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A Two-Step Catalytic Depolymerization of Alkali Treated *Pennisetum glaucum* L. and *Melia dubia* cav. into Low Molecular Weight (LMW) Aromatics

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The potential of lignin and its challenge for valorization has become the gold-rush nowadays for emerging bio-refineries. In the present investigation, alkaline H_2O_2 pre-treated two lignocellulosic biomass (LCB), agro residue (pearl millet) and hardwood (*Melia dubia*) were subjected to catalytic depolymerization. Of the catalysts optimized, Ru/C 1% recovered higher monomeric yield of 67% over Ni/C on carbon supports. The alkaline H_2O_2 pre-treatment of pearl millet and *M. dubia* showed less than 40% of biomass conversion into aromatics with more than 50% cellulose and hemicellulosic derivatives. The solid cox and gaseous loss for alkaline H_2O_2 pearl millet biomass sample were found to be 16.13% and 4.42 % for Ru^- and 30.00% and 35.43 % for 1% Ru^+ respectively with highest monomeric (97.84%) and least polymeric (2.16%) yield. Sugar derivatives such as diols and acids were detected more compared to lignin derivatives in alkali pretreated pearl millet. On the other hand, the alkaline H_2O_2 pre-treated *M. dubia* lignin registered a solid cox of 16.97%, gaseous loss of 12.95% and highest monomeric yield of 69.53% for 1% Ru^+ which includes p-propyl syringol (0.32 $mg.ml^{-1}$), p-propyl guaiacol (0.27 $mg.ml^{-1}$), tetra-hydrofurfurol (0.12 $mg.ml^{-1}$), p-ethyl syringol (0.08 $mg.ml^{-1}$), syringol (0.05 $mg.ml^{-1}$) and so on. From the results obtained, it can be concluded that alkaline H_2O_2 pre-treated *M. dubia* is a suitable candidate for lignin based bio-refineries for high value platform chemicals, whereas alkaline H_2O_2 pretreated pearl millet can be employed for bio-ethanol production.

Key words: Lignocellulosic-biomass, Alkaline H_2O_2, Catalysts, Depolymerization, Aromatics

Lignocellulosic biomass (LCB), a complex carbohydrate biopolymer is composed of cellulose, hemicellulose, lignin, and pectin in major proportions. Of which, lignin being an abundant heterogeneous biopolymer cementing cellulose and hemicelluloses became a potential source to unlock many value-added green chemicals. The pretreatment of LCB helps in separating lignin from other cellulosic and hemicellulosic components which can further be depolymerized using the suitable methodology to achieve diverse chemicals. Therefore, a special pretreatment processing should be adopted for the delignification of LCB. In the past decades several pretreatment techniques such as kraft pulping (Sixta, 2006), soda pulping (Prinsen *et al.*, 2013), organosolv pulping (Muurinen, 2000), acidic pretreatment (Noureddini and Byun, 2010), ammonia treatment (Kim and Holtzapple, 2005), AFEX treatment (Lau *et al.*, 2010), ozonolysis (de Barros *et al.*, 2013), microwave treatment (Ma *et al.*, 2009), and biological pretreatment (Liu and Wyman, 2005) were employed for removal of cellulose and hemicelluloses with enhanced enzymatic hydrolysis. Alkaline pretreatment was found to be advantageous over acidic pretreatment such as no washing is required after pretreatment, preventing corrosion of the reactor and do not generate furfural, as it prevents from repolymerization of LCB (Karunanithy and Muthukumarappan, 2011). In general, lime (calcium hydroxide) and sodium hydroxide (NaOH) are commonly employed for alkaline pretreatment of lignocellulosic biomasses (LCB). Alkaline pretreatment at mild reaction condition prevents condensation of lignin resulting in high solubility and removal of lignin from LCB (Sharma *et al.*, 2013). Hence alkaline pretreatment is considered to be a promising methodology as it enhances enzymatic hydrolysis owing to altered structural properties of LCB. Above all, alkali-based pretreatment holds highly promising for agricultural residues and grasses compared to woody biomass (Yang and Wyman, 2008). The pre-treated lignin fraction can be used to derive high-value fine chemicals by depolymerization.

