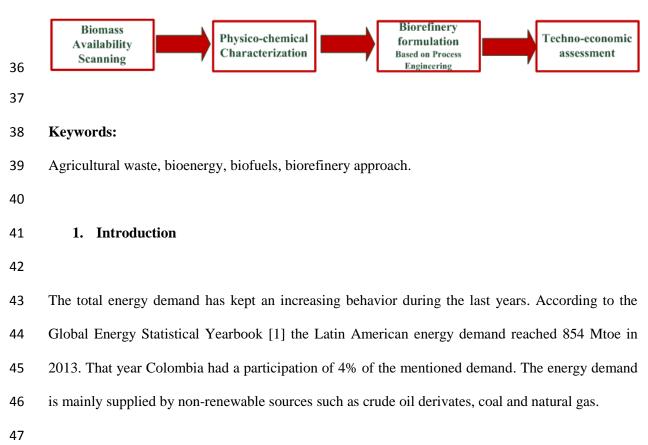
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4	Energy Biorefineries for Agricultural Waste Management: The
5	Colombian Case
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# 24 Abstract

25 In this study a techno-economic analysis of energy producing biorefineries from two different 26 agricultural wastes: Rice Husk (RH) and Plantain Pseudostem (PP) was developed. Considering the 27 wastes availability and the experimental characterization results were evaluated two energy 28 producing biorefineries considering ethanol, electricity and biogas production. The higher holocellulose (cellulose and hemicellulose) content 57% and 60% of RH and PP respectively makes 29 30 interesting these raw materials. The economical results allow concluding about the potential of 31 bioethanol production together with other energy products from agricultural wastes in tropical 32 countries.

33

### 34 Graphical Abstract



Considering environmental factors and the depletion in resources availability, the research focused on non-conventional energy sources has been increasing based on the advantages provided by nonrenewable energy sources such as high efficiency, easy transportation and huge power generation capability. In this sense the production of liquid, gas and solid biofuels as well as electricity can be an interesting alternative for biomass use.

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54 Bioenergy producing biorefineries are referred to these schemes in which one or different types of raw materials are used to produce energy (liquid biofuels, gaseous biofuels, solid biofuels, and/or 55 56 electricity). The use of liquid biofuels, as bioethanol and biodiesel, has been increased during the 57 past few years. In this sense the Colombian Government has regulated the use of gasoline blends 58 with 7-10% of bioethanol [2]. Bioethanol can be obtained from conventional and non-conventional 59 sources. The production process considers the pretreatment, fermentation, distillation and 60 dehydration processes [3]. Gaseous biofuels can be generated through anaerobic digestion (AD), 61 where methane and carbon dioxide are produced. It consists in three main steps (Hydrolysis-62 acidogenesis, acetogenesis and methanogenesis) [4]. Hydrolysis stage involves the biological 63 decomposition of organic polymers. In the acidogenesis stage some fermentative bacteria degrades glucose, xylose and xylans to produce ethanol, acetate, propionate, lactate and butyrate as mainly 64 products. Digestate is the main residue from anaerobic digestion. This residue is widely used in 65 66 land-applications due to its capability to enhance the soils nutrients retention [5]. Besides lignocellulosic residues, sugars like glucose have been tested as substrate for anaerobic digestion 67 68 under different schemes [6]. Electricity is considered as a secondary energy source based on the 69 flow of electrical power. Electricity can be produced from biomass through different termochemical 70 technologies which includes gasification or combustion [7].

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For products definition purposes it is necessary to consider the physical and chemical compositionof raw materials which can be classified in first, second and third generation. First generation raw

materials are referred to the edible crops used for food or agribusiness purposes [8], [9]. Second generation raw materials are mainly composed by lignocellulosic materials (cellulose, hemicellulose and lignin rich material) produced during different extraction or transformation stages such as seeding, cropping and harvesting. Other sources of second generation raw materials are the non-edible crops [10]. Finally, Microalgae are recognized as third generation raw materials [11]

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81 1.1 Colombian Context

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Colombia is a country located in a tropical region between the Pacific and Atlantic Oceans in the northern side of South America. Some geographical special features made Colombia a country assorted of a biodiversity composed by a variety of soils, hydric resources among others. Due to some geographical restrictions, different parts in the country exist under isolation conditions (for example the Amazon rainforest, high mountains regions, etc.). Infrastructure and Unsatisfied Basic Needs (UBN) represents the main gaps for isolated regions.

