

A NEW WAY OF USING SPENT COFFEE GROUND

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Abstract

Coffee is a drink enjoyed by millions of people worldwide and progressively more studies are made to prove its benefits, this drink however has a high production of waste, the coffee grounds. The coffee grounds represent a biodegradable waste and with high richness chemistry that should be valued. The present study aims to contribute to the development of scientific knowledge on the chemical composition of spent coffee ground (SCG) and isolate the holocellulose from this by-product, to assess its potential for the production of cellulosic pulp or type I cellulose. Cellulose was isolated using Kürschner and Hoffer method and characterized by X-ray diffraction (with 66.1% of crystallinity) and ¹³C NMR CP/MAS. SCG holocellulose was prepared by two types of oxidative cooking: with alkaline hydrogen peroxide and with peracetic acid.

Key words: *Chemical composition, holocellulose, Liquefaction, spent coffee ground, 13C NMR, FTIR and XRD*

1. INTRODUCTION

The need for sustainable energy alternatives has been fuelled by the depletion of fossil fuel reserves, coupled with the increase of global energy demand and the environmental concerns raised by the prolonged and increased use of fossil fuels (Nigam & Singh 2011). The utilization of biomass to produce liquid biofuels has been interesting the scientific and economic communities due to its renewability, abundance and lack of carbon impact (Peterson et al. 2008). The most viable options for the production of liquid biofuels are by using edible crops – corn or sugarcane in the case of bioethanol, and vegetable oils in the case of biodiesel – and that causes negative impacts on food supplies [2,3] (Peterson et al. 2008; Minowa, Kondo & Sudirjo 1998). As such, research efforts have shifted towards the use of biological matter such as animal manure, agricultural or forest-based residues, food processing and municipal waste in the production of liquid biofuels (Appell et al. 1972; Teri, Luo & Savage 2014; Panisko et al. 2015; Wang, Huang & Zhang 2014; Azadi & Farnood 2011; Luo, Fang & Smith 2014; Theegala & Midgett 2012). By taking advantage of waste streams in the production of biofuel, local pollution is reduced, greenhouse gas emissions are decreased and less waste is stored on landfills.

America, Japan and Europe are some of the worlds' large consumers of coffee (Mussatto, Machado, et al. 2011; Kondamudi, Mohapatra & Misra 2008). The global coffee production has increased by 6% since 2010 and in 2014, 142 million bags of coffee were produced, with a total of 9.6 million tonnes (ICO 2016). With the increase of coffee brewing, the amount of spent coffee grounds, hereinafter referred to as SCG, has increased accordingly. These biomass residues are massively underutilized, even though they are produced in increasingly larger quantities, with most of the residues being dumped in landfills or being used, albeit to a very small extent, in composting (Liu & Price 2011; Valipour 2015a, 2015b). And even these uses have been found to be adverse to the environment, with complex organic substances such as caffeine, tannins and polyphenols found in the coffee residue having a negative impact on the land it is disposed on (Mussatto, Machado, et al. 2011; Valipour et al. 2015). Other methods of non-wasteful disposal have also been researched but without success, due to the hazardous gases the combustion of coffee logs or pellets generates, especially high nitrogen oxidants, in comparison to the combustion of wood pellets (Valipour 2015a, 2015b). This invalidates the direct use of SCG as a solid fuel, but new interests have recently arisen concerning the use of SCG for the production of liquid biofuel, a field in which they are also ineffective due to their low average oil content ranging from 10 to 15% mass fraction. This makes it necessary to use a solvent in the

extraction of the useable matter so the option is economically unviable. This has been researched by Kondamudi *et al* (Kondamudi, Mohapatra & Misra 2008), who have extracted coffee oil from SCG for biodiesel production. Mussato *et al.* (Valipour *et al.* 2015) also researched the production of bioethanol from SCG, but the ethanol production yield was low at 26% mass fraction while fermenting the SCG through three different yeasts. A fast pyrolysis process has been used by other researchers (Romeiro *et al.* 2012; Bok *et al.* 2012; Li, Strezov & Kan 2014) with promising results, with the coffee oil yield being as high as 54.9% mass fraction, but the high energy consumption costs of pre-drying the fairly high moisture SCG make it so the solution isn't economically viable. Furthermore, the oil produced with this process of pyrolysis isn't of a satisfactory quality, with relatively high oxygen of about 35.2 to 59.5% mass fraction resulting in lower HHVs, in a range from 17 MJ kg⁻¹ to 23 MJ kg⁻¹, the results being altered by the composition of feedstock and the conditions of the pyrolysis process. As such, the research of other approaches of utilizing the SCG waste in an efficient and economical way is essential. However SCG represents a biodegradable residue with high chemistry richness that should be valued.

