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Physicochemical characterization of lignin isolated from agricultural vegetable residues for the study of its properties as fuel and estimation of its energy potential

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Abstract

Lignin is one of the main constituents of plant biomass and is generated as a by-product in the production of bioethanol. However, it has important energy properties that convert it as a potential fuel, and its use can improve the competitiveness of biomass as a source of renewable energy. In Baja California-Mexico, there is a preponderance agricultural activity that generated in 2016 around 102,960 t of wheat straw and 48,315 t of cotton stalk. Therefore, the objective of this research was to determine the percentage of lignin in wheat straw and cotton stalk, to valorize the amount of lignin available in Baja California and estimate the energy potential of this region. The analyses included isolation and determination of the lignin percentage; morphological analysis; proximate analysis; higher heating value determination; elemental analysis by electrons dispersed of X-rays; analysis of the majority of elements by X-rays fluorescence; analysis by Fourier transform infrared spectroscopy. It was found that wheat straw contains 20.81% lignin, with a higher heating value of 22.91 MJ/kg, while cotton stalk 22.33% and 24.99 MJ/kg. By 2016, Baja California had 114,571 t of lignin from both wastes, giving it an energy potential equivalent to 2,644 TJ or 80,120 tons of anthracite coal.

Agricultural Wastes, Energy Properties, Higher Heating Value, Physicochemical Characterization, Lignin

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Introduction

Plant residues from agriculture are a type of lignocellulosic biomass consisting essentially of cellulose, hemicellulose, and lignin. There is now a growing interest in the deposition of these wastes as renewable energy sources. The production of bioethanol from this type of waste is one of the main objectives in many investigations around the world. (Mohapatra et al., 2017; Chng et al., 2016). However, the process for the production of bioethanol presents a major drawback that increases its production. The plant material must be delignified before hydrolyzing and fermenting the cellulose. (Baskar et al., 2016).

The elimination of lignin is an indispensable step in the production of bioethanol because its presence in the material affects the process of transformation of the biomass into fermentable sugars in two ways. Firstly, lignin can irreversibly absorb hydrolytic enzymes by blocking their action on cellulose. And secondly, lignin has a hydrophobic character that prevents or reduces swelling of the cellulose, decreasing the surface accessible to the enzymes. (Palonen et al., 2004; Chang & Holtzapple, 2000). Therefore, the fermentation of plant biomass for the production of bioethanol inevitably generates large amounts of lignin as a by-product.

Lignin is a complex, branched and an amorphous polymer composed of three monomeric units, syringyl propane (3,5-dimethoxy-4-hydroxyphenylpropane), guaacyl-propane (4-hydroxy-3-methoxyphenylpropane) and 4-hydroxyphenylpropane. (Bittencourt et al., 2010; Monteil et al., 2013; Singh et al., 2015). This polymer has important energetic properties that can be harnessed for the production of thermal and/or electric energy (Cotana et al., 2014).

Their use can contribute to lower bioethanol production costs and improve the competitiveness of residual agricultural biomass as a source of renewable energy, especially in regions with intense agricultural activity (Buranov & Mazza, 2008).

The state of Baja California, Mexico has devoted extensive areas to wheat and cotton crops, making this region one of the most active sites of Mexican agriculture. This characteristic represents a significant potential for the development of renewable energies, such as the production of lignocellulosic bioethanol and, consequently, the generation of large amounts of lignin as a by-product. In 2016, 102,960 ha of wheat and 10,931 ha of cotton were grown (SIAP, 2016). Generating approximately 741,312 t of wheat straw and 48,315 t of cotton stalk, considering a residue generation index of 7.2 t/ha and 4.42 t/ha for wheat and cotton crops, respectively (Gemtos & Tsiricoglou, 1999; SENER, 2016).

Therefore, the objective of this work was the study of the energetic properties and physicochemical characteristics of lignin isolated from vegetable residues of wheat and cotton crops in the State of Baja California. It also quantifies the amount of available lignin and its energy potential as a biofuel of the region.

Methodology

This research was developed in four steps: (a) preparation of the sample; (b) determination of the lignin percentage; (c) physicochemical characterization and energy properties determination and (d) estimation of the energy potential lignin. In all cases, these samples were analyzed in triplicate.

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Preparation of the sample

200 g of *Triticum aestivum L genus* wheat straw and 200 g of *Gossypium hirsutum L* genus cotton stalk were collected from a cropland of the Mexicali Valley that is located in the State of Baja California. The samples were finely milled using a GRINDOMIX GM 300 Retsch mill series and homogenized in a sieve Nº 35.

