

LIGNIN, POTENTIAL PRODUCTS AND THEIR MARKET VALUE

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ABSTRACT

Lignin is one of the important components in the valorization of lignocellulosic biomass. Lignin-based materials and chemicals represent potential value-added products for biorefineries. Lignin products have numerous applications and can be divided into three main groups. Group, in which lignin is fragmented into smaller aromatic compounds such as phenol or benzene, toluene and xylene, is less developed than group where lignin is used as macromolecule, but has greater potential. Lignin as macromolecule is used as additive or polymer blend. Last group of lignin products are carbon materials, which include carbon fibres.

KEYWORDS: Lignin, market value, bio-economy, market, products.

INTRODUCTION

With increasing prices and exhaustion of sources of fossil fuels, the society has started to focus on alternative sources of energy and chemicals. BP p.l.c. recently released its Statistical Review of World Energy 2015 (2015) and found that consumption of fossil fuels in 2014 continued to increase. Global fuel consumption in 2014 represented million tonnes oil equivalent: 4211.1 for oil, 3065.5 for natural gas, 3881.8 for coal, 574.0 for nuclear energy, 879.0 for hydroelectricity and 316.9 for renewables. World Fossil fuel reserves-to-production ratios at end 2014 are estimated on 52.53 years for oil, 55 years for natural gas and 110 years for coal. Total proved reserves of oil are 239.8 thousand million tonnes, for natural gas 187.1 trillion cubic metres and coal reserves are estimated 891 531 million tonnes (estimate from year 2014). Biomass, thanks to its complexity, is a great renewable source of chemicals and energy. It is relatively cheap and its processing does not increase percentage of greenhouse gasses. Weight of dry biomass on Earth is estimated to $(1.85 - 2.4) \times 10^{12}$ tons. Every year $(150 - 180) \times 10^9$ tons of photosynthesis biomass is produced (Khim 1975; Blažej and Košík 1993; Rosillo-Calle et al. 2007). Global primary production can

be estimated from satellite observations. Satellites scan the normalised difference vegetation index over terrestrial habitats, and scan sea-surface chlorophyll levels over oceans. This results in 56.4 billion tonnes C/yr (53.8 %), for terrestrial primary production, and 48.5 billion tonnes C/yr for oceanic primary production (Field et al. 1998). Approximately 75 % of all biomass is composed of saccharides, and another 20 % is made of biopolymer named lignin (Rosillo-Calle et al. 2007). The total lignin availability in the biosphere exceeds 300 billion tonnes and annually increases by around 20 billion tonnes. (Gregorová et al. 2006, Rosillo-Calle et al. 2007) That makes significant amount of energy about 800 EJ, but except energetic function, lignin has many other applications.

Lignin structure

Lignin forms aromatic part of wood composites. Lignin acting like adhesive in plant cell walls holds cellulose and hemicellulose, as main parts of lignocellulose matrix, together (Zakzeski et al. 2010; Watkins et al. 2014). Important to mention is, that structure of protolignin or native lignin is still unknown. Protolignin is untreated lignin, which can be found directly in plants (Zakzeski et al. 2010). However, it is known that lignin is composed of three types of phenylpropane monomers: Coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol. These are also known as monolignols. Except these major monolignols, some other lignols may be present in smaller amounts. Percentage of components differs from plant to plant (Norgren and Håkan 2014).

Extraction processes

Extraction process used to separate lignin from lignocellulosic biomass has significant influence on the lignin structure, properties and purity. Lignin can be extracted by physical and/or chemical and biochemical methods (Ibrahim et al. 2014; Jablonský et al. 2014a; Minu et al. 2012; Mosier et al. 2005; Sun et al. 2011; Šurina et al. 2015; Tejado et al. 2007; Thakur and Thakur 2014; Toledano et al. 2010a, b). Fractionation of biomass, however, is not easy (Tab. 1).

Tab. 1: Properties of different type of lignins and their potential applications (Jablonský et al. 2014a, b, c; Vishtal and Kraslawski 2011).

