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AGRI-WASTES – FEEDSTOCK FOR BIOREFINERY

BY

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Abstract. Straws and stalks are important categories of lignocellulosic agri-wastes. The availability of these materials is high, taking into account their extended cultivation. Their chemical composition represents an argument for their use as feedstock for papermaking fiber production. In this study, soda pulping process was employed for delignification of wheat straws (*Triticum aestivum*), corn stalks (*Zea mays*), rapeseed (*Brassica napus*) and sunflower (*Helianthus annuus*). The obtained pulps have been characterized from the perspectives of papermaking. Lignin separated from spent liquors resulted from pulping of agri-wastes is an alternative to increase overall process feasibility. In such context, the separated spent liquors were acid treated for lignins separation, which were further characterized by UV and IR spectroscopy techniques and gel permeation chromatography. The obtained results are important in establishing the potential usage of such lignins.

Keywords: straw; stalks; pulp; paper; lignin.

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1. Introduction

In pulp and paper industry, wood is traditionally the preferred fiber source, but a series of environmental impacts such as deforestation, soil erosion, depletion and acidification are associated (González-García *et al.*, 2010). In such context, the use of secondary fiber sources as feed-stocks for the production of papermaking pulp fibers and valorizing the currently underexploited resources deserves serious consideration.

Agri-waste lignocellulosic biomass is a renewable resource, globally available, recognized as important feedstock for bio-based industries (Fernández-Rodríguez *et al*., 2017). Lignocellulosic agri-waste (LAW) resulted as side-streams from harvesting of cereals present a particular interest due to their availability (Snelders *et al*., 2014). Yields of LAW collection are a good reflection of their availability: wheat straw: 1.4 - 2.5 t/ha; corn stalks: 1.7 - 4.5 t/ha; sunflower stalks 1.9 - 5 t/ha; rapeseed stalks 1.7 - 3.5 t/ha (Kadam and McMillan, 2003; Glithero *et al.*, 2013).

Pulping to papermaking pulp is a good example of fractionation of lignocellulosic biomass to materials such as cellulose fiber, lignin and hemicelluloses. While pulp is recovered and further processed by bleaching, beating and papermaking, lignin and hemicelluloses and their degradation products contained by the spent liquor are used in chemical recovery for energy generation by burning (Martin-Sampedro *et al*., 2014). In efforts to maximize the outputs in terms of economic efficiency, some authors (Rousu *et al.*, 2002; Sánchez *et al*., 2010; Snelders *et al*., 2014) pointed out that agricultural wastes are to become an economically feasible source of virgin fiber for the papermakers if integrated fiber based biorefinery concepts are implemented (Araceli *et al*., 2011). In other words, the recovery of lignin, hemicelluloses, sugars and derivatives could be a promising pathway to the accomplishment of such objectives.

Lignin is the second abundant natural polymer after cellulose and it is considered for valorization in production of different materials and as an ecological source of chemicals (Tamminen *et al*., 2010; Jääskeläinen *et al*., 2017). Characterization of the chemical potential of this aromatic resource is therefore important in establishing its prospective technical applications (El Mansouri and Salvadó, 2007).

Two objectives were taken into account in this paper: the characterization the pulps obtained by soda pulping of wheat straws (*Triticum aestivum*), corn (*Zea mays*), rapeseed (*Brassica napus*) and sunflower (*Helianthus annuus*) stalks and to study the lignin separated from spent liquors.

2. Experimental

2.1. Raw Materials

The raw materials such as straws of wheat (*Triticum aestivum*), stalks of rapeseed (*Brassica napus*), sunflower (*Helianthus annuus*) and corn (*Zea mays*) used in the study have been collected by the authors from local farmers. These materials have been pre-conditioned by drying up to 8-10% moisture and chopped to adequate dimensions before pulping trials. Portions of each type of raw material were milled for the following chemical analysis: moisture content (TAPPI T 664 om - 88); holocellulose (Wise, 1946), cellulose (Kürschner and Hoffer, 1931), pentosans, (TAPPI T233 cm - 01), lignin (TAPPI T222 om - 02), extractives (TAPPI T204 om - 88) and ash (TAPPI T211 om - 85). All reagents used were of analytical grade.

2.2. Methods

Pulping experiments were performed in a stainless steel laboratory rotating batch reactor, equipped with electric heating and automatic temperature control. Amounts of 400 g of raw materials (o.d. mass) and a solid to liquid ratio of 5:1 were used. Heating time was 30 min, while cooking time was 60 min at a temperature of 170ºC. The alkali charges were kept constant - 20% expressed as NaOH. Cooking liquor was prepared by dissolving analytical grade sodium hydroxide in tap water. After cooking, the digester was degassed and cooled to an appropriate temperature to allow removal of pulp for disintegration, washing and squeezing for water removal up to a consistency of about 30%. Furthermore, yield (gravimetric method) kappa number (ISO 302:2004) and intrinsic viscosity (ISO 5351:2010) were measured.

