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# Solvothermal conversion of spent aromatic waste to ethyl glucosides

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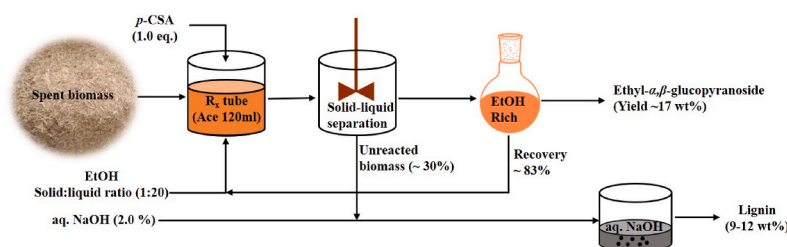
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## HIGHLIGHTS

- A *solvothermal* approach for production of ethyl glucosides from spent aromatic waste.
- Xylose and lignin were obtained as co-products.
- *p*-Cymene-2-sulphonic acid (*p*-CSA) in ethanol was used as a reaction media.
- Ethyl- $\alpha,\beta$ -glucosides obtained in good yields (~17%) under the optimized condition.
- High selectivity in product formation with no side products and black tar.

## GRAPHICAL ABSTRACT



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## ABSTRACT

On-farm extraction of commercially important essential oil from aromatic crops generates huge spent aromatic waste. This massive waste is often disposed in the unregulated landfills or burned in the open air to vacate the fields. Hence, a new method for processing of aromatic spent waste has been developed to obtain platform chemicals, such as, xylose and ethyl glucosides. The thermochemical liquefaction of acid pre-treated palmarosa (*Cymbopogon martini*) biomass furnished a mixture of ethyl glucopyranosides in good yield (~17 wt% relative to biomass) and selectivity (~77%) by heating with *p*-cymene-2-sulphonic acid (*p*-CSA) in the presence of ethanol as a solvent. The detection, quantification and isolation of ethyl glucosides may provide a new application of spent aromatic biomass for use as a feed stock in the production of value added chemicals.

## 1. Introduction

The plants belonging to genus *Cymbopogon* (Family- Gramineae) are cultivated around the world for their commercial essential oils useful to cosmetics, pharmaceuticals, and perfumery (Dwivedi et al., 2018a). The lemongrass species, such as *Cymbopogon flexuosus* and *C. citratus*, are currently under a large scale cultivation in the Congo, Republic of Madagascar, and the Comoros Island (Avoseh et al., 2015). *Cymbopogon* species are widely cultivated throughout the Asia, Africa, and America

due to their speciality to grow in the moderate to extreme temperature conditions (Thakker et al., 2016a, 2016b; Singh et al., 2017). On-farm extraction of aroma oil from *Cymbopogon species* results in the generation of spent waste which currently have very limited applications. Major portion of spent waste is disposed in landfill or left for a natural way of biodegradation while a handful of this is burned to generate steam during the essential oil extraction from the plants. Open burning of spent aromatic waste may cause the environmental pollution due to the release of gases (e.g., CO<sub>2</sub>, CH<sub>4</sub>, CO, etc.), particulate matters (PM),

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aerosols, organic carbon, black carbon, etc., into the atmosphere (Singh et al., 2020).

High calorific value and a good composition of natural polymers (cellulose, hemicellulose, and lignin), make spent aromatic waste a suitable feedstock for conversion to variety of the value added chemicals (Yadav et al., 2013). Earlier, it has been investigated for the production of bio-ethanol through the microbial fermentation, wherein, the volatile residues (e.g., monoterpenes, limonoids, etc.) have been cited for posing inhibitory effects on *Saccharomyces cerevisiae* progression (Helal et al., 2006). Fuel fungible properties of the volatile constituents occurring in lemongrass oil has also been evaluated (Alagumalai, 2015). Other reports on spent waste involve, studies on improvement of soil productivity, nutrients availability, recycling, and recovery of fertilizer components (Saha et al., 2019), and conversion to value added chemicals (Singh et al., 2019), e.g., levulinic acid, 5-(chloromethyl)furfural (CMF), monosaccharides, 5-(hydroxymethyl)furfural (HMF), etc.