Non-Interconnected Zones (NIZ) are those isolated regions composed by the zones, towns and 89 90 municipalities non-interconnected to the national grid of energy generation and distribution. These zones represents approximately the 52% of the national area [12]. These zones are characterized by 91 92 their low population density, difficult access, poor infrastructure, as well as the Ethnic and 93 Afrodescent native communities. According to the 'Instituto de Planificación y Promoción de 94 Soluciones Energéticas para las Zonas no Interconectadas-IPSE', which is the govern agency 95 dedicated to planning strategies to integrate the NIZ [13], the electricity access represents a key 96 equity factor to promote the development and economic growth in the country based on 97 sustainability, competitiviness and efficiency.

99	In this sense the purpose of this work was to evaluate the production of three different energy forms
100	taking advantage of lignocellulosic biomass from agricultural wastes as an alternative for its
101	management and adequate disposal.

- 103 1.2 Agricultural waste Availability
- 104

105 **1.2.1 Rice Husk** 

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Rice represents one of the most relevant crops for Colombian agriculture preceded by coffee and sugarcane given the production scales and the harvested areas [14]. Rice is cultivated in more than 20 Colombian regions. This crop is developed under three different culture mechanisms classified according to the water irrigation and technification scales in irrigated, non-irrigated mechanized and non-irrigated manual areas.

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Rice Husk is the non edible agricultural residue generated during the whole grain de-husking process. Per each ton of rice processed can be generated approximately 0.23 tons of this residue [15] [16]. According to official statistics provided by agriculture ministry [17] from 2008 an stable area of about 500.000 Has producing 2,8 millions tons of rice is identified in the country. The production shares according the harvesting mechanism were 65%, 31% and 4% of irrigated, nonirrigated mechanized and non-irrigated manual.

119

120 This residue has restrictions in feed production due to its nutritive properties degradation 121 restrictions[18]. Ethanol, concrete and ceramics, agglomerates and adsorbent production as well as 122 energy generation are some of the potential uses for rice husks [19]. This residue can be used as 123 fertilizer being applied in averages quantities of 8 kg/m<sup>2</sup> [20].

### 125 1.2.2 Plantain Pseudostem

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Plantain culture represents a traditional sector in Colombian agriculture for internal as well as external market. In 2013 Colombia was the third world's exporter losing the leading role against Guatemala and Ecuador [21]. This crop has been traditionally cultivated by small farmers (less than 3 has) mainly associated to other crops such as coffee, cocoa, cassava and fruit crops. Plantain is cultivated in 31 Colombian regions and it is widely consumed in the diet playing an important role in food security [22].

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The plantain biomass is composed by an edible and a non-edible part. Approximately 20% of total 134 135 plantain biomass is represented by the edible part called plantain bunches, while the non edible part 136 is composed by mainly plantain pseudostem (representing the 50% of total biomass) [23]. The 137 remaining 30% is constituted by rachis and low quality edible parts [24]. Plantain Pseudostem is 138 commonly used as nutrient support for new plants during the agronomic stage [24]. According to 139 official statistics provided by agriculture ministry [17] about 2,7 millions tons of plantain bunches 140 are actually produced in the country. Considering the ratio pseudostem: bunches approximately 6,8 141 millions of tons of plantain pseudostem were produced. Near to 79% of the total residue is left in 142 lands.

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144	2.	Methodology
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146 2.1 Raw Material
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Rice Husk (RH) samples from *Oryza sativa* variety were obtained from a small farm from Saldaña
town 3°55′45″N 75°00′56″W located in Tolima region. Pseudostem plantain (PP) samples from *Musa paradisiaca* variety were obtained from Bugalagrande town located in Cauca Valley region.

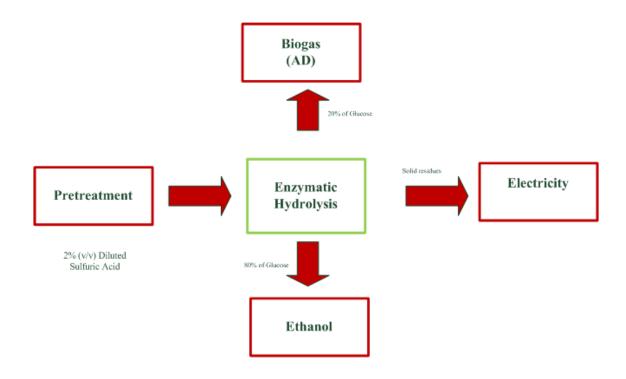
- 152 2.2 Experimental Characterization
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154 These raw materials were chemically characterized to determine its extractives, cellulose, hemicellulose, lignin and ash content. The samples were dried using a convective furnace at 50°C 155 and then milled to reduce the particle diameter below 0.85 mm. The extractives determination were 156 157 developed following the ASTM Standard Test Method E 1690 "Determination of Ethanol 158 Extractives in Biomass" [25] by using ethanol at 45°C for 24 h. Holocellulose (cellulose and 159 hemicellulose fractions) was determined through the chlorination method described by 160 Rabemanolontsoa and Saka [26]. The alpha-cellulose fraction was determined from the 161 holocellulose residue through sodium hydroxide and acetic acid treatment [27]. The total lignin (soluble and non-soluble fractions) was determined by acid treatment with  $H_2SO_4$ . Finally the ash 162 163 content was determined by sample ignition at 575°C according to the TAPPI standard T211 [27]. 164 All the experimental procedures were carried out by triplicated.