The present study aims to contribute to the development of scientific knowledge on the chemical composition of the general chemical composition of some SCG and isolate the holocellulose of this by-product, to assess their potential for the production of cellulosic folders and as a cellulose native (type I cellulose).

2. MATERIAL AND METHODS

2.1. Sample Preparation

Testing was done on SCG. The sampling was divided into three fractions, being grounded and sieved previously, fractions composed of > 40 Mesh (> 0.425 mm), from 40 to 60 Mesh (0.425 to 0.250 mm) and 60-80 Mesh (0.250 - 0.180 mm) and < 80 Mesh (< 0.180 mm). All the fractions had been dried previously in an oven at 100°C for at least 24 hours before testing.

2.2. Chemical Composition Determination

The results of the testing determined the SCG ash content, extractives while used with ethanol, dichloromethane or hot water, tannins, cellulose, proteins, hemicellulose and lignin. By calcinating the material at 525°C according to the standard procedure Tappi T 211 om-93 (TAPPI, 2012), the ashes content was determined. After wet digestion, metal cations were analysed by ICP, with the analysis being made on a Leco CHNS-932 Elemental Analyzer.

For the determination of the extractive content in ethanol and dichloromethane, Soxhlet extraction was used according to standard Tappi T 204 om-88 (TAPPI, 1996). A solution of ammonium citrate (10g/L) was used in conjunction with hot water to determine its extractives by carrying out the tests for 1 hour under reflux (in a liquid to solid ratio of 100).

In extractives-free spent coffee grounds, the protein content was determined by treatment with 1% pepsin solution in 0.1 M HCl at 37°C for 16 hours, after extraction with acetone.

The tannin analysis was conducted with extractive- and protein-free stalks by the reflux, with 0.3% NaOH solution (with a liquid to solid ratio of 100) under a nitrogen atmosphere, for 1 hour. After extraction, the material was filtered off and washed under hot water with a neutral reaction of filtrate, and lately dried at 60°C to a constant weight. The tannin content was assessed by comparing the weight difference of starting and extracted materials. Precipitation of the alkaline extract was done by adding 3M H₂SO₄ until the pH measure was at 3. Precipitated tannins were centrifuged and washed with water after 24 hours, until they reached pH 5. The tannin fraction was then freeze dried.

The cellulose materials were determined by 4 consecutive treatments of spent coffee grounds. Treatments consisted of a HNO₃:EtOH mixture (1:4 ratio, v/v) under reflux for 1h each, according to the Kürschner and Höffer method (Browning, 1967).

Lignin content in extractive-, protein- and tannin-free spent coffee grounds was determined after extraction with acetone, by treatment with 1% pepsin solution in 0.1 M HCl at 37°C for 16 hours.

All determinations were carried out in triplicate. The 40 mesh fraction was used for these tests.

2.3. X-ray analysis of cellulose

The cellulose isolated by the Kürschner and Höffer method was analyzed by X-ray scattering on a Philips X'Pert MPD diffractometer using Cu-K α source ($\lambda = 0.154$ nm) in the 2θ range 2-40° and scanning step width of 0.02°/scan. Cellulose was analysed as textured sample and the degree of crystallinity was corrected for the presence of non-cellulosic polysaccharides based on sugars analysis (Figueiredo, Evtuguin & Saraiva 2010).

2.4. Holocellulose

To obtain SCG holocellulose two types of oxidative treatment were performed, baking with alkaline hydrogen peroxide (AHP) and with peracetic acid (PA). The essays were conducted in a 250 mL erlenmeyer flask with temperature-controlled and equipped with a mechanical stirrer adding 5 grams of SCG into the erlenmeyer flask, adding 50 mL of AHP during 90 minutes. The second essays were made in a 250 mL erlenmeyer flask with temperature and magnetic stirring, adding 10 grams of coffee grounds to 50 mL of PA. The tests were carried out under the following conditions: PA concentration of 11.69%, reaction time of 90 minutes, the temperature of 80° C and at a pH of 4. After treatment with PA, the resulting materials were filtered and washed with water distilled water and acetone until the pH neutral.

