



Bio-oil from pyrolysis of Tunisian almond shell: Comparative study and investigation of aging effect during long storage



Najla Grioui^a, Kamel Halouani^{a,*}, Foster A. Agblevor^b

^a UR: Micro-Electro Thermal Systems – ENIS-IPEIS, University of Sfax, Route Menzel Chaker km 0.5-B.P. 1172, 3018 Sfax, Tunisia

^b USTAR, Biological Engineering, Utah State University, Logan UT, 4105 Old Main Hall, Logan, UT 84322, USA

ARTICLE INFO

Article history:

Received 23 April 2013

Revised 10 April 2014

Accepted 24 May 2014

Available online 10 July 2014

Keywords:

Almond shell

Fast pyrolysis

Bio-oil

Storage

Aging

ABSTRACT

Bio-oil from fast pyrolysis of Tunisian almond shell (TN-AS) in fluidized bed reactor was investigated. TG (Thermogravimetric) and DTG (Derivative Thermogravimetric) analyses were performed to quantify the kinetic of its thermal degradation by comparison with other Mediterranean almond shell feedstocks from Spain (SP-AS) and Turkey (TR-AS).

The obtained bio-oil was characterized in terms of its composition and energy content using FTIR, ¹³C NMR and GC-MS. The analyses showed that TN-AS bio-oil was similar to the Turkish one and was slightly different from the Spanish bio-oil.

Aging effect at room temperature over a long storage period (5 years) was also investigated to assess bio-oil stability. The aged TN-AS bio-oil had a higher viscosity ($705.16 \pm 3.76 \text{ mm}^2 \cdot \text{s}^{-1}$ at 50 °C) while pH, water content and HHV remained unchanged. The increase of viscosity may be due to the increase in the molecular weight resulting of re-polymerization reactions taking place during the long storage period.

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Introduction

Biomass, as renewable material, contributes to global energy sustainability since it can be a potential substitute for petrochemical derivatives used for industrial applications. Different thermochemical conversions such as combustion, gasification and pyrolysis were successfully used to recover energy from lignocellulosic materials. These technologies were considered as a highly attractive way especially when environmental concerns are of importance during energy production. Recently, pyrolysis process is becoming a potential technology which has proved its efficiency through the energy conversion of various types of feedstocks. Moreover, almond shell (AS) is a relatively abundant lignocellulosic agricultural by-product in Tunisia with a production of about 60000 tons in 2011 (FAOSTAT data, 2011) but it is not much valorized. Like most biomass residues, AS is biodegradable material composed of cellulose, hemicelluloses and lignin. Cellulose is a high molecular weight and linear polymer of β -(1 → 4)-D-glucopyranose units. Hemicelluloses are a mixture of various polymerized monosaccharides whereas lignin is a cross-linked polymer consisting of an irregular array of hydroxy- and methoxy-substituted phenylpropane units. Given its higher carbon

content and the stability of its aromatic rings, lignin is thermally more stable than cellulose and hemicelluloses (Raveendran et al., 1996; Worasuwannarak et al., 2007). When cellulose, hemicelluloses and lignin are heated in an inert atmosphere, they decomposed into various pyrolysis products (char, gases, and oils) depending on the operating conditions principally temperature and heating rate (Bridgwater et al. 1999).

Although several pyrolysis studies have been conducted on AS (Caballero et al., 1996; Chen et al., 2010; Conesa et al., 1997; Front et al., 1990, 1994; González et al., 2005, 2006; Önal et al., 2014), none of them have addressed geographic variation in feedstock composition. Agricultural residues such as AS vary in composition because of climatic and geographic location, harvest time and harvest practices, storage and other conditions prevailing in the farming community. According to our knowledge, there have been no publications on bio-oil production from TN-AS pyrolysis. Thus, we propose in the present work to explore TN-AS suitability for bio-oil production by comparison with those from two other locations (Spain and Turkey).

The bio-oil produced from AS pyrolysis is a result of various thermolytic degradation reactions of polymers (cellulose, hemicelluloses and lignin chains) and their interactions during thermochemical process. The main reactions of these polymers are depolymerization, decarboxylation, cracking and splitting of depolymerization products. The bio-oil derived from pyrolysis reactions is a complex mixture of alkanes, alkynes, aromatic compounds, esters, acids, alcohol, phenols.

* Corresponding author. Tel.: +216 98954415; fax: +216 74246347.

E-mail addresses: najla_grioui2001@yahoo.fr (N. Grioui), kamel.halouani@ipeis.mu.tn (K. Halouani), Foster.agblevor@usu.edu (F.A. Agblevor).

Potentially this complex mixture can be refined into liquid fuels or converted to other chemicals such as resins and bioplastics if the bio-oil can be stabilized.