The obtained pulp samples were further used for laboratory sheet forming before and after beating. Laboratory beating of pulps was performed according to ISO 5264-3:1979 procedure in a Yokro mill. Handsheets were obtained according to ISO 5269-2:2004 on a Rapid Köthen laboratory sheet former and were subjected to tensile strength (ISO 1924:2008) and burst strength (ISO 2758:2001) determinations.

Lignin separation from black liquor. Black liquors resulted from pulping of agri-waste were used for lignin separation by precipitation with 1 N hydrochloric acid to pH 2 (Lin, 1991a) and centrifugation. The obtained lignin samples were dried in a vacuum oven at 40°C.

UV spectra were recorded by using a Jasco V550 spectrometer in quartz cells with 10 mm path. The lignin samples were dissolved in 0.2 M NaOH solution (lignin concentration 0.08 g/L) and spectra were recorded by using solvent as reference. The ionization differential spectra were recorded in the range 200 - 600 nm using lignin dissolved in buffer solutions (pH 6, 12 and

0.2 M NaOH). The data were used for the determination of the phenolic hydroxyl content (Gärtner *et al*., 1999).

FTIR spectra of the lignins were recorded by using a Digilab Scimitar FTS 2000 and KBr pellet technique. The IR absorption was recorded in the range 4000 - 400 cm^{-1} with 64 scans at 4 cm^{-1}. The pellet was prepared with a mixture of 1% mg sample/mg KBr and 2 mg of lignin sample. FTIR data were processed using ACD Labs software.

High performance size exclusion chromatography analysis of the lignins was performed after each of the lignin samples was derivatized by acetyl bromide method (Asikkala *et al*., 2012). Sample volumes of 200 μL (0.5%) were injected in the chromatography system equiped with a TSKgel GMHHR column calibrated with polystyrene standards (Fluka, 266-10^6Da). The detection was performed at 280 nm.

3. Results and Discussion

The studied raw materials show a high variability in chemical composition depending on the plant species. As shown in Table 1, the highest total polysaccharides content expressed as holocellulose was found in sunflower stalks while the lowest was found in corn stalks. Cellulose content was found to be the highest in wheat straw as well as pentosans content. In terms of lignin content the rapeseed stalks show the highest values while straws have the lowest content. These data show that chemical composition of agri-waste is close to that of hardwoods (Petrovici and Popa, 1997).

Table 2 lists the results for yield, kappa number and intrinsic viscosity of soda pulps obtained from the considered raw materials. It can be observed that highest yield values were obtained for rapeseed stalks and wheat straw. Lower yield in corn and sunflower stalks pulps are explainable by taking into account the chemical composition of the proposed feedstock types – higher content of extractives may be observed. The obtained pulps Kappa number varies from 15.2 to 63.0; this is an indication of suitability for fiber production. The intrinsic viscosities values obtained for wheat straw and corn stalk pulps were above 800 cm^3/g, while lower values of viscosity rapeseed and sunflower stalks.

The results regarding strength properties of agri-waste soda pulps in both unbeaten and beaten state are revealed in Table 3. For all pulp samples beating obviously improved the mechanical strength of the testes sheets. Better results were obtained for the corn stalks and wheat straw pulps. This is in correlation with the obtained values for pulp viscosity and kappa number.

Table 1
Chemical Composition of Raw Materials

Components [%]	Type of raw material			
	Wheat straw	Corn stalks	Sunflower stalks	Rapeseed stalks
Holocellulose	74.2	66.7	82.7	72.1
Cellulose	43.2	39.3	35.6	41.2
Pentosans	27.7	18.7	21.5	23.4
Lignin	17.5	18.2	19.9	21.6
Solvent extractives	5.5	3.9	11.2	4.7
Ash	5.3	4.1	8.7	5.8

Table 2
Pulping Results in Terms of Yield, Kappa Number and Intrinsic Viscosity

Type of raw material	Pulping Yield [%]	Kappa number	Intrinsic viscosity [cm^3/g]
Wheat straw	40.3	15.2	810
Corn stalks	35.1	27.3	1050
Sunflower stalks	38.2	63.0	670
Rapeseed stalks	44.0	47.2	620

Table 3
Strength Properties of Agri-Waste Soda Pulps

Pulp source	Beating degree, [ºSR]	Tensile index [N.m/g]	Burst index [$kPa.m^2/g$]
Wheat straw	20	39.3	2.6
	31	55.1	3.9
Corn stalks	25	47.48	2.24
	42	73.6	4.59
Sunflower stalks	23	22.7	0.78
	62	46.46	1.66
Rapeseed stalks	19	23.5	1.1
	28	45.3	2.1

The recorded lignin UV spectra (Fig. 1) present the characteristics of alkali lignins. In case of wheat straw lignin the maxima were observed at 214 nm and 285 nm; in corn stalks lignin maxima at 220 nm, 290 nm; for sunflower stalks lignin 214 nm and 287 nm and for rapeseed stalks lignin 220 nm and 295 nm. This maxima are affected by the presence of different substituents on the aromatic rings in lignin's structure. The presence and ratio of different units such as p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) may induce either bathochromic - presence of high number of (H) units - or hypsochromic (S) shifts in the range 270 - 290 nm (Lin, 1991b; Petrovici and Popa, 1997). The

ionised differential spectral data was used for calculation of the content of phenolic hydroxyl groups – Fig. 2. Absorbance values at 300 nm and 350 nm were taken into consideration for the calculus. Higher values were obtained for the wheat straw lignin as a result of the more intense cleavage of aryl-ether linkages in this type of lignin during pulping.

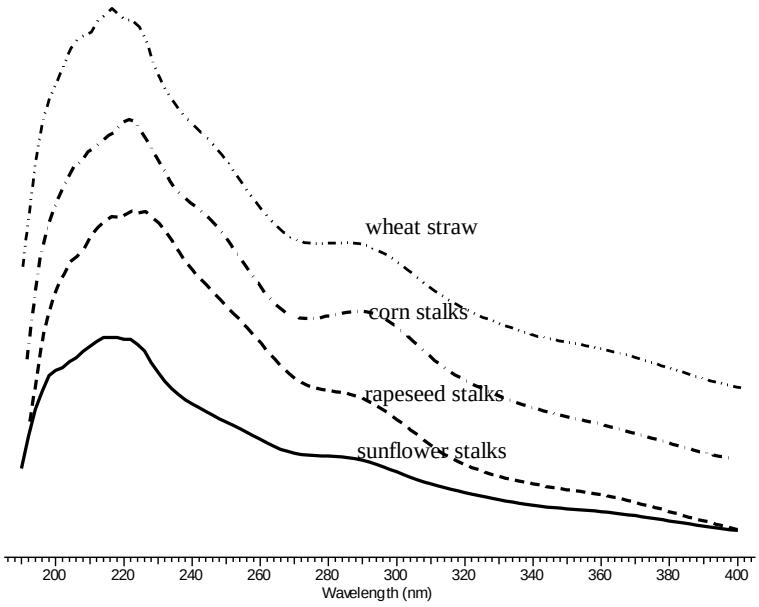

Fig. 1 − UV spectra of agri-waste soda lignins.

The agri-waste lignins' FTIR spectra are presented in Fig. 3. Assignment of the most important peaks (Faix, 1992): ~1710cm^{-1}- unconjugated C=O; conjugated C=O at ~1610-1650 cm^{-1}; ~1510 and ~1460 cm^{-1} - aromatic ring; ~1330 cm^{-1} - characteristic for syringyl (S) units found in hardwoods and nonwoods; ~1267 cm^{-1} guaiacyl unit; ~1150 cm^{-1} and 817 cm^{-1} shoulders correspond to CH in-plane deformation; ~1220 cm^{-1} C–O deformation in secondary alcohols and aliphatic ethers; ~1040 cm^{-1} C–O bands in primary alcohols. These bands showed different intensities as a result of different initial structure of lignin and different behavior during pulping.

As it observable in Table 4, all of the lignins samples showed a high polydispersity, with polydispersity index (PDI) ranging from 2.76 in corn stalks' soda lignin to 4.07 in rapeseed stalks' lignin. The lowest number average and weight average molecular weight (Mn and Mw) values were also revealed for the corn stalks lignin.

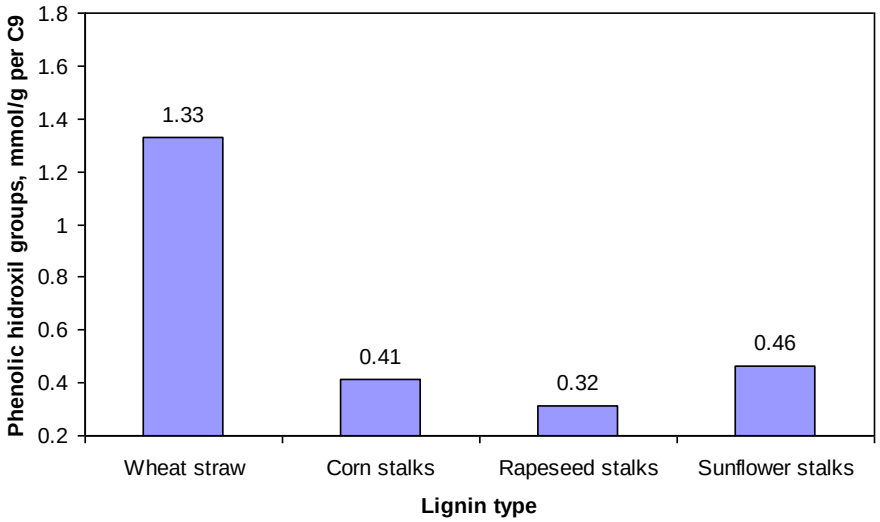

Fig. 2 – Total phenolic hydroxyl content
of agri-waste soda lignins.