Alkyl glucosides represent an important class of non-ionic compounds that exhibit excellent surfactant properties. Owing to their low toxicity, biodegradable nature, and benign environmental character, these bio-based molecules are widely used as the emulsifiers in variety of cosmetics, food, and pharmaceutical products (Li et al., 2019). In general, the alkyl glucosides are synthesised from sugars and higher alcohols via the Fischer glycosidation (Aronow et al., 2019) in presence of acids as catalyst. Earlier, a variety of acids such as HCl, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, NH<sub>2</sub>SO<sub>3</sub>H, C<sub>7</sub>H<sub>7</sub>SO<sub>3</sub>H, etc., have been tested for conversion of sugars to alkyl glucosides at high temperatures (200–280 °C) and pressure (3–5 MPa) by using a stainless steel reactor (von-Rybinski and Hill, 1998; Hughes and Lew, 1970; Deng et al., 2011). However, corrosion effects of homogeneous acids, high cost of the materials used for the construction of the reactors, non-selectivity of products, gypsum formation during neutralization after reaction with H<sub>2</sub>SO<sub>4</sub>, and formation of inhibitory by-products are some potential drawbacks (Ma et al., 2017). In addition, the metal impurities, coloured side products, etc., often pose difficulty in product purification from reaction matrix. Moreover, the progress of such technologies is greatly hindered by high product price, low recovery, and recyclability. Other methods, e.g., Koenigs-Knorr reaction (Singh and Demchenko, 2019), ketal alcoholysis (Adero et al., 2018), use of tin tetrachloride (Konstantinovic et al., 2001), etc., have the limited industrial applications due to a complex chemistry and requirements, e.g., expensive metal catalyst, excessive solvents, etc. Some auxiliary synthesis methods, such as ultrasonic and microwave-assisted synthesis (Richel et al., 2011) in presence of catalysts, e.g., phosphomolybdic acid, NaHSO<sub>3</sub>·H<sub>2</sub>O, ionic liquids (Saito et al., 2018), etc., with high reacting efficacy have also been prospected.

In recent years, the biomass liquefaction in presence of solvents under mild temperatures (~150–200 °C) has greatly attracted the chemist and technologists (Marinkovic and Estrine, 2010; Seguin et al., 2012; Hausser et al., 2013). Earlier, Ma et al. (2017) reported an acid catalysed liquefaction of bamboo biomass in ethanol to afford alkyl-xylosides/glucosides as product. However, conversion of raw biomass under such a short reaction period may instigate an early decomposition of hemicelluloses before the cellulose, thus, results in a low selectivity of products. Ethyl xylosides are formed predominantly while ethyl glucosides are obtained as minor due to a partial breakdown of cellulose. One wise way to increase the selectivity in product formation is to overcome the biomass recalcitrance factors, such as cellulose crystallinity and lignin. Various physical and chemical methods, e.g., milling, energy irradiation, steam expansion, use of acids, NaOH, urea, ionic liquids, etc., have been prospected. Biological pre-treatment, such as the application of ligninolytic enzymes has also been reported (Baruah et al., 2018). Earlier, we investigated a green approach for conversion of spent aromatic biomass to levulinic acid (Singh et al., 2019) by the action of *p*-cymene-2-sulphonic acid (*p*-CSA). However, the process was limited due to essentiality of a mineral acid as reaction media for an efficient *in situ* conversion of glucose to levulinic acid.

The compound *p*-CSA is a promising non-foaming, biodegradable,

and recyclable biogenic equivalent of petrochemical derived *p*-toluenesulfonic acid (PTSA). It can readily be synthesised directly from *D*-limonene as a renewable feed stock from citrus fruit waste (Dwivedi et al., 2018b) under an atom economical approach. *p*-CSA is soluble in various organic solvents and water, thus, can mimic the PTSA as a catalyst in most of the organic transformations. It is benign environmental and produces less corrosive and toxic effects compared to the mineral and other organic acids. Therefore, the use *p*-CSA in biomass processing can reduce the potential waste production and dependence on fossil fuels for production of efficient chemicals.

This manuscript describes a green and efficacious protocol for liquefaction of spent aromatic waste by reaction with *p*-CSA in ethanol to afford a mixture of ethyl glucosides as product in good yields and selectivity. Also, *D*-xylose and lignin are obtained as the co-products during the processing of the biomass to alkyl glycosides. To the best of our knowledge, very limited efforts so far have been made to valorise this abundant spent waste. Additionally, in compared to the traditional processing methods that result in a single product (either furfural or ethanol), application of the approach describe herein, may enable an easy access to multiple economic products from lignocelluloses.

## 2. Experimental

### 2.1. Materials and methods

Oven dried glassware (1 h at 100 °C) were used to run the reactions. Standards of ethyl- $\alpha$ -D-glucoside (EAGP) and ethyl- $\beta$ -D-glucoside (EBGP) procured from Carbosynth Limited, UK were used in calibration studies. All reagents and solvents, such as, monosaccharides, carboxylic acids, and ethanol, were purchased from Sigma Aldrich (Merck). Silica gel coated aluminium plates were obtained from MP Biomedicals, USA for Thin Layer Chromatography (TLC). Detection and quantification of liquid products, such as, xylose, glucose, arabinose, carboxylic acids, etc., was carried out using Agilent Hi-Plex H column (300 mm length; 8 mm porosity) in a HPLC system (Agilent, Model 1260). XRD analysis (Panalytical X'PERT PRO) was carried out to determine the crystallinity of lignin at scattering angle (2 Theta) versus intensity, step size 0.001°, working voltage 45 kV with a Cu K $\alpha$  Ni-filtered radiation ( $\lambda = 1.5406 \text{ \AA}$ ). IR analysis was carried out on a FT-IR spectrophotometer (Agilent Technologies Cary 600) to establish the functional groups in the isolated lignin samples. EDS analyser (Model XFlash-6130, Bruker) was used to establish the elemental composition of the lignin after plating with gold, working voltage 0–5 keV.

