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Full Length Article

Valorization of citrus wastes by fast pyrolysis in a conical spouted bed reactor

Jon Alvarez[a], Bahar Hooshdaran[b], Maria Cortazar[a], Maider Amutio[a], Gartzen Lopez[a], Fabio B. Freire[c], Masoud Haghshenasfard[b], Seyyed Hossein Hosseini[d], Martin Olazar[a,*]

[a] University of the Basque Country UPV/EHU, Department of Chemical Engineering, P.O. Box 644, E48080 Bilbao, Spain
[b] Department of Chemical Engineering, Isfahan University of Technology, Isfahan, Iran
[c] Department of Chemical Engineering, Federal University of São Carlos, C.P. 676, 13565-905 São Carlos, SP, Brazil
[d] Department of Chemical Engineering, Faculty of Engineering, University of Ilam, Ilam, Iran

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ABSTRACT

The fast pyrolysis of the juice squeezing derived orange waste has been carried out in a continuous pyrolysis bench-scale plant consisting of a conical spouted bed reactor (CSBR). A prior study performed in thermobalance and a kinetic model consisting of a multi-component mechanism allowed determining the contents of pectin (35 wt%), hemicellulose (16.6 wt%) and cellulose (17.1 wt%), but that of lignin could not be satisfactorily determined as its degradation curve overlapped with other compounds such as sugars, proteins and fats. In the bench scale experiments, the bio-oil yields were very high in the 425–500 °C range (close to 55 wt%) due to the suitable features of the CSBR (high heat and mass transfer rates and short residence time of the volatiles), but they are lower for higher temperatures due to the promotion of secondary cracking reactions. Compared to lignocellulosic biomasses, the orange waste produced a bio-oil with more methanol and furfural and less phenolic species, which is an encouraging fact for its stability and valorization by catalytic cracking or steam reforming. The high concentration of CO_2 in the gas is a drawback for use for energy production. The char yield (33–27 wt%) was high in the whole range of temperatures studied and its high carbon content (71–73 wt%) and HHV (≈ 27 MJ kg^{-1}) are suitable for use as fuel.

1. Introduction

Strategies for the production of bio-fuel and bio-based chemicals are essential in order to gradually replace fossil fuel derived counterparts and so reduce the environmental impacts associated with the emission of greenhouse gases [1]. Amongst the different agro-forestry wastes generated during harvesting or industrial processing [2,3], citrus fruit wastes are a source of abundant, inexpensive and readily available renewable energy [4]. These wastes are composed of seeds, peels and pulp and are the main by-product of juice industries, accounting for about 50 wt% of the raw fruit processed, with their moisture content being approximately 82 wt% [5]. Brazil is the world's largest producer of orange juice, accounting for approximately 53% of the orange juice produced worldwide and 80% of the international trade in this product [5]. Accordingly, a large amount of waste results from the juice processing industry, which in 2011 reached about 9.3 million tons [6]. In Spain, approximately 500,000 t of citrus wastes are produced per year, with over 60% being derived from orange juice squeezing [7].

These wastes have no commercial applications, and they are usually spread on soil areas adjacent to the orange juice industries, used as compost, for animal feed or they are just burned in open fields [5,8]. Therefore, they are an unavoidable waste from the juice industry, involving serious environmental concerns [4]. Currently, some biochemical processes (anaerobic digestion, ethanol fermentation, recovery of flavonoids and chemicals) and thermochemical ones (pyrolysis, gasification and/or combustion) have been proposed as environmentally friendly routes for the valorization of these wastes [9,10]. Although each technique has its advantages and drawbacks, pyrolysis, and specifically fast pyrolysis, has been widely used to convert biomass and organic residues into diverse products (bio-oil, gas and char) [11,12]. This technology is versatile, simple and has a low investment cost, which allows decoupling its deployment on a moderate scale in the regions where the raw material is available from the further upgrading of the bio-oil in large-scale bio-refineries [3].

Most of biomass pyrolysis studies have been focused on lignocellulosic wastes, which are made up of hemicellulose, cellulose and

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[*] Corresponding author.
E-mail address: martin.olazar@ehu.es (M. Olazar).

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lignin. The chemical composition of citrus juice wastes differ from lignocellulosic ones, as citrus peels have also an significant content of pectin in addition to cellulose, hemicellulose and lignin [13]. Furthermore, they also contain other constituents, such as sugars, fats and proteins, in a significant amount [14]. Pectin is a primary constituent in the cell wall structure of terrestrial plants, and basically consists of 4-linked D-galacturonic acid units with several degrees of methylation of the carboxyl group [15]. According to the relevant literature, pectin decomposes at lower temperatures (between 150 and 250 °C) than hemicellulose or cellulose, which decompose between 220 and 315 °C and between 315 and 400 °C, respectively [16–18]. Therefore, the thermal degradation behavior and the products derived from the fast pyrolysis of pectin-containing wastes, especially those in the bio-oil, will be different from those commonly obtained in the pyrolysis of lignocellulosic materials [19]. In fact, Kim et al. [13,16] predicted that the higher content of pectin (16–43 wt%) and lower of lignin (0.8–9 wt %) in citrus wastes than in woody biomasses leads to larger amounts of methanol and lower of aromatics in the bio-oil.