Catalytic depolymerization mediated by hydro genolysis was considered to be a promising technology for lignin valorization of novel chemicals since the 1930s (Galkin and Samec, 2016) where Nickel (Ni), Molybdenum (Mo) and Ruthenium (Ru) serves as catalysts in the presence of hydrogen. The challenges of catalytic depolymerization under chemical pretreatment conditions showed high cost

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*Corresponding author's email: usivakumartnau@gmail.com and catalytic deactivation. Hence, the integrated bio-refinery concept on lignin valorization has been fascinating in the 21st century for a feasible low-cost technology for modern bio-refineries. Therefore, the present investigation mainly focuses on two-step catalytic depolymerization of alkaline pretreated LCB to achieve increased monomeric yield and to prevent repolymerization of depolymerized lignin.

Material and Methods

Source of alkali pretreated LCB

Alkaline hydrogen peroxide pre-treated pearl millet (*Pennisetum glaucum* L.) and Malabar neem (*Melia dubia* cav.) lignin obtained from Department of Bioenergy, Agricultural Engineering College and Research Institute, Tamil Nadu Agricultural University, Coimbatore were used for catalytic depolymerization experiments. The biomass was dried at ambient temperature and finely powdered using shredder and grinder prior to the pretreatment process passed through a sieve to get the 212µ size.

Monosaccharide content in alkali pretreated LCB by HPLC

Monosaccharide content in alkali pretreated LCB was quantified in HPLC on ‘Millichrome A-02” with 2*75 mm column and “Nucleosyl 5 – S18” as reverse phase sorbent powder after acidic hydrolysis. The air-dried LCB sample was treated with 80% H_2SO_4 for 2.5 h at room temperature followed by the addition of 5% H_2SO_4 and boiled for 5h. Solutions of water and acetonitrile with 0.1%TFA (Trifluoroacetic acid) was used as eluents. The hydrolysates were pretreated by derivatization with 2,4-dinitrophenylhydrazine (2,4 DNPH) at 65°C for 1.5h.

FT-IR analysis of alkali pretreated LCB

The compositional analysis of alkali pretreated LCB was carried out using FT-IR - 6800 type A (JASCO, Japan) with ATR PRO ONE accessory and TGS detector. Registration was carried out in the region between 400 – 4000 cm^{-1} (resolution 4 cm^{-1} with 40 scans per sample). The processing of result was done using Origin Pro® 8.0 software for deconvolution of various shifts in the functional groups of compounds.

Characterization of catalysts

Two different catalysts Nickel (Ni) and Ruthenium (Ru) at the rate of 1% and 3% each, supported on Sibunit-4, a porous carbonaceous material (Omsk, Russia) of 3-4 nm in diameter were employed. The catalysts on C support were reduced using hydrogen (H_2) by heating from ambient to 300⁰C (dry heat) with a ramp rate of $1^0C.min^{-1}$, held for 6 h after the supply of argon (Ar) and nitrogen (N) for 30min and cooled down to ambient temperature. The catalyst was then stored under the reduced condition and the size and reduction ability were analyzed in Transmission Electron Microscopy (TEM).

Depolymerization process

The alkali pre-treated LCB of pearl millet and Malabar neem (500 mg) was depolymerized in an autoclave with 250 mg of optimized catalyst (1% Ru^+), where alkali pretreated LCB without catalyst served as control (Ru^-). The reaction was carried out under hydrogen (10 atm) at 260°C for 6 h at 1000 rpm in an autoclave reactor (45 ml capacity). Et-OH (96% v/v) was used as a solvent and a ring made of Teflon® (polytetrafluoroethylene - PTFE) served as reactor gasket (Chikunov *et al*., 2018)

Product analysis of depolymerized LCB in GC-MS

The analytical methods of gravimetry and spectroscopy were carried out for the compositional analysis of solid, liquid and gaseous phases after catalytic depolymerization process.

