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Name and address of patentee(s):

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Title of invention:

A METHOD FOR LIGNIN EXTRACTION FOR BIOENERGY APPLICATIONS

Name of inventor(s):

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Term of Patent:

Eight years from 30 July 2021

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Physiochemical characterization and thermal kinetics of lignin recovered from sustainable agrowaste for bioenergy applications

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Highlights

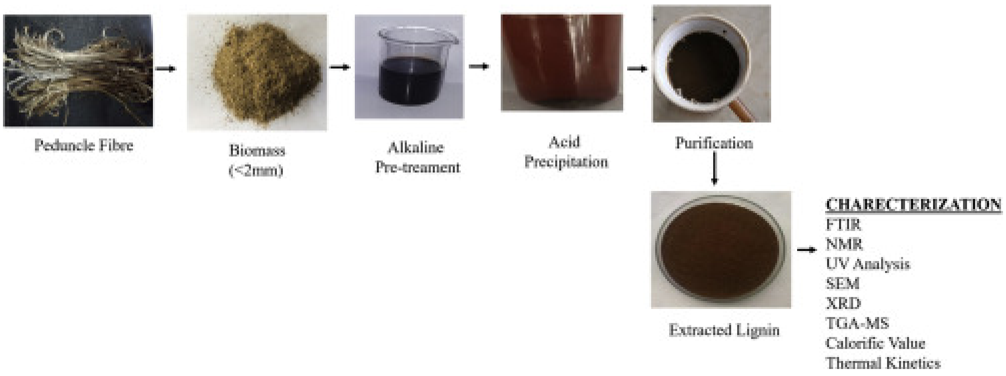
- Banana peduncle used as renewable source of lignin and potential source of energy.
- Extracted lignin showed characteristics of herbaceous lignin.
- Morphological analysis showed high surface area, hollow spherical structures.

- Calorific value of 21.43 MJ/kg of extracted lignin equivalent to sub-bituminous coal.

Abstract

In this study, lignin, one of the commonly occurring natural polymers, is extracted from banana agro-waste. Lignin is recovered from the spent liquor produced during alkaline pre-treatment of agro-waste and precipitated by acidification. This study focuses on the physio-chemical characterization and thermal degradation behaviour of lignin extracted from agro-waste biomass. The extracted lignin yield accounts for nearly 12% of the biomass composition. Spectral analysis, FTIR and NMR explain purity and carbon skeleton characteristics of herbaceous lignin monomers, majorly G and S units. Morphological analysis by SEM showed hollow spherical structures with large surface area for the extracted lignin. The calorific value of extracted lignin was experimentally found to be 21.4276 MJ/kg, which suggests the possible use of extracted lignin as an alternative to sub-bituminous coal. Thermal studies of lignin showed that lignin degrades in a wide temperature range releasing CO_2, CH_4, H_2O, CO and H_2. The volatile content of extracted lignin is found to be 31.42%, which suggests its possibility for gasification process. The overall outcome supported that recovered lignin from agro-waste is a potential resource for bioenergy.

Graphical abstract



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Introduction

On following a linear economy for above 150 years, a one-way approach of production, consumption and disposal has been realized to be an unfavourable choice for sustainable future. Transition to circular economy develops a sustainable society as per its key principles; valorisation of waste and by-products, minimization of disposal, dematerialization of economy and reduced energy dependence on fossil hydrocarbon. One of the major moves to achieve circular economy is to replace fossil resources with potential lignocellulosic resources from various primary (field-based) and secondary (processing based) sources.

Agro-residue is assumed to be an energy derivable source contributing to sustainable energy generation [1]. Agriculture is the largest sector in the world economy, contributing 1/3rd of global GDP and 26.81% of global employment and 38.14% of land area. In India, over 600 million tons of agricultural residues are produced every year [2]. These include field waste, animal waste and agro-industrial waste. Primary and secondary crop wastes mainly comprise of stalks, cob, straws etc. which contains energy rich constituents that could meet the energy demands [3].

In the year 2017, approximately 5.6 million hectares of land are under banana production globally, producing 20.20 tons/ha of banana fruit yearly. The banana plantation generates residues such that the ratio of crop residue to product is 2.13:1 [4]. The non-edible fractions generated in these farms are managed in many countries by mass burning, disposing at field, open dumping and discarding into water bodies [5]. These result in loss of nutrients. The impact of this on soil and water properties has been studied elsewhere [6]. However, the major ways of reuse of biomass are in fodder, briquetting, biogas/composting, domestic fuel, textile, paper, cutlery, bedding material, roofing etc. Agricultural residues for advanced techniques are also been studied in the form of biochar for application in effective composting and as additives in concrete piles [7], synthesis of porous graphitic biochar in removal of organic pollutants [8], biosorbents for pesticide removal [9] etc.