165

### 166 2.3 Process Description

167 After chemical characterization, were selected the routes to obtain different energy products as 168 bioethanol, biogas and electricity. These routes allow the design of the simulation strategy and 169 implementation to be used. The figure 2 shows the proposed biorefinery scheme.



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#### 173 2.3.1 Bioethanol Production

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175 The raw materials were submitted to pretreatment, enzymatic hydrolysis, fermentation and 176 separation stages. During pretreatment stage the raw materials were dried and milled and then were 177 sent to a diluted sulfuric acid (2% v/v) pretreatment at  $121^{\circ}\text{C}$  during 1.5h. The kinetic parameters 178 were reported by *Esteghillian* et al [28]. From this stage were separated two phases: the liquid phase 179 (mainly composed by xylose with furfural) and the solid phase (composed by non-soluble fraction 180 rich in cellulose). This stream was detoxified for further fermentation and the xylose fraction 181 disposed as co-product. Then, the filtrated residual biomass were destined to enzymatic hydrolysis, applying conditions reported by Morales-Rodriguez et al [29]. Enzymatic hydrolysis was developed 182 by cellulases and beta-glucosidase enzymes at  $50^{\circ}$ C, transforming the cellulose fraction into 183 184 glucose.

Later, the produced glucose was used as substrate to produce ethanol through submerged
 fermentation by *Saccharomyces cerevisiae* at 30°C [30]. After fermentation stage the fermentation

187	products were sent to the separation zone composed by three distillation columns. The outgoing
188	ethanol concentration reaches the azeotropic point (96% wt). Then, the azeotropic mixture was sent
189	to the dehydratation process with molecular sieves to obtain anhydrid ethanol (99.6 % wt) [31].
190	
191	2.3.2 Biogas Production
192	
193	Biogas production was evaluated considering a glucose portion from enzymatic hydrolysis as
194	substrate. The production process for anaerobic digestion (AD) is developed as complex multistage
195	system involving acidogenesis, acetogenesis and methanogenesis. The kinetics for these reactions
196	was proposed by Kalyuzhnyi and Davlyatshina [32] using anaerobic sludge as preinoculum. The
197	digestion was developed at 35°C with a initial glucose concentration of 2 g/l. As AD products were
198	obtained mainly methane and carbon dioxide followed by acetate and propionate in low amounts
199	[32].
200	
201	2.3.3 Electricity Production
202	
203	A gas turbine cogeneration system as described by Rincón et al [33] with the aim of producing
204	electricity and steam for process requirements. In this scheme the gases produced during biomass
205	combustion were passed through a turbine to obtain energy.
206	
207	2.4 Process Simulation
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209	Aspen Plus V8.2 (Aspen Technology Inc., USA) was used for simulation purposes. Some
210	physicochemical properties of non-included compounds were obtained from the National Institute
211	of Standards of Technology. Aspen Plus database for biofuels components developed by the

212	National Renewable Energy Laboratory [34] was used for hexoses properties specifications. The	he
213	thermodynamic models used for simulation were the Non-Random Two-Liquid (NRTL). }	

The total production costs were estimated using the commercial software Aspen Process Economic Analyzer V8.2 (Aspen Technology Inc., USA) assuming the depreciation of capital for 12-year period beneath the straight-line method. The economic parameters such as income tax, interest rate, labor salaries, electricity and water costs corresponded to the Colombian context. From this stage, the capital costs as well as the operating, raw materials, utilities, equipment and other general and administrative costs were estimated. All the inputs, referred to enzymes, low pressure steam and medium pressure steam are presented in the Table 1

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#### **Table 1. Input Prices**

Feature	Value	Units	Reference
Water	0.74	USD/m <sup>3</sup>	Moncada et al [35]
Electricity	0.14	USD/kW	Moncada et al [35]
LP Steam	1.57	USD/Ton	Moncada et al [35]
MP Steam	8.18	USD/Ton	Moncada et al [35]
Nutrients	1	USD/kg	This Work *

\*proposed as an average price of the needed nutrients

225

226 **3. Results and discussion** 

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228 3.1 Experimental Characterization

The chemical composition of RH and PP are presented in the Table 2 and Despite the similar compositions, the high initial moisture 83% represents the main disadvantage for the use of PP. This moisture content could imply higher energetic costs related to the drying process. Besides, the costs associated to the PP logistics of the harvesting can reduce the profitability potential of PP as raw material.