Although some papers deal with the pyrolysis of citrus peel wastes, most of these studies have been performed in thermogravimetric equipment [4,13,16], semibatch/fixed bed reactors [2,10,19,20] or rotary kilns [21]. However, none of them have been performed in fluidized bed or conical spouted bed reactors (CSBR), which can operate in continuous mode, under isothermal regime, with very high heat and mass transfer rates between phases, without segregation and low residence time of the volatiles (conditions required for maximizing bio-oil production and minimizing gas formation [22,23]). The CSBR technology is an alternative to conventional fluidized beds, and performs well in the fast pyrolysis of different types of lignocellulosic wastes [3,24–26], sewage sludge [23], as well as other waste materials, such as tyres [27] or plastics [28]. The main advantage of the CSBR is the fact that the vigorous cyclic movement of the solid allows handling particles that are bigger than those allowed in fluidized beds, of irregular texture, fine materials and sticky solids, with no agglomeration and segregation problems [29]. Accordingly, the costs derived from orange waste grinding and milling are considerably reduced. Furthermore, this reactor has a simple design (no distributor plate) and requires lower volumes than fluidized beds for the same throughput [30].

It should be remarked that few papers deal with a qualitative composition of the bio-oil derived from orange/tangerine peel, but none of them have determined quantitatively the concentration of each compound in the liquid. For example, Lopez-Velazquez et al. [4] detected by simultaneous TGA-FTIR analysis the presence of carboxylic acids, aldehydes/ketones, alcohols and phenolic compounds in the volatiles evolved from orange waste pyrolysis. Kim et al. [9] observed large amounts of acids, ketones and aldehydes, a low amount of phenols and the presence of some nitrogen species in the bio-oil from the non-catalytic pyrolysis of tangerine residue. Likewise, they also identified certain tangerine peel pyrolytic products by Py-GC/MS and the major areas observed in the chromatograms corresponded to acetic acid and methanol [19]. Besides, the same authors [13] concluded in a later study that *Citrus Unshui* peel fast pyrolysis produced larger amounts of furans, ketones and methanol than wood powders [13].

This study focuses on the valorization of orange waste by continuous flash pyrolysis in a CSBR with the objective of maximizing the bio-oil yield at temperatures between 425 and 600 °C. A quantitative analysis of the bio-oil composition has been carried out in order to assess different bio-oil upgrading routes. In addition, the characteristics of the gas and char (and their possible applications) are also evaluated in order to improve the overall economy of the process for a successful industrial implementation. Given that the composition of orange wastes differs from that of typical biomasses, this study also provides a methodology for the quantification by thermogravimetry of the main chemical components of these types of wastes (pectin, hemicellulose, cellulose and lignin), which is based on a previous one developed by Amutio et al. [18,31] for other biomass materials.

Table 1
Properties of the orange wastes used.

Ultimate analysis[a] *(wt%)*	
Carbon	42.7
Hydrogen	6.4
Nitrogen	1.0
Oxygen[b]	47.6[b]
Proximate analysis[a] *(wt%)*	
Volatile matter	74.1
Fixed carbon	23.6
Ash	2.3
Moisture (wt%)	1.5
HHV (MJ kg^{-1})	19.4
Chemical analysis of ashes (wt%)	
SiO_2	0.29
Al_2O_3	0.33
Fe_2O_3	0.09
MgO	4.78
CaO	29.47
Na_2O	1.98
K_2O	30.9
TiO_2	0.02
P_2O_5	8.34
SO_3	3.46

[a] On a dry basis.
[b] Calculated by subtraction.

2. Materials and methods

2.1. Orange wastes characterization

Orange wastes were collected from an orange juice dispenser. The samples were dried in an oven for 24 h at 60 °C in order to reduce the moisture content and at the same time avoid the release of some extractives. After the drying process, the water content in the orange peel was reduced to 1.5 wt%. Next, these wastes were ground in a mill (Retsch ZM 100) and sieved in order to remove particles finer than 1 mm, which may easily elutriate from the reactor without being completely reacted. The main properties of the orange wastes are summarized in Table 1. The ultimate and proximate analyses have been carried out in a LECO CHNS-932 elemental analyzer and in a TGA Q500IR thermogravimetric analyzer, respectively. Table 1 also includes the ash chemical composition determined by X-ray fluorescence (model AXIOS, PANalytical).

Moreover, the analysis of the data obtained by TGA enabled the determination of the main chemical constituents of this waste (pectin, hemicellulose and cellulose and lignin + proteins + fats). The kinetic model implemented is based on a multi-component mechanism, which describes the volatile formation by means of four concurrent (independent and parallel) reactions corresponding to the decomposition of the four main biomass pseudo-components. According to Boluda-Aguilar et al. [7], pectin decomposes between 180 and 300 °C, hemicellulose between 200 and 300 °C and cellulose between 315 and 430 °C, whereas the remaining components (lignin, proteins and fats) decompose in a wider temperature range, 150–700 °C. Similar decomposition temperatures for each pseudo-component were reported by Kim et al. [16,19] (210, 270 and 368 °C for pectin, hemicellulose and cellulose, respectively). Given that lignin decomposes in a wide range of temperatures, and fats, sugars and proteins overlap in the DTG curve, one of the pseudo-components is assigned to the sum of lignin, sugar and protein content in the orange waste. Details about the approximation considered and on the multi-component mechanism have been reported in a previous paper [18], in which the authors successfully determined the concentration of each pseudo-component (hemicellulose, cellulose and lignin) in forestry residues from the Portuguese Central Inland Region following the same procedure.

Hence, the overall kinetic model studied considers four parallel independent reactions of first order as follows: