shen et al. (2015) reviewed two hybrid processes, including the characteristics of fermentative substrates produced in the thermochemical stage and microbial utilization of these compounds in the fermentation stage.

Zang et al. (2011) analyzed the cassava residues pretreatment with distillery wastewater mixture by anaerobic digestion, using a microbial consortium as inoculations in batch bioreactors at 55°C. Results showed that maximum methane yield of 259.46 ml g⁻¹ volatiles materials for cassava residues was obtained for 12 h pretreatment by a microbial consortium, which was 96.63% higher than control, i.e. 131.95 ml g⁻¹ volatiles materials.

Biogas production

Biogas is produced from anaerobic digestion (AD) of organic materials by microbes. AD is a microbial decomposition process of organic materials in oxygen

absence for biogas production. AD occurs in four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Wang et al., 2012). Biogas is constituted mainly by methane, carbon dioxide and hydrogen sulphide traces, ammonia, hydrogen and nitrogen. Methane is the component that provides the high energy value (Balat and Balat, 2009). High heating value (HHV) of biogas ranges from 5000 to 7000 kcal m⁻³ (depends on methane content). In practice, different substrates spectrums are combined into AD process. This AD process is called anaerobic co-digestion (ACD) process. ACD processes are known for biogas synergistic yield, because combination yield is higher than sum of AD individual yields (Khalid et al., 2011). Adelekan and Bamgboye (2009) studied the ACD productivity of several mixture ratios of cassava peels with livestock wastes (poultry, piggery and cattle) and concluded that for each case, ACD produced improvement in the biogas yield. Also it was observed that each mixture provided the best yield in the 1:1 constituents ratio by mass. For any ratio, ACD with piggery wastes presented the best yield, followed by cattle and poultry wastes.

Thermal pretreatment

According to Ferrer et al. (2004), thermal pretreatment can increase the biogas production and methane yield of certain substrates, but is not an effective technique in all cases. For example, thermal pretreatment of hyacinth water at 80°C increased slightly the solubility, with few or no effect on the anaerobic digestion (Ferrer et al., 2004). Pasteurization process of abattoir wastes at 70°C for 1 h, produced a four-fold increase in methane yields, but the application of this pretreatment cannot be generalized for the different biomasses (Faloye and Kana, 2017). For Chandra et al. (2012), temperatures below 100°C are used to breakdown plant cells, increase membrane fluidity and hydrolyze polymers, resulting in a soluble COD release of approximately 35%. This thermal method causes modifications in the chemical equilibrium of the exopolymers in the lignocellulosic biomasses.

Thermal pretreatment was applied by Aruwajoye et al. (2017) for the optimal release of fermentable sugar from cassava husks. The authors used the response surface design method to investigate the effect of immersion temperature, immersion duration and autoclave, acid concentration and solid loading on the sugar yield reduction, obtaining optimal pretreatment conditions and immersion temperature of 69.62°C. Thermal pretreatment may be used for cassava residues, but their cost must be weighed against the benefits derived from increased biogas production rates (Norberg, 2004).

Ultrasonic pretreatment

Pretreatments based on ultrasound irradiation has been

employed as isolated technique or combined with other technologies. Such combinations include acid pretreatments, alkaline, ionic liquid and ozone or with a physical technique, for example, microwave irradiation, thermal and supercritical carbon dioxide, for the pretreatment of lignocellulosic biomasses and wastes for improving biofuel production (Saifuddin and Fazlili, 2009; Erden and Filibeli, 2010; Tian et al., 2016). Ultrasound present a spectrum ranging between 20 and 10 MHz, and their tone is above human hearing, which can detect sounds up to 16 kHz (Mood et al., 2013). This process catalyzes the depolymerization of biopolymers, emulsification, and extraction of tanning vegetables oils from almond, ginger, and wood seeds (Bundhoo and Mohee, 2017).

Tian et al. (2016) reported that some applications of the irradiation processes via ultrasound can be implemented on municipal wastewater pretreatment to disrupt flocks, production of biodiesel from microalgae and bioethanol from cassava chips. Laboratory scale studies using ultrasonic pretreatment showed that solubilisation degree was between 30 and 90% and increase in the biogas production from 5 to 70% (Bundhoo and Mohee, 2017). Lehne et al. (2000) reported that use of this technique promote a reduction in the average particle size, increasing the disintegration degree of the sewage sludge samples; however this cannot be suitable for energy crops such as cassava.