Type of lignin	Mw (g.mol ⁻¹)	Polydispersity	Sulphur/Ash (%/%)	Application
Soda lignin	1000 - 3000 (to 15000)	2.5-3.5	0/0.7-2.3	Production of phenolic resins, animal nutrition, dispersants, polymer synthesis
Kraft lignin	1500 - 5000 (to 25000)	2.1-3.5	1.0-3.0/0.5-3	Fertilizer and pesticide carrier, carbon fibers, addition to thermoplastic polymers, binders, resins, activated carbon. Chemical - vanillin, hydroxylated aromatics, quinine, aldehydes and fatty acids
Hydrolysed lignin	5000 - 10000	4.0-11.0	0-1.0/1.0-3.0	Preparation of polymeric materials, dispersants, deflocculation agents
Organosolv lignin	500 - 10800	1-4.7	0.0/1.7	Additives for paints, varnishes, paints and create new substances

Lignosulfonates	1000 - 50000 (to 150000)	4.2-7.0	3.5-8.0/4.0 - 8.0	colloidal suspensions, stabilizers, dispersants, binders, detergents, adhesives and components of feed, particle board, surfactants, adhesives and additives for cements
Ionic liquid lignin	≈2000		/0.6-2.0	Chemicals
MWL	5500 - 20000	1.8-2.5	0/1.5	Chemicals
Steam explosion lignin	107000 - 19300	5.2-11.4		Chemicals such as phenols or biodiesel
Lignin pyrolyses	620-1320	1.8-2.7		Pyrolysis products, chemicals, liquid fuels

MODIFICATION OF LIGNIN

Extracted lignin can be used as an unchanged macromolecule or can be further modified. Unmodified lignin is used as additive in materials in order to improve their properties and has many other uses discussed below. On the other hand, we can modify lignin molecule, and produce various compounds (Laurichesse and Avérous 2014). Lignin can be modified in three ways: Depolymerization / fragmentation; modification of functional groups and modification of hydroxyl groups.

Depolymerization / Fragmentation

It is commonly known that lignin is possible source of low molar mass compounds. As fossil sources of these compounds are running out and also their price is rising, focus of the science is on the renewable sources of chemicals (Laurichesse and Avérous 2014). Different processes of fragmentation of lignin have been studied; these are shown in the Fig. 1, where we can also see some products of these methods.

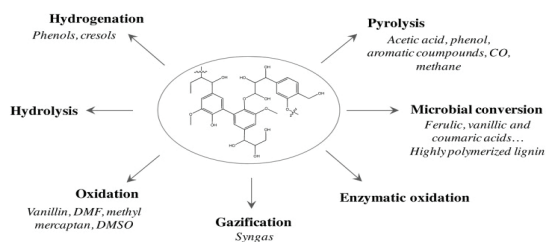


Fig. 1: Fragmentation methods of lignin and their potential products (Laurichesse and Avérous 2014).

Significant are products of oxidation, which are today commercially produced. Pyrolysis produces liquid also known as bio-oil, also it produces phenol and acetic acid. Market prices of these pyrolysis products are displayed in Tab. 4. Next fragmentation process used to produce low mass compounds is oxidation. Well-known lignin product, vanillin, is produced this way. Also it gives chance to obtain phenolic derivatives. Yield of products, in this case aldehydes and acids, depends on the oxidant. Usually used oxidants are nitrobenzene, metallic oxides, air and oxygen. These protect aromatic rings and form various aromatic compounds including vanillin, vanillic acid, syringic acid and aldehyde, hydroxybenzaldehyde and others (Laurichesse and Avérous 2014; Vishtal and Kraslawski 2011; Zakzeski et al. 2010). Some products of oxidation and their

price range is shown in Tab. 4. Other processes as hydrogenation, hydrolysis and microbial conversion are used to transfer lignin to high-valued chemicals. Also, using gasification, syngas can be produced from lignin. Significant are products of microbial conversion, such as vanilic acid (Laurichesse and Avérous 2014). Price of this acid and other products is shown in the following Tab. 2.

Tab. 2: Fragmentation methods, their products and their price.

Fragmentation methods	Product	Price (USD/MT)	Note
Pyrolysis	Acetic acid	350-750	*1, *2
	Phenol	1000-2000	*2, *3
	Methanol	350-500	*3, *5
	n-Propanol	1800-2300	*1
Oxidation	Vanillin	15-40 USD/kg	*1
	DMF	800-1000	*1
	DMSO	1-5 USD/kg	*1
	Syringic acid	10-100 USD/kg	*1
	4-Hydroxybenzaldehyde	9500-11100	*1
Microbial conversion	Vanillic acid	15-80 USD/kg	*1
	Ferulic acid	10-100 USD/kg	*1
	p-Coumaric acid	10-100 USD/kg	*1

*1 – www.alibaba.com, *2 www.sunsirs.com, *3 www.apic2014.com, *4 www.methanex.com.