Determination of the lignin percentage

Before determining the percentage of lignin, samples of wheat straw and cotton stalk were dried according to ASTM E871 to determine their humidity content. Two extractions were then performed, one in hot water and other in ketone, according to the standards established in TAPPI T207 and PATTI T264, respectively. The percentage of lignin was determined as the amount of sulfuric acid insoluble material according to the methodology established in ASTM D1106.

Physicochemical characterization and energy properties determination

Five analyses were carried out to the physicochemical characterization and energy properties determination of the wheat straw, and cotton stalk, each of them described below.

a. Higher heating value

The higher heating value (HHV) was determined using an IKA C2000 series isoperibolic bomb calorimeter. This equipment was set at 25ºC through the isoperibolic method according to the ASTM 711 standard.

b. Proximate analysis

The proximate analysis was carried out to quantify the solid, gaseous, and non-fuel fraction from the agricultural wastes.

This analysis includes determinations such as the volatile material, fixed carbon, and ash according to the ASTM E872, ASTM E870, and ASTM E830 standards.

c. Analysis by scanning electron microscope

The morphology of the lignin powders and the distribution of elements were characterized by a scanning electron microscope (SEM) using a JEOL JSM-6010LA series microscopy. This instrument consists of an energy dispersive X-ray analyzer and a retro-dispersed electrons detector to capture images. It was operated under conditions of low vacuum and a voltage from 15 kV to 20 kV.

d. X-ray fluorescence spectrometry

The isolated lignin powders of wheat straw and cotton stalk were analyzed by the X-ray fluorescence spectrometer of dispersed energy, using a SHIMADZU EDX-7000 equipment. The X-ray generator consists of a tube that uses the Rhodium (Rh) element as a target, and it was set at 50 kV and 283 μA.

The operation characteristics allowed determining the majority of elements found in the samples in a range that covers from sodium to uranium. The X-ray fluorescence lines emitted by the samples were identified using a silicon drift detector (SDD).

e. Analysis by Fourier transform infrared spectroscopy

The wheat straw and cotton stalk isolated lignin was characterized by the infrared spectrometry, using a Perkin Elmer Spectrum One FT-IR Spectrometer, which consists of a detector of attenuated total reflection (ATR). The spectra were collected in the range from 400 to 4000 cm^{-1} with a spectral resolution of 4 cm^{-1}, and 16 scans were performed for each sample.

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Estimation of the energy potential lignin

The amount of available lignin were calculated according to the Eq. (1), where the calculated lignin percentage is multiplied for each residue per the amount of agricultural waste (no humidity and total extractions) generated in 2016. The residue production index of wheat straw considered was 7.2 t/ha and 4.42 t/ha for cotton stalks (Gemtos & Tsiricoglou, 1999; SENER, 2016).

$$A = [B \times (1 - \%H - \%E)] \times \%L \quad (1)$$

Where:
A: Amount of recovered lignin
B: Tons of residues generated in 2014
% H: Humidity percentage
% E: Total extractions
% L: Percentage of lignin in wheat straw

The potential energy was estimated considering the amount of available lignin from the wheat straw and the cotton stalk in 2016. It was calculated according to the yield of available lignin that corresponds to each residue regarding its higher heating value; that was measured in MJ/kg.

Results
Morphological analysis

The lignin was isolated from the vegetable materials as the insoluble residue in sulfuric acid, and it was filtered and dried at 40°C. As a result, a brown powder of soft texture was obtained. The color of the wheat straw lignin was darker than the cotton stalk lignin. The morphology of the isolated lignins was analyzed by SEM, and the captured images are illustrated in Figure 1. These images indicate some important differences of the isolated materials, even though both residues were treated similarly in the lignin separation process.

The wheat straw lignin is like a micrometric powder that agglomerates in layers with micro-metric sizes smaller than 25 µm. The cotton stalk lignin presents densely packed microparticles. These microparticles have a defined structure and a high porosity.

The porous structure observed in the isolated lignins provides a major superficial area available for gasification reactions. The high porosity favors the mass transference inside of the material, which facilitates the carbonating agents penetration, e.g., CO_2 and H_2O. It causes an increase in the reaction speed during gasification, desirable characteristics in thermochemical processes (Butterman & Castaldi, 2012; Rincón et al., 2011).

Typical cellulose and hemicellulose micro fibers were not observed in the SEM images depicted in Figure 1. Therefore, it could be assumed that the treatment of agricultural wastes with 72% w/w sulfuric acid dissolved those components.