### 2.2. Preparation of biomass

Aromatic spent waste was obtained from Center of Innovative and Applied Bioprocessing (CIAB) farm, Mohali-140,306, Punjab, India. The waste was shade dried till the moisture content reached <7 wt%. Grinding of the shade dried material with a commercial grinder furnished the pieces of biomass in reduced size (~0.5 mm, 30 mesh). Laboratory analytical procedures of National Renewable Energy Laboratory (NREL) were followed to determine the carbohydrates and lignin (LAP 009), ash (LAP 005), and moisture content (LAP 012).

### 2.3. Biomass pre-treatment

The grounded spent biomass was reacted with the Brønsted acid, *p*-CSA (Dwivedi et al., 2018b), following the method reported in literature (Singh et al., 2019). Filtration of the hydrolysate with a muslin cloth provided the unreacted solid fibres which after usual workup, such as, washing and drying steps, furnished the pre-treated biomass in dry form.

### 2.4. Production of ethyl- $\alpha$ - and $\beta$ -glucopyranosides

A high pressure glass tube (120 mL, Ace Glass, USA) containing

ethanol (20 mL), and *p*-CSA (1.0 g) was loaded with pre-treated biomass (1.0 g). After complete loading, the glass tube was sealed with a silicone stopper followed by refluxing at 180 °C for 5 h. After completion, the heating was terminated, and the tube was taken out of the oil bath (Ma et al., 2017). Application of cold water enabled the fast cooling of the glass reactor to room temperature. Centrifugation of reaction mixture caused the pellet formation. Pellet was removed, dried, and kept separately. Retentive ethanol phase comprising liquid products was validated by HPLC method of analysis to detect and quantify the small chain carboxylic acids, monosaccharides (such as, glucose, fructose, xylose, and arabinose), and their esterified products (such as ethyl- $\alpha$ - and  $\beta$ -glucopyranosides).

### 2.5. Recovery of lignin from residual biomass

Round bottomed flask containing a dilute solution of NaOH (2%) was added with the dry pellet recovered from the previous step. The reaction was heated at 100 °C for 2 h under a constant stirring condition. After completion, the heating was discontinued, and the flask containing the reaction liquid was cooled to room temperature. Further, subjecting the reaction mixture for centrifugation followed by the separation of retentive aqueous phase furnished a back liquid, wherefrom, lignin was precipitated at pH 3.0 by the application of a dilute solution of 0.5 N H<sub>2</sub>SO<sub>4</sub> (Schulze et al., 2016). Lignin in the form of precipitate was collected over filter paper and dried in an oven. Amount of lignin was estimated by formula given under following.

$$\text{Lignin yield (wt\%)} = \frac{\text{Recovered lignin (g)}}{\text{Initial spent aromatic biomass (g)}} \times 100$$

### 2.6. Detection and quantification of liquid products by HPLC analysis

Liquid products including monosaccharides (such as, glucose, xylose, and arabinose), carbohydrate degradation products (e.g., acetic acid, formic acid, levulinic acid, etc.), and alkyl glucosides (ethyl- $\alpha$ -D-glucoside and ethyl- $\beta$ -D-glucoside) in the biomass hydrolysate were quantified by the HPLC method of analysis (Feng et al., 2015). A direct comparison was made with the commercial analytical standards of monosaccharides, carboxylic acids, and ethyl glucosides. Chromatographic settings followed are detailed as: Hi-Plex H column (Agilent), 300 mm length, 8 mm porosity, 5 mM H<sub>2</sub>SO<sub>4</sub> mobile phase, flow rate 0.6 mL/min. Refractive index (RI) detection was performed at 65 °C with 40 min run time. Ethyl- $\alpha$ -D-glucosides, and ethyl- $\beta$ -D-glucosides in the biomass hydrolysate were determined quantitatively by drawing a calibration curve plotted between concentration versus area obtained from RI chromatograms.

## 3. Results and discussions

The study herein, was performed to establish a chemical process for the assembly of xylose, ethyl glucosides, and lignin as the value added products from spent waste. The method recruited comprises: (a) acid pre-treatment of biomass for recovery of xylose; (b) thermochemical liquefaction of pre-treated biomass to ethyl glucosides; (c) isolation of lignin.