2.5. FTIR and ¹³C CP/MAS NMR analyses

¹³C CP/MAS NMR spectra were registered on a Bruker Avance 400 spectrometer (magnetic field of 9.4 T). Samples were spun in a zirconia's rotor at 7 kHz. The acquisition parameters were as follows: proton pulse of 4 μ s (90°), contact time of 2 ms, recovery delay of 4 s and 7000 scans were accumulated. The FTIR spectra were obtained on a Mattson FT-IR spectrometer Model 7300 using KBr pellets at 4 cm⁻¹ resolution and acquiring 128 scans per set.

3. RESULTS

3.1. Chemical Composition Determination

Aiming a better understanding of the results, the general chemical composition of the SCG has been done. Table 1 presents the SCG chemical composition. This sample presents 55% of moisture. The chemical characterization showed that SCG is a lignocellulose material in which tannins are the major component (with around 30.4 %), followed by hemicelluloses (with around 28.4%) and cellulose (with around 10.8 %). It's important to highlight the high presence of extractives in dichloromethane and in water (with around 6.6%).

The ash percentage 1.8% obtained in this work is similar to the presented by Mussatto (Mussatto, Carneiro, et al. 2011) (1.6%) as well as the celluloses 10.8% comparing to 8.6% obtained by Mussatto (Mussatto, Carneiro, et al. 2011). The lack of information in relation to other analyses performed, proteins, tannins, etc, doesn't allow a better comparison.

Table 1. Chemical Composition of SCG (% dry material).

Parameters	Content (%)	
Ashes	1.80	
Extractives	Ethanol	0.95
	Dichloromethane	6.68
	Water-soluble	6.64
Proteins	9.28	
Tannins	30.36	
Lignin <i>Klason</i> ^c	10.72	
Cellulose <i>Kürscher - Höffer</i>	10.78	
Hemicelluloses	28.36	

^a Corrected for the extractive content and ash,

^b Corrected for the extractive content, ash, proteins.

^c Corrected for the extractive content, ash, proteins and tannins

3.2. Cellulose

Cellulose, one of the most abundant polymers, was isolated by the method *Kürscher* and *Höffer* and characterized by X-ray diffraction for knowledge of their crystalline structure, Figure 1.

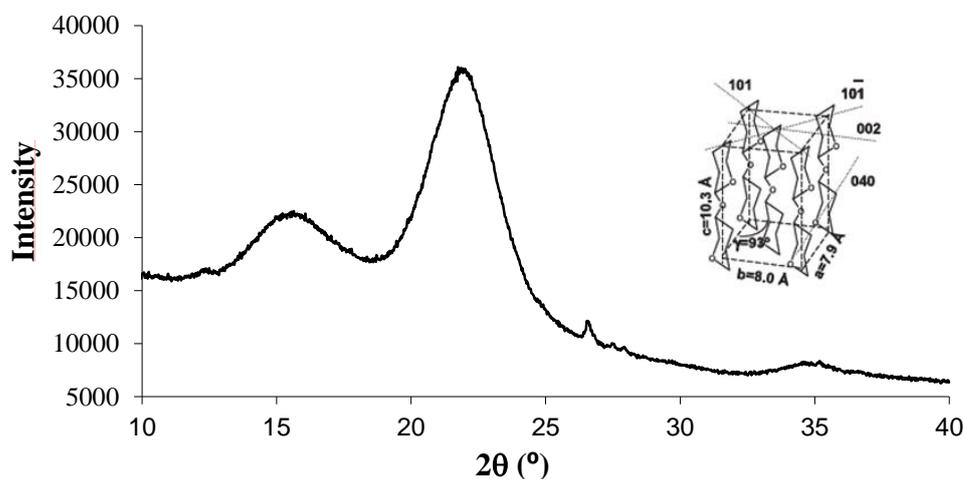


Figure 1. X-ray diffractogram of cellulose isolated by the *Kürscher* and *Höffer* method.

The diffractogram showed it is cellulose I (native cellulose) with high degree of crystallinity, 66.1%. This presents values higher than those obtained from wood.

3.3. Holocellulose

The holocellulose (constituted mostly by cellulose and hemicelluloses) obtained from the SCG when subjected to oxidative treatment with PA reveals a 72% yield. The SCG and holocellulose samples were characterized by FTIR (Figure 2) and ^{13}C NMR CP/MAS (Figure 3).

