Fuel Processing Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Evolution of chars during slow pyrolysis of citrus waste

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ARTICLE INFO

Article history:
Received 3 December 2016
Received in revised form 10 January 2017
Accepted 11 January 2017
Available online xxxx

Keywords:
Citrus waste
Pyrolysis
Char reactivity
Downdraft gasification

ABSTRACT

Conversion of agro-wastes into energy can be key to a circular-driven economy that could lead to models for sustainable production. Thermochemical processing is an interesting alternative for the upgrading of agro-wastes to energy. However, owing to the complex and largely unknown set of reactions occurring during thermal breakdown, to ensuring consistent quality of the final products is still a goal to achieve at industrial level. The present study investigates the evolution of solid products of pyrolysis, to gain some insights in these complexities. Chars derived from slow pyrolysis (200–650 °C) of citrus pulp in a horizontal reactor have been characterized by means of Fourier Transform Infrared spectroscopy (FT-IR), X-Ray Diffraction (XRD), Thermo Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). Results are discussed also in light of similarities with coal thermal breakdown.

At temperatures below 300 °C, changes in solid matrix are mainly due to breaking of aliphatic compounds. Significant changes in char structure and behavior then occur between 300 °C and 500 °C mainly related to secondary char-tar reactions. Above 500 °C, changes appear to occur mainly due to recombination reactions within matrix, which thereby becomes progressively less reactive.

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1. Introduction

During the past 200 years, several methods have been proposed to efficiently gasify biomass. Different types of gasifiers potentially suitable to the different types of biomass, desired power and general conditions have been designed. Downdraft and updraft gasifiers are more suitable to small scale applications [1] and hence particularly desirable in rural areas where conversion to energy of abundant agro waste would offer a significant support to local economies while contributing to solve existing disposal issues [2].

Despite gasification has been known for a long time, although extensive research effort and significant incentive schemes have been implemented in several countries in order to support its industrial and commercial development, current lack of fundamental knowledge on biomass thermal breakdown still impedes the widespread of the technology [3,4].

The gasifying section of downdraft set-ups normally follows a pyrolysis stage in which biomass experiences increasing temperatures in a non-oxidative environment to break down into a solid carbonaceous material (char) and a hot mix of reactive vapors and non-condensable gases. The extent and type of the numerous reactions occurring within the hot fluid and between the fluid and the solids is highly dependent on the system set-up [5,6]. In moving bed systems, such as downdraft gasifiers, a relatively tall stack of chipped or shredded, typically inhomogeneous, biomass is piled up to slowly undergo thermal breakdown as temperature rises towards the gasification section. While solids move downwards through an increasingly hot bed, they experience different fates depending on the sequence of events that they undergo. The complexity at hand is exacerbated by significant heat and mass transfer limitations [7,8] as well as synergistic effects among the macro-constituents of ligno-cellulosic feedstock [9,10].

In summary, efficient gasification of chars that evolve out of the pyrolysis stage of a downdraft set-up, largely depends on the specific, reactor's related, pyrolysis process that the chars have come out of [11].

Several authors have studied the evolution of chars in different type reactors: Zhao and co-workers [12] investigated the effect of pyrolysis temperature on char structure in an entrained flow reactor and found that pyrolysis between 500 and 900 °C resulted in ring condensation, which produces large aromatic ring systems containing six or more fused benzene rings. Song and coauthors [13] recently investigated the reactions among fresh coal and biomass tar with biomass chars to find that the aromatic structures in tar are more reactive with char than the non-aromatic structures, especially at temperatures above 800 °C. Xin and coauthors [14] observed how dehydration due to

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http://dx.doi.org/10.1016/j.fuproc.2017.01.015
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Please cite this article as: R. Volpe, et al., Evolution of chars during slow pyrolysis of citrus waste, Fuel Processing Technology (2017), http://dx.doi.org/10.1016/j.fuproc.2017.01.015

cleavage of intra- and inter-molecular hydrogen bonds (H-bonds) was the primary reaction in pyrolysis of cellulose at temperatures below 300 °C and that above 300 °C dehydration occurred principally intermolecularly along with decarbonylation, ring-opening and aromatization. In a recent study, the present authors have investigated the pathways that influence the reactivity of chars produced in a horizontal batch set-up simulating the pyrolysis stage of a downdraft gasifier [15]. While that work highlighted how chars evolve depending on the evolution of C and H in solids, further investigation is required to continue develop the argument and shed some additional light into the factors that govern the physical and chemical characteristics of solid products of pyrolysis especially at temperatures between 300 and 650 °C.

The present study tackles this issue, by providing a FT-IR, XRD, TGA and SEM characterization of pyrolysed lemon and orange pulp in search for clues on reactions among volatiles and solids and within the solids themselves during thermal decomposition. The results are discussed also in light of early research on coal. As reported in previous works [6,15], the comparison between coal and biomass thermal breakdown deserves investigation and the subsequent analysis will attempt at highlighting similarities. The study is also intended to support operators who look for indications to design real scale set ups and set operational parameters of existing reactors.