### 3.1. Acid pre-treatment of biomass for recovery of xylose

The crystallinity of cellulose and lignin are the two major recalcitrance factors obstructing the conversion of spent aromatic waste to biofuels and products. Therefore, the pre-treatment by acids is a common practice for overcoming the biomass crystallinity. It makes the polysaccharides locked in the intricacy of plants cell wall easily accessible and amenable. In recent years, the use of homo-/hetero-geneous Brønsted acids as reagent or catalyst has been a hot issue in the field of biomass processing due to their benign environment character, easy

separation, recyclability, and selectivity in product formation (Megias-Sayago et al., 2021). The biomass derived homogenous Brønsted acid catalyst such as, *p*-cymenesulfonic acid (*p*-CSA) can be readily prepared in good yields from the citrus oil (contains >95% *D*-limonene) via the steps of dehydrogenation and sulfonation (Dwivedi et al., 2018b). A lower production cost and the stronger biological affinity of *p*-CSA in compared to the toluene sulfonic acid (*p*-TSA), a petrochemical product, demonstrates its efficacy in the hydrolysis of xylan-polysaccharide giving *D*-xylose as a product with good selectivity and yields (Singh et al., 2019). Therefore, a dry and powdered spent waste of palmarosa was reacted with *p*-CSA in water (solid liquid ratio, 1:10) under the autoclave condition. After completion, the reaction mixture was allowed to come at room temperature. Unreacted biomass was filtered out from reaction mixture. Concentration of monosaccharides (e.g., xylose, glucose, arabinose, etc.) and degradation products (e.g., acetic acid, formic acid, etc.) in the biomass hydrolysate were validated by HPLC analysis. Results established a pre-dominant formation of *D*-xylose as the major product (~16% yield) due to a selective hydrolysis of biomass contained xylan polysaccharides while glucose, arabinose, acetic acid, etc., were all together obtained in a very low concentration. Further, *in vacuo* concentration of the hydrolysate to half of the original volume was performed in order to recover xylose through precipitation in presence of a low boiling alcohol. The precipitate after usual workup, and crystallization resulted in a good recovery of *D*-xylose (~10% isolated yield).

### 3.2. Thermochemical liquefaction of pre-treated biomass to ethyl glucosides

The alkyl glucosides are generally synthesised from carbohydrates, e.g., glucose, starch, cellulose, etc., via processing at elevated temperature (~200–250 °C) and pressure (3–5 MPa) under homo- and heterogeneous conditions (Chung et al., 2016). Despite an ease in transformation under mild reaction condition in compared to the cellulose, the sugars, such as, glucose and starch being the components of food supply, cannot be used as substrates for production of alkyl glucosides. In recent years, lignocelluloses obtained as by-product of several crops, e.g., wheat, rice, soya, spent waste, etc., have been prospected for having a great potential for conversion to value-added chemicals (Sadh et al., 2018; Philippini et al., 2020). However, reports on synthesis of alkyl glucosides using biomass as a renewable feed stock are limited (Kishimoto et al., 2019) and suffers from disadvantages, such as, formation of complex by-products, and dark colours that require additional steps for product purification, thereby, increase the cost of down-streaming (Ma et al., 2017). Therefore, pre-treated biomass with enhanced characteristics, e.g., enriched cellulose and lignin along with the lower ashes, was investigated as a substrate for thermochemical liquefaction to alkyl glucosides. In a representative reaction, 1.0 g pre-treated palmarosa biomass, *p*-CSA, and ethanol were refluxed in a high pressure glass tube reactor for 2 h in an oil bath. After cooling to room temperature, reaction liquid was centrifuged for the pellet formation. Organic fraction was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> followed by HPLC analysis which established the formation of ethyl- $\alpha$ - and  $\beta$ -glucopyranosides as major (18.7 mg, ~2% yield) while glucose, levulinic acid, and formic acid were observed as minor products.

To access a mixture of ethyl- $\alpha$ - and  $\beta$ -glucopyranosides as product in high yields, the reaction conditions were optimized regarding the influence of temperature, time, and reagent concentration. Thermochemical liquefaction of biomass in ethanol without *p*-CSA could not be successful as no liquid products were detected in HPLC analysis. However, addition of *p*-CSA to the reaction liquid, even at a low equivalent, caused a noticeable change in the reaction outcome, such as, ethyl- $\alpha$ - and  $\beta$ -glucopyranosides could be detected readily in HPLC analysis of the organic phase (Table 1). This suggested that the *p*-CSA not just stimulates the yield of ethyl glucosides in reaction liquid, but also, directs the faith of reaction towards pre-dominant formation of ethyl

**Table 1**

Reaction optimization for the synthesis of ethyl glucopyranosides from palmarosa spent waste.

SN	<i>p</i> -CSA (g)	Biomass (g)	Liquid products <sup>a</sup>					
			Glucose	Xylose	Ethyl- $\alpha$ -D-glucopyranoside	Ethyl- $\beta$ -D-glucopyranoside	FA	LA
1.	Blank	1.0	ND	ND	ND	ND	ND	ND
2.	0.5	1.0	1.56	1.97	2.92	1.23	ND	0.10
3.	0.75	1.0	2.35	1.94	3.74	1.55	ND	0.14
4.	1.0	1.0	4.17	0.56	11.89	5.19	<0.1	0.28
5.	1.25	1.0	3.29	0.58	9.79	3.40	<0.1	0.43

LA, Levulinic acid; FA, Formic acid.

