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A study of pyrolysis oil from soluble coffee ground using low temperature conversion (LTC) process

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ABSTRACT

The pyrolysis process using the low temperature conversion (LTC) conditions was applied in a sample of soluble coffee ground at 380 °C and produced four fractions: pyrolysis oil, pyrolytic char, gas and acidic fraction in relative amounts of 50, 29, 15 and 6% [w/w], respectively. The composition chemistry of the pyrolysis oil was studied by FTIR: ^{1}H and ^{13}C NMR and GC–MS. The density, viscosity, sulfur content, calorific value and water content of the pyrolysis oil were also determined.

1. Introduction

The pyrolysis process can be generally classified into three types: conventional, fast and flash, depending upon the operating conditions employed in the process, such as time, temperature and heating rate [1,2].

The thermochemical conversion, low temperature conversion or simply LTC, of biomass and sludge into char and fuel oil was originally developed and patented in Germany by Prof. Ernst Bayer [3]. Besides oil and char other products are produced, e.g., gas and water fraction to a lesser amount. Basically mimics the formation of fossil fuels in petroleum. Consists of heating the material, previously dry, to the temperature varying of 380–420 °C, in inert atmosphere, for a period of 2 h. The temperature used in the process is considered so low a time that the pyrolysis can occur in the band of temperature of 350–1000 °C.

The LTC process has been applied to diverse biomasses of urban, industrial and agricultural origins, in order to transform them into potential commercial products [4–14]. The first material used by the Bayer's group was the sludge from wastewater treatment plants trying to obtain a kind of fuel with similar properties to diesel. Because it is not fossil fuel, the process produces no greenhouse gases and provides an alternative for the disposal of biomass.

The oil fraction has potential as a fuel and in other applications including greases, lubricants, resins, and in fine chemistry. Another application that has been studied is the use of pyrolysis oil blended with biodiesel and diesel to optimize the properties of pyrolysis oil as fuel [15]. The solid fraction can also be used as a fuel, as well as in ceramics, components of building blocks, soil remediation, and with suitable activation as active char. The gaseous fraction can be also used as a fuel.

The LTC process involves only thermal decomposition not using solvents or chemical reagents. Other methods to produce alternative fuels are more sophisticated relatively to instruments required. The LTC process produces pyrolysis oil that is constituted of oxygenate compounds amongst others. These oxygenate compounds can increase the lubricity of the diesel oil like that observed in the case of fossil fuels (diesel) and methyl fatty ester (biodiesel), which are mixed.

The soluble coffee is a form of instant coffee with various manufacturing processes, which suffers dehydration and can be found in the form of powder or granules. These can be rehydrated using hot water. The benefits of the soluble coffee are the speed of preparation and the biggest conservation of the aroma and the flavor. The natural coffee under the dust form with the time loses its flavor ant its essential oil evaporates. These characteristics of coffee have made its use expanded in the global market.

In industrial production of soluble coffee solid waste known as "soluble coffee ground" is produced. According to NBR 10004 [16] they are classified as "Class II Waste – non-inert". In the industrial process, the coffee bean is generated from roasting and grinding. The soluble coffee ground has high concentration of organic substance and high content of acidity. Normally this residue is set free in the environment or used as combustible in boiler, in general, in the industry itself. One of the best applications of the soluble coffee ground is as a fuel with calorific value of 20.9 MJ/kg (dry)

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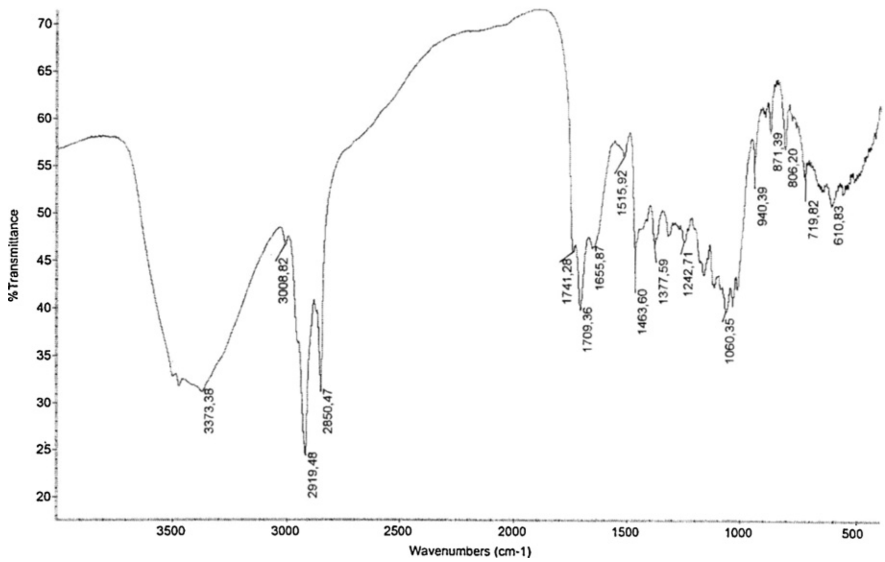

