Journal of Analytical and Applied Pyrolysis 107 (2014) 17–24

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Pyrolysis of apricot kernel shell in a fixed-bed reactor: Characterization of bio-oil and char

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ARTICLE INFO

Article history:
Received 6 August 2013
Accepted 22 January 2014
Available online 11 February 2014

Keywords:
Apricot kernel shell
Pyrolysis
Bio-oil
Char
Characterization

ABSTRACT

The pyrolysis of apricot kernel shell was studied for determining the main characteristics and quantities of liquid and solid products. Experiments were carried out in a static atmosphere with heating rates of 10 °C/min and 50 °C/min, pyrolysis temperatures of 400, 450, 500 and 550 °C and sweep gas flow rates of 50–200 cm^3/min. The maximum bio-oil and char yields were 26.3 (500 °C) and 35.2% (400 °C), respectively. The TG-DTG analyses were applied on the raw material to investigate the thermal degradation of apricot kernel shell. The elemental analysis and heating value of the bio-oils were determined, and then the chemical composition of the bio-oil was investigated using chromatographic and spectroscopic techniques such as column chromatography, ^{1}H NMR, and FTIR. In addition, the char was characterized by elemental, BET and scanning electron microscopy (SEM) analyses. According to the experimental results the liquid products can be used as liquid fuels and the solid product seems to be suitable for adsorption purposes due to its high surface area.

1. Introduction

Renewable energy should be considered in order to renovate the energy sources and to keep the sustainable development safely due to the fact that energy consumption is increasing and limited fossil fuels are nearly exhausted with increasing population and economic developments [1]. Among the technologies concerning clean energy conversion, the energy exploitation of biomass is an interesting challenge since biomass is available in large quantities, renewable and clean (zero net CO_2 emission, low sulfur, nitrogen and metal content), and it minimizes the disposal problems associated with the generation of agricultural by-products. Moreover, biomass exploitation allows the possibility of generating added value products such as chemicals or activated carbons which means an attractive economic and technological solution [2].

Biomass may vary significantly in its physical and chemical properties due to its diverse origins and types [3]. Biomass, a composite material mainly comprised of cellulose, hemicellulose, lignin and minor amounts of other organics, is an ideal renewable resource for the generation of heat and power via thermochemical processes [4]. Recently, many researchers have carried out obtaining and characterization studies of ligno-cellulosic biomass such as pyrolysis, gasification, and combustion in order to design efficient and environmentally sustainable processes [5].

One of the most promising thermochemical processes is pyrolysis which produces solid (char) and volatile (gas and liquid) products [2,6–8]. The yield of gas, char and liquid product (tar) obtained in the pyrolysis process is due to the decomposition of the raw materials and the interactions of the intermediates. Numerous parameters affect the pyrolysis rate and the yields, composition and properties of the products. The products proportion is influenced by feedstock properties (chemical composition, ash content and composition, particle size and shape, density, moisture content, etc.) and operation parameters (such as temperature, heating rate, type of sweeping gas, residence time, etc.). To obtain high yields of valuable liquid products, the biomass particles must be rapidly heated and the residence time of volatile products must be short [3,6,8–11].

The most interesting product from the energetic point of view is the gas (mainly composed of H_2, CO, CO_2, CH_4, C_2H_4, etc.) which has a higher heating value (HHV) high enough to be used for the total energy requirements of a biomass waste pyrolysis plant and might also be employed in internal combustion engines, gas turbines and other operating applications and technologies [2]. Bio-oil, with H/C molar ratio higher than 1.5, mainly contains alkanes, aromatic hydrocarbons, phenol derivatives and little amounts of ketone, ester, ether, amine, furans, sugar and miscellaneous, as well as alcohol [12–16]. This bio-oil can be used both as an energy source and a feedstock for valuable chemical products. However, drawback in the utilization of biomass pyrolysis oils in fuel applications is their chemical and physical characteristics. Biomass pyrolysis oils are highly oxygenated, viscous, corrosive, relatively unstable

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0165-2370/$ – see front matter
http://dx.doi.org/10.1016/j.jaap.2014.01.019

and chemically very complex [17,18]. The direct substitution of the biomass derived pyrolytic oils for conventional petroleum fuels may therefore be limited. Consequently, research has developed for upgrading the oils by catalytic treatment to produce a derived fuel product with similar quality to a refined petroleum fuel [17]. The solid product from pyrolysis contains char, ash and unchanged biomass material, and it is known as char. The char is a solid carbonaceous residue, with a high content in fixed carbon (>75%), which can be used directly as fuel or briquettes, or as precursor for the activated carbon production [2,19].

Biomass is the world's largest and most sustainable energy resource. Estimation shows that ∼220 billion dry tones of annual available biomass in the world [20]. Currently biomass covers approximately 10 percent of the global energy supply, of which two-thirds is used in developing countries for cooking and heating. The remaining energy use of biomass takes place in industrialized countries where biomass is utilized both in industrial applications within the heat, power, and road transportation sectors and for heating purposes in the private sector [21].

Turkey has a rich agricultural biomass potential. Various agricultural residues are available. One of the main important biomass sources in Turkey is food processing industry wastes. Apricot stone, hazelnut shell, grapeseed and chestnut shell are important biomass residues obtained in Turkey and they have a great importance as being a source of energy [22].