But an effective utilization of biomass is limited, as major portion of lignocellulosic biomass fails to meet the quality standards for its commercialization due its complexity in structure in the form of cellulose, lignin, hemicellulose and extractives. Lignin is a major barrier for effective utilization of crop biomass. Difficulty in commercialization of biomass is that lignin increases the fibre indigestibility in cattle when used as fodder [10], inhibition in fermentation as well as accessibility to cellulose in bioethanol production [11], yellowing of products in paper and pulp industries [12] and hinder the spinning process in textile industry [13]. These limitations can be resolved by pre-treatment for delignification prior to utilization.

Delignification can overcome the recalcitrance of feedstocks efficiently and thereby increases the porosity of the biomass. Various pre-treatment technologies such as physical (mechanical or ball mill), chemical (alkali/dilute acid/ionic liquid), biological (enzymatic) and physicochemical (microwave, ultrasound along with chemical treatment) techniques remove most of the lignin along with some amount of hemicellulose from the biomass. The lignin can be removed by extraction as well as by degradation.

Alkaline pre-treatment methods solubilise most of the lignin from biomass into the solution due to its affinity to lignin than to other components. It can be carried out under milder condition of temperature, pressure [14,15]. This is due to the fact that, under acidic conditions, that are typically utilized during the organosolv and acidic pre-treatment process, limited lignin selectivity is observed due to the acidic hydrolysis of the cellulose component [16]. Similarly, the acidic conditions catalyse lignin depolymerization simultaneously with condensation reactions that can also limit lignin extraction. Acid conditions also concurrently produce inhibitory products such as furfurals, aromatic acids, and ketones which makes it a less attractive method [17]. In fact, variation in the structure and composition of lignin among different plants is considered to determine the selection of extraction technique. Alkaline treatment is more effective for delignification of herbaceous biomass [18]. Among various alkaline solvents, sodium hydroxide is considered to have high reaction rate, less solvent concentration under low temperature and pressure [18,19]. Sodium hydroxide cleaves the dimer containing syringyl units more rapidly than guaiacyl dimers. ie, lignocellulosic biomass containing more syringyl unit can be delignified under higher pH.Lignin-carbohydrate complexes of herbaceous plants contains ferulic bridges between lignin and carbohydrate. Ferulic acid attached to lignin with ether linkage and to carbohydrate with ester linkage, which can be easily cleaved by alkali [19]. Thus, alkaline treatments are highly selective for lignin separation, and pulping process of herbaceous plants and it can be used to extract large fraction of lignin with relatively high purity.

In this paper, non-edible banana agro-waste in the form of powder is treated in alkaline medium, to extract lignin from biomass leaving a cellulose rich residue. NaOH solution breaks the bonds, and then lignin fraction dissolves in the solvent, forming black liquor [20]. Lignin is recovered from the black liquor by acid precipitation. Physicochemical characterization and thermal kinetics of extracted lignin, using Friedman's method is used to derive the kinetic parameters like activation energy using TGA data is investigated.

Section snippets

Theory

The thermal degradation of lignin is a complex process because of the presence of aliphatic and aromatic monomers. The single component decomposition may occur in parallel with each other or in successive paths during the thermal decomposition. Therefore, an overall pyrolysis reaction mechanism [21] can be expressed asLignin $_{(Solid)}$ → Volatiles $_{(Gases)}$ +Oil$_{(Liquid)}$+Char $_{(Solid\ residue)}$

The conversion of lignin into product is assumed to be a single step process. Therefore, according to Arrhenius …

Materials and methodology

In this study banana peduncle from organic farm was selected as lignocellulosic biomass and processed as reported in our previous study [2]. The banana peduncle was dried in direct sunlight for initial drying, then powdered using mechanical grinder (Bajaj GX-1500) and sieved using 40-mesh size. 4g of sieved biomass was incubated with 150mL, 0.8N NaOH under 60°C for 2h at

100rpm. After reaction, the slurry was filtered through a Whatman filter paper. The dissolved lignin is precipitated…

Results and discussion

The extracted lignin yield accounted for 11.83±1.8% of the biomass composition and 78.76% of the total lignin in biomass. Proximate analysis showed moisture (8.38±1.56%), ash (1.98±1.81%), fixed carbon (11.75±2.51%) and volatile matter (77.89±2.32%). Ultimate analysis based on weight % showed C (37.27%), H (5.15%) N (1.61%), S(1.34%) and O(54.61%). The biomass consisted of cellulose (43.02±2.36%), hemicellulose (23.65±6.22%), lignin (15.07±1.37%) and extractives (6.23±2.6%).…

Summary and conclusions

In this work, thermal characteristics of lignin extracted from banana agro-waste by alkaline pre-treatment, followed by acid precipitation were studied. The extracted lignin yield accounted for 11.83±1.8% of the biomass composition. The lignin purity was studied by UV spectroscopy. Spectral analysis, FTIR and NMR showed characteristics of herbaceous lignin monomers majorly G and S units. Morphological analysis by SEM showed high surface area, hollow spherical structures for the extracted…

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