i) *Gaseous phase*: The gaseous phase (CH_4, CO_2, and CO) from the reactor was collected using gas collection assembly containing hydrochloric acid (pH 3.0) and was analyzed in Gas Chromatograph Kristall 2000M (Chromatec®, Russia) equipped with a flame ionizing detector (FID) and a methanator with an injection port temperature of 110°C. The column (2 m x 2 mm) was filled with Chromosorb 102 and argon (Ar) acted as a carrier.

ii) *Solid phase*: The presence of lignin in the solid phase was determined by the gravimetric method. Final weight was obtained after vacuum filtration of autoclaved product using filter paper (20 µ) and the lignin content was estimated by fitting the values in the following equation.

Loss of lignin as solid cox=Final weight of solid cox-Initial weight of lignin sample (1)

iii) *Liquid phase* : The distribution of lignin over the liquid phase of depolymerized LCB was analyzed in GC-MS Agilent ® 7000B equipped with mass spectra at scanning mode between 40-650 m/z. Probe (1.0 ml) was dry evaporated, filled with 100µl of pyridine and 100µl of BSTFA whereas ionol (10.0 µg) served as internal standard. The prepared probe was heated it for 1h at 70°C. The GC-MS Operating condition is as follow: 80°C (3 min), then 8°C up to 300°C, helium as a carrier gas with a flow rate of 1.2 ml min^{-1}, evaporator 300°C, discharge 1:5 and sample volume 1µl.

Results and Discussion

Proximate composition of alkali pretreated LCB

The proximate analysis (NREL protocol) of raw and pre-treated pearl millet (*Pennisetum glaucum* L.) and Malabar neem (*Melia dubia* cav.) revealed the presence of all the three major biopolymers. In the present experiments, alkaline pretreated pearl millet showed cellulose (42.25%), hemicelluloses (25.58%) and lignin (8.14%) with biomass extractives, moisture and ash content of 18.08%, 5.95% and 0.007% respectively whereas the raw pearl millet had 41.6% cellulose, acid soluble lignin (5.49%) and acid insoluble lignin (16.32%) with 8.00% moisture and 6.27% ash content. Similarly, alkali pretreated *M.*

Table 1. The functional group assignment of corncob samples detected in FT-IR

Band length (cm-1)	Apm	Amd	Assignments	Reference
1728/-	-	+	Xylan unit of hemicelluloses (unconjugated C=O)	Evans, 1991
1599/-	+	+	Aromatic skeletal ring of lignin with C=O stretching	Pandey and Pitman, 2003
1454/-	+	-	Possibly CH_2 deformation vibration and benzene vibration-Lignin and heteroxylan	Fahey *et al.*, 2017; Harrington *et al.*, 1964; Marchessault and Liang, 1962
1425/-	-	+	-CH3 and –CH2 asymmetry of carbohydrate and deformation in C-H in lignin	Pandey and Pitman, 2003; Scholze and Meier, 2001
1327/1325	+	+	C=O stretching of syringyl nuclei - lignin	Le *et al.*, 2017; Sammons *et al.*, 2013; Scholze and Meier, 2001
1238/-	-	+	Possibly C-O stretching in guaiacyl nuclei	Le *et al.*, 2017; Sammons *et al.*, 2013; Scholze and Meier, 2001
1108/-	+	-	Possible stretching of aromatic and C=O	Pandey and Pitman, 2003
1029/1026	+	+	C-O deformation in primary alcohol, C=O stretch, aromatic C-H deformation in guaiacyl ring: 1025-1033 cm^{-1}	Faix, 1991; Le *et al.*, 2017; Scholze and Meier, 2001
841/-	+	-	Deformation of 1,3,4,5 – substituted rings of syringyl unit	Evans, 1991

+ represents the presence of a peak at particular wave number (cm^{-1})

- represents the absence of a peak at particular wave number (cm^{-1})

(Amp – Alkaline H_2O_2 pretreated *M. dubia*; Apm – Alkaline H_2O_2 pretreated pearl millet)

dubia has registered an increased cellulose content (45.35%), and reduced hemicelluloses (15.46%) and lignin (27.46%) with biomass extractives, moisture and ash content of 7.93%, 3.80%, and 0.006% respectively (Fig 1).