Most of bio-oils are unstable because of the large fraction of oxygenated compounds and polymerization reactions leading to phase instability during storage therefore do not lend themselves easily to conventional petrochemical unit operations. The storage stability is one of the most important factors influencing the introduction of a new fuel into commercial markets. Some authors studied the different condition storage effect of bio-oils. They found that the aging reactions result in undesirable changes in physical properties, such as increase in viscosity and water content with a corresponding decrease in volatility. Czernik et al. (1994), Diebold and Czernik (1997), Oasmaa and Kuoppala (2003); Oasmaa et al. (2011), Elliott et al. (2012), Chaala et al. (2004), Hilten and Das (2010) and Kim et al. (2012) measured the degree of instability of aged bio-oil during storage period between 2 days and 1 year by increasing storage temperature between 20 and 90 °C. Czernik et al. (1994; 1997) concluded from aging data, that the aging reactions are relatively similar over the 37 to 90 °C temperature range and therefore, chemical changes during accelerated aging are representative of the changes that occur during normal aging. They demonstrated that equivalent viscosities are obtained in oak pyrolysis oil after 3 months of aging at room temperature, 4 days of aging at 60 °C or 6 h of aging at 90 °C. In the same way, Chaala et al. (2004) reported that the increase in molecular weight observed after heating softwood bark pyrolysis oil for 1 week at 80 °C is equivalent to keeping the sample for 1 year at room temperature. Kim et al. (2012) found the same results than those previous authors for yellow poplar wood bio-oil during 10 weeks of storage at 23 °C. They concluded that the average molecular weight of pyrolytic lignin increased by re-polymerization with low molecular weight compounds present in the aged bio-oil. Diebold and Czernik (1997), Oasmaa and Kuoppala (2003); Oasmaa et al. (2011) and Elliott et al. (2012) have shown that the increase in viscosity during aging correlated very well with the increase in molecular mass. They also investigated that the aging rate is dependent on the feedstock, pyrolysis conditions, efficiency of solids/ash removal and product collection. Diebold (2002) reported that possible chemical reactions occurring within bio-oil include: esterification of organic acids with alcohols; homopolymerization between aldehydes; hydration of aldehydes or ketones with water; formation of hemiacetals or acetals from aldehydes and alcohols; resin formation from aldehydes and phenols; olefinic condensation; and air oxidation of alcohols and aldehydes to form carboxylic acids. However, the chemical reactions in bio-oil have been essentially postulated on theoretical basis, with a few studies being carried out experimentally for confirming the occurrence of these reactions.

All the majority studies on aged bio-oil stability were investigated during maximum period 1 year of the storage and at an accelerated aging (study temperature between 60–90 °C) to demonstrate the aging properties of a particular pyrolysis liquid in the short time. But, the studies on the bio-oil stability during a long period of storage (above 1 year) were practically absent. However, the effect of storage duration on bio-oil properties depends of the time and the storage temperature.

In this paper we propose two principal sections. The first section is devoted to a kinetic study of TN-AS pyrolysis and a physico-chemical characterization of the produced bio-oil to investigate its suitability as raw material for added value products applications. To show climatic and geographic location impact on the physico-chemical properties of bio-oil, the obtained results will be particularly compared with those of SP-AS and TR-AS bio-oils. In the second section, we propose to study the aging effect on bio-oil stability during a long period storage (5 years) at room temperature. FTIR, ¹³C NMR and GC–MS analysis will be performed to investigate the changes in the composition of TN-AS bio-oil. Some reaction mechanisms will also be proposed to explain the changes in the chemical structure of the aged bio-oil.

Materials and methods

Plant material

The AS used in the present study was arranged from Sfax City in Tunisia. The shells were ground and sieved to a 0.841 mm particle size. The sample of AS was shipped to Galbraith Analytical Laboratory, (Knoxville, TN) where it was analyzed to determine its elemental compositions and higher heating value (HHV, ASTM D5865). These results were shown in Table 1.

Thermobalance

A Setaram thermobalance Labsys apparatus was used for thermogravimetric analysis. The experiments were carried out in dynamic conditions at heating rate of 10 °C·min⁻¹ from 298 K to 823 K. 30 mg of ground and sieved TN-AS was loaded into the platinum pan and pyrolyzed under nitrogen atmosphere at a nitrogen flow rate of 30 mL·min⁻¹.

Fast pyrolysis in fluidized bed reactor

The fast pyrolysis of TN-AS was conducted using a bubbling fluidized bed reactor. Fig. 1 shows a schematic diagram of the fast pyrolysis unit. The reactor was made from stainless steel pipe having 50 mm internal diameter and 500 mm height. The fluidizing medium was silica sand with average particle size of 252 μm. The reactor tube was externally heated with a three-zone electric furnace.

The dried AS of 0.841 mm particle size was loaded into a K-Tron volumetric feeder and conveyed by a twin-screw into an entrainment compartment where high velocity N₂ gas was used to entrain the feed and carry it through a jacketed air-cooled feeder tube into the fluidized bed.

The pyrolysis was carried out at two different temperatures, 473 °C and 537 °C, and the apparent pyrolysis vapor residence time was 3.25 s. During the pyrolysis, a feed rate of 200 g·h⁻¹ and a N₂ fluidizing gas flow rate of 18 L·min⁻¹ were maintained constant. The temperatures in top, medium and bottom of reactor were measured and controlled by three K-thermocouples inserted into a thermal well in the reactor.

The pyrolysis vapor exiting the reactor was condensed in a series of ethyleneglycol/water-cooled condensers and an electrostatic precipitator (ESP). Most of the liquid product was condensed in the condensers maintained at a temperature below –20 °C. However, the aerosol which was not condensed in the ethyleneglycol/water-cooled condenser was collected in the ESP.

The char fraction was separated in a hot gas filter. The mass balance of the liquid, solid, and gas products was performed gravimetrically by weighing the reactor, filter, condensers and ESP before and after each experiment. All experiments were performed in triplicates to ensure reproducibility.

Oil production analysis

Physicochemical properties of pyrolytic bio-oil

The pyrolytic TN-AS bio-oil product was characterized for its physicochemical properties determination following the standard test methods (Table 3). The elemental compositions of the bio-oil were determined using thermo Scientific Flash 2000 organic elemental analyzer. The sample size was 2–4 mg and the oxygen content of the bio-oil was determined by difference. pH value of bio-oil was measurement by a pH meter (COMBI pH/mV/Temp Bench Meter) at room temperature. The instrument was calibrated with liquid calibration standards of pH 4 and 7 prior to the measurement. HHV was measured using a bomb calorimeter (Parr 6400) according to the ASTM D 240 standard. Water content is recommended to be analyzed according to ASTM E

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