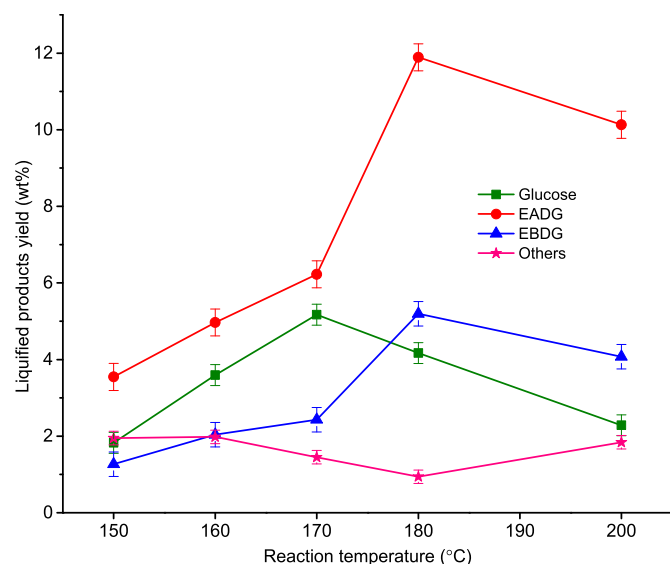
ND, Not detected.

<sup>a</sup> In weight %.

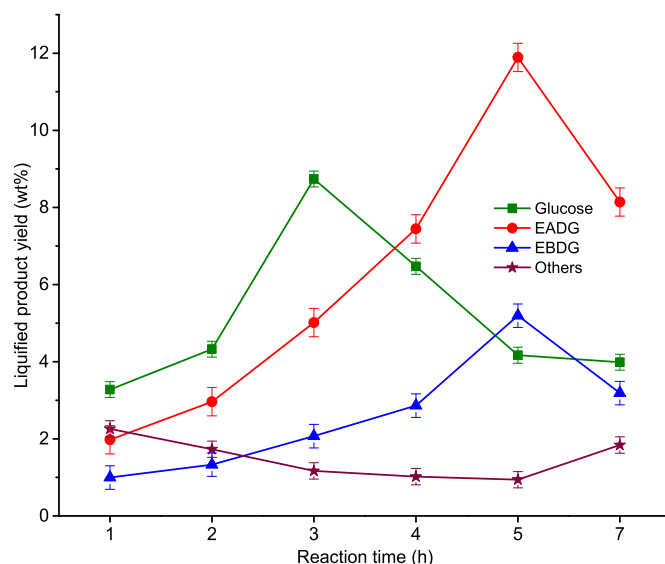
glucosides under refluxing condition. Thus, *p*-CSA greatly enhanced the product selectivity in thermochemical liquefaction of biomass. Increasing the concentration of *p*-CSA in the reaction mixture resulted in an enhanced yield of ethyl glucosides which soon reached to a maximum beyond which it could not be enriched unless the reaction time and processing temperature were not raised up significantly (Climent et al., 2016). A lower yield of ethyl glucosides was observed on lowering the temperature. As evident from Fig. 1, the highest yield of ethyl glucosides from the biomass was observed at 180 °C temperature. Increasing the reaction temperature more than 180 °C caused a dramatic decrease in the yield of ethyl glucosides as product. This could be due to the secondary reactions like the formation of numerous by-products, e.g., levulinic acid (LA), formic acid (FA), humins, unidentified soluble materials, etc.

The *p*-CSA induced thermochemical liquefaction of biomass in ethanol under positive N<sub>2</sub> pressure was also studied. However, no significant increase in the yield of ethyl glucosides could be observed by carrying out reaction under positive N<sub>2</sub> pressure (ranged between 1.0 and 3.0 MPa) using a stirred pressure vessel steel reactor (Parr Instrument Company). Instead, N<sub>2</sub> pressure beyond 3.0 MPa resulted in a decreased yield of ethyl glucosides. This could be due to the generation of more solid residues by the re-polymerization of the liquid products under the pressure.

The reaction time also displayed a profound effect on yields of ethyl glucosides from biomass under heating condition. A short reaction time, such as, less than 5 h resulted in a poor yield product due to an incomplete degradation of cellulose. Likewise, no substantial increase in product yield was observed by running the reaction beyond 5 h (Fig. 2).



**Fig. 1.** Effect of temperature on biomass liquefaction at 5 h reaction time. EADG: Ethyl- $\alpha$ -D-glucopyranoside; EBDG: Ethyl- $\beta$ -D-glucopyranoside; Others: xylose, formic acid and levulinic acid.



**Fig. 2.** Effect of reaction time on biomass liquefaction with *p*-CSA at 180 °C. EADG: Ethyl- $\alpha$ -D-glucopyranoside; EBDG: Ethyl- $\beta$ -D-glucopyranoside; Others: xylose, formic acid and levulinic acid.