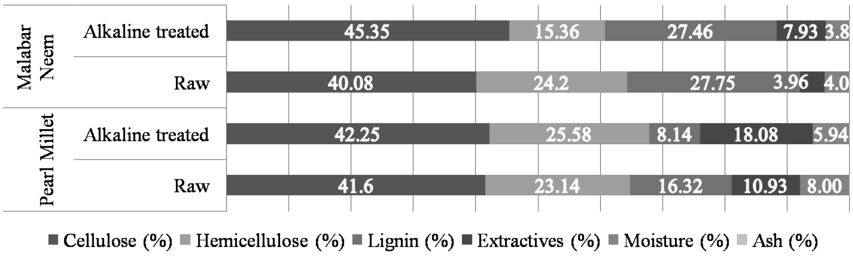

Fig 1. Proximate composition of raw and alkaline H_2O_2 pretreated biomass

(The proximate analysis (NREL protocol) of raw and alkaline H_2O_2 pre-treated LCB was represented in the above table. Increase in cellulose in both the pre-treated lignin and decreased lignin in pre-treated pearl millet and no significant change in pre-treated *Melia dubia* was found. Decreased hemicelluloses were detected in alkaline pre-treated *M. dubia*).

The proximate composition of lignocellulosic biomasses varies from plant species to species. A steady increase in cellulose content was observed in alkali pre-treated pearl millet (42.25%) over raw pearl millet (25.00%) with significant lignin reduction of 39.70% and increased hemicelluloses (25.58%) over raw pearl millet (24.5%). Similarly, alkaline H_2O_2 pretreated *M. dubia* showed increased cellulose (5.27%), reduced hemicelluloses (11.11%) and almost the same lignin content (27.46%) over raw Malabar neem. The alkaline H_2O_2 used for pre-treatment might have removed the cellulose and hemicellulose and thereby achieved considerable lignin reduction. In the previous study conducted by Maheshwari and Subburamu (2016) on alkaline hydrogen peroxide pre-treatment of pearl millet, H_2O_2 enhanced the removal of cellulose and hemicelluloses from LCB. The removed cellulose and hemicelluloses in the hydrolyzate yielded ethanol (Et-OH) which can be blended with petroleum (bio-diesel). The remaining solid portion corresponding lignin was further characterized and used for the production of low molecular weight (LMW) aromatics by catalytic depolymerization (1%Ru$^+$).

Monosaccharide content in alkali pretreated LCB

The HPLC chromatogram revealed that alkaline hydrogen peroxide-pretreated pearl millet has 14.6% glucose, 1.53% galactose, 0.21% arabinose and 0.1% xylose whereas alkaline treated *M. dubia* showed 23.2% glucose, 3.2% galactose, 0.56% mannose and 0.57% xylose. An additional peak with characteristic retention time close to C_6-saccharides was found and its intensity is close to or even exceeds the area of glucose peak for alkali treated pearl millet lignin sample (Fig 2). The pre-treated LCB contains a different proportion of monosaccharides / reducing sugars which can be easily converted to value-added chemicals *via*, fermentation or depolymerization.

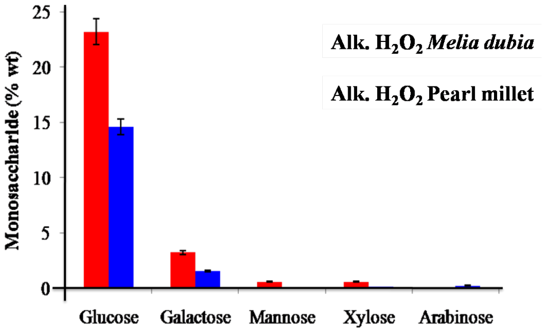

Fig 2. HPLC analysis on the distribution of monosaccharides in Pearl Millet and *M. dubia*

(Alkaline H_2O_2 pretreated *Melia dubia* shows maximum glucose (23.20%) and galactose (3.20%) compared to alkaline pretreated pearl millet. Also, hemicellulosic derivatives, mannose, and xylose are detected only in alkaline *M. dubia,* not in the other. The bars indicate ±SE and the data were analyzed by one-way ANOVA and p-value < or 0.05 was considered significant).