Modification of functional groups

Hydroxyl, methoxyl, carbonyl and carboxyl groups are lignin functional groups. These groups can be improved to increase their application range (Jablonský et al. 2014c). Methoxyl group is processed in Tab. 3, where we can also see content of elements and ash.

Tab. 3: Elemental analysis, ash content and higher heating value of lignins, and content of methoxyl groups (Jablonský et al. 2014c, 2015).

Samples of lignin isolated with	N (%)	H (%)	S (%)	C (%)	Ash (%)	HHV (MJ.kg ⁻¹)	OCH ₃ (mmol.g ⁻¹)
H ₂ SO ₄ , pH 5	1.13	5.52	1.04	57.41	6.93	23.34	13.5
H ₂ SO ₄ , pH 4	1.13	5.5	1.31	57.61	-	23.42	
H ₂ SO ₄ , pH 3	1.14	5.5	1.68	57.88	6.81	23.53	13.1
H ₂ SO ₄ , pH 2	1.09	5.36	1.87	56.49	4.64	22.97	13.8
HNO ₃ , pH 5	2.14	5.63	0.0	57.53	-	23.39	
HNO ₃ , pH 3	1.85	5.91	0.01	62.06	1.91	25.23	15.2
HCl, pH 5	1.2	6.03	0.03	63.24	1.31	25.71	15.7
HCl, pH 3	1.20	5.72	0.01	58.69	2.13	23.86	15.8
CH ₃ COOH, pH 4.3	1.21	5.93	0.00	62.48	5.99	25.40	14.0
Kraft lignin Bukóza	0.28	4.62	3.91	55.68	3.85	23.62	11.1

Many modification pathways have been investigated and so far, the most known is process of alkylation or dealkylation, because demethylated lignins are by-product of DMSO production. Also formaldehyde-free wood adhesives have been developed using dealkylation processes. Next department that uses lignin as substitute to fossil chemicals is phenolic wood production. Lignin

is used in synthesis of phenol-formaldehyde resins and some other adhesives (Gonçalves and Benar 2001). After substitution, lignin-phenol-formaldehyde (LPF) resin is produced. Varying reaction conditions and formaldehyde/lignin ratio produces LPF's with different properties. Lignin active sites can be modified by amine alkylation provided by Mannich reaction (Arend et al. 1998). Products of this reaction have two main applications; first they are used as cationic surfactants, and second preparation of composites that improve properties of PVC/wood-floor composites. In non-aqueous solvents with nitrating agents, nitrolignin is formed. It is amorphous powder with 6-7 % of nitrogen content (Zhang and Huang 2001). Nitrolignin was successfully used in synthesis of graft interpenetrating polymer networks from polyurethane (Laurichesse and Avérous 2014).

Phenolic hydroxyl groups have significant effect on reactivity of the material, because they are the most reactive functional groups. Modification of these groups is key step to improve lignin's solubility (Bouajila et al. 2006). Different types of lignins have different amount of phenolic hydroxyl groups and comparison of particular lignins is summarized in Tab. 4 (Jablonský et al. 2014b, c, Šurina et al. 2015).

Tab. 4: The content of non-conjugated, conjugated and total amount of phenolic hydroxyl groups for lignins (Jablonský et al. 2014b, c, Šurina et al. 2015).

Samples of lignin	Non-conjugated phenolic structures (I+III) (mmol.g ⁻¹)	Conjugated phenolic structures (II+IV) (mmol.g ⁻¹)	Total amount of phenolic hydroxyl groups (mmol.g ⁻¹)
Lignin (H ₂ SO ₄ , pH 3)	2.24	0.31	2.55
Kraft lignin Bukóza	3.13	0.39	3.52
Lignin (HNO ₃ , pH 3)	2.20	0.23	2.43
Lignin (CH ₃ COOH, pH 4.3)	1.30	0.16	1.46
Lignin (HCl, pH 3)	1.33	0.18	1.52

One way to modify hydroxyl groups is esterification. Esterified lignins are mainly used in the synthesis of polyesters, elastomeric materials and epoxy resins. Process where lignin reacts in acidic medium with phenol is called phenolation. This process is used in phenol-formaldehyde synthesis. Using etherification lignin can be transferred to in organic solvents soluble polyol. Polyols can be potentially used to produce new materials as lignopolyols (Ahvazi et al. 2011; Thielemans and Wool 2005), polyurethane foams or epoxy resins (Laurichesse and Avérous 2014).

