Fuel Processing Technology 159 (2017) 160–167

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

In-situ catalytic pyrolysis of peanut shells using modified natural zeolite

L.I. Gurevich Messina [a,b], P.R. Bonelli [a,b], A.L. Cukierman [a,b,c,*]

[a] Programa de Investigación y Desarrollo de Fuentes Alternativas de Materias Primas y Energía—PINMATE, Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Intendente Güiraldes 2620, Ciudad Universitaria, C1428BGA Buenos Aires, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Godoy Cruz 2290, C1425FQB Buenos Aires, Argentina
[c] Cátedra de Tecnología Farmacéutica II, Departamento de Tecnología Farmacéutica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Junín 956, C1113AAD Buenos Aires, Argentina

ARTICLE INFO

Article history:
Received 21 June 2016
Received in revised form 9 January 2017
Accepted 18 January 2017
Available online 26 January 2017

Keywords:
Catalytic pyrolysis
Peanut shells
Clinoptilolite
Bio-oil quality improvement

ABSTRACT

In-situ catalytic pyrolysis of peanut (*Arachis hypogaea*) shells was investigated employing modified clinoptilolite. Likewise, conventional pyrolysis of the shells was explored to quantify the deoxygenation degree of bio-oil. Two solid catalysts obtained from natural clinoptilolite were used: one which retained most of the native cations and another one subjected to ion exchange treatment to develop Brønsted acid sites. These catalysts were characterized using different techniques, such as scanning electron microscopy with X-ray microanalysis, Fourier transform infrared spectroscopy by pyridine adsorption, and nitrogen sorptometry. Assays in a bench scale installation based on a fixed bed reactor were conducted at 500 °C and the yields of the three kinds of pyrolysis products (bio-oil, bio-char and gases) were determined. Likewise, the composition and other physical properties of the bio-oil and gases were investigated. Both catalysts led to reduce the oxygen content of the bio-oil, improving its high heating value. On the other hand, catalytic pyrolysis promoted a slight reduction in bio-oil production at expenses of an increase in gases generation. The catalyst subjected to ion exchange performed better than the native form as less water was generated in the catalytic cracking.

1. Introduction

Argentina is one of the largest producing countries of peanut (*Arachis hypogaea*) with an estimated annual production of over 1 Mt [1]. Industrial processing of peanut generates a large amount of shells, accounting for approximately one fourth of the annual production of the legume. This waste is normally burned, releasing into the atmosphere toxic gases, such as dioxins [2–4]. Waste burial, which is also employed to dispose the hulls, could lead to changes in soil pH and may result in groundwater pollution. Bioenergy production from biomass resources would minimize these practices, contributing at the same time to generate green energy [5–8].

As the peanut shells are rich in lignin, biochemical processes, such as anaerobic digestion or alcoholic fermentation, are not appealing because of their lower organic matter degradation capacity. On the other hand, thermochemical processes such as gasification or pyrolysis, could decompose lignin and also attain higher reaction rates [9]. Despite being a more mature technology, gasification produces gases with a low energy density and which are expensive to transport and storage. By contrast, biomass pyrolysis generates a high energy density liquid fuel, known as bio-oil, which could be used as substitute of fuel-oil [10]. This biofuel has been tested in boilers and gas turbines, reaching a high degree of combustion efficiency [11].

However, bio-oil shows some disadvantages mainly due to its high oxygen content. The oxygenated compounds present in the liquid lead to a high chemical polarity, which reduces its miscibility with conventional hydrocarbon fuels. Furthermore, most of the oxygen is in the form of reactive groups (hydroxyl and carboxyl groups) that might react among them, lowering the bio-oil stability. In addition, the high oxygen content brings about a low heating value of the bio-oils [8,9,12,13].