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The results obtained are slightly different compared to the reported by *Quintero* et al and *Cordeiro*et al. In both cases, cellulose followed by hemicellulose contents was identified as the main
component. It shows a high potential of the selected raw materials to be transformed to sugars
platform. However, the higher lignin content of RH represents the main drawback as raw material
for sugar production. Nevertheless, its lignin content confers to RH the potential to be used in
concrete and construction materials.

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#### Table 2. Rice Husk Characterization

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Feature	This Work	Literature	Reference
Moisture	$11 \pm 0.5\%$	11.7 %	Srinivas and Reddy
			[36]
Extractives <sup>(db)</sup>	$7 \pm 1\%$	3.35 %	
Cellulose <sup>(db)</sup>	40 ± 2%	26.45 %	
Hemicellulose <sup>(db)</sup>	16 ± 3%	27.29 %	Quintero et al [37]
Lignin <sup>(db)</sup>	$26 \pm 7\%$	28.03 %	
Ash <sup>(db)</sup>	11 ± 1%	14.89 %	

- 245
- 246

248 Despite the similar compositions, the high initial moisture 83% represents the main disadvantage 249 for the use of PP. This moisture content could imply higher energetic costs related to the drying 250 process. Besides, the costs associated to the PP logistics of the harvesting can reduce the 251 profitability potential of PP as raw material.

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# Table 3. Plantain Pseudostem Characterization

Feature	This Work	Literature	Reference
Moisture	83 ± 3%	85 %	<i>Pérez</i> [23]
Extractives <sup>(db)</sup>	$19 \pm 1\%$	8.1 %	
Cellulose <sup>(db)</sup>	41± 7%	40.2 %	
Hemicellulose <sup>(db)</sup>	19± 5%	25 %	Cordeiro et al[38
Lignin <sup>(db)</sup>	14± 4%	14.6 %	
Ash <sup>(db)</sup>	8± 0.1%	15.6 %	

# 255 (db): Dry Basis

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### 257 3.2 Techno-economic Assessment

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Ten tons per hour of each raw material were defined as basis calculation for simulation purposes. Then, based on preliminary analysis the produced glucose was distributed in 80% and 20% to ethanol and biogas plants respectively. Considering the moisture contents the available hemicellulose and cellulose varies affecting the ethanol and biogas yields. In both cases the ethanol production process gave a positive profit margin compared to the reported market prices [39] of 0.92 USD/kg. The ethanol profit margins obtained were 5% and 2%. These profit margin values are still lower and can be strongly affected by inputs and raw materials costs.

Products		
	RH	PP
Ethanol (USD/kg)	0.88	0.91
Biogas (USD/m <sup>3</sup> )	5.37	6.81
Electricity (USD/kWh)	0.0097	0.0099

For understanding the prefeasibility of the proposed technology, in the case of biogas Table 5 presents the prices comparison between some conventional biogas sources. Biogas production costs from RH and PP are higher compared with the reported by *Gissén* et al[40]. This behavior might be explained by the fewer amount of glucose considered by this work using just 20% of the total availability. However, if the xylose is also used for these purposes, the total biogas yield can be considerably higher and the costs dramatically reduced. The xylose production was 135.4 kg/ ton RH and 56.4 kg/ ton PP of xylose.

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# Table 5. Biogas Comparison

Source of Biogas	USD/m <sup>3</sup>	Reference
RH	5.37	This work
PP	6.81	This work
Natural Gas	0.41	Gissén et al[40]
Dairy	0.09	Gissén et al[40]

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Another interesting co-product to be considered is the highly diluted anaerobic sludge, which in this work was produced at rates of 6918 kg/ton RH and 3590 kg/ton PP of anaerobic sludge as coproducts. This co-product can represent additional incomes enhancing the biorefinery economical performance.

The electricity production, being one of the most important targets allowed due to the positive incomes. The low production costs could contribute to enhance the electricity access in different regions with limited access. In this sense, the use of agricultural wastes which has a huge availability in the country (isolated and non-isolated regions) would have strong applicability for NIZ.

293

# **4.** Conclusions

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The results showed that it is possible take advantage of agricultural wastes under biorefinery scheme considering additional products such as xylose derivatives and sludge from AD. The moisture content represents one bottleneck for waste valorization considering the increases in costs associated to drying process and low available dry matter to be transformed. Finally, this type of raw materials can be used under biorefiney scheme for those isolated zones with high rates of NBU considering the production of basic supplies and other value-added products as energy.

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