Table 2. Major monomeric compounds detected in GC-MS for alkaline pre-treated LCB

Compound	Alk. H_2O_2 Pearl millet mg.ml^{-1}	Alk. H_2O_2 *M. dubia* mg.ml^{-1}
Hydroxyl-3-methylvaleric acid	0.66	-
p-Propyl guaiacol	-	0.27
1-Octanol	0.25	-
Caproic acid	0.21	-
p-Ethyl guaiacol	0.14	0.04
Tetrahydrofurfurol	-	0.12
Octanoic acid	0.09	-
4-Ethyl phenol	0.09	-
Syringol	0.09	0.05
p-Propyl syringol	0.07	0.32
1-Dodecanol	0.06	-
4-Methyl valeric acid	0.05	0.04
Succinic acid	0.05	0.01
Pyrocatechol	-	0.04
p-Ethyl syringol	0.04	0.08
Sinapyl alcohol	-	0.04
Coniferyl alcohol	-	0.03
2-Hydroxyvaleric acid	0.20	0.03
3-Hydroxycaproic acid	0.03	-
Methyl succinic acid	0.02	-
Guaiacol	0.02	-
p-Methyl syringol	0.01	0.03
Phenol	0.01	-

In the present investigation also, the analysis of monosaccharides using HPLC showed the presence of glucose (14.6%), galactose (1.53), arabinose (0.21) and xylose (0.1%) being released by the cellulosic and hemicellulosic proportion which coincides with the FT-IR banding pattern with characteristic peaks at 1454 cm^{-1}, 1108 cm^{-1}, 1029 cm^{-1}. Alkaline H_2O_2 treated *M. dubia* also registered glucose (23.2%), galactose (0.56%), mannose (0.56%) and xylose (0.57%) with a characteristic peaks at 1728 cm^{-1}, 1425 cm^{-1} and 1029 cm^{-1}. The glucose content is more in case of alkali treated *M. dubia* which might be due to the influence of more cellulose content as it is a hardwood as reported by Anbu (2014) (Fig 3).

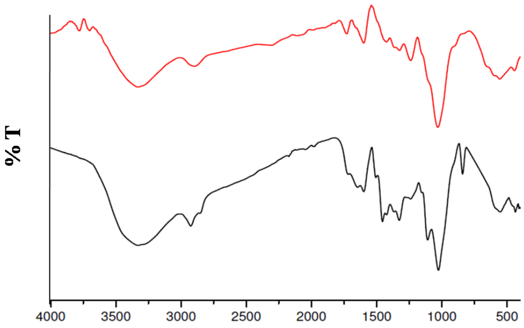

Fig 3. Band spectrum of alkaline H_2O_2 pre-treated pearl millet (top) and *M. dubia* (bottom)

(The characteristic banding pattern varies for alkaline H_2O_2 pretreated pearl millet and *M. dubia* between 1100cm^{-1} and 1700 cm^{-1})

The FT-IR analysis of alkali pretreated pearl millet and *M. dubia* biomass (Fig 3) revealed that the peaks of alkaline pearl millet lignin biomass showed syringyl unit (1328 cm^{-1}, 841 cm^{-1}), guaiacyl unit (1026 cm^{-1}) and lignin units at 1599 cm^{-1} 1454 cm^{-1} with some possible carbohydrate and other hydroxyl vibrations (1025 cm^{-1}). On the other hand, the alkaline *M. dubia* showed intense peaks at 1029 cm^{-1} corresponding to a deformation in C=O in primary alcohol, C=O stretching and aromatic deformation in guaiacyl nuclei. In addition, the additional peaks revealed the presence of guaiacyl units (1238cm^{-1},