Thus, the optimum yield of ethyl glucosides in the process may be due to a combined effect of *p*-CSA, reaction time and temperature. Since, the developed protocol displays a high selectivity towards the formation of ethyl glucosides, hence, they are formed predominantly while levulinic acid, formic acid, etc., are obtained only in traces (Supporting Fig. S1). All these products being soluble in reaction media, remains present in the biomass hydrolysate. Their quantification in weight percentage compared to pre-treated biomass has been shown in Table 2. The highest concentration of ethyl glucosides (~17% yield) from thermochemical liquefaction of pre-treated palmarosa biomass was observed under a temperature condition of 180 °C, 5 h reaction time, and use of 1.0 equivalent *p*-CSA as reagent.

The solid liquid ratio for the thermochemical processing of spent biomass was also optimized. Generally, a gradual decrease in the yield of ethyl glucosides could be observed by increasing the initial biomass loading to the glass tube reactor. This indicated that a high loading may cause an incomplete exploitation of biomass due to the unavailability of adequate amount of solvent. This could cause a poor decomposition of biomass and also create difficulty while mingling of the fibers in the glass tube. Hence, the solid liquid ration 1:20 was maintained in all the experiments for an efficient thermochemical liquefaction.

The unique property of *p*-CSA could be accountable for a predominant formation of ethyl-D-glucopyranosides (EDGP) from biomass with minimum side products. The solid obtained after the reaction was solubilized in methanol to detect the formation of black tar during the thermochemical liquefaction. In the plausible mechanism for such a highly selective degradation of cellulose to EDGP, it may be assumed

**Table 2**  
Selectivity of products in thermochemical liquefaction of spent biomasses.

SN	Biomass	Products selectivity <sup>a</sup>						Conversion <sup>b</sup> (%)
		GLU	XYL	EADG	EBDG	FA	LA	
1.	Palmarosa	18.87	2.54	53.83	23.49	0.45	1.27	55.06
2.	Lemongrass	19.26	2.87	53.18	21.20	0.57	3.49	42.55
3.	Citronella grass	19.57	3.33	54.15	18.73	0.50	4.22	54.16

GLU, Glucose; XYL, Xylose; EADG, Ethyl- $\alpha$ -D-glucopyranosides; EBDG, Ethyl- $\beta$ -D-glucopyranosides; FA, Formic acid; LA, Levulinic acid.

<sup>a</sup> In weight %.

<sup>b</sup> Based on glucan content in substrate.

that the *p*-CSA causes a rapid degradation of cellulose to glucose (Fig. 3). EDGP in the reaction mixture is formed by a direct reaction of glucose with ethanol. EDGP once formed in the reaction matrix, is sufficiently stable to the acidic condition, such as its further isomerization to ethyl- $\alpha$ -D-fructofuranoside (EDFF) and dehydration to EMF could not be observed. Once the protocol was successfully established for the selective conversion of palmarosa biomass to afford EDGP in high yields, it was next applied to other biomasses, such as lemongrass and citronella grass (Supporting Fig. S2), results summarized in Fig. 4.

### 3.3. Isolation of lignin

The pellets separated from the reaction liquids obtained after the thermochemical liquefaction of biomasses were reacted with a dilute solution of NaOH in round bottomed flasks at 100 °C for 2 h. After completion, the reaction mixtures were allowed to come at room temperature. Filtration of reaction mixtures furnished clear black liquids. Lignin from different biomasses were precipitated from their respective black liquids by the process of neutralization through adding a dilute solution of sulphuric acid (Fig. 5). The precipitates were collected on filter papers followed by processing to the usual workup steps which furnished dark brown powder in good yields (~124 mg, 12.4% isolated yield). FT-IR, EDS, and XRD analysis were carried out for complete characterization of isolated lignin and comparisons were made with the standard lignin purchased from Sigma-Aldrich (MERCK). FT-IR spectrum of palmarosa lignin (Supporting Fig. S3) displayed a close similarity to the lignin standard by exhibiting maximum absorption in the region 3500  $\text{cm}^{-1}$  (phenolic groups), 2800-2900  $\text{cm}^{-1}$  ( $-\text{CH}_2-$  and  $>\text{C}-\text{H}$  stretching), 1600-1780  $\text{cm}^{-1}$  (carbonyl group), 1400  $\text{cm}^{-1}$  (aromatic ring), 1300-1100  $\text{cm}^{-1}$  (syringyl and guaiacyl residues), and 800  $\text{cm}^{-1}$  (aromatic  $>\text{C}-\text{H}$  bending). In the X-ray diffraction (XRD) analysis (Supporting Fig. S4), the isolated lignin displayed diffraction peaks centred at 19.03°, 28.06°, 29.03°, 32.05° and 33.93° which were typical for lignin. The EDS analysis of lignin recovered from thermochemical liquefaction of biomasses exhibited an elemental composition: C,