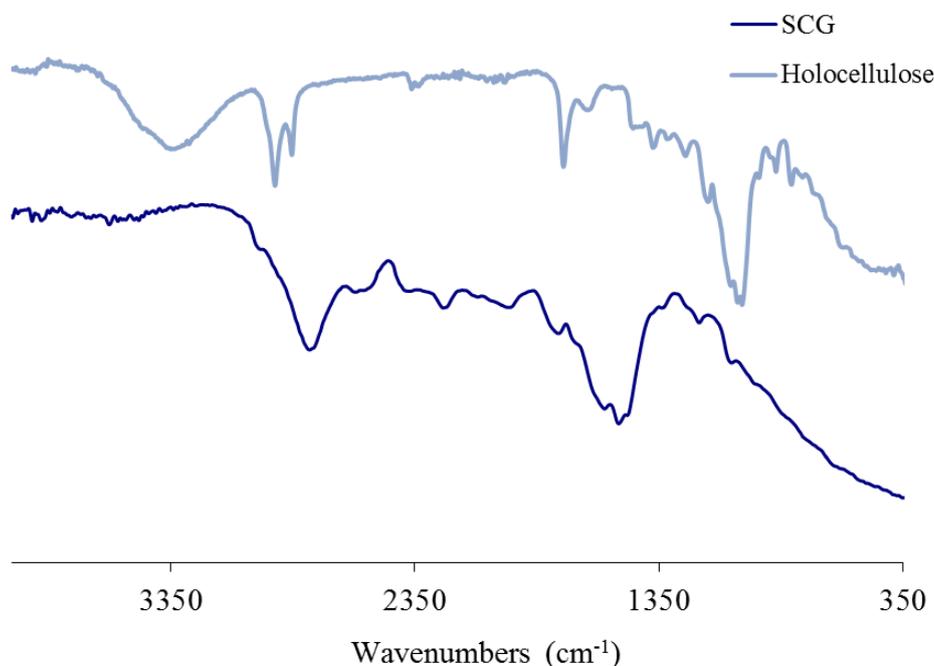


Figure 2. FTIR spectrum of SCG and holocellulose.

The FTIR spectrum obtained for the SCG revealed a band at about 2760 and 2582 cm^{-1} suggest the presence of the C-H stretch vibrations present in lignin, cellulose and hemicellulose. The presence of polysaccharides, including hemicelluloses, is confirmed by the peak at 1742 cm^{-1} , which is assigned to C = O elongation in esters (Hernes & Hedges 2004; Pandey & Pitman 2004). The peak at about 1473 cm^{-1} corresponds to the elongation of the C = C bonds and can be attributed to aromatic compounds, possibly lignin or tannins and the peak about 1197 cm^{-1} is assigned to C-O groups which are present in lignin and polysaccharides. The holocellulose spectrum shows a broad band at about 3344 cm^{-1} that includes many vibration modes mainly attributed to OH groups with a minor contribution of NH functional groups (Kante et al. 2012). The presence of methyl and methylene groups is confirmed by the two sharp peaks at 2920 cm^{-1} and 2855 cm^{-1} attributed to asymmetric and symmetric stretching of CH bonds in aliphatic chains. These peaks have been previously identified in roasted coffee and attributed to the presence of caffeine (Craig, Franca & Oliveira 2012). However, these peaks can likely be attributed to lipids which are present in the coffee samples in a large amount. The sharp band at 1746 cm^{-1} is associated to the carbonyl vibration C=O in aliphatic esters (Lyman et al. 2003) or in triglycerides (Kemsley, Ruault & Wilson 1995). Therefore, this band can be attributed to lipids. The low intensity band at 1636 cm^{-1} and 1545 cm^{-1} are due to C=C vibration of lipids and fatty acids and C=C vibration of aromatic rings from lignin moieties, respectively (Wang & Lim 2012). The band at 1452 cm^{-1} represents the symmetric deformation of C-H on cellulose and hemicelluloses; the band at 1302 cm^{-1} assigned to the C = O elongation in esters, possibly in xylenes; and the typical band 834 cm^{-1} attributed to deformation C-H in cellulose. The FTIR spectrum in the holocellulose materials reveals than, typical lignin bands (1473 and 1182 cm^{-1}) are not present, which indicates that the PA treatment is effectively used to remove lignin.

