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Content

Characterization and determination of the S/G ratio via Py-GC/MS of agricultural and industrial residues

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Given the energy crisis and global warming, agricultural residues (olive tree pruning, almond shell and apple tree pruning) and industrial residues (kraft liquor) as source or biomass have been regarded as a promising alternative to fossil fuels, due to its renewability and extensive distribution [1].

Lignin is a three dimensional cross-linked polymer consisting of various phenylpropane units, which constitutes a lignocellulosic materials together with cellulose and hemiculloses. It is well known that lignin structure depends on the plant origin. Softwood lignins are composed essentially of guaiacyl units whereas hardwood lignins are based on varying ratios of guaiacyl (G) and syringyl (S) units . Finally grass lignins are composed of G, S and p-hydroxyphenyl units (H) with different compositions.

In this work lignin extracted by different fractionation processes (kraft, organosolv, acetosolv, acetosolv/formosolv) and from different agricultural residues (apple tree pruning, olive tree pruning and almond shell) and industrial residues (kraft black liquor) were characterized by FITR, HPLC, GPC and with especial interest on Py-GC/MS with the motivation of knowing which lignin had the highest syringyl and guaiacyl units for further depolymerization.

Table 1. Summary of the results obtained by Py-GC/MS for the different raw material lignin

	OOL	KL	AAL	ASAFL
H	5.26	0.49	7.25	0.83
G	26.07	23.80	27.72	45.43
S	68.67	75.70	64.54	53.74
S/G	2.63	3.18	2.33	1.18

The results in Table 1 revealed that the lignin from olive tree pruning and almond shell had the highest and most equal amounts of guaiacyl and syringyl units and were the ones chosen for further depolymerization.

References

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Content

Evaluating residual lignins from bioethanol and pulping olive tree pruning industry

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Among different lignocellulosic feedstocks, olive tree pruning (OTP) has shown a great potential for bioethanol production and pulp and paper manufacture. Lignocellulosic bioethanol production comprises pretreatment, saccharification, sugars fermentation, separation of lignin-rich fermentation residues, and distillation. A great part of lignin-rich residues is necessary in order to obtain energy for processing plant, mainly by combustion. The rest of lignin could be transformed into value-added products including bio-based aromatic chemicals, as well as building blocks for materials. In the same way, the traditional pulp and paper industry (Kraft and Soda-AQ pulping) is looking for new value-added products from their residual lignins. Thus, the adaptation of these processes into biorefineries will help to enhance the profitability of bioethanol plants and paper mills. In this context, a good understanding of lignin quality is necessary prior to its valorization.

The present study focused on the characterization of different residual lignins from olive tree pruning bioethanol production (residual lignins collected from steam explosion with water or phosphoric acid as catalysts, followed by simultaneous saccharification and fermentation process) and alkaline pulping (residual lignins recovered from Kraft and Soda-AQ black liquors). In addition to the composition and purity, the lignin structures (S/G ratio, interunit linkages) were investigated by spectroscopy techniques such as FTIR, solid state ¹³C-NMR, and 2D-NMR.

Spectroscopy techniques revealed different structural characteristics depending of the industrial procedure. Then, certain content of alkyl-aryl ether and resinol linkages were observed in bioethanol lignins compared to pulping lignins, which showed a dramatical reduction of alkyl-aryl ether and, consequently a higher hydroxyl phenolic content. This higher phenol content of pulping lignins makes them suitable for resin applications, a field where the hydroxyl groups of lignins are key functional groups for its reactivity. By contrast, the higher content of alkyl-aryl ether linkages of bioethanol lignins lead to high molecular mass lignins, which could be an advantage in lignin-based dispersants and composites. Contamination by sugars and protein impurities was also determined in these residual lignins.

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Content

Lignin, the most important aromatic polymer in the nature, contributes between 15-40% of the dry matter content in biomass [1]. The lignin functional groups constitute the key for its transformation into high added value products. The main functional groups in lignin are the hydroxyl, methoxyl, carbonyl and carboxylic groups and those have the great impact on the reactivity of lignin molecule [2].

Four industrial lignins were used to develop this study. Soda lignin from wheat straw (Protobind 1000), kraft lignin from pine, straw organosolv lignin (Avidel process) and Indulin AT kraft lignin.

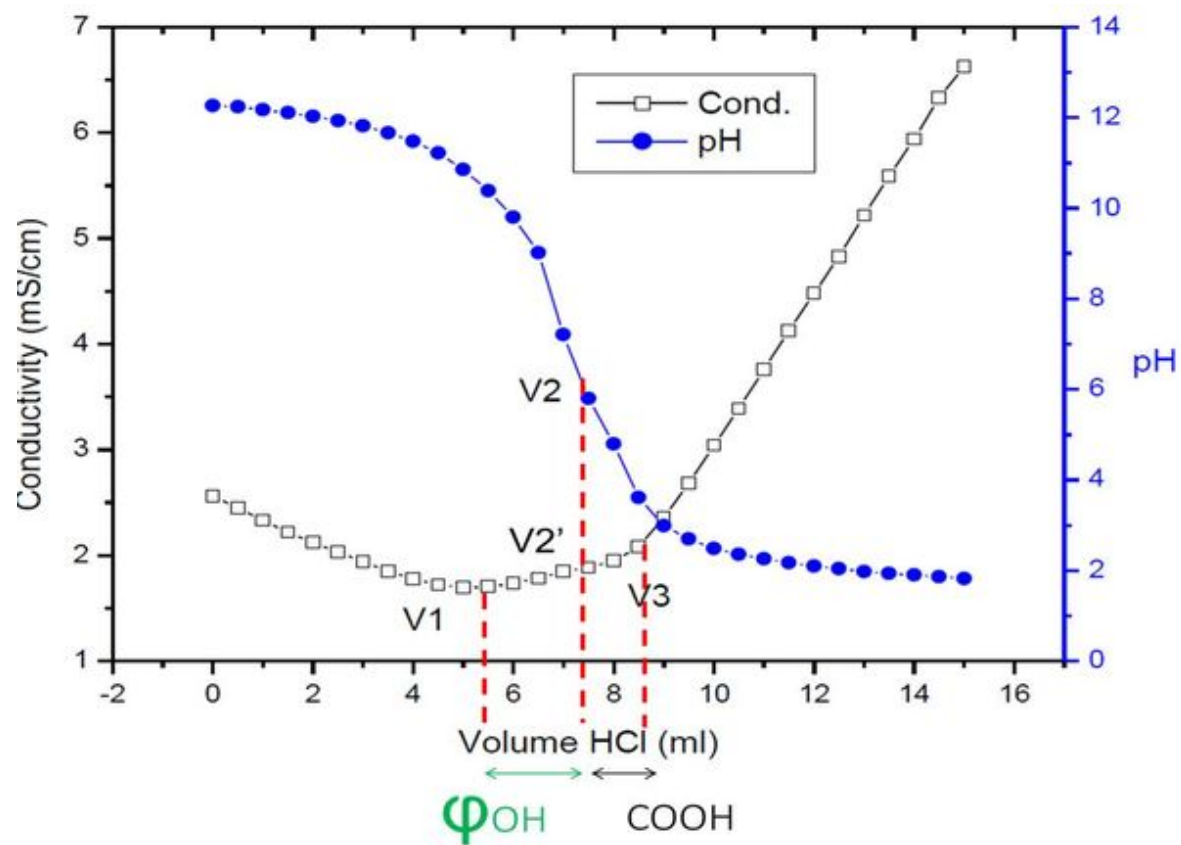
A rapid method in aqueous media based on simultaneous conductometric and acidic titration by pH was evaluated to determine the amount of phenolic hydroxyl groups and compared with six traditional methods (amynolysis, UV-method, Folin Ciocalteu method, ^{13}C -NMR, ^1H -NMR, ^{31}P -NMR). At the same time, this method provides the carboxyl groups amount.

During the titration three different inflexion points can be differentiated (Figure 1). Using simultaneous conductometric and acidic titration by pH it becomes possible to distinguish the amount of each functional group. The titration of free phenols with pKa's in a range of 8-11.5 can be obtained by the difference volume between V2, corresponding to pH 7, and V1. The remaining acidic groups, i.e. carboxylic groups, correspond thus to the difference volume between V3 and V2.