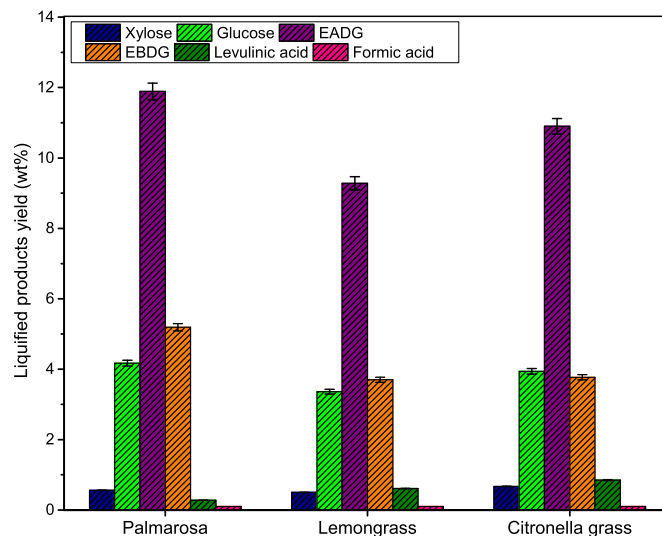


Fig. 4. Yield of liquid products by thermochemical liquefaction of biomasses with *p*-CSA.

62.37%; O, 31.42% (Supporting Fig. S5-S7).

In order to access the economic and environmental prospective, an input/output balance in the developed biorefinery process has been shown in Table 3. Foremost the liquefaction products were ethyl- $\alpha$ -D-glucopyranoside, ethyl- $\beta$ -D-glucopyranoside, xylose, glucose, levulinic acid, formic acid, etc. A considerable amount of lignin (~10–15 wt%) was degraded during thermochemical liquefaction and only small amount, such as 9–12 wt% could be recovered when spent biomass conversion to liquid products ranged between 17 and 22 wt%. In the process, solvent recoveries were always >80 wt% due to an ease in the distillation of low boiling alcohol. About ~25–30% weight loss in the process may be linked to the occurrence of the volatile residues

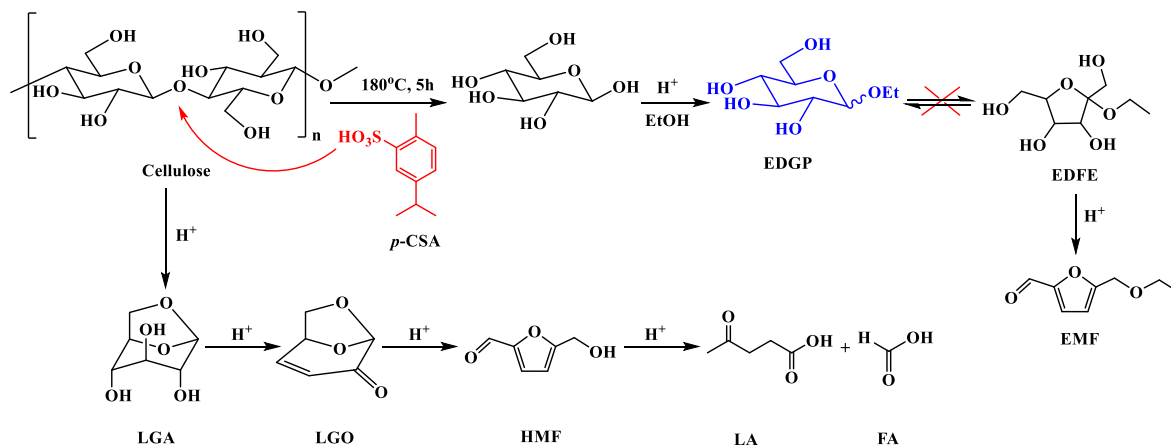


Fig. 3. Proposed reaction pathway for cellulose conversion to liquid products in ethanol-rich medium.