LIGNIN MARKET VALUE

Lignin as part of biomass is renewable source of chemicals and other products. This is one of the reasons why lignin has relatively stable prices through the years and seasons. Price range starts with low purity lignin, with wide range 50-280 USD/MT, and is closed with high purity lignin, which price can go up to 750 USD/MT. In between are other kinds of lignins such as lignin from Kraft process with market value about 260-500 USD/MT and lignosulphonates starting as low as 180 USD/MT and ending at 500 USD/MT. From sulphur-free lignins is cheaper soda lignin with price range of 200-300 USD/MT. Organosolv lignin has little higher price with start at 280 USD/MT on end at 520 USD/MT (*1), (Gosselink 2011).

LIGNIN AS SOURCE OF AROMATIC COMPOUNDS

The interesting part of lignin is that it can be broken down in to several building blocks and from reduction of them the primal substances as benzene, toulene, xylene and phenol can be produced.

Benzene, toluene and xylene

Benzene, toluene and xylene (BTX) have large-scale of applications. Therefore it has great potential in chemical industry. Lignin-based BTX is similar to BTX from petroleum and so can be used as a replacement for it. BTX represents 60 % of all aromatics on market and 24 % of the global petrochemical market (Smolarski 2012). Today market value of BTX and their derivatives is shown in Tab. 5. Products with bubbles that have location higher on Y axis have better potential for development of new production technologies. Every product in the Fig. 2 is represented by a bubble, which displays minimum and maximum price of the product on the market in 2014. As the area of the bubble is bigger, the price range is higher for the product. Bubbles with larger areas represent products with unstable market prices. This is a consequence of different production methods and costs of the production technology of the product. Higher bubble positions on the Y axis and the smaller diameter creates a greater potential for the development of technologies based on lignin.

Tab. 5: Prices of benzene, toluene, xylene and their derivatives.

Chemical / Price	Derivative	Price (USD/MT)	Note
Benzene (800-1200 USD/MT) *5, *6	Cumene	1000-1500	*7
	Styrene	1300-1700	*7,*8
	Adipic acid	1300-1700	*1
	Caprolactam	1500-2000	*1
	Cyclohexanone	1500-2200	*1
	Cyclohexane	1500-3000	*1
Toluene (700-1200 USD/MT) *2	Benzoic acid	1000-1500	*1
	Toluene diisocyanate	2000-2700	*1, *8
Xylene (800-1500 USD/MT) *9	Isophthalic acid	1600-2200	*1
	Terephthalic acid	500-1100	*10

*1 www.alibaba.com, *2 www.sunsirs.com, *5 www.platts.com, *6 www.globalrubbermarkets.com,
*7 www.chemweek.com, *8 www.icis.com, *9 www.osterman-co.com, *10 www.platts.com,
*11 www.plasticnews.com.

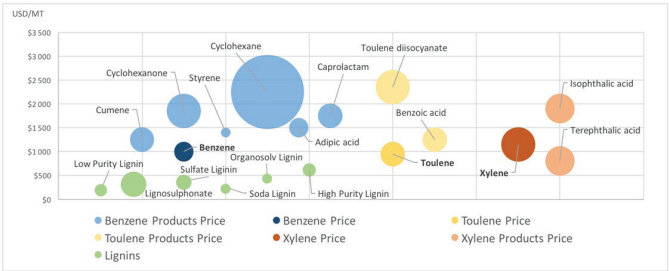


Fig. 2: Comparison of price different products and lignins. Individual bubbles represent minimum and maximum price of compounds.

Phenol

Phenol is important in plastics production and other materials. Main applications of phenols are in production of phenol-formaldehyde resins, polyurethane foams or polyurethanes for automobile industry. Today market value of phenol is approximately 1000 – 2000 USD/MT (*2). In 2012 annual production of phenol reached 8 million tonnes. Main advantage of production phenol from lignin is that nowadays phenol prices are depending on oil prices. Lignin as part of renewable source has relatively stable market value (Smolarski 2012). Phenol has many derivatives and some of them and their prices are shown in Fig. 3. Price of nitrophenols represents p-nitrophenol and aminophenols, cyclohexanone and bisphenol (*1).