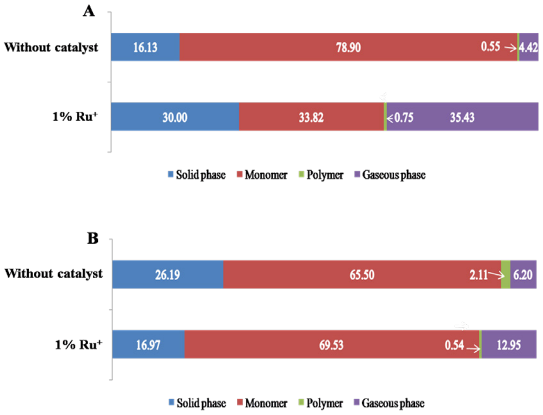

Fig 4. Compositional analysis of catalytically depolymerized alkaline pre-treated pearl millet (A) and *M. dubia* (B)

(A. The decrease in monomeric yield by 45.08% is evident for 1% Ru/C catalytic depolymerization with more losses in solid and liquid phases over control. B. The monomeric yield was increased by 4.03 % on metal-catalyst depolymerization: 1% Ru/C over control)

1029cm^{-1}) and syringyl units (1325cm^{-1}) along with hemicellulose component, heteroxylan (1728cm^{-1}, 1454cm^{-1}) and carbohydrate (1425cm^{-1}) were also detected (Table 1).

Depolymerization of alkali pretreated LCB

Optimization of metal catalysts for depolymerization

The metal catalysts, Nickel-59 (1% & 3%) and Ruthenium-101 (1% & 3%) were used for optimization studies based on their mean size, reducing the ability and adhesive nature with carbonaceous support. The Transmission Electron Microscopy (TEM) analysis revealed that all the catalysts studied have a mean size of 7.3nm (1%Ni), 4.5nm (3%Ni) and ~ <1nm (1% and 3% Ru) and was found embedded in sibunit-4 in the highly reduced state. Ruthenium (1% Ru$^+$) was found to be most promising while optimizing the depolymerization process with organosolv birchwood lignin (Nishanth, 2018). The active depolymerization using 1%Ru/C might be attributed due to its smaller mean size (~ <1nm) and highly reduced state. Ruthenium (Ru/C) was found to be an active catalyst on cellulose conversion using H_2 as reported by Kobayashi *et al.* (2011).

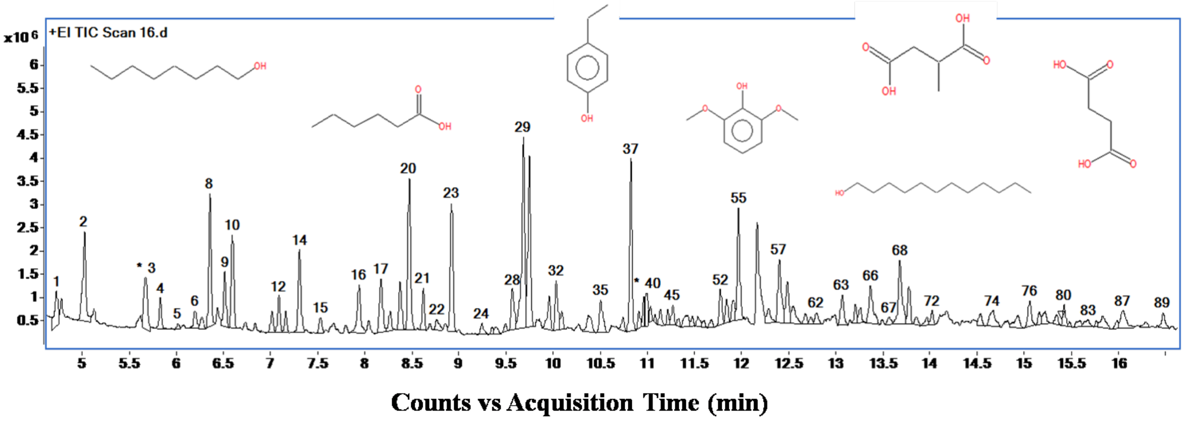

Fig 5. GC-MS chromatogram of catalytically depolymerized alkaline pre-treated pearl millet

(The chromatogram of alkaline H_2O_2 pre-treated pearl millet after depolymerization with 1% Ru/C showed maximum peaks intensities corresponding to different monomers: hydroxyl-3-methyl valeric acid, 1-octanol, caproic acid, p-ethyl guaiacol, octanoic acid and traces of lignin derivatives along with phenol compounds).