Turkey is the leading fresh and dry apricot producer in the world. Apricot is one of the most popular ones of the temperate tree fruit species. The total world production of apricot is about 3.8 million tons. Turkey is the leading country in apricot production (676,138 tons), and Iran (452,988 tons) and Italy (263,132 tons) are the other main producers [23,24].

The apricot kernel shell is an agricultural by-product obtained in large amounts. Many years ago these by-products were used as a fuel in rural areas but now the preparation of activated carbon and liquid fuel production has been encouraged. Therefore, it is important to evaluate apricot kernel shell in liquid fuel and activated carbon productions since it is a cheap precursor [25–30].

In this study, the apricot kernel shell was selected as a feedstock for bio-oil and char production and the aims of the study are: (i) to determine the effects of pyrolysis temperature, heating rate and sweeping gas flow rate on product yields, (ii) to characterize the bio-oil obtained under optimum pyrolysis conditions to investigate if it can be used instead of conventional fossil fuels or chemical feedstocks, and (iii) to characterize the chars as solid products for their possible use of solid fuels or activated carbon.

2. Experimental

2.1. Raw material

Apricot kernel shell chosen for this study has been taken from the city of Konya located in the Central Anatolian region. Prior to its use, the samples were air dried, ground with a high speed rotary cutting mill and sieved into fractions of 0.425 mm < Dp < 0.600 mm in size. The main characteristics of the apricot kernel shell are shown in Table 1.

Table 1
Properties of the apricot kernel shell.

Characteristics	Standards	Percentage (wt.%)
Moisture content	ASTM D2016	8.30
Proximate analysis[a]		
Volatiles	ASTM E 872-82	75.00
Ash	ASTM D1102-84	0.95
Fixed carbon[b]	By difference	15.75
Ultimate analysis[a]		
Carbon		47.33
Hydrogen		6.37
Nitrogen		0.37
Oxygen[b]	By difference	45.93
Empirical formula	Calculation	$CH_{1.62}O_{0.73}N_{0.01}$
H/C molar ratio	Calculation	1.62
Lignocellulosic composition		
Cellulose	TS 4431	29.57
Hemicellulose	By difference	17.01
Lignine	ASTM D 1106-96	47.97
Higher heating value ($MJ\,kg^{-1}$)	ASTM D 240	20.58

[a] Weight percentage on dry basis.
[b] By difference.

2.2. Pyrolysis experiments

All pyrolysis experiments were performed with exactly 20 g of dried apricot kernel shell in a stainless steel (#316) fixed-bed Heinze reactor with a length of 104 mm and an internal diameter of 70 mm, equipped with an inert gas (nitrogen) connection. The reactor was heated externally by an electric furnace, with the temperature being controlled by a NiCr–Ni thermocouple inside the bed. More detailed descriptions of the pyrolysis procedure can be found elsewhere [31,32].

The experiments were carried out in two groups. The first group of experiments was carried out in a Heinze reactor under self-pyrolysis atmosphere [33]. To determine the effect of pyrolysis temperature and heating rate on the yields of apricot kernel shell pyrolysis, each 20 g air-dried sample, of 0.425 < Dp < 0.600 mm size, was placed in the reactor and the temperature was raised to the final temperatures of 400 °C, 450 °C, 500 °C, and 550 °C. The two heating rates of 10 and 50 °C/min were applied and the final temperatures were held for a minimum of 30 min until no further significant release of gas was observed. After reaching the final pyrolysis temperature the reactor was set to cool to room temperature. The flow of gas released was measured using a soap film throughout the experiments. Liquid products were condensed in ice cooled traps at about 0 °C using salty ice and recovered with DCM (dichloromethane) washing. The aqueous phase was separated from oil phase with a separating funnel. The bio-oil and solvent mixture was passed over dry sodium sulphate to make it water free and then the solvent was recovered from bio-oil by rotary evaporator. After pyrolysis, the char was removed and weighed. The yield of products was calculated by using the following equation:

$$\text{Yield\%} = \left[\frac{\text{Desired product (bio-oil or char, g)}}{20 \times (1 - (\%\,\text{ash} + \%\,\text{moisture}))}\right] \times 100 \quad (1)$$

The gas yield was determined by an overall material balance.

The second group of experiments was performed to establish the effect of sweep gas flow rate (nitrogen) on the pyrolysis yields. The experiments were conducted at sweep gas flow rates of 50, 100, 150 and 200 cm^3/min. For all of these experiments, the heating rate and the final pyrolysis temperature were 50 °C/min and 500 °C, respectively, based on the optimum results of the first group of experiments. All the yields were calculated on a dry ash free (daf) basis. In order to determine if results were reproducible, each experiment was performed three times with the experimental error less than ±1%, and the averaged values were used for analysis.

2.3. Thermal analysis

The thermal behavior of apricot kernel shell was studied using Perkin Elmer Diamond thermogravimetric analyzer. The sample, weighing approximately 10 mg, was heated from room temperature to 1000 °C with a constant heating rate of 10 °C/min in air atmosphere.