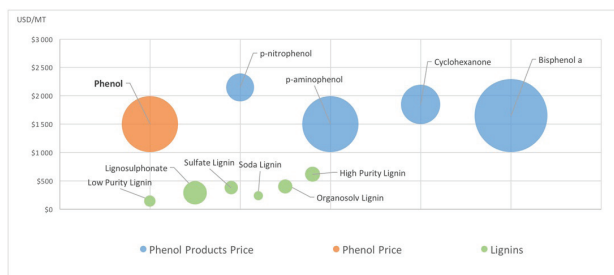


Fig. 3: Price of phenol and its derivatives in comparison with lignin prices. Individual bubbles represent minimum and maximum price of compounds.

Vanillin

Vanillin is well-known product of lignin treatment. Commercially has been vanillin produced for almost 80 years. But today only 20 % of vanillin on market is produced from lignin and other 80 % is produced from crude oil. Market value of vanillin depends on the source. Highest price has natural vanillin produced from Madagascar vanilla. Vanillin from lignin and crude oil have similar prices and on the market their value is according to Smolarski approximately 12 000 USD/MT (Smolarski 2012). Other sources report price in USD per kilogram and it is somewhere between 15-40 USD/kg (*1). For natural vanillin it is about 600 000 USD/MT (Smolarski 2012).

LIGNIN AS A MACROMOLECULE

Polymer blends

Unmodified lignin does not have properties to be used as material. On the other hand it can be blended with other synthetic or bio-based polymers. Lignin usually acts like UV degradation stabilizer or thermo-oxidation stabilizer. This functions lignin fulfils if it is blended with polyethylene, polystyrene, polypropylene or natural rubber (Lawoko and Duval 2014).

Adsorbents from lignin

Lignin has potential to adsorb heavy metals ions. This fact leads to studies about lignin as potential adsorbent for wastewater purification. Main role in sorption process play phenolic hydroxyl groups. Lignin's adsorption has been studied against chromium, cadmium, lead, zinc, nickel, mercury and cobalt (Lawoko and Duval 2014).

Hydrogels

Biopolymeric hydrogels are one of the most popular materials for biological, biomedical and environmental applications (Liang et al. 2013; Karaaslan et al. 2010; Thakur and Thakur 2015). Hydrogels are polymer-based networks with ability to absorb water or other solvents up to thousands of times their dry weight without being dissolved. They consist of many hydrophilic groups. The size of hydrogels depends on the amount of swelled water and synthesis methods. Properties such as swelling ratios or water uptake differ with different type of lignin. Interesting is that some properties of hydrogels are very similar to living tissues. Lignin as biorenewable polymer has the potential to be used as starting material for natural polymer-based hydrogels. Many applications are known; for example, hydrogel polymers are used in water purification process, biomedical field, drug delivery devices and some other (Thakur and Thakur 2015; Upadhyaya et al. 2014)

Phenol-formaldehyde resins

Synthetic polymeric materials that have great heat and moisture resistance and strength. They have been introduced to market in early twentieth century. And since then they have been used in numerous fields. In industry as wood bonding, insulation, lamination or plywood adhesives. They are also used in electronics, airspace or railway, not forgetting building and construction industries. In 2010 was phenolic resin market valued at 10 billion USD, with annual value from 4.5 to 6 billion USD. In PF resins production phenol can be substituted with lignin. This substitution could improve effect of this industry on global warming issue. The reason why lignin isn't commercially used for PF resins production is that yield does not cross 50 %. This fact is caused by lignin's complex structure. Reactivity of lignin can be improved by various modifications such as phenolation or methylation. The market price of PF-resins is somewhere between 1100 to 2300 USD/MT (*1). Price, of course, may be higher or lower, that depends on the purity, quality and application of final resin.

CARBON MATERIALS

Lignin consists of about 50-60 % of carbon. It can be directly used as a precursor for carbon materials. Interesting applications are activated carbons and carbon fibers.