Fig. 1. Infrared spectroscopy (FTIR), CHCl3 film, of the soluble coffee grounds.

and 14.6 MJ/kg (wet) [17,18]. It is consequently necessary to dry the product previously. However, these methods of reuse of the soluble coffee ground are not environmentally and economically satisfactory. In the first case, the organic substance present in the residue, still unstable, needs to be degraded before being poured in the environment. And when used as fuel in boilers, what is observed is the generation of particles, with implications for air quality in the vicinity of the industry.

Brazil is the largest producer and exporter of the natural coffee and the soluble coffee in the world; therefore, it generates a large quantity of waste, which would be the most benefited.

2. Objective

This work aims to investigate the possibility of reuse the soluble coffee ground using the LTC process to generate products with fuel characteristic. The pyrolysis oil will be study relatively to their chemical composition and physical–chemical properties.

3. Methods

3.1. Low temperature conversion (LTC) process

A sample of the soluble coffee ground, light brown, mixed texture (between powder and granular), with a faint smell of coffee and with no apparent moisture content was maintained at 105 °C to constant weight.

The dry sample of the soluble coffee ground was subjected to a Low Temperature Conversion process at 380 °C. The experiments were repeated ten times, using 300 g of material each time, and results for the ten repeats were averaged. Each sample was placed in the central region of a cylindrical glass tube, which was then introduced to the reactor coupled with the condensing system. Nitrogen gas was continuously applied, at 500 mL/min, before the start and during the course of the process. After 10 min of gas purging, heating was initiated at a rate of 10 °C/min and the temperature was then maintained at 380 °C for 3 h. The condensable gas, pyrolysis oil and water fractions, after passing through the condenser are collected in a graduated tube and separated by different densities. The pyrolitic char is retained in the middle of the reactor and collected after cooling. The non-condensed gas is passed through three traps containing, successively, NaOH 10% (w/v), $NaHCO_3$ 10% (w/v) and HCl 10% (w/v) solutions, to retain compounds with acidic (strong and weak) and basic characteristics.

The parameters such as temperature, time of reaction and flows of nitrogen were pre-established prior to this work by Romeiro and coworkers [6–9], where these values were determined as the best due to the higher yield of oil, less time required for total conversion of raw material and smaller amount of energy spent.

The conversions were carried out in a Heraus R/O 100 batch scale instrument constituted by: (1) oven; (2) dried sample; (3) glass wool; (4) electric resistance; (5) gas N_2 inlet; (6) condenser; (7 and 8) separator funnel and (9) gas washing.

3.2. Analytical methods

The pyrolysis oil generated during the LTC process of soluble coffee ground at 380 °C was analyzed by gas chromatography/mass spectrometry (GC/MS). Conditions used in the GC part of the GC/MS set-up were: column: 25 m × 200 μm × 0,33 μm; heating: 10 °C/min from 80 °C to 260 °C, and subsequently at 260 °C for 20 min; carrier gas: helium at 0.6 mL/min; temperatures: detector 290 °C and injector 240 °C. ^1H NMR and ^{13}C NMR were recorded using a Varian-Unity Plus 300 spectrometer, in $CDCl_3$ solution with TMS as the internal standard. The FTIR spectra were obtained using a Perkin Elmer Spectrometer model 1420 in KBr discs for solids or films for liquids (polystyrene was used for calibration).

3.3. Physical–chemical analysis

The calorific value was determined according to ASTM D-1989 using a Leco-AC 350 model. The sulfur content was measured using a Leco®-SC 432 model by the ASTM D-4239 method. The viscosity was performed in the viscometer seybolt Petrotest model by the ABNT MB-293 method. The water content was measured using a 633 Karl Fischer by the ASTM D-1744 method.

4. Results and discussion

4.1. Studies of the soluble coffee ground before the LTC process

A preliminary assessment of the sample before the pyrolysis process provides important data to understand what happens during the thermo decomposition at 380 °C. Some water, ash and sulfur content and calorific value results were compared to