Vera et al. (2004) used an ultrasound 20 kHz and the power supply of 500 watts to disintegrate sewage sludge and, consequently, to increase the fermentation rates, but cannot be suitable for lignocellulosic biomass. For the cassava biomass, the use of ultrasound pretreatment cannot be ideal due to the requirement of a high energy for disintegrating of the cell walls (Clarke, 1999; Saifuddin and Fazlili, 2009).

Wet explosion pretreatment

The wet explosion process was developed as a combination of thermal and chemical oxidation to treat biomasses with high concentrations of sugars. However, biogas production was not significantly increased by this technique (Chandra et al., 2012). Wang et al. (2012) used wet explosion pretreatment for enhancing methane production from energy crops, such as cassava and other agricultural residues. The results showed an increase in the sugars release after pretreatment, but not implying at higher methane yield (Wei et al., 2015).

Steam explosion pretreatment

Steam explosion pretreatment is an extensively investigated thermomechanical and chemical method, involving the structural components breakdown of lignocellulosic materials by steam-heating and shearing

Table 4. Effects of different pretreatments on the chemical composition and structural of lignocellulosic biomasses and their limitations (Mood et al., 2013).

Pretreatment method	Increase specific surface	Hemicellulose removal and solubilization	Lignin removal	Inhibitor compounds formation	Drawback and disadvantages
Physical	++	–	–	–	High energy consumption
Acid	++	++	+	++	Equipment corrosion, degrading produce sugar
Alkaline	++	+	++	+/-	Neutralization of pretreated slurry
Ionic liquid	++	+	+	–	High cost of ionic liquid
Organosolv	++	++	++	–	Recovery and recycle of solvent by evaporation, high cost
Steam explosion	++	++	+/-	++	Incomplete disruption of lignin–carbohydrate matrix,
CO ₂ explosion	++	++	–	–	High pressure requirement, does not affect on lignin and hemicellulose
Biological	++	+/-	++	–	Low hydrolysis rate, large space requirement, watchful control condition of microorganism growth

mechanical, that is due to sudden decompression, moisture evaporation and auto-hydrolysis of glycosidic bonds (Mood et al., 2013; Cai et al., 2017). In this process, biomass particles are heated using pressurized steam, with pressure between 20 and 50 bar, and temperature ranging from 160 to 270°C, during few minutes. After this step, the pressure is released to atmospheric pressure, condensed moisture evaporates and lignocellulosic matrix desegregation takes place (Mabee et al., 2006; Mood et al., 2013). Okudoh et al. (2014) related that this pretreatment causes hemicellulose hydrolysis, lignin transformation due to high temperature and increases cellulose crystallinity, promoting crystallization of the amorphous portions.

Comparison between the effects of different pretreatments on the chemical composition and structure of lignocellulosic biomasses and their possible limitations are presented in Table 4.

THERMOCHEMICAL CONVERSION PROCESSES

Current technologies available for converting

biomass into fuels can be classified into four categories based on their methodologies: biochemical, chemical, thermal, and thermochemical conversion. Thermochemical processes are commonly employed for converting biomass into biofuels with high heating value (Phillips et al., 1990; Ferreira et al., 2017). Biomass thermochemical conversion includes a great number of processes, such as direct combustion, liquefaction, gasification, pyrolysis and oxy-fuel combustion (Bridgewater, 2001; Park et al., 2012). From techniques presented, pyrolysis is the more usual of the biomass thermochemical conversion processes to produce solid and liquid fuels, both are easy to handle and transport (Van de Velden et al., 2010). Figure 2 shows the possibilities of converting the stored energy within biomass directly into heat via combustion/co-firing or transformed into solid fuels (charcoal), liquid (bio-oils) or gaseous (synthetic gas) with various utilization purposes (Bridgewater, 2001).

One of the disadvantages of using biomass as fuel in thermochemical processes is their high moisture content (Phillips et al., 1990). Although the combustion reactions are exothermic

processes, the water evaporation is endothermic (Park et al., 2012). For maintaining the self-sustaining combustion process, moisture content of biomass fuels cannot exceed 65% (Science Daily, 2010). Even with moisture content within the acceptable maximum limit, the fuel high heating value (HHV) is negatively correlated with the amount of water (Quaak et al., 1999).

