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Isolation of lignin by organosolv process from different varieties of rice husk: Understanding their physical and chemical properties

Sandip K. Singh, Paresh L. Dhepe *

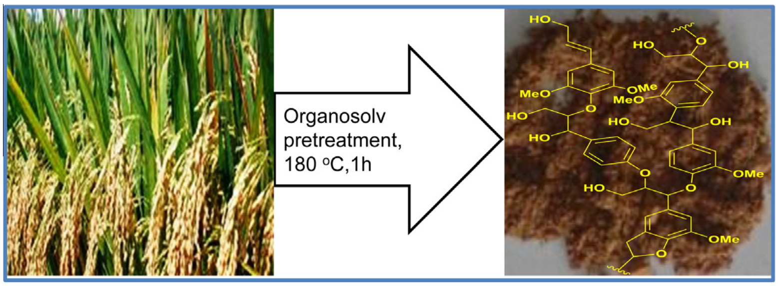
Catalysis & Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India
Academy of Scientific and Innovative Research (AcSIR), New Delhi 110 025, India

HIGHLIGHTS

- Organosolv method used to isolate lignin from 3 rice husk to understand properties.
- XRD analysis proves extracted lignin is not contaminated with polysaccharides.
- ATR and NMR revealed presence of *H*, *G*, *S* & T substructures in varying concentrations.

GRAPHICAL ABSTRACT

Organosolv lignin from 3 rice husks were isolated and studied for their physico-chemical properties.



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ABSTRACT

The aim of this work was to study the difference in properties of lignins, those (organosolv lignins (ORGLs, 12 ± 3% yield and 93 ± 5% mass balance) were isolated from diverse rice husk (RH) substrates using organosolv procedure (water:ethanol, H_2SO_4) carried out at 180 °C for 1 h. To identify the possible alterations in lignin structures several bulk and molecular level advanced characterization tools were employed. Even though lignins were extracted using common isolation procedure from three varieties of similar species of RH; from XRD, GPC, and elemental analysis it was found that those have comparable properties on bulk level. But molecular level analysis conducted using UV–vis, ATR, 1D/2D HSQC NMR techniques could help disclose that isolated lignins have varying concentrations of *G*, *H*, *S* and *T* substructures. Additionally, the double bond equivalence of 4.4–4.7 reveals that few of the aromatic rings are devoid of substituent.

1. Introduction

Due to obvious drawbacks associated with the use of fossil feedstocks (Long et al., 2013; Zakzeski et al., 2010a) for the synthesis of chemicals it is crucial to develop methods based on renewable feedstock for future chemical needs (Ragauskas et al., 2014). In view of this, the sole renewable feedstock, biomass which has several benefits associated with it such as, carbon neutrality, abundant & sustainable availability, homogeneous distribution around globe etc. can be used for chemicals synthesis (Ragauskas et al., 2006). However, in particular among all types of biomass available (plant or animal derived and edible or non-edible) in recent times, use of lignocellulosic biomass has attracted lot of attention from researchers due to its huge availability (ca. 2 × 10^6 MMT/year) (Deepa and Dhepe, 2015; Kobayashi and Fukuoka, 2013; Maki-Arvela et al., 2011) and non-edible characteristic. It is made

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* Corresponding author at: Catalysis & Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India.
E-mail address: pl.dhepe@ncl.res.in (P.L. Dhepe).

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up of polysaccharides such as, cellulose (40–50%) & hemicelluloses (15–30%) and aromatic polymer, lignin (10–25%) and is for long processed in paper and pulp industries to isolate cellulose for paper manufacture. In recent times, the cellulosic part of third generation feedstock, lignocelluloses is considered for ethanol production to trounce the food vs. fuel dispute associated with 1st and 2nd generation feedstocks (Huber et al., 2006). Moreover, synthesis of value added chemicals from cellulose and hemicellulose through several methods is a rapidly growing research area (Bhaumik and Dhepe, 2016; Corma et al., 2007; Tathod and Dhepe, 2015). Though, cellulose finds a number of applications as mentioned above, (Fukuoka and Dhepe, 2006; Hussin et al., 2014) another principal constituent of lignocelluloses, lignin is just burned to produce heat or used as an additive in cement industry (Ragauskas et al., 2014). However, in several forums it is debated that until high value added products such as fine, specialty and bulk chemicals are extracted from lignin, it would be unviable to commercialize celluloses to ethanol process and thus valorization of lignin becomes imperative for economic profitability of biorefinery (Huber et al., 2006; Kobayashi and Fukuoka, 2013). Lignin, an only naturally available aromatic polymer has a 3-D amorphous structure consisting of methoxylated phenylpropane structure in general and in particular is made up of three major units; *p*-coumaryl, coniferyl and sinapyl alcohols (Section S1, Supplementary data), connected through numerous linkages such as $\equiv$C—O—C$\equiv$ (β-O-4, α-O-4, 4-O-5 etc.) and $\equiv$C—C$\equiv$ (β-5, β-1, β-β, etc.) (Nimz, 1974; Zakzeski et al., 2010a). Up on depolymerisation of lignin facilitated by hydro (cracking), reduction, oxidation, hydrolysis, gasification reactions etc. several industrially relevant rich in functional groups (—OH, —CHO, —alkoxy etc.) low molecular weight platform and intermediate value added aromatic compounds can be obtained (Deepa and Dhepe, 2015; Singh and Dhepe, 2016). Nevertheless, compared to other bio-polymers such as starch, cellulose, hemicelluloses etc. lignin is very intricate molecule since its structure and bonding between various units varies according to plant species, age of plant, type of plant, growing conditions (temperature, humidity, soil quality, time, etc.) and most importantly isolation procedure employed for its extraction. As a result of this complexity associated with the structure, very little attention is paid towards its catalytic conversions to yield value added chemicals.