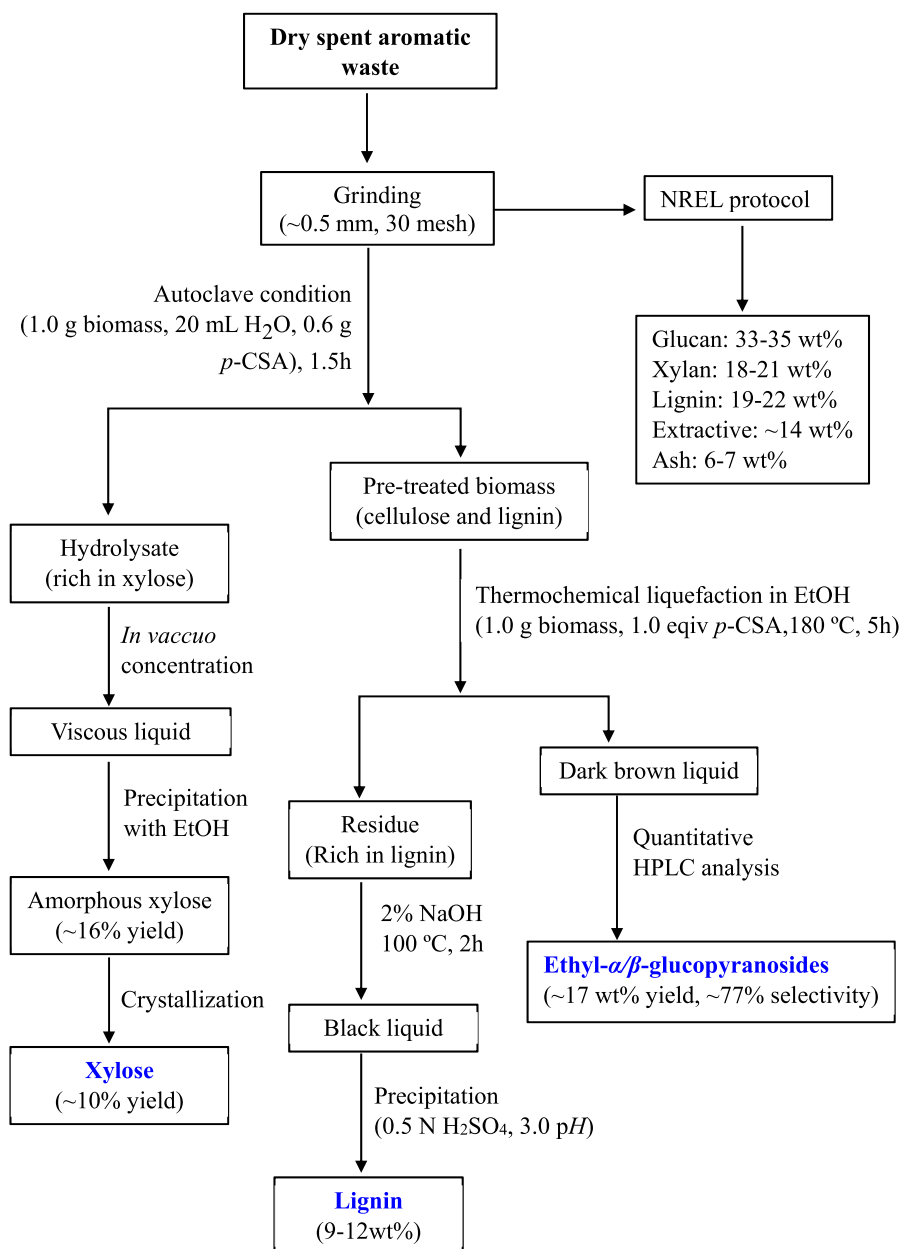


Fig. 5. Flow diagram for the recovery of xylose, ethyl glucosides and lignin from spent aromatic waste.

Table 3

Material balance analysis.

SN	Input		Output					
	Type of Biomass	Biomass loading (g)	Liquid products (wt%)	Solid residue <sup>a</sup> (mg)	Biomass conversion <sup>b</sup> (wt%)	Recovered lignin <sup>c</sup> (wt%)	Carbon balance (wt%)	Ethanol recovery (%)
1	Palmarosa	1.0	22.09	~315	59.4	12.45	54.32	~83
2	Lemongrass	1.0	17.45	~324	54.1	9.72	44.11	~83
3	Citronella grass	1.0	20.13	~307	53.7	9.56	53.47	~84

<sup>a</sup> Residue left after production of ethyl glucopyranosides.

<sup>b</sup> Conversion with respect to the biomass loading.

<sup>c</sup> Lignin recovered from solid residue.

(essential oil constituents), organosolv lignin, and their degraded products. Obviously, the material balance could not go close to 100% due to the losses in the form of untraceable compounds generated from biomass after thermal decomposition, solids stick to the filter paper

while filtration, and compounds residing on the wall of funnel during activities of filtering, washing, and drying, hence, could not be assembled.

#### 4. Conclusion

The investigation demonstrates that the aromatic spent biomass which is generally considered as a waste, can be exploited efficiently to produce platform chemicals, such as ethyl glucosides and xylose. A quantitative yield of ethyl glucosides (~17 wt%) with high selectivity (~77%) could be achieved at relatively low temperature (180 °C). The process also furnishes a significant amount of lignin that can be valorized further into biomaterials, hydrocarbon and fuels, thus, strengthens the process economy. On sustainability point of view, the methodology displayed efficacy in product formation by using a renewable Brønsted acid *p*-CSA instead of mineral acids and the recyclability of reaction solvent. However, further studies are required to understand the reaction pathway, and the fundamentals of thermochemical liquefaction to arrive at an appropriate processing condition to afford platform chemicals from biomass with the minimum side products.

#### Author contribution statement

Mangat Singh: Validation, Methodology, Investigation. Nishant Pandey: Methodology, HPLC validation. Pooja Negi: XRD, EDS and other analysis. Jyoti: IR analysis, Writing - original draft. Christian Larroche: Writing - review & editing. Bhuwan Bhushan Mishra: Conceptualization, Supervision, Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2021.133428>.

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