Industrial Crops and Products 97 (2017) 252–259

Contents lists available at ScienceDirect

Industrial Crops and Products

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

# Formosolv fractionation of hemp hurds

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ARTICLE INFO

*Article history:*
Received 25 July 2016
Received in revised form
12 December 2016
Accepted 18 December 2016

*Keywords:*
Hemp
Formic acid
Fractionation
Organosolv
Deformylation

ABSTRACT

Effects of the main variables of the Formosolv fractionation of hemp hurds (formic acid and hydrochloric acid concentrations and treatment time) on delignification and hemicellulose solubilisation were quantified. The conditions that provided a pulp with low lignin content and high cellulose content, while recovering the maximum possible amount of lignin by precipitation, are 30 min of treatment time, 86.6%w formic acid, and 0.095%w hydrochloric acid. Under these conditions, 93.2% hemicellulose removal and 72.1% delignification were achieved. The residual solid from the Formosolv treatment contained a high proportion of formate groups (8.7%w). Four total chlorine-free treatments were used to eliminate the formate groups. Only alkaline treatments (oxygen and sodium hydroxide) completely removed the formate groups. However, the ozone treatment produced a solid with the highest delignification rate (34.7%, 80.1% global) and crystalline index.

## 1. Introduction

Use of lignocellulosic materials (LCMs) for the production of energy and new materials through environmentally friendly processes is a field of growing interest. A wide variety of processes and techniques can be used to obtain chemicals, materials, fuels, electricity, and heat from biomass. Chemical methods have proven to be useful tools for this purpose. Thus, by chemical reactions, separation of the major components of the plant tissues (i.e. cellulose, hemicelluloses, and lignin) can be achieved. This is called fractionation. Fractionation can be performed in several ways, but the overall idea is to arrange the methods by increasing the severity of the chemical attack to sequentially extract the main components from the solid matrix. By increasing the severity of these attacks in a controlled manner, it is possible to preserve part of the chemical characteristics of the components that are to be separated. This fractionation method involves processes of delignification and hydrolysis of hemicelluloses, which must be placed at a suitable stage of the overall process (Behera et al., 2014). Several processes (including organosolv procedures (Zhang et al., 2016)) are able to 'clean' the pulp by two simultaneous mechanisms: delignification and solubilisation of the hemicelluloses.

Organosolv methods are used for the treatment of lignocellulosic materials (Zhang et al., 2016; Dussan et al., 2015; Gandolfi et al., 2014; Li et al., 2012; Villaverde et al., 2010; Zhao et al., 2009; Li et al., 2016). Formic acid (FA) is among the most active agents used in organosolv delignification because of its proven ability to delignify a variety of LCMs, acting simultaneously as an acid and as a solvent for lignin. In aqueous mixtures, it can act alone or with small additions of a mineral acid, typically hydrochloric acid (HA) (Li et al., 2012; Villaverde et al., 2010). When a small amount of mineral acid is added, the system can achieve a high lignin solubilisation at atmospheric pressure. Mixtures of FA, water, and HA at its normal boiling point can result in fractionation of LCM, yielding pulps with very few non-glucose sugars and remarkable degrees of delignification (Myint et al., 2013; Dussan et al., 2015; Li et al., 2012; Villaverde et al., 2010).

Industrial hemp (*Cannabis sativa* (L.)) is used worldwide as a source of fibre and oil to produce a wide range of products. Many schemes were proposed for the use of this natural resource (Sen and Jagannatha Reddy, 2011; Barberà et al., 2011). Hurd is the name given to the internal fraction (core) of the hemp stalks that remains after separating the bast fibres (which consist of shorter and narrower fibres that are of no use in the textile industry but are used as animal bedding, for mulching, in specialty papers, and as biocomposites) (Carus and Sarmento, 2016).

Our objective was the Formosolv fractionation of hemp hurds to obtain delignified cellulose pulps with the lowest possible content of non-glucose sugars and to provide a mathematical description of the effects of process variables on several parameters affecting delignification and hydrolysis of the hemicelluloses. Furthermore, Formosolv pulps show a significant degree of formylation, which is

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http://dx.doi.org/10.1016/j.indcrop.2016.12.021

undesirable in many of the subsequent operations; therefore, we also investigated which stages of total chlorine-free (TCF) bleaching are the best to remove formate groups from the pulps and continue the delignification process.

## 2. Materials and methods

### 2.1. Raw materials

The LEPAMAP research group at the University of Girona (Spain) supplied the hemp hurds. The material had the appearance of small chip-like particles of varying sizes (no larger than 2 cm along the largest dimension). A mill equipped with a cutting-grinding head (IKA MF 10.1) and a 2-mm sieve at the outlet was used for milling the hurds. The milled material was dried in air until moisture equilibration (9.2%) before use in the experiments.

### 2.2. Analytical methods

Analysis of the raw material was performed using standard procedures. TAPPI (Technical Association of the Pulp and Paper): T222 for acid insoluble lignin, T211 for ash, and T204 for extractives. Other standard procedures were also used to characterize the pulps: T236 for the kappa number and UNE 57039-1:1992 for determining the limiting viscosity number in the cupriethylenediamide solution.

Quantitative hydrolysis was performed on the pulps to determine the monosaccharide, and acetic acid content using high performance liquid chromatography (HPLC). A two-step sulphuric acid method was used: 72% sulphuric acid at 15 °C for 2 h, then lowering the acid concentration to 4% and autoclaving at 120 °C for 1 h.

