Assessment and comparison of thermochemical pathways for the rice residues valorization: pyrolysis and gasification

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1. Introduction

The energy security is a key item to minimize the environmental impact generate by the fossil fuels use promoting sustainable energy supply to the communities (Jain et al., 2022). In search of new alternatives for the energy matrix diversification, lignocellulosic biomass as agricultural and agro-industrial solid wastes have an important role due to their availability and composition. These residues show a significant trend towards non-conventional energy generation and production being a possible solution to the high demand that currently exists on the planet (Y. Zhang et al., 2023). In the last years, different processes have been studied for the valorization of solid wastes that allow the bioenergy production, where thermochemical and biochemical technologies are the most promising (Wu et al., 2022). Thermochemical conversion processes are based on obtaining gaseous, liquid and solid products, such as syngas, bio-oil and bio-char respectively, through exothermic and endothermic reactions of biomass degradation and devolatization, being pyrolysis (400 – 800 °C), and gasification (800 – 1000 °C) the most scientifically recognized processes (García et al., 2017).

In the context of the rice industry, the main residues generated are straw (agricultural waste) and husk (agro-industrial waste) which have a high energy potential and where its structure is mainly composed by cellulose, hemicellulose and lignin fibers and can be exploited via thermochemical pathways. Currently, husk and straw represent one of the biggest problems for rice farmers due to these correspond to 20% by weight of total production approximately. According to the National Administrative Department of Statistics (DANE) in the country for the first half of the year 2021 were harvested 1.208.599 tons of mechanized rice which generated 241.719,8 tons of husk. So far, do not exist industries focused on the management of this kind of residues or have developed a productive process that ensures its suitable use commercial purposes. In this sense, this work aims to carry out an assessment and comparison of thermochemical pathways for the rice residues (straw and husk) valorization through a techno-economic analysis in two different scenarios, i) gasification and ii) pyrolysis.

2. Material and methods

The rice husk and rice straw were provided by a milling placed at San Marcos - Sucre, in the northern region of Colombia. The residues were sun-dried and milled until a particle size of 0.425mm (mesh 40). The physicochemical characterization (*i.e.,* chemical, proximate and elemental analysis) of feedstocks was carried out in triplicate. Initially, the chemical composition of feedstock was determined using NREL standards (National Renewable Energy Laboratories) for moisture, extractives (NREL TP-510-42619), ashes (NREL TP-510-42622) calculation. Then, the determination of holocellulose and cellulose, and Klason's lignin were carried out according to ASTM D1104 and ASTM D1106, respectively. The proximate analysis involves four measures, ash, volatile matter, moisture and fixed carbon. The determination of ash, volatile matter and moisture was carried out through the protocol reported on the ASTM E1755 – 01, ASTM E872 – 82 and ASTM E871 – 82, respectively. Finally, the fixed carbon was estimated as the difference between the ash and volatile matter content on dry basis. The ultimate or elemental analysis allows the quantification of C/H/O in a sample. In this work, this analysis was carried out using standard ASTM D591-92 with the EMA 502 Elemental Analyzer CHNS-O. The Calorific value was determined using an IKA C-6000 bomb calorimeter based on ASTM E711 - 87.

An experimental thermogravimetric analysis (TGA) for both residues was carried out to generate kinetic parameters for the pyrolysis process at 10°C/min and 30°C/min.