To value add lignin, in bio-refinery concept first step is to isolate lignin from lignocellulosic materials and hence quite a few methods such as, Kraft, soda, lignosulphate, hydrolysis, milled wood lignin, enzymatic, ionic liquids process etc. are developed for the isolation of lignin from lignocelluloses (Lange et al., 2013; Zakzeski et al., 2010a). All these isolation methods use varying conditions like pH, temperature, pressure, reagents, time, solvents etc. and thus these parameters strongly influence the structural and chemical properties of isolated lignin. Subsequently, these properties alter the product distribution up on depolymerisation. The most prevailing isolation method used commercially is Kraft lignin method and in this method, aqueous solution of NaOH and Na_2S are employed at 150–180 °C for 1–2 h (Chakar and Ragauskas, 2004; Mansouri and Salvado, 2006) and consequently isolated lignin is by and large contaminated with Na and S (Mª Jesus de la Torre et al., 2013). Under the employed conditions, most of $\equiv$C—C$\equiv$ linkages survive and lignin obtained has number average molecular weight (M_n) in the range of 1000–3000 Da. In a lignosulfonate method, sulphite precursors of calcium and magnesium are employed at wide range of pH. Lignin isolated by the sulphite coking process contains HSO_3^- and SO_3^{2-} ions with *Mn* of 5000–60,000 Da depending on the source of lignin whether softwood or hardwood (Belgacem et al., 2003; Mansouri and Salvado, 2006). In yet another important isolation method, organosolv (org), lignocelluloses are treated with organic solvents like ethanol or ethanol/water mixtures at mild conditions to obtain lignin with *Mn* of 1000–3000 Da. Besides these methods, several other processes like acid hydrolysis (0.2 M HCl in aqueous 1,4-dioxane), soda or soda-anthraquinone (>155 °C, >30 min), pyrolysis (450 °C), enzymatic acid hydrolysis (alkaline phosphatase) in ionic liquids, enzymatic mild acidolysis (EMAL, 3% w/v dry matter, 45 °C, 50 mM sodium acetate pH 5), steam explosion (180–250 °C, >1 MPa), ammonia fibre expansion (1–2 kg of ammonia/kg of dry biomass, 90 °C), ammonia lignin (aqueous ammonia 15% w/v, 180 °C, 20 bar, pH 2), ionic liquid dissolution etc. are known for the isolation of lignin (Kumar et al., 2009; Lange et al., 2013; Wahlstrom and Suurnakki, 2015; Zakzeski et al., 2010a). Depending on the method used for isolation, properties of lignin alter as reviewed earlier (Bharadwaj et al., 2011) and as summarized in Tables 1 and 2.

From Table 1 it is evident that with a change in isolation procedure, properties of lignin vary. Likewise, even if a same isolation procedure is applied to diverse substrates, properties of lignin alter. Therefore, identification and quantification of different functional groups and linkages present in lignin is still a substantial challenge ahead of researchers. In view of this complexity, most researchers use model compounds of lignin (dimmers, trimers) synthesized in laboratories or available commercially for demonstrating depolymerisation efficiencies of catalysts. Nonetheless, these model compounds would be devoid of any impurities (as discussed above) generated during isolation processes and thus the depolymerisation catalysts developed with these model compounds may face difficulties once applied to depolymerise real lig-

Table 1
Comparison study of lignin characteristics using same isolation process with different substrates and same substrate with different isolation processes.

	Isolation process[a]	Substrate	*Mw* (g mol^{-1})[b]	*Mn* (g mol^{-1})[c]	PDI[d]	Ali-OH[e]	Ph-OH[f]	Refs.
Same process	EMAL	Spruce	13,700	3100	4.4	3.85	0.59	Rahikainen et al. (2013)
		Wheat	3600	2000	1.8	3.78	0.66	
	Org	Wheat	1960	450	4.4	1.27	2.54	Constant et al. (2016)
		Poplar	2180	570	3.8	1.83	2.59	
		Spruce	2030	420	4.9	1.21	2.73	
Same substrate	MWL	Loblolly pine	13,500	7590	1.77	4.2	1.0	Sannigrahi et al. (2010)
	OSMWL		16,800	6530	2.57	4.7	3.3	
	EOL		5410	3070	1.77	7.3	2.7	
	OEOL	Switch grass	4200	980	4.3	2.92	1.7	Hu et al. (2012)
	OTBM		5750	1580	3.6	2.0	1.9	

[a] EMAL: enzymatic mild acidolysis process; Org: organosolv; MWL: mild wood lignin; OSMWL: organosolv mild wood lignin; EOL: ethanol organosolv lignin; OEOL: organosolv ethanol pretreatment; OTBM: organosolv treated ball milled lignin.

[b] *Mw*: weight average molecular weight.

[c] *Mn*: number average molecular weight.

[d] PDI: polydispersity index (*Mw*/*Mn*).

[e] Ali-OH: aliphatic alcohol.

[f] Ph-OH: phenolic hydroxyl group.