Activated carbons

They are great adsorbents of organic and inorganic substances. They can be used both for liquid or gaseous phase. Different activated carbon materials are characterized by surface area and the size of pores. Also carbon black has been produced from lignin. Carbon black is used as pigment and tire additive (Lawoko and Duval 2014). Market price of activated carbon materials depends on properties and application. Activated carbon used for water purification has price around 1500 USD/MT [79]. Price of activated carbon with surface not smaller than 900 m².g⁻¹ starts at 500 USD/MT and can rise up to 2500 USD/MT (*1). Price of final products as carbon filters is as high as 35 000 - 62 000 USD/MT (*1).

Carbon fiber

Carbon fibers are very valuable composite material. It is based on their properties such as low density, but extreme strength and stiffness (Lawoko and Duval 2014). Carbon fibers already have wide range of applications, and it is increasing. Forecasts say, that demand for carbon fibers will

be 140 000 tonnes by 2020. The problem is price of carbon fibers; industry is not willing to pay more than 7 - 11 USD/kg. Today prices of carbon fibers for automotive industry is somewhere between 18-26 USD/kg (*11). The main cause of high price is, that precursor for carbon fiber is polyacrylonitrile (PAN). And it makes 50 % of all production costs. There comes lignin's chance to make production cheaper. Lignin can be used as alternative to PAN and therefore make the process a lot cheaper. Applications include civil engineering, automobile industry, aircrafts and sport goods (Smolarski 2012).

SUMMARY

Collected information about market values and prices from earlier chapters are summarized in Fig. 4. Brown coloured bubbles in chart represent price ranges of lignins obtained by different processes. It is obvious that different type of preparation and isolation techniques makes differences between lignin prices. A wide range of lignin prices from 50 to 750 \$ makes it suitable for further use. To these prices we compare price ranges of several potential lignin products and their derivatives, such as benzene and its derivatives. According to Tab. 1 phenol-formaldehyde resins are produced from soda lignin. Price of soda lignin is somewhere around 250 USD/MT, therefore production of PF resins with price starting at 1100 USD/MT would be very efficient. Similar results we can see with phenol or activated carbon materials. However production of methanol as primary product from lignin would probably not make high profit.

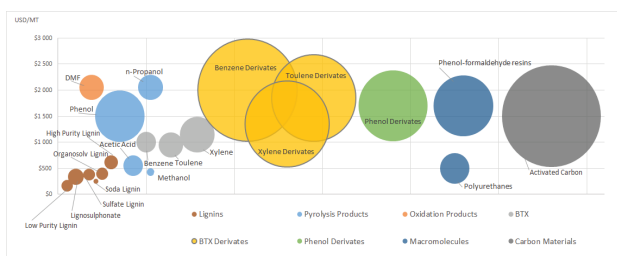


Fig. 4: Price of lignins and potential products and their derivatives I. Individual bubbles represent minimum and maximum price of compounds.

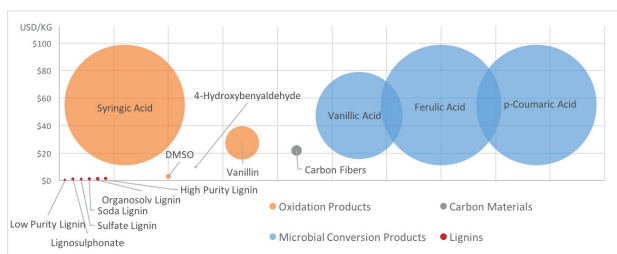


Fig. 5: Price of lignins and potential products and their derivatives II. Individual bubbles represent minimum and maximum price of compounds.

Lignin products with higher prices, which are available in USD/kg are displayed in chart below in Fig. 5. Production of these substances is very efficient. Carbon fibers for example have many applications but their actual price on market is too high for industry. Carbon fibers

produced from lignin could have lower price and could be therefore used in industry more often.

Not all products have potential for high profit, on the other hand lignin prices are usually stable, and that makes lignin better substance for further processing than are the fossil fuels. Because fossil fuels have unstable prices, which are constantly increasing and therefore prices of final products are still changing.

CONCLUSIONS

Lignin is interesting part of biomass and it is considered a biodegradable renewable source of energy and chemicals. Green chemistry department is daily researching new ways to utilize lignin's role in industry and material chemistry. Lignin's ability to be source of aromatic compounds has the greatest potential to become an essential substance in the future, because in some ways it can substitute for fossil fuels as source of these chemicals. Lignin already has several applications; however these do not have high market value in comparison with aromatics or carbon materials, such as carbon fiber, which can also be produced from lignin.

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