Aqueous titration for measurement of carboxyl groups is already well-known and reliable method. The results of this study proved that measurement of phenolic hydroxyl groups for technical lignins can be simultaneously measured providing a fast, easy and economical method compared to traditional ones.

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Content

For more efficient and economic 2nd generation biorefineries a complete valorization of lignocellulose is essential, but still challenging due to the recalcitrance of lignin against simple degradation. To monitor and evaluate chemically catalyzed lignin degradation, gel permeation chromatography (GPC) is used as standard technique. However, the determined lignin molecular weight depends on the biomass type and the isolation procedure, such as acidolysis (Klason process), organosolv or Kraft pulping, which additionally influence the chemical properties of lignin leading to unwanted solubility, association, adsorption, and ion-exclusion effects. Therefore, this work compares and optimizes GPC-UV/RI methods for various lignin types in order to predict and reduce secondary separation effects.

To this end, the composition of Kraft- (KFL), Klason- (KLL), Organosolv- (OSL) and Organocat (OCL) lignins isolated from beech wood as well as their solubility in GPC eluents were determined. The eluent additives monosodium phosphate, LiCl, polyethylene glycol (PEG), and polystyrene sulfonate (PSS) were tested for their capability to prevent lignin association on aqueous- and organic GPC. High performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) was applied to detect potential lignin degradation products under alkaline conditions (pH 12) of aqueous GPC accompanied by molecular changes of lignin [1].

The composition of KLL and OSL could be balanced to 100 % with acid insoluble lignin contents of about 90 % and low carbohydrate impurities of less than 5 %, whereas the acid insoluble lignin content of OCL and the commercial KFL was found to be only 50 % probably due to solvent residues and formulation agents. Increasing salt concentrations in the eluent resulted in significantly decreased molecular weight of all lignins on both aqueous and organic GPC methods. Association of KLL in the aqueous eluent could be halved by the addition of PEG 6000 to the eluent. The addition of PEG 1500 and PSS 70000 even resulted in almost no lignin association and a reproducible molecular weight for all lignins. Furthermore, negligible lignin degradation in the alkaline GPC eluent was detected using HPAEC-PAD. Similar molecular weight distributions for the respective lignin were gained with different GPC methods (eluent, column material), calibration standards (PEG, PSS) and detectors (UV, RI). In summary, GPC methods with high accuracy and reproducibility for chemically diverse lignins could be optimized and applied for lignin characterization.

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Content

Olive tree biomass is an agricultural residue generated every year in huge amounts after harvesting olives and must be eliminated to avoid environmental problems. This lignocellulosic residue with high content of fermentable sugars, mainly glucose, can be considered as an interesting raw material for bioethanol production. However, its high extractives content, the presence of lignin and the cellulose crystallinity make difficult some process stages such as pretreatment and enzymatic saccharification.

This biomass has been traditionally characterized according to National Renewable Energy Laboratory (NREL) methods to determine its content in cellulose, hemicellulose, lignin, extractives and ashes. In this work, additional analytical techniques, such as Fourier transformation infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Thermogravimetric analysis (TGA) have been used. FTIR gives an overall picture on the lignin purity and extractives. This technique allows to see how some important infrared absorption bands of lignin, carbohydrates and extractives affect on olive tree biomass structure. The crystallinity of cellulose is an essential factor that affects its enzymatic digestibility. In this study, the XRD diffractograms were used to understand the interactions of cellulose in olive tree biomass. Furthermore, XRD allowed to determine the crystallinity index of original olive pruning biomass and after different process stages. Concerning TGA, the weight-loss curve of biomass materials shows mass changes that can be related to hemicellulose and cellulose decomposition in olive tree biomass after the process stages.

The aim of this work was to achieve a deeper knowledge of the structure of original olive tree biomass and its evolution along the bioethanol conversion process. Thus, these techniques were applied to raw olive tree biomass, after a water extraction (121°C, 60 min), after sulfuric acid pretreatment (164°C, 10 min, 0.9 % H₂SO₄) and after enzymatic hydrolysis (Martínez-Patiño et al., 2017).

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