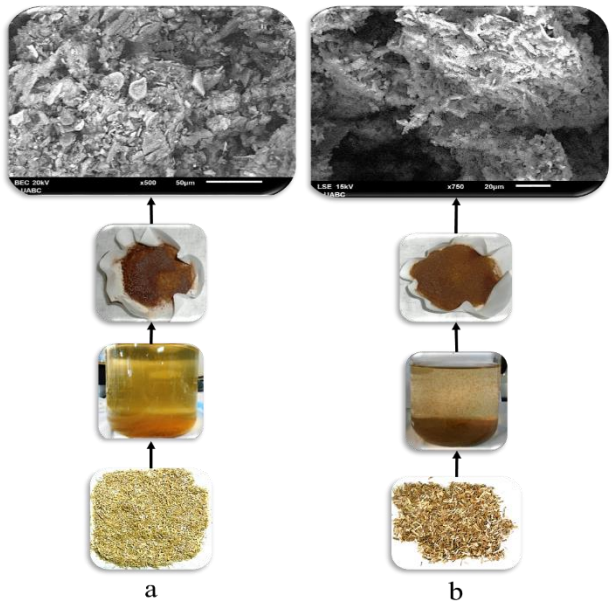

Figure 1 Lignin extraction process and SEM images of (a) wheat straw and (b) cotton stalk.

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Lignin percentage, proximate analysis, and higher heating value

The cotton stalk contained 6.28% of humidity and 11.57% of the extractable material. This waste had 22.33% of lignin as part of their structural compounds. The higher heating value of the lignin was 24.99 MJ/kg. The experiment results are exhibited in Table 1.

The wheat straw contained 8.83% of humidity and 25.91% of the extractable material. This waste had 20.81% of lignin as part of their structural compounds. The higher heating value of this lignin was 22.91 MJ/kg. The experimental results are displayed in Table 1.

The values obtained of volatile material, ashes, fixed carbon, and the HHV in both lignins are in the range of values according to the literature (Horst et al., 2014; Blunk et al., 2000). Regarding the proximate analysis results, the high amounts of volatility found in the lignins revealed important thermal properties. These lignins provide a high reactivity and burn at low temperatures. Therefore, they do not require staying a long time in the furnace. These properties increase the efficiency of the combustion process (Nogués et al., 2010).

Analysis	**Cotton stalk**		**Wheat straw**	
	Average	SD	Average	SD
Humidity	6.28	0.01	8.83	0.14
Extract	11.57	0.33	25.91	0.36
Lignin	22.33	0.31	20.81	0.22
Analysis	Isolated lignin		Isolated lignin	
	Average	SD	Average	SD
VM	70.25	0.33	69.15	0.59
FC	29.51	0.37	27.54	0.80
Ash	0.78	0.09	2.29	0.20
HHV*	24.99	0.15	22.91	0.06
* Expressed in MJ/kg				

Table 1 Lignin in cotton stalk and wheat straw and its physicochemical characteristics in dry base.

The quantification of the ashes content is important in a fuel material because the ashes decrease the heating value and the combustion efficiency. The isolated lignin of both materials has a low content of ashes. It means that diminishes the occurrence of problems related to the powder emissions, maintenance difficulties, crud formation, corrosion, and deposits in the heat exchangers. The low contents of ashes also make its grinding process and transportation easier (Suramaythangkoor & Gheewala, 2010).

The fixed carbon refers to the amount of material that burns slightly without igniting a flame. Its value is related to the time required to complete the oxidation of the material. It is important to determine the feeding speed to the furnace. The fact that the cotton stalk lignin contains a higher percentage of fixed carbon than the wheat straw lignin implies that the HHV of the cotton stalk lignin is higher than the HHV of the wheat straw lignin (Nogués et al., 2010).

The results of the approximate analysis and the high-energy contents of the isolated lignins are similar to the characteristics of the sub-bituminous coals according to the Standard Classification of Coals by Rank (ASTM D338). Therefore, it is possible to convert the energy of the residual lignin generated in Baja California by using more efficient conversion systems such as gasification or co-firing with these coals (Suramaythangkoor & Gheewala, 2010). The lignin can be pelletized and densified to make its transportation easier and cheaper, which makes its final arrangement possible into far places from the agricultural lands.

Elemental analysis

After performing the elemental analysis by EDX, it was found that the cotton stalk lignin contains 74.83% of carbon and 24.83% of oxygen.

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The EDX analysis of the wheat straw lignin revealed 63.56% of carbon and 32.94% of oxygen. These results are disclosed in Table 2, and they support the results of HHV where the cotton stalk lignin has a higher amount of energy per unit of mass, compared to the wheat straw lignin.