Monosaccharide, FA, formic and acetic acid determinations were performed using a Waters HPLC Breeze 2 system equipped with a Waters 2414 refractive index detector (at 30 °C) and a Waters 2489 UV/Visible detector. The column was a BioRad Aminex HPX-87H operating at 60 °C and eluted at 0.6 mL/min with 0.004 M $H_2SO_4$.

To precipitate lignin, the cooking liquors were diluted with water in a volumetric ratio of 1:10 (Ligero et al., 2008). The precipitated lignin was washed with water until pH was neutral and then lyophilized for gravimetric determination of the yield. Moreover, the liquor was analysed by HPLC before and after the post-hydrolysis (30 min, 120 °C, 3% $H_2SO_4$) to determine the amount of oligosaccharides present (obtained after subtracting the content of each individual sugar before and after treatment).

### 2.3. Formosolv treatment

Mixtures of hemp hurds, water, and FA were heated to the boiling point in Pyrex flasks. HA was added when boiling started, and this time (t) was noted as t = 0. The mixtures were refluxed with stirring at atmospheric pressure for different times. At the end of the reaction, the flasks were removed from the heat and rapidly vacuum filtered. Pulp washings were performed with FA aqueous solutions at room temperature as follows: two washings with 98% FA and two washings with 80% FA. Finally, the pulps were washed with water until the pH of the filtrates were neutral.

### 2.4. Deformylation of formosolv pulps

The peracetic acid stage (Pa-stage) was performed by soaking the pulps in commercial peracetic acid (AppliChem, 15% w/w) according to the consistency indicated for each experiment (Table 5), placed in polyethylene zip bags, and submerged in a water bath at the desired temperature. Each batch was kneaded at approximately 5 min intervals. The pulps were filtered under vacuum, washed with 15% peracetic acid, and finally washed with water until the pH of the filtrate was neutral.

For the alkaline stage (E-stage), the same methodology was followed as for the Pa-stage using the appropriate volume of NaOH solution instead of peracetic acid. The pulps were filtered and washed with 4% NaOH and water until the pH of the filtrate was neutral.

The pressurized oxygen stage (O-stage) was performed in a PARR reactor (4560 series) equipped with a paddle stirrer and temperature controller (4842 series). The pulps were soaked with the appropriate volume of 4% NaOH and the amount of water required for the predetermined consistency; they were then introduced into the reactor vessel. The reactor was purged with a stream of oxygen, and the oxygen pressure was set to reach 4 bar at the desired reaction temperature. At the end of the reaction, after releasing the pressure, the pulps were filtered, washed with 4% NaOH, and washed with water until filtrate was neutral.

The ozone stage (Z-stage) was performed in a system comprising an ozone generator (ECOLAB 5000), a rotameter, and three parallel lines (one line leads to the reaction vessel and a 1 M potassium iodide solution trap to determine the amount of unconsumed ozone, one line determines the ozone produced by the generator (with the same 1 M KI trap), and one line vents and equilibrates the system before the reaction). All of the pulps were soaked before ozonation with a mixture of acetic acid-water (volumetric ratio of 4:1). Following ozonation, the pulps were filtered and washed twice with the same mixture used for soaking and then with water until the pH of filtrate was neutral.

### 2.5. FTIR spectroscopy

FTIR spectra were obtained using a PerkinElmer Spectrum 2000 spectrophotometer with the attenuated total reflectance (ATR) technique. Spectra were recorded in the 4000–600 $cm^{-1}$ range with 16 scans at a resolution of 4.0 $cm^{-1}$ and an interval of 1.0 $cm^{-1}$. The FTIR spectra were normalized with respect to area and baseline corrected before any calculations were performed.

### 2.6. X-ray diffractometry

X-ray diffraction (XRD) measurements were performed on the pulp samples with a Siemens D5000 diffractometer equipped with a Cu target X-ray tube ($K\alpha = 1.5406$ Å) and a diffracted beam monochromator (graphite). The X-rays were generated by supplying a 40 kV and 30 mA current to the anode. The measurements were performed as a continuous scan from 5° to 40° (2θ), with a step size of 0.020° (2θ) and 5.0 s per step.

Deconvolution of the X-ray diffractograms was performed by nonlinear curve fitting using the MagicPlotStudent software (Ibbett et al., 2008). Gaussian distributions were used to simulate the full diffractogram. In principle, each of these functions were fixed in the following positions: $2\theta = 14.8°$ for {1,0,1}, $2\theta = 16.8°$ for {1.0,–1}, $2\theta = 20.5°$ for {0,2,1}, $2\theta = 22.6°$ for {0,0,2}, $2\theta = 34.8°$ for {0,4,0}, and a final broad peak accounting for the non-crystalline contribution centred at $2\theta = 20.1°$. For the mathematical fitting, the position, amplitude, and intensity of each function were allowed to vary.

The apparent crystallinities were expressed as crystallinity indices (CIs) by two methods. The Segal CI is based on the measurement of intensities at 22.7° (contribution of planes {0,0,2}) and 18.5° (contribution of non-crystalline fraction) (Segal et al., 1959; Ibbett et al., 2008):

$$CI = \frac{I_{002} - I_{\text{non crystalline}}}{I_{\text{non crystalline}}} \times 100 = \frac{I_{22.7^\circ} - I_{18.5^\circ}}{I_{18.5^\circ}} \times 100$$