Figure 3 shows the negative linear relationship between the moisture content and HHV. As the moisture content increases, both the HHV and Low Heating Value (LHV) decrease (Phillips et al., 1990). HHV and LHV are used to describe the heat production of a unit fuel amount during their complete combustion. In determining the HHV and LHV of a fuel, liquid and vapor phases from water are selected as the reference states, respectively (Goyal et al., 2008). As HHV incorporates the heat condensation of water vapor during combustion, it is noted that the HHV curve is always above LHV (Quaak et al., 1999).

Direct combustion

Many studies have been devoted to agricultural

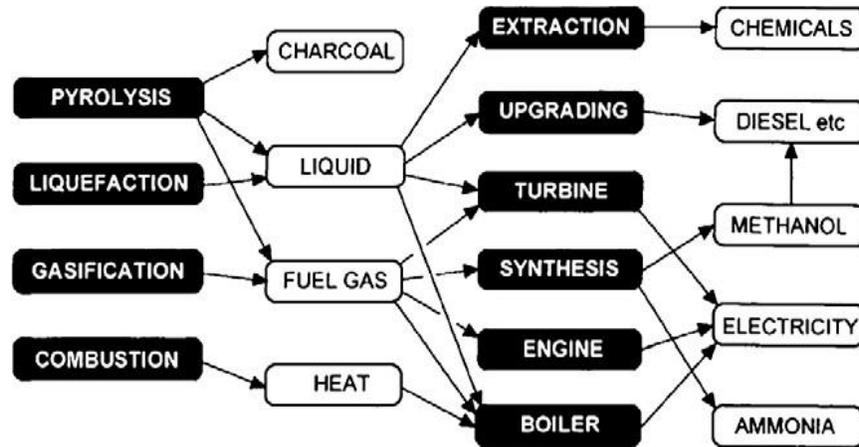


Figure 2. Thermochemical processes for bioenergy production and their corresponding products.
Source: Bridgewater (2001).

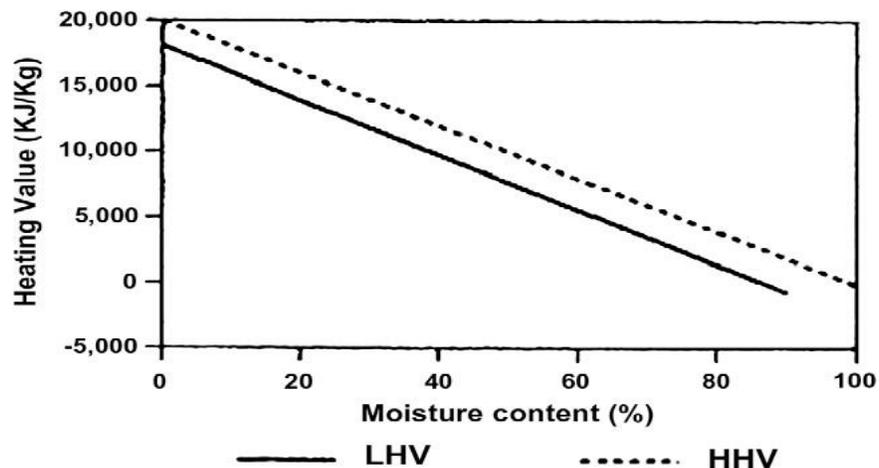


Figure 3. Relationship between heating value and moisture content of biomass fuel (Quaak et al., 1999).

wastes combustion in fluidized bed systems with sand (Kaynak et al., 2005; Madhiyanon et al., 2010; Pécora et al., 2014). These studies focused mainly on fluorinated gas emissions, efficiency and ash related problems, such as fouling and bed agglomeration (Zhang et al., 2011). Combustion performance in terms of efficiency and emissions has been reported to depend heavily on fuel properties as well as on system design characteristics and operating parameters, such as fluid velocity, bed temperature, fuel feed rate, etc (Isahak et al., 2012; Karan et al., 2011).

Combustion is a process widely used to convert stored chemical energy into biomass then into heat, mechanical energy or electricity, using various processes and equipments, such as stoves, ovens, boilers, steam turbines, turbo generators, etc (Demirbas, 2000; IEA,

2006). This is a known technology, although improvements in performance are still possible (Quaak et al., 1999). Biomass combustion produces hot gases at temperatures between 800 and 1000°C and it is possible to burn any biomass type. However, this process is more reliable for application with moisture content below 50% (McKendry, 2002).