Pyrolysis and gasification as thermochemical pathways were assessed for husk and straw, namely, four process scenarios, where the experimental physicochemical characterization was the base line to generate the mass and energy balances via simulation procedures using the software Aspen Plus (Aspen Technology, Inc., USA). Peng Robinson was taken as thermodynamic method. A set of indicators were used to evaluate the energy performance of each process (Aristizábal-Marulanda et al., 2020). The software Aspen Process Economic Analyzer (APEA) v10 was used to calculate the process cost (CAPEX and OPEX). This analysis was estimated in US dollars considering the straight-line depreciation method and using economic parameters of Colombian context. The effect of different capacities in the economic profitability (*i.e.*, production cost) was evaluated. In this analysis were included concepts as, Minimum Processing Scale for Economic Feasibility (MPSEF) that represents the point where NPV is equal to zero across the total project lifetime; and equilibrium point where the gains and expenses are equal (NPV keeps constant after zero time) (Serna-Loaiza et al., 2018). Based on this analysis, the contribution of the main economic parameters as CAPEX (based on fixed capital costs of equipment), OPEX (calculated as the sum of costs of raw materials, utilities, maintenance, labor, fixed and general costs and overhead) and the general profits from the product were discussed (García-Velásquez et al., 2018).

3. Results and discussion

The proximate, elemental and chemical analysis, and calorific value allow to determine the most adequate route for the energetic valorization of the waste (Solarte Toro, 2017). In this sense, **Table 1** indicates the experimental physicochemical characterization of rice husk and rice straw, which due to their availability and composition can be used as an energy vector by valorizing them through thermochemical routes such as pyrolysis and gasification (Basu, 2013). This is due to the properties that the products obtained from pyrolysis or gasification processes such as bio-oil, bio-char and syngas can have a high heating value than biomass when subjected to direct combustion. (Basu, 2013), (Chen et al., 2011) report that the bio-oil obtained from the pyrolysis of rice husk presents a high heating value of 22 - 23 MJ/kg, which is higher than that obtained in the same analysis for other biomasses.

Table 1. Physicochemical characterization of rice husk and rice straw (% dry basis).

Component	**Rice husk**		**Rice straw**	
	%	**(±)**	**%**	**(±)**
Proximate analysis				
Volatile matter	69,9466	0,2164	72,6451	0,5444
Fixed carbon	10,1886	0,1449	12,0776	0,1092
Ash	19,8648	0,0409	15,2773	0,0154
Elemental analysis				
Carbon	31.6587	-	37.4308	-
Hydrogen	4.3268	-	5.1879	-
Nitrogen	0.7290	-	0.9486	-
Oxygen		-		-
Sulphur	<0.01	-	<0.01	-
High heating value HHV (MJ/kg)	14.6395	0.0389	14.7550	0.0976
Chemical analysis				
Moisture	4.5797	0,1759	5.8128	0.1270
Ash	10,9201	0,0409	9,3708	0,0154
Holocellulose	38.5664	0.8442	40.2993	1.4414
Lignin	39.4088	4.5179	32.3866	2.1291
Extractives	6.5250	0.6892	12.1305	0.8660

The results also show that rice husk and rice straw have a very similar calorific value and that the C/H ratio indicates that are promising biomasses for bioenergy production from gasification or pyrolysis. As related to the productivity of the main products in pyrolysis process, the yields for rice husk have been defined as ranges of 26.8 - 41.92 %, 34.8 - 39.61 % and 18.47 - 34.1 of biochar, bio-oil and gases, respectively (S. Zhang et al., 2018), (Abu Bakar & Titiloye, 2013). Likewise, for rice straw these vary between 31.0 - 41.5 %, 38.5 - 51.8 % and 17.2 - 20.0 % of biochar, bio-oil and gases, respectively (Park et al., 2014), (Faisal et al., 2022).

On the other hand, the yields of rice husk gasification present values of 73.3 - 85.8 % for syngas, 7.8 - 14.5 % for solids (ash and biochar), and 4.2 - 12.2 % for tar (G. Zhang et al., 2018). In the case of rice straw gasification, the yields are 41.1 - 64.0 % for syngas, 16.6 - 19.3 % for solids (ash and biochar) and 7.3 - 12.23% of tar (Pei et al., 2020).

4. Conclusions

Energy, technical and economic analysis for pyrolysis and gasification processes it is evident that these are promising routes for the energetic valorization of rice residues ensuring socio-economic growth, transforming waste into viable products to be integrated into the production system, providing access to clean energy, and bringing economic growth to communities.

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