Catalytic depolymerization of pearl millet and M. dubia

The compositional analysis of depolymerized pre-treated pearl millet lignin with 1% Ru$^+$ was found to be distributed among solid, liquid and gaseous phases as revealed by GC-MS. The solid cox for alkaline hydrogen peroxide pearl millet biomass sample was found to be 16.13% for Ru$^-$ and 30.00% for 1% Ru$^+$. The GC analysis revealed maximum gaseous loss of 35.43% for 1% Ru$^+$ (30.66%, CH_4; 3.74%, CO_2; and 1.03%, CO) and the least value of 4.42% for Ru$^-$ (1.08%, CH_4; 1.96%, CO_2 and 1.38%, CO). GC-MS analysis of liquid phase showed highest monomeric (78.90%) and least polymeric (0.55%) yield for Ru$^-$ whereas 1% Ru$^+$ registered 33.82% and 0.75% of monomers and unknown compounds respectively (Fig 4). In general, sugar derivatives, diols, and acids were detected in the highest level in alkali pretreated pearl millet compared to lignin derivatives.

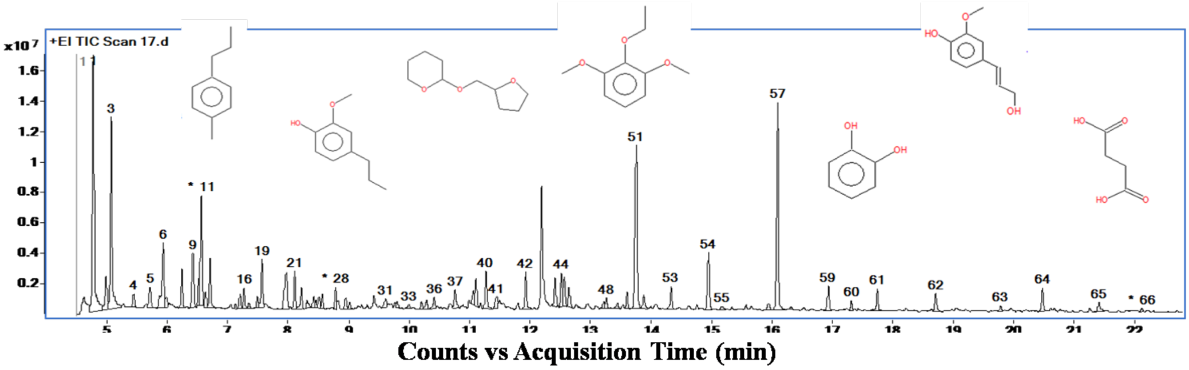

Fig 6. GC-MS chromatogram of catalytically depolymerized alkaline pre-treated *M. dubia*

(The chromatogram of alkaline H_2O_2 pretreated *M. dubia* after depolymerization with 1% Ru/C showed maximum peaks intensities corresponding to different monomers: p-propyl syringol, p-propyl guaiacol, tetra-hydro furfurol, p-ethyl syringol and syringol. More than 60% of the compounds detected are the derivatives of cellulose)

The major lignin derived monomers detected in depolymerized alkali pretreated pearl millet are hydroxyl-3-methylvaleric acid (0.66 mg.ml^{-1}), 1-octanol (0.25 mg.ml^{-1}), caproic acid (0.21 mg.ml^{-1}), p-ethyl guaiacol (0.14 mg.ml^{-1}), octanoic acid (0.09 mg.ml^{-1}), 4-ethyl phenol (0.09 mg.ml^{-1}), syringol (0.09 mg.ml^{-1}), p-propyl syringol (0.07 mg.ml^{-1}), 1-dodecanol (0.06 mg.ml^{-1}), 4-methyl valeric acid (0.05 mg.ml^{-1}), succinic acid (0.05 mg.ml^{-1}), p-ethyl syringol (0.04 mg.ml^{-1}), 3-hydroxycaproic acid (0.03 mg.ml^{-1}), methyl succinic acid (0.02 mg.ml^{-1}), guaiacol (0.02 mg.ml^{-1}), p-methyl syringol (0.01 mg.ml^{-1}) and phenol (0.01 mg.ml^{-1}) (Fig 5).The alkali pre-treated *M. dubia* lignin has solid cox of 26.19% for Ru$^-$ and 16.97% for 1% Ru$^+$. Further, Ru$^-$ registered lowest gaseous loss of 6.20% (0.70%, CH_4; 2.54%, CO_2; 2.96%, CO) and highest of 12.95% for 1% Ru$^+$ (4.62%, CH_4; 1.80%, CO2; 6.53%, CO). Ru catalyst at 260^{o}C might specifically hydrogenate and hinder complete gasification off hydrolytic lignin. The liquid phase analysis showed highest monomeric yield of 69.53% for 1% Ru$^+$ followed by Ru$^-$ (65.50%) as presented in Fig 5. On contrary highest polymeric yield (2.11%) was observed in Ru$^-$ and least in Ru$^+$. Some of the predominant monomers for 1% Ru$^+$ include p-propyl syringol (0.32 mg.ml^{-1}), p-propyl guaiacol (0.27 mg.ml^{-1}), tetra-hydrofurfurol (0.12 mg.ml^{-1}), p-ethyl syringol (0.08 mg.ml^{-1}), syringol (0.05 mg.ml^{-1}), 4-methyl valeric acid (0.04 mg.ml^{-1}), p-ethyl guaiacol (0.04 mg.ml^{-1}), pyrocatechol (0.04 mg.ml^{-1}), sinapyl alcohol (0.04 mg.ml^{-1}), 2-hydroxy valeric acid (0.03 mg.ml^{-1}), coniferyl alcohol (0.03 mg.ml^{-1}), p-methyl syringol (0.03 mg.ml^{-1}) and succinic acid (0.01 mg.ml^{-1}) (Table 2 and Fig 6).

In both the alkaline pre-treated biomass, lignin-derived chemicals were detected in smaller proportions while comparing with the yields of sugars, diols, and acids. However, alkaline pre-treated *M. dubia* biomass recorded major monomers of alkylated guaiacyl and syringyl derivatives such as p-propyl syringol, p-propyl guaiacol, syringol, p-ethyl guaiacol, and p-methyl syringol. Alkaline pre-treated pearl millet showed comparatively lesser lignin derivatives such as p-ethyl guaiacol, syringol, p-propyl syringol, p-ethyl syringol, guaiacol and p-methyl syringol. The reason for achieving the lower amount of monomeric lignin derivatives in alkali treated pearl millet might be due to incomplete or partial pretreatment by alkaline H_2O_2. Hence alkaline H_2O_2pre-treated LCB be utilized for bioethanol production rather than LMW lignin monomers. The results are in preponderance with the findings of Maheshwari *et al.* (2017). The alkaline H_2O_2 pre-treated biomass had more stable structure, redistribution, condensation and partial removal of lignin and favors more yield of fermentable sugars.

Conclusion

Lignocellulosic biomass (LCB), a major source for high value low molecular weight (LMW) aromatic compounds can be explored for sustainable bio-refineries. In this perspective, an efficient catalytic depolymerization strategy involving hydrogenolysis developed for the LCBs, Pearl millet and *M. dubia* resulted in unique end-products of industrially important monomeric and polymeric units. The alkali pretreated pearl millet yielding more fermentable sugars can be used for bio-ethanol production, while the hardwood *M. dubia* could be a potential candidate for lignin- dependent bio-refineries.

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