The atomic O/C ratio is usually used as a parameter to evaluate the efficiency of fuels in the different processes of energy conversion (Ohm et al., 2015). The O/C ratio of the cotton stalk lignin was 0.33, and the O/C ratio of the wheat straw lignin was 0.52. An increase of 0.20 in the O/C ratio meant a decrease in the HHV of 2.08 MJ/kg. This ratio indicates that the cotton stalk lignin will provide a higher reactivity in the pyrolysis processes, direct combustion, or gasification (Wang et al., 2010). The higher O/C ratio is also related to the decrease of liquid fuel produced by the liquefaction processes (Hayamizu & Ohshima, 1985; Saxby, 1980). Nevertheless, several studies indicate that the increase in this ratio increases the total efficiency of gaseous products through the hydropyrolysis processes in carbonaceous materials (Strugnell & Patrick, 1995).

Analysis	Elements	Lignin Source	
		Cotton stalk	Wheat straw
Elemental analysis	Carbon	74.83	63.56
	Oxygen	24.82	32.94
	Sulfur	ND*	0.09
	Silicon	0.34	3.41
	O/C	0.33	0.52
Analysis of the majority elements	Silicon	41.035	76.341
	Sulfur	34.851	10.856
	Bromine	6.925	2.400
	Calcium	6.771	3.678
	potassium	5.980	3.562
	Iron	2.592	1.964
	Copper	1.847	0.219
	Zinc	-	-
	titanium	-	0.477

Table 2 Percentage of elements in the lignin and relative concentration of majority elements (w/w).

Fuels are usually composed of elements that are responsible for the emission of pollutants and elements related to corrosion problems in the combustion systems, for instance: nitrogen, chlorine, and sulphur. These elements were not found in the isolated lignin, but it was found sulphur in the wheat straw lignin.

However, the low sulphur concentrations in the wheat straw make its combustion or co-firing easier with other fuels without high environmental risks.

Analysis of the majority elements

This analysis allowed classifying the elements of the inorganic fraction in the isolated lignin, as it is indicated in Table 2. During the combustion of the lignin, it is expected the formation of oxides of silicium, sulphur, calcium, and potassium.

Although the wheat straw lignin had a higher relative amount of sulphur, it also had the higher amount of calcium, which means that a great part of sulphur oxides generated from the combustion, will remain in the calcium oxides. This decreases the emission of polluting and corrosive products to the environment. It is also expected that the ashes of the cotton stalk lignin burn at higher temperatures than the wheat straw lignin because it has the higher content of silicon oxides and the lower content of potassium oxides (Melissari, 2012).

On the other hand, heavy metals were not found in the isolated lignin, except for the zinc in the cotton stalk lignin. The determination of the elements present in the inorganic fraction of biomass is important because such elements have a catalytic effect on the pyrolysis and gasification reactions.

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Furthermore, they may react with the carbonating agent and impact on the reactivity of the carbonaceous residue and the thermal decomposition of the vegetable material. The calcium, sodium, potassium, and magnesium are components present in the ashes and have a catalytic effect over the gasification (Butterman & Castaldi, 2012; Hattingh et al., 2011).

FT-IR analysis

FT-IR spectra of isolated lignin powders in wheat straw and cotton stalk are illustrated in Figure 2, and the principal absorption bands are indicated in Table 3. The absorption spectrum values of the wheat straw lignin were lower than the spectrum values of the cotton stalk lignin. It may be caused by changes or damages in the chemical structure of lignin during the isolation process.

Nevertheless, both spectra reveal the characteristic functional groups in this biopolymer. Coming from the vibration of OH stretching groups in the aromatic and aliphatic compounds, a strong absorption at 3323/3350 cm^{-1} was observed. Two absorption bands at 2921/2917 and 2852/2832 cm^{-1} were assigned to the asymmetric and symmetric vibrations, respectively, of the saturated CH_2.

Other bands at 1710/1706 cm^{-1} are part of the non-conjugated carbonyl groups, whereas the others at 1645/1650 cm^{-1} are part of the conjugated carbonyl. Moreover, the rings or aromatic skeleton absorption at 1603/1599 and 1513/1500 cm^{-1} were noticed (Li, Wu, 2012; Kang et al., 2012; Balagurumurthy et al., 2014). The absorption bands associated to the monomers that form the lignin of vegetable materials may be noticed in the spectrograms.

In the spectrum of the cotton stalk lignin, there are bands at 1376, 1263, and 1218 cm^{-1} that correspond to the G units, the typical bands of S units appear at 1376 and 1110 cm^{-1}, and the characteristic bands of H units are present at 824 and 933 cm^{-1}.