2. Materials and methods

2.1. System set-up

A horizontal fixed-bed type reactor, derived from the standard Gray-King (GK) assay test on coal was purposely modified to conduct pyrolysis tests. The reactor design and full details of set-up are described in [16,17]. Briefly, the system consists of a quartz-made cylindrical reactor 340 mm long and 20 mm i.d. closed at one end. A special quartz cap equipped with an 8 mm i.d. quartz inner tube allows a flow of inert gas through the feedstock to sweep volatiles away into a cold trap (mix of glycol, dry CO_2 and water bath kept at −27 °C) used to collect condensable products for mass balances.

2.2. Sample preparation

Peel waste from lemon, “Femminello” variety, and blonde orange, “Tarocco” variety, were collected as a wet pulp, right after being processed at factory located in Messina province, Sicily. The pulps were oven dried for 48 h at 60 °C and then 6 h at 105 °C to get rid of moisture. Lemon and orange pulp (LP and OP) showed respectively 83.7% and 78.9% moisture by weight (as received basis). LP contained also approximately 7.5% by weight (%*w*/w db) of seeds while no seeds were present in OP. Dried LP and OP were milled and again oven dried for 12 h prior to grinding and sieving to <850 μm particle size. The feedstock was then oven dried again at 105 °C and then sieved to select particle size range between 200 and 850 μm and then pyrolysed in order to produce the chars for subsequent analyses.

2.3. Test run

A series of pyrolysis experiments (150 °C–650 °C peak temperatures) have been carried out under a flow of 1.5 L min^{-1} of Nitrogen (Airliquide 5.0 Alphagas 1); a detailed description is provided on [17]. Approximately 10 g (db) of sample were heated to the desired peak temperature at 50 °C min^{-1} heating rate and held at peak value for 30 min. Gas residence time was calculated to be approximately 3.3 s. Bio oils were condensed in a cold trap held in a thermostatic bath kept at −27 °C while non-condensed gases were filtered and vented out safely. At end of run, chars were left to cool naturally to room temperature and collected for further analyses. Char yields (M_{char}/M_{raw}%w/w db) were calculated to compare results obtained in previous studies only with the purpose of validating the runs. Runs showing char yields out of a ± 5% error range were repeated. Neither bio-oil nor gases were analyzed in the present study.

2.4. Analytical determinations

Proximate analyses were conducted on raw materials, as well as chars, in a TA Instruments Discovery TGA, Q50. Moisture content (MC), volatile matter (VM), and ashes of solid samples were determined according to the following thermal program:

1) 20 °C/min ramp to 105 °C in N_2, hold time 30 min to eliminate and determine any residual MC;
2) 15 °C/min ramp from 105 °C to 900 °C in N_2, hold time 7 min to determine VM;
3) 15 °C/min cooling down to 500 °C in N_2;
4) 15 °C/min ramp to 900 °C in air and isothermal for 10 min to determine ash content.

Fixed carbon (FC) was evaluated by difference via the following formula:

$$FC = M_i - MC - VM - Ash \tag{1}$$

where all numbers are expressed in grams and M_i indicates the original ‘as received’ mass of sample.

Ultimate analyses were performed using a CE Instruments Flash EA 1112 analyzer at Medac Ltd. laboratories in Woking UK. Higher heating values (HHV) were evaluated according to the CEN/TS 14918 standard by means of a LECO AC500 calorimeter.

FT-IR study was carried out on a Perkin Elmer FT-IR 100 spectrometer. The spectrometer was set to work in transmission mode. Background subtracted spectra were collected at room temperature by co-adding 64 scans at 4 cm^{-1} resolution. The data were baseline corrected using Spectrum 10™ software.

The evolution of aromaticity in samples was calculated as the ratio I_{ar}/I_{al} between the intensities at:

- I_{ar} wavenumber associated to the stretch of C=C bonds ($\nu C = C$), and
- I_{al} wavenumber associated to the C—H stretch in aliphatic bonds (νCH_{al})

X-ray diffraction (XRD) analysis was performed on an X'Pert Pro PANalytical. Diffraction patterns were recorded with Cu Kα radiation (40 mA, 45 kV) over a 2ϑ-range of 5 to 60° and a position-sensitive detector using a step size of 0.05° and a step time of 120 s. The XRD patterns were further processed using the accompanying software in the equipment, X'PertHighscore Plus.

Finally, SEM micrographs were taken using a JEOL JSM6400 scanning electron microscope.

3. Results and discussion

Table 1 presents proximate and ultimate analysis of the samples investigated. Data show the expected decrease in VM with temperature and subsequent increase of FC and C. H shows limited reduction up to 300 °C to then decrease significantly above that temperature.

3.1. FT-IR

Fig. 1 shows the FT-IR patterns of samples while Table 2 reports the principal components associated with the different wavenumbers relevant to present study [18,19].

The patterns show that thermal treatment produced clear changes in the chemical functionalities and therefore in the chemical composition of the chars for both feedstocks. Remarkably, the intensity of the hydroxyl groups, of the C—H stretching associated to aliphatic compounds and the carbonyl band C=O decreased with increasing

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