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Bio-oil production from rice husk fast pyrolysis in a conical spouted bed reactor

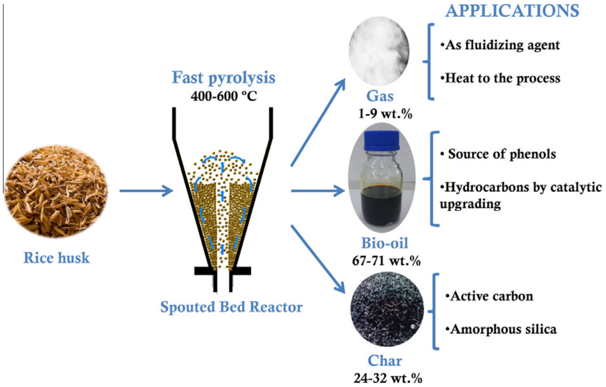
Jon Alvarez, Gartzen Lopez, Maider Amutio, Javier Bilbao, Martin Olazar *

University of the Basque Country UPV/EHU, Department of Chemical Engineering, P.O. Box 644, E48080 Bilbao, Spain

HIGHLIGHTS

- The CSBR is suitable for fast pyrolysis of rice husk obtaining high bio-oil yields.
- The maximum bio-oil yield (70 wt.%) is achieved at 450 °C, with low gas yield (4 wt.%).
- The bio-oil is a mixture of oxygenated compounds with interesting applications.
- The char is of good quality for the production of active carbon and amorphous silica.

GRAPHICAL ABSTRACT



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ABSTRACT

The fast pyrolysis of rice husk has been performed in the 400–600 °C range in a continuous pyrolysis bench-scale plant equipped with a conical spouted bed reactor (CSBR) with continuous removal of the char. In this paper it is studied the influence of temperature on product yields and products composition (gas, bio-oil and char) as well as the effect over the char properties. Bio-oil yield is very high (70 wt.% at 450 °C) due to the high capacity of mass and heat transfer as well as the reduced residence time of the CSBR. Moreover, bio-oil yield decreases slightly with temperature owing to the increase of gas yield, which is very low in the whole range of temperature studied. These results evidence the suitability of CSBR for the fast pyrolysis of rice husk, with the aim of obtaining bio-oil and char. The char can be upgraded by obtaining amorphous silica and activated carbon.

1. Introduction

The use of bio-based energy is an essential strategy to replace fossil derived fuels gradually in order to reduce the CO_2 net emissions [1]. Rice husk (RH) is a by-product from rice mills and is one of the most widely available agricultural residues because rice is a primary source of food for billions of people, with an annual production over 600 million tons, from which more than 90% are cultivated in Asia [2,3].

The RH has a hard surface, small bulk density and high amorphous silica content (the highest among the Gramineae plants) [4]. Its final disposal in landfills gives way to a source of pollution, i.e., eutrophication and perturbations in the aquatic and terrestrial life. Additionally, its uncontrolled combustion could cause environmental and accumulative health problems due to the formation of crystalline silica (quartz and cristobalite) particles, which remain suspended in the air [5].

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* Corresponding author. Tel.: +34 94 601 2527; fax: +34 94 601 3500.
E-mail address: martin.olazar@ehu.es (M. Olazar).

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Fast pyrolysis is an attractive treatment for lignocellulosic biomass valorization, which has attained a high degree of technological development for large-scale production of bio-oil [6,7]. Bio-oil can be used as fuel blended with diesel [8], for the manufacture of value-added products [9,10]; or as feedstock for the production of hydrocarbons in catalytic reaction units [11,12], and subjected to steam reforming for obtaining hydrogen [13–15]. Furthermore, the pyrolysis process can be performed on a moderate scale in rural regions where lignocellulosic biomass is collected and the bio-oil produced can be transported to the corresponding refinery units for the large-scale production of commercial fuels or hydrogen [16,17].

The essential features of a fast pyrolysis process for producing liquids are: (i) very high heating and heat transfer rates, (ii) carefully controlled temperature (around 500 °C), (iii) short vapor residence times (typically below 1 s), (iv) rapid removal of the char from the reaction environment and (v) rapid cooling of the pyrolysis vapors [18].

Fast pyrolysis of different kinds of lignocellulosic biomasses usually produce bio-oil yields in the 60–80 wt.% range, a gas yield of 5–25 wt.% and a char yield in the 15–35 wt.% range, depending on the amount of ash in the raw material [19–22]. Generally, the main objective in the fast pyrolysis is obtaining the highest bio-oil yield, whilst the gas can be used to satisfy the energy requirements of the pyrolysis process itself [23]. The char or solid residue can also be used as fuel to provide heat to the process or as raw material for producing activated carbons with high adsorption capacity to remove toxic gas streams and treat polluted liquid effluents [24,25]. Moreover, porous carbon materials also play a significant role in new applications, such as catalytic supports, battery electrodes, capacitors and gas storage [26–28].

The chemical composition of bio-oils is very complex because they are mainly composed of water and a mixture of oxygenated compounds formed by the fragmentation and depolymerization reactions of cellulose, hemicellulose and lignin by their rapid heating [21,29]. The composition of oxygenated compounds in the bio-oil depends on the content of cellulose, hemicelluloses and lignin in the biomass [30], and the major compounds in the bio-oil from RH fast pyrolysis are phenolic ones, including phenols, cresols, guaiacols and benzenodiols as well as ketones [31–35].

Fluidized bed reactors have been widely used in the biomass fast pyrolysis due to its isothermicity, high heat and mass transfer rates, reduced residence time of the volatiles, simplicity of design and scaling up capabilities [36,37]. The conical spouted bed reactor (CSBR) is an alternative to fluidized beds and has been proven to be a versatile reactor for biomass fast pyrolysis, which allows obtaining high bio-oil yields thanks to its high heat and mass transfer rates and very short residence times [19,20,38].

This paper deals with aspects concerning RH fast pyrolysis. The interest of the study carried out lies in the CSBR capability to handle low density materials with a highly irregular texture, such as RH, whose pyrolysis also produces high yields of char with a great content of siliceous ashes. The cyclic movement of the particles characteristic of the CSBR minimizes bed segregation, and the peripheral circulation of the char in the bed allows it continuous separation and removal from the reaction environment. Furthermore, the reduced residence time of the volatiles is suitable for minimizing the gas fraction formed by the cracking of oxygenate compounds in the bio-oil, which in the case of RH pyrolysis is enhanced by the high ash content acting as a catalyst in the process [31,39,40].

This paper focuses on the production of bio-oil and the knowledge of its composition for a wide range of temperatures, paying also attention to the properties of the gas and solid, since the economic viability of the pyrolysis process also requires the valorization of these two fractions. Much attention has been paid to the composition of the char due to its great interest for obtaining activated carbon and amorphous silica [41]. The silica obtained from RH has a great commercial interest as raw material for industries associated with ceramics, construction materials, glass, rubber, electronics, catalysis, pharmaceutics and others [42,43]. Given the common routes for removing the silica contained in the RH are extraction and combustion [42,44], pyrolysis could be an attractive alternative because the char obtained as by-product could also be used for the production of silica, thus complementing the economy of the global process. Moreover, the separation of the silica contained in the char has lower energy requirements and generates less environmental problems than the production of silica from the raw RH. Furthermore, rice husk based activated carbons have proven to perform well in the adsorption of many metal ions [45] and organic molecules [46,47]. The separation of the silica from the char is recommended as a preliminary stage in the physical or chemical activation of the char in order to improve the adsorption properties of the activated carbon [41,48,49].

2. Material and methods

2.1. Raw material

The *Brillante* brand RH has been supplied by Ebro Foods S.A and has been ground (Retsch ZM 100) and sieved to a particle size in the 0.63–1 mm range. Grinding requirements are only necessary in a laboratory scale because the feeding system device cannot feed materials with a large particle size; however, a CSBR is especially suitable for handling particles with wide range of sizes. The main characteristics of RH are summarized in Table 1. The ultimate and proximate analysis has been carried out in a LECO CHNS-932 elemental analyzer and in a TGA Q500IR thermogravimetric analyzer, respectively. The calorific value has been measured in a Parr 1356 isoperibolic bomb calorimeter. The chemical composition of the ash (Table 2), including silica and major metal compounds, has been determined by X-ray Fluorescence (model AXIOS, PANalytical).

2.2. Pyrolysis plant and experimental procedure

The continuous bench-scale plant used to perform RH fast pyrolysis is shown in Fig. 1. The design has been based on the extensive knowledge acquired in previous studies in the pyrolysis and gasification of other waste materials, such as waste tyres, plastics and other types of biomasses like sawdust and forestry residues [50–52].

The feeding system consists of a vessel equipped with a vertical shaft connected to a piston placed below the material bed and allows the continuous feeding of up to 200 g h^{-1} of RH. Nitrogen has been used as fluidizing agent, and its flow rate is controlled

Table 1
Properties of the RH.

Ultimate analysis (wt.%)[a]	
Carbon	42.0
Hydrogen	5.4
Nitrogen	0.4
Oxygen	39.3
Proximate analysis (wt.%)[b]	
Volatile matter	70.5
Fixed carbon	16.6
Ash	12.9
Moisture (wt.%)	1.1
HHV (MJ kg^{-1})	16.8

[a] On wet basis.
[b] On dry basis.