Bands of G (1313, 1114 cm^{-1}) and S (1266, 1214 cm^{-1}) units are also noticed in the wheat straw lignin. However, just one band at 925 cm^{-1} is noticed, which could be caused by the H monomer. This result indicates a lower concentration of H units in wheat straw lignin that corresponds to the results given by other authors (Monteil et al., 2013; Watkins et al., 2015; Bauer et al., 2012).

The determination of the chemical lignin composition is strongly affected by the methods and extraction solvents used. For that reason, the lignin spectra of the same vegetable material may have differences concerning the absorption band and the intensities. The spectra obtained in this study differ with the spectra of isolated lignin using dioxane (Sun et al., 2005) or sodium hydroxide (Ahvazi et al., 2011). Nonetheless, they maintain greater similarities to the spectra of isolated lignin with sulfite (Sahoo et al., 2011) or using a sulphuric acid treatment supported by microwaves (Monteil et al., 2013).

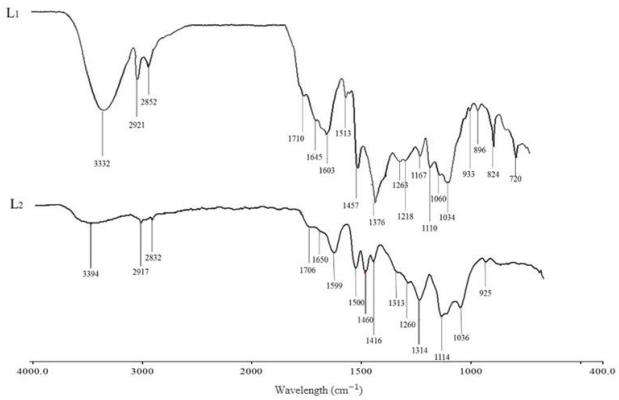

Figure 2 FT-IR spectrum of cotton stalk lignin (L1) and wheat straw lignin (L2).

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Wavelength (cm^{-1})	Vibration type		
Cotton stalk lignin	**Wheat straw lignin**	**Functional groups**	**Origin**
3332	3394	O-H stretching	Phenolic and alcoholic groups
2921, 2852	2917, 2832	C-H symmetric and asymmetric stretching	$–CH_3$, $–CH_2$ –CH
1710	1706	C=O stretching	Non-conjugated carbonyl groups
1645	1650	C=O stretching	Conjugated carbonyl groups
1603, 1513	1599,1500	C=C stretching	Aromatic ring or skeleton
1457	1460	C-H bending	Asymmetric deformation in $–CH_3$ and $–CH_2$
1376	-	C-H bending	Syringyl or guaiacyl units
-	1313	C-H bending	Syringyl units
1263	1260	=C-O-R stretching	$–OCH_3$ y –OH guaiacyl units
1218	1214	C-C, C-O and C=O stretching	Condensed and esterified guaiacyl units
1110	1114	C-H in-plane bending	Typical syringyl units
1034	1030	C-H and C-O bending	Aromatic ring, $-OCH_3$, primary alcohol
933	925	=CH- out-of-plane bending	Alkenes

Table 3 FT-IR absorption bands of the isolated lignins

Available lignin

In 2016, the lignin that might has been recovered from cotton stalks in Baja California was 8,940 t that is equivalent to 223 TJ taking into account the HHV experimentally determined. For the same year, it was estimated that about 105,631 t of lignin from wheat straw could be obtained that are equivalent to 2,421 TJ based on the experimental HHV.

The cotton stalk and wheat straw lignins totalized 114,571 t, this quantity represents an approximate total energy potential of 2,644 TJ. And this potential is equivalent to the energy that would be obtained from 80,120 t of anthracite coal.

Conclusions

The separation of the lignin from the rest of the fibers present in the cotton stalk and wheat straw`s cell wall was achieved. The lignins recovered from both agricultural wastes were physicochemically characterized, and the energy properties were determined. The quantified lignin in the cotton stalk was 22.33% and 20.83% for the wheat straw. The results highlighted that the lignins have a high heating value and a high carbon content. The wheat straw lignin has sulphur and calcium. The sulphur oxides generated from a combustion process will remain in the calcium oxides. This decreases the emission of polluting and corrosive products to the environment.

The lignin is a renewable resource that could be exploited for the energy supply through more efficient conversion systems such as the gasification or the co-combustion. Furthermore, its high energy density, compared with the source biomass, has a positive impact on the transport costs.

The amount of lignin available from wheat straw and the cotton stalk was 114,571 t, equivalent to 2,644 TJ or 80,120 t of anthracite coal. The lignin represents a renewable energy resource for the State of Baja California. However, the separation of this polymer implies processes or operations that involve additional costs. Those processes allow the obtainment of various products, which add value to the agricultural wastes and promote the economic development of the rural sector.

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