Fixed or fluidized beds and drag reactors are three typical combustion systems, with an increase in the velocity of the carrier gas inside the reactor (Laursen and Grace, 2002). A higher gas velocity implies an intensive mixing of the feedstock, which improves combustion efficiency and heat exchange rate (Madhiyanon et al., 2010). The flushed flow systems are expected to exhibit the best performance among these three types of combustion systems (Pattiya et al., 2012). However, no

study about direct combustion of cassava residues was found.

Pyrolysis

Pyrolysis is a thermal decomposition process that takes place in the absence of oxygen (inert atmosphere) to convert biomass into solid charcoal, liquid (bio-oil) and gases at elevated temperatures. Pyrolysis is considered an industrially realized process for biomass conversion (Truman et al., 2004; IITA, 2005). This process can be divided into three subclasses, that is slow, flash and fast pyrolysis (Karan et al., 2011; Pattiya et al., 2012). According Zabaniotou and Ioannidou (2008) the slow pyrolysis occurs under a low heating rate, which obtain more charcoal yield, while the flash pyrolysis is a rapid heating rate process occurring at moderate temperatures (400 to 600°C), obtaining maximized volatile products at short residence time and occurs at high temperature and longer residence times, increasing the biomass conversion and returning more gas product.

For Weerachanchai et al. (2011), the first stage, also called pre-pyrolysis, occurs between 120 and 200°C with a slight weight loss, where some internal rearrangements, as bond breakage, free-radicals appearance, and formation of carbonyl groups are observed, with a release of small amounts of water (H₂O), carbon monoxide (CO), and carbon dioxide (CO₂). The second-stage is itself a pyrolysis process, during which solid decomposition occurs, accompanied by a significant weight loss from the initially fed biomass (Jiménez and Ballester, 2006). Finally, in the last stage occurs the continuous char devolatilization caused by the further cleavage of C–H and C–O bonds (Maschio et al., 1992).

Karan et al. (2011) investigated the pyrolysis process of cassava rhizome, utilizing flue gas in the lab-scale metal kiln. It was reported that the charcoal yield for the dry cassava rhizome ranged from 26 to 35%, depending on the pyrolysis temperature and the fast pyrolysis time was found from 19 to 38 min. In particular, fast pyrolysis favours the formation of liquid products, but inhibits solid chars formation (Maschio et al., 1992). Their liquid products (bio-oils) are composed of an aqueous phase, which contains several organo-oxygen compounds of low molecular weight, and a non-aqueous phase (tar), which includes a variety of insoluble aromatic organic compounds of high molecular weight (Yanik et al., 2009; Zhang et al., 2011).

Some studies on the utilization of cassava residues for the bio-oil production by pyrolysis process have been reported (Pattiya, 2011; Pattiya et al., 2012). Pattiya and co-workers used rhizome and stalk of cassava as feedstocks to obtain bio-oil by fast pyrolysis process in two reactors: fluidized bed reactor (Pattiya, 2011) and free fall reactor (Pattiya et al., 2012). Weerachanchai et

al. (2011) carried out slow pyrolysis from cassava pulp residues and palm kernel cake and their formed products, included solids, liquids and gases.

Pattiya et al. (2012) used the fast pyrolysis of agricultural residues, i.e. cassava plantations, in free fall reactor of laboratory scale to investigate effects of this biomass and the pyrolysis conditions, such as reactor temperatures, condensation, nitrogen flow rate and execution duration in the distribution from pyrolysis products. For maximizing the bio-oil yield, optimum reactor temperatures were reached between 350 and 450°C. It was observed that for the reactor temperature of 450°C and condensation primary temperature of 10°C, about 70% weight bio-oil yield for the cassava stem pyrolysis was obtained. It was also verified that the minimum nitrogen flow rate for obtaining high bio-oil content was 1.5 L min⁻¹.

Suttibak et al. (2012) reported experimental proceeding of rapid pyrolysis from cassava rhizome in a fluidized bed reactor incorporated with a hot steam filter. Results showed that ideal pyrolysis temperature was around 472°C, which produced a maximum bio-oil yield of 63.23% on a dry basis.