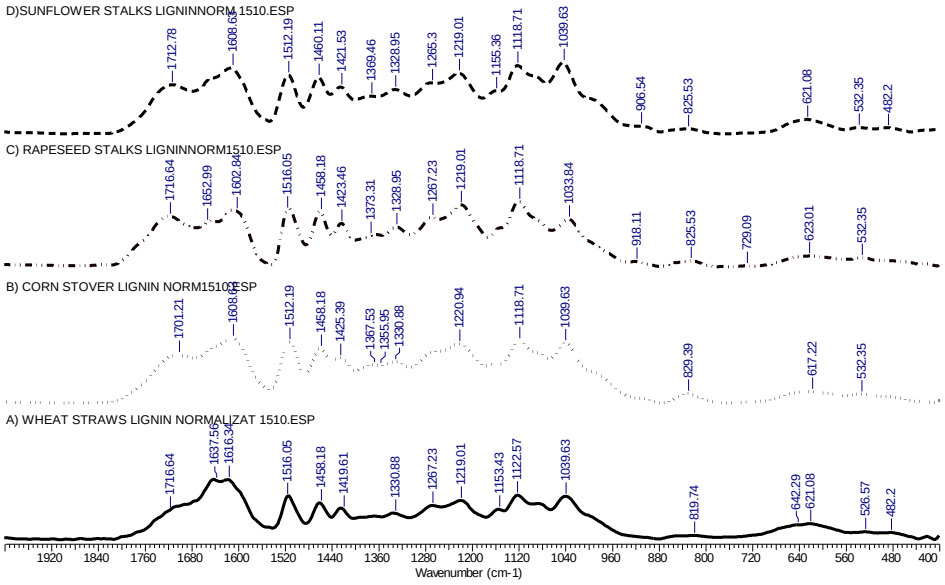

Fig. 3 − FTIR spectra of agri-waste soda lignins.

Table 4
Calculated Values of Number Average and Weight Average Molecular Weight (Mn, Mw) and Polydispersity Index (PDI) of Agri-Waste Soda Lignins

Lignin source	Mn	Mw	PDI
Wheat straw	3166	9240	2.92
Corn stalks	1837	5078	2.76
Rapeseed stalks	4300	17537	4.07
Sunflower stalks	2334	7409	3.17

4. Conclusions

Chemical composition of studied agri-waste categories points out that these materials could be an alternative fiber source for pulping. Soda pulping of the proposed types of agri-wastes leaded to different types of pulps in terms of yield (35 - 44%), kappa number (15 - 63) and viscosities (620 - 1050 cm^3/g). The results on strength properties indicated that beating improved strength properties for all the pulps. Taking into account these results wheat straw and corn stalks seemed more attractive for fiber production.

Analysis of lignins separated by acid precipitation from spent liquors revealed different values of UV absorption maxima and phenolic hydroxyl content, with wheat straw having the highest content. FTIR data showed the presence of the characteristic bands of lignin. HPSEC chromatography revealed that the studied lignins presented high polydispersity indexes. The differences between data are a consequence of native lignin structure as well as of its behavior during pulping.

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DEŞEURILE AGRICOLE – MATERIE PRIMĂ PENTRU BIORAFINARE

(Rezumat)

Paiele și tulpinile provenite din diferite culturi agricole sunt categorii importante de deșeuri agricole lignocelulozice. Disponibilitatea acestor materiale este ridicată ca rezultat al cultivării extinse. Compoziția chimică a acestora reprezintă un argument în ceea ce privește utilizarea ca materii prime la fabricarea celulozei. În studiul de față s-a realizat dezincrustarea natron a paielor de grâu (*Triticum aestivum),* tulpinilor de porumb (*Zea mays*) a celor de rapiță (*Brassica napus*) și respectiv de floarea soarelui (*Helianthus annuus*). Celulozele obținute au fost caracterizate din perspectiva utilizării ca materie primă la fabricarea hârtiei. Separarea ligninei din leșia neagră rezultată la fierbere poate constitui un mijloc de creștere a fezabilității economice a procesului. În acest context, leșiile negre au fost tratate cu acid în vederea separării ligninelor, care au fost ulterior caracterizate prin intermediul spectroscopiei UV și IR și respectiv prin cromatografie de excluziune sterică. Rezultatele obținute sunt importante în contextul stabilirii potențialului de utilizare al acestor lignine.