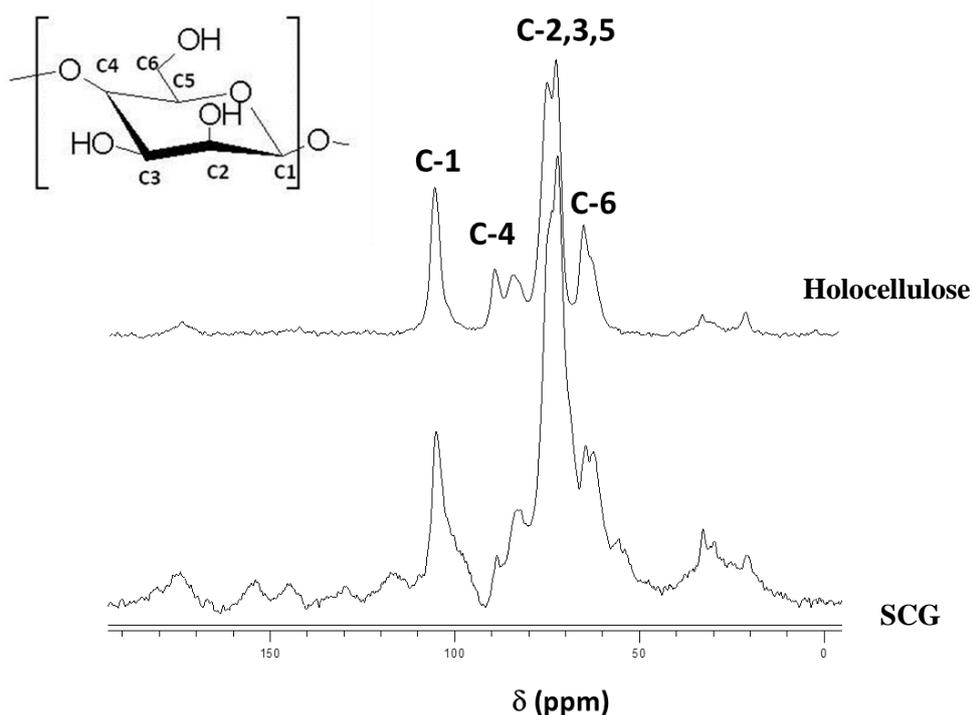


Figure 3. ^{13}C CP/MAS NMR of SCG and holocellulose.

The analysis of the spectrum reveals that the signals between 62-64 ppm correspond to C-6 of cellulose and hexosans and to C-5 of xylans, while resonances between 70-80 ppm are attributed to C-2,3,5 of cellulose, hexosans and C-2,3,4 to xylans. The C-4 of cellulose can be observed between 84 and 90 ppm, and the C-1 of cellulose and xylans between 101-104 ppm (Farinella, Matos & Arruda 2007; Oliveira et al. 2007; Atalla & VanderHart 1999). The peaks at about 174 ppm, 21 ppm are related with acetyl group resonances of hemicelluloses (Farinella, Matos & Arruda 2007). Methoxyl groups (OCH_3) of structural lignin units give a signal about 56 ppm. The region between 100 and 125 ppm is characteristic of tertiary carbons. On the other hand, the non-oxygenated quaternary carbons of lignin give signals between 126-136 ppm, whereas the oxygenated carbons of lignin cause signals between 136 and 156 ppm (Farinella, Matos & Arruda 2007; Oliveira et al. 2007). The analysis of the spectrum from holocellulose baking with AP is essentially composed of cellulose and xylans. This ^{13}C CP/MAS NMR spectrum also consolidates the conclusions obtained by the FTIR spectrum, in that no typical lignin signals are observed, allowing us to conclude that cooking with AP is effective.

4. CONCLUSIONS

The chemical composition shows that SCG is a lignocellulose material in which tannins are the major component (with around 30.4 %), followed by hemicelluloses (with around 28.4%) and cellulose (with around 10.8 %). The cellulose obtained is cellulose I (native cellulose) with high degree of crystallinity, 66.1%. In oxidative treatment of SCG, just with the AP treatment the results were satisfactory, i.e. obtaining a holocellulose with a yield of 72%. The ^{13}C CP/MAS NMR and FTIR spectra allowing us to conclude that holocellulose is mainly composed by cellulose and xylans.

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