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Density and rheology of acid suspensions of peanut waste in different conditions: An engineering basis for bioethanol production

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ABSTRACT

The current world-wide energetic situation implies in researches about new resources and technologies capable of producing biofuels, such as the peanut processing residues. To design operations associated to bioethanol processing, understanding material properties, as density and rheology, is necessary. In this study, peanut shells were firstly chemically characterized, showing 37.1% cellulose, 33.4% hemicellulose and 15.0% lignin. Aqueous acid suspensions of powdered peanut shell were prepared and their physical properties were determined. Rheological parameters and density could be correlated with solid content and temperature by exponential and quadratic equations, respectively, while pH did not present significant effect on these parameters. Dilute suspensions showed Newtonian behavior, but at concentration above 8% (*w*/w) of solids, a non-Newtonian behavior was observed, showing yield stress and shear thinning. By evaluating the relative viscosity behavior with increasing solids concentration, Farris effect was also evidenced in suspensions above 8% of solids due to the presence of fine particles. Such result indicates the possibility of processing peanut shells for biofuel production in solids concentration higher than 10%, without a significant influence on viscosity.

1. Introduction

Nowadays, with the high exploitation of fossil fuels, one of the biggest environmental worries is the fuel supply [1]. It has influenced many studies to bring new technologies and renewable sources to produce energy, mainly from lignocellulosic materials. Biomass is the more suitable and available source able to produce biofuels, as bioethanol and biodiesel in a short time [2,3].

Agro-industrial residues, wood and some urban residues are the examples of biomass, with a dry matter composed of cellulose, hemicellulose and lignin. Agro-industrial wastes are an interesting biomass source due to its low cost and abundance in agriculture producing countries as Brazil [4].

Currently in Brazil, peanut processing can generate more than 90 thousand tons of waste, considering the average shell/grain ratio of 30% [5] and an annual production, of around 320,000 tons in 2014 [6]. Thus, its polymeric composition of fermentable material is attractive to develop new treatments and processes. The peanut shells, currently used as fertilizers and fodder in poultry farms, could be used as raw material in bioethanol conversion/preparation processing after physical, chemical, biological or even combined pretreatments.

The major step of bioethanol production consists into the breakdown of hemicellulose and the crystalline structure from the cellulose for sugars release, which will be fermented into ethanol and later distilled. All these steps generally occur in stirred bioreactors using acid medium [7–9].

A correct understanding of the material properties, as density and rheology, is necessary to design cost-effective treatment processes [10] during fermentation and handling agro-industrial residues. Rheology is also used to understand the product's structural behavior [11], besides its importance on designing pipes and process equipment.

Rheological/structural behavior depends on a number of factors, including chemical composition, particle size and shape, surface effects and/or additives presence. These factors are generally heterogeneous in biomass suspensions, once particles vary in terms of composition, size and shape [12]. The flow characteristics of suspensions can be defined both by the continuous or dispersed phase, and even by the influence of one in another [13]. Considering that the combination of these facts makes unique the properties of each suspension, the need of published physical properties data of such systems is emphasized.

So, this study intended to characterize and evaluate the rheological behavior and density of acid suspensions of peanut shell powder in different conditions of biomass concentration, temperature and pH.

2. Materials and methods

2.1. Peanut shell preparation

Cleaned and dried peanut (*Arachis hypogaea* L.) shells were obtained from Agro-industrial Cooperative — COPLANA (Jaboticabal, São Paulo,

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Brazil). Using a knife mill MA380 (Marconi, Piracicaba, Brazil), the shells were milled and separated by Tyler sieves (mesh 12 and 24) to obtain a particle size distribution between 1397 and 701 μm.

2.2. Chemical characterization

Analysis of moisture, dry matter, cellulose, hemicelullose, lignin and total sugars were done aiming the characterization of the peanut shell. Moisture and dry matter were determined by a vacuum oven, according to AOAC 926.12 method [14].

Cellulose, hemicellulose and lignin content were determined using a method on reflux extraction with neutral detergent or acid detergent solutions for 90 min [15,16]. Filtrate was washed with hot distilled water and ethanol, then oven-dried until constant weight. The percentage of each washing represents the neutral detergent fibers (NDF) and acid detergent fibers (ADF). To determinate the lignin amount, sulfuric acid (72% *w*/w) was added to the samples under magnetic stirring at 20 °C every hour, during 3 h. After washing with hot distilled water until a sulfuric acid concentration of 3% (*w*/w), the filtration residue (lignin) was dried and weighed. The difference between NDF and ADF indicates the hemicellulose content, and subtracting the lignin percentage from ADF results in the cellulose content.

Total sugars content was determined from the acid hydrolyzed samples of NDF and ADF, by high-performance liquid chromatography (HPLC) according to the AOAC 982.14 method [14]. Hydrolyzed sample was centrifuged at 1850 × *g* for 2 min at 20 °C. After removing the supernatant, sugars were extracted into 50% ethanol, passed through a Sep-Pak® C18 cartridge (Waters Associates, Milford, MA, USA) and then filtered through a 0.45 mm nylon disk. Separation and quantification were carried out on a μbondapak-NH_2 column (30 cm × 3.9 mm i.d., Waters, Milford, MA, USA) and a refractive index (IR) detector, using CH_3CN and H_2O (80:20 v:v) as mobile phase. Concentrations were calculated based on prepared external standards.