Among the different alternatives to improve the bio-oil quality by lowering its oxygen content, zeolite cracking is one of the most promising options [14,15]. By means of this process, bio-oil deoxygenation is accomplished through dehydration, decarbonylation, decarboxylation, and cracking. The acid nature of zeolites is the main motive of their catalytic activity as it seems to promote the rupture of C—C and C—O bonds through the acid sites [16]. The zeolite based catalysts could be used to improve the bio-oil in different ways. The bio-oil upgrading might be carried out in a different reactor than the one used to carry out the pyrolysis, allowing to make react the vapours or the bio-oil with the catalysts. On the other hand, the same reactor where the pyrolysis is performed could be employed to accomplish catalysis. This scheme is known as *in-situ* catalytic pyrolysis [17].

* Corresponding author at: Programa de Investigación y Desarrollo de Fuentes Alternativas de Materias Primas y Energía—PINMATE, Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Intendente Güiraldes 2620, Ciudad Universitaria, C1428BGA Buenos Aires, Argentina.
E-mail address: analea@di.fcen.uba.ar (A.L. Cukierman).

http://dx.doi.org/10.1016/j.fuproc.2017.01.032
0378-3820/

Synthetic zeolites, such as ZSM-5, mordenite and faujasite, are usually employed to develop the catalysts [15,18]. Nevertheless, the cracking could also be performed employing natural zeolites, therefore, reducing the cost of the process. Clinoptilolite, being the most abundant zeolite in the earth crust, is an attractive option to develop cheap catalysts [19]. However, only few works on the subject have explored zeolite cracking with clinoptilolite as a way to improve pyrolysis products. Pütun et al. [20] compared the catalytic pyrolysis of residues of olive oil production using ZSM-5 and clinoptilolite. They concluded that, although the synthetic zeolite was more effective to deoxygenate the bio-oil than the clinoptilolite, less coke was produced employing the latter as catalyst. Moreover, Rajić et al. [21] explored the synergy between metal oxides and clinoptilolite in lignin pyrolysis for phenol production. In later works, they compared the performance of phenol production between the modified clinoptilolite and the modified ZSM-5 [22,23], finding that phenol production depended mainly on the metal cations in the zeolite and not on the type of acid sites. Nevertheless, the quantity and type of acid sites (Lewis and Brønsted sites) has been reported to exert a strong influence on the cracking process [24]. However, to the best of our knowledge, there are no works in the literature devoted to examine exhaustively the influence of the different acid sites of clinoptilolite on the pyrolysis products.

Within this context, this work comparatively studies the conventional pyrolysis of peanut shells and catalytic pyrolysis of this lignocellulosic biomass using two catalysts developed from clinoptilolite. One of the catalysts retained most of the cations present in the natural clinoptilolite while the other was subjected to an ion exchange treatment in order to protonate it and increase Brønsted acid sites concentration. Pyrolysis of the shells was performed employing a fixed bed reactor at pre-established conditions. Yields of the different pyrolysis products were obtained. The gases and bio-oils generated were also characterized.

2. Materials and methods

2.1. Peanut shells

Commercial peanut (*Arachis hypogaea*) shells, abbreviated as PS, were cleaned, milled, and screen-sieved in order to obtain samples of different particle diameters. The fraction ranging from 250 μm to 500 μm was selected for the fixed bed reactor experiments, while that of particle diameter between 44 and 74 μm was used for thermogravimetric studies. The elemental composition of the biomass samples was determined using an automatic elemental analyzer (Carlo Erba model EA 1108) and the content of main biopolymers of the shells was estimated by Van Soest analysis. The elemental content [wt%, dry and ash-free basis] of the hulls was C: 49.6; H: 6.5; N: 1.8; O: 42.1. Moreover, the biopolymer composition [wt%, dry and ash-free basis] was the following: lignin: 30.9; cellulose: 54.6; hemicellulose: 14.5.

2.2. Natural zeolite and catalyst development

Natural clinoptilolite, shortened CL, provided by Minera CMA was employed. It was milled and sieved. The aforementioned particle sizes (44–74 μm and 250–500 μm) were employed.