Gasification

According to Couto et al. (2013), gasification is the carbon based solid material conversion into gaseous fuels at high temperatures, usually from 800 to 900°C, in order to optimize gas production. Gas produced with a LHV ranging from 4 to 6 MJ Nm⁻³ can be directly burned or used as fuel for engines and gas turbines (McKendry, 2002). Badin and Kirschner (1998) found that high efficiencies, approximately 50% are achievable using combined cycle gas turbine systems, where the residual gases of the turbine are recovered to produce superheated steam for using into a steam turbine. Most commercial gasifiers are downdraft type, fluidized bed systems and upstream type, such classification depends on the biomass feed-way, which can be from top, bottom or side of the gasifier (Rezaiyan and Cheremimoff, 2005). Another important aspect is the bed type, for example ice beds or fixed. One reactor specific type is not necessarily suitable for the full power ranges, for example each reactor is operated in an adequate range. For example, fixed bed (upflow and downdraft) is suitable for smaller scales, which ranges from 10 to 10 MW; fluidized bed is more suitable for intermediate units from 5 to 100 MW; while trailed bed reactors are used for large scale power plants higher than 50 MW (Basu, 2010).

A detailed comparison between biomass gasification and combustion was provided by Rezaiyan and Cheremimoff (2005) and is summarized in Table 5. Generally, combustion aims on heat generation, whereas the gasification creates valuable gaseous products that can be used directly for combustion or stored for other

Table 5. Comparison between gasification and combustion processes (Rezaiyan and Chereminoff, 2005).

Features	Gasification	Combustion
Purpose	Creation of valuable, environmental friendly, usable products from waste or lower value material	Generation of heat or destruction of waste
Process type	Thermal and chemical conversion using or no limited oxygen	Complete combustion using excess oxygen (air)
Pressure	Atmospheric to high	Atmospheric
Raw gas composition (before gas cleanup)	H ₂ , CO, H ₂ S, NH ₃ , and particulated materials	CO ₂ , H ₂ O, SO ₂ , NO _x , and particulate materials
Solid byproducts/products	Char or slag	Bottom and fly ashes

applications (Mok et al., 1992). Fixed bed generally produces low heat synergies and is suitable for small or medium scales in thermal applications (Pattiyia, 2011). Since there is no mixing within the reactor, reaction uniform temperatures are difficult to be achieved (Moster et al., 2005). Fixed bed fans include upstream (countercurrent), downdraft (concurrent), crossflux and gas open (Araque et al., 2008).

Oxy-fuel combustion

Peng et al. (2016) discovered that the CO₂ emissions can be reduced by different ways, i.e., water absorption at high pressure, combustion in the presence of calcium oxide, oxy-fuel combustion, and electrical absorption. Among the CO₂ reduction methods cited, oxy-fuel combustion is considered as one of the most important and promising options for CO₂ sequestration, due to their ability for a significant reduction in the operating costs (Taniguchi et al., 2002). It was known that oxy-fuel combustion of pulverized biomass in O₂/CO₂ atmosphere can result in an increasing of the char conversion amount and combustion efficiency (Peng et al., 2016; Cruz and Crnkovic, 2016). Taniguchi et al. (2002) reported that NO_x emissions under O₂/CO₂ atmosphere are about 25% those emitted in air atmosphere. In addition, coal oxy-fuel combustion

makes it possible to capture and sequester carbon, using technology already available in conventional pulverized coal boilers, and to capitalize on the enormous quantities of money invested in the existing boilers (Riaza et al., 2012). Some researchers (Sengupta and Basu, 1991; Stenseng et al., 1995; Iavarone et al., 2017; Gaikwad et al., 2017) focused their attentions on the development of mathematical models to predict coal combustion, gaseous emissions and combustion chambers performance. It was observed that biomass oxygen emissions are not extensively investigated and applications of oxy-fuel combustion using cassava residues were not found.

FINAL CONSIDERATIONS

After extended research about the several known ways for biochemical and thermoconversion from cassava harvest residues and agricultural residues in bioenergy or biofuels, it was observed that many information and specific applications for this biomass are still lacking, which leads the researchers to the developing of studies that are more applicable to the real situations in each Country. In Brazil, for example, cassava harvest wastes present a great potential for use as bioenergy alternative source, but some care should be taken when these are used as biofuel,

due to the high occurrence of ashes in this biomasses, which can cause incrustation in thermal systems. Furthermore, because of the high moisture content presented at the time of harvest, a drying process should be provided before the wastes can be used as biofuel.

Finally, it is understood that correct and adequate use of cassava harvest residues in a sustainable and environmental friendly way, is an important factor for a socio-environmental conscience more concerned with the future of the Planet.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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