2.3. Zeta (ζ) potential

The zeta (ζ) potential of the suspensions of powdered peanut shells was determined using a Zetasizer Nano ZS equipment (Malvern Instruments, Worcestershire, UK). Suspensions containing 0.01% (*w*/w) of powdered peanut shells were previously prepared at different pH (3.0, 4.0, 5.0, 6.0 and 7.0) using 0.05% (*w*/w) H_2SO_4 solutions. Each sample was transferred to the cuvettes for zeta potential measurements, which were done in triplicate.

2.4. Particles size distribution

Particle size distribution of the peanut powder, separated by Tyler sieves mesh 12 and 24, was evaluated by laser diffraction (LD) using a Mastersizer S model MAM 5005 (Malvern Instruments Ltd., UK), with distilled water as dispersing medium. Each sample was evaluated in 6 replicates. Diameter of samples was represented as the volume weighted mean diameter ($D_{4,3}$), defined by Eq. (1) and surface weighted mean diameter ($D_{3,2}$), defined by Eq. (2). Polydispersity was evaluated according to span value, given in Eq. (3).

$$D_{4,3} = \frac{\sum n_i \cdot d_i^4}{\sum n_i \cdot d_i^3} \tag{1}$$

$$D_{3,2} = \frac{\sum n_i \cdot d_i^3}{\sum n_i \cdot d_i^2} \tag{2}$$

$$\text{span} = \frac{D_{9,0} - D_{1,0}}{D_{5,0}} \tag{3}$$

where, n_i is the number of particles with d_i diameter, $D_{1,0}$, $D_{5,0}$ and $D_{9,0}$ are diameters at 10%, 50% and 90% cumulative volume, respectively.

2.5. Optical microscopy (OM)

Particle morphology was analyzed through optical microscopy (OM). Using microscope slides and glass cover slips, particles were observed at 10, 40 and 100× magnification using a Carl Zeiss Model Axio Scope A.1 (Zeiss, Germany). Images were also evaluated using the public domain software Image J v1.36b. The pixel-scale values were converted into microns by a scaling factor and the group of particles present in the captured images were measured. The length (L) and the width (w) were the dimensions determined for the fibers, and the aspect ratio (a_r) was calculated by $a_r = L/w$.

2.6. Rheological measurements

Suspensions were prepared with different solids content: 0, 2; 4; 6; 8; 10 and 12% (*w*/w) using an analytical balance (model AUX220, Shimadzu, Japan). Solutions with varying pH (3.0; 4.0; 5.0; 6.0 and 7.0) were used for dispersing the suspensions. These solutions were prepared and stabilized for 3 days with distilled water and diluted sulfuric acid (H_2SO_4) at 0.05%. The suspensions were prepared and insert immediately into the equipment.

Rheological measurements were done in a AR-G2 rheometer (TA Instruments, USA) with SPC (Starch Pasting Cell) geometry to avoid the particles sedimentation. Samples of approximately 28 cm^3 were required in each run and shear rate ramps were set from 0 to 260.5 s^{-1} in steady flow. Sample temperature (1, 10, 20, 30, 40, 50 and 60 °C) was controlled by the equipment bath. Shear stress data were extracted by data acquisition system Universal Analysis 2000 version 4.7 (TA Instruments, USA).

Chlorobenzene was the standard substance in calibration. The measurements in Table 1 did not present significant difference ($p_{value} > 0.050$) with the ones published in literature [17], indicating that the equipment is properly calibrated.

2.7. Density analysis

Density (ρ, kg/m^3) was determined for the same suspensions used in rheological determination. Analyses were carried out in a volumetric standard picnometer DIN ISSO 3507 (Brand, Wertheim, Germany), equipped with a lid and a graduated thermometer with sensibility of 0.1 °C. Sample temperature was changed and stabilized using a thermostatic bath MA-159 (Marconi, São Paulo, Brazil). For each measurement, the picnometer was calibrated with distilled water according to the procedures described in ASTM-D1480 [18].

Experimental measurements were done in triplicate, using a 50 mL picnometer and an analytical balance with 0.0001 g of precision (model AUX220, Shimadzu, Japan).

2.8. Data modeling

Rheograms were plotted, obtaining shear stress as function of shear rate. Rheological behavior was evaluated using flow models with 1 to 3 parameters (Eqs. (4)–(7b)) and their adjusted correlation coefficient (R^2). Newton (1 parameter), Bingham and Power Law (2 parameters) and Herschel–Bulkley model (3 parameters) are represented by Eqs. (4)–(7b), respectively. Whereas τ (Pa) is shear stress (Pa), $\dot{\gamma}$(1/s) is shear rate, k (Pa.s^n) is the consistency coefficient, n (dimensionless) is the flow behavior index, τ_0 (Pa) is the initial yield stress to start the flow, μ (Pa.s) is Newtonian viscosity, η_B (Pa.s) is plastic viscosity and η_{app} (Pa.s) is apparent viscosity at a fixed shear rate [11,19].

$$\tau = \mu\dot{\gamma} \tag{4}$$