An alkaline catalyst (Z1) was obtained by calcinating the clinoptilolite at 500 °C for 24 h. On the other hand, in order to obtain a protonated catalyst (Z2), the zeolite was submitted to ion exchange with NH_4Cl. This treatment was accomplished using 20 mL of a 0.5 M NH_4Cl solution per gram of clinoptilolite. The ion exchange was carried out in a beaker without agitation and at ambient temperature by 8 h. Afterwards the material was filtered and washed until absence of Cl^-, which was verified with a $AgNO_3$ solution. Finally, the material was calcinated for 24 h in order to decompose NH_4^+ into H^+ [25]. Before the catalytic experiments, the catalysts were activated heating the samples at 400 °C for 1 h.

2.3. Zeolite and catalyst characterization

The clinoptilolite and the catalysts phases were identified by means of X-ray diffraction (XRD) using a Siemens D5000 diffractometer with Cu Kα radiation (λ = 1.54056 Å). The scanning angle was in the range 5–60° of 2θ with a step size of 0.05° and a scanning speed of 2.0 s $step^{-1}$.

In addition, both the native zeolite and the catalysts were analyzed by scanning electronic microscopy (SEM) in a Zeiss Supra 40 coupled with an Oxford-Instrument energy dispersive X-ray (EDS) spectrophotometer. Prior to the analysis, the samples were placed on an aluminum holder, supported on conductive carbon tape, dried under vacuum, and sputter coated with Au-Pd.

pH of the samples was measured suspending 1 g of each one in 20 mL of distillated water and letting boil for about an hour. Then, the solution was cooled to room temperature and the pH value was assessed using a portable Orion 290A pH-meter.

Concentrations of Brønsted and Lewis acid sites were quantified by pyridine adsorption coupled to FT-IR spectroscopy. The concentration (C) was calculated as:

$$C = (A \cdot s_d)/(\varepsilon \cdot W_d) \quad (1)$$

The integrated absorbance (A) of peaks corresponding to Brønsted (1545 cm^{-1}) and Lewis (1445 cm^{-1}) sites was used. W_d and s_d represent, respectively, the weight and the area of the sample disk which was mounted on the spectrophotometer. The molar extinction coefficients (ε) measured by Emeis [26] were employed: 2.22 cm μmol^{-1} for Lewis sites, and 1.67 cm μmol^{-1} for Brønsted sites. The strength of the different acid sites was determined quantifying the adsorbed pyridine after desorption at different temperatures (100 °C, 200 °C, 300 °C, and 400 °C).

Moreover, N_2 adsorption isotherms of the materials at −196 °C were determined using an automatic Micromeritics ASAP-2020 HV volumetric sorption analyzer. Before the analysis, the samples were outgassed at 120 °C for 2 h. Textural properties were assessed from the isotherms, according to conventional procedures depicted in detail in previous studies [27]. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was determined by the standard BET procedure and total pore volumes (V_t) were estimated from the amount of nitrogen adsorbed at the relative pressure of 0.95 ($p/p_0 = 0.95$). Mean pore radius (R_m) was calculated as

$$R_m = 2\,V_t/S_{BET} \quad (2)$$

2.4. Thermogravimetric assays

Measurements of the pyrolysis behavior of the peanut shells, individually and in the presence of each catalyst (biomass to catalyst ratio of 2:1), were carried out in a simultaneous thermal analyzer (TG-DSC/DTA TA Instruments SDT Q600). The samples were thermally treated under a constant flow of N_2 (100 mL min^{-1}) from ambient temperature up to 500 °C. Experiments were performed for samples' masses of 10 mg, fractions of 44–74 μm particle diameter, and heating rate of 10 °C min^{-1}. For these conditions, negligible diffusional effects were thoroughly verified from preliminary experiments.

2.5. Conventional and in-situ catalytic pyrolysis assays

In order to obtain the pyrolysis products and determine their yields, pyrolysis experiments were carried out in a bench-scale fixed bed reactor (2.5 cm I.D., 110 cm total length) made of AISI 316 stainless steel (Fig. 1). Peanut shells, individually and mixed with each one of the catalysts (biomass to catalyst ratio of 2:1), were first placed at room temperature in a sample carrier located in a zone above the reactor, that