Sustainable Environment

Catalytic Conversion of Kraft Lignin into Substituted Phenols and Aromatics

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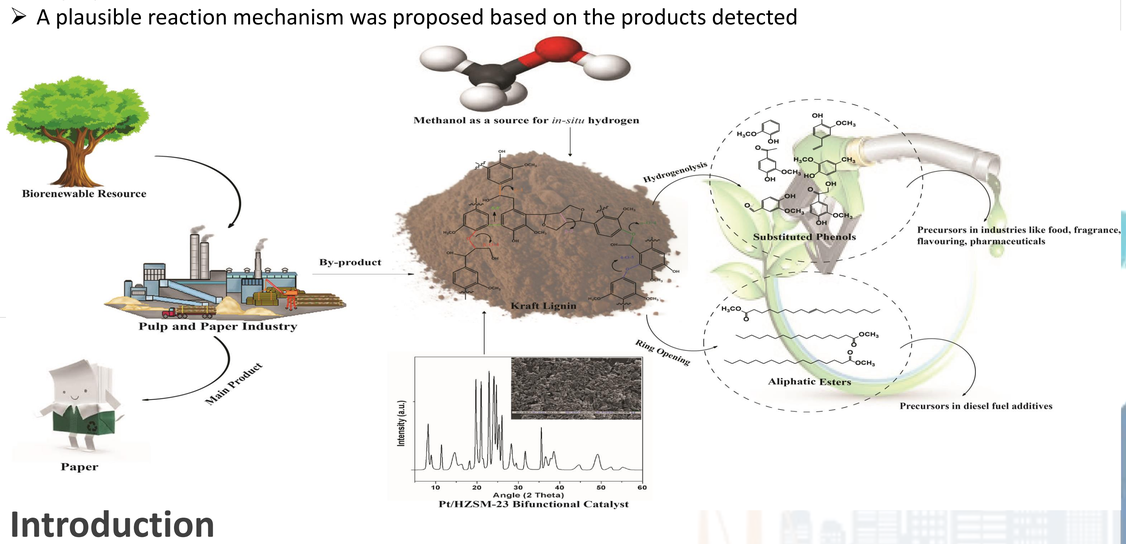
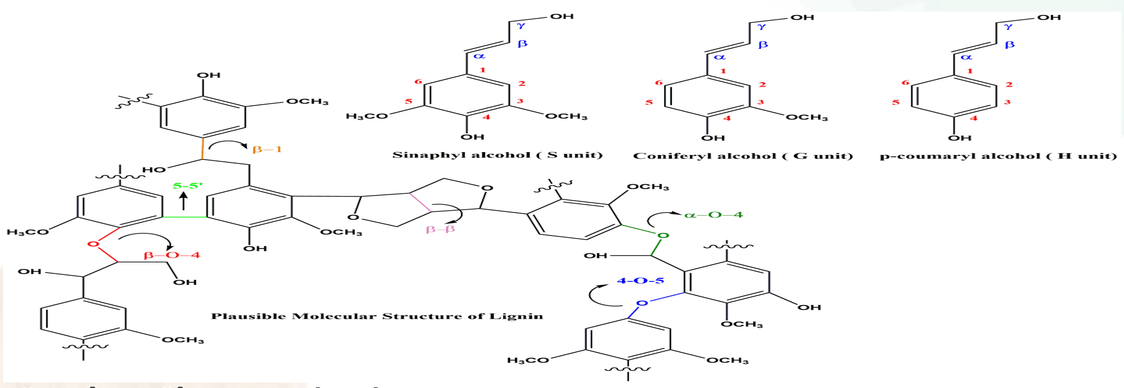
Abstract

- In the present study, Kraft lignin which is a major by-product of pulp & paper industry is converted into substituted phenols, aromatics and aliphatic esters via reductive depolymerization over Pt/HZSM-23 catalyst
- Experiments were performed in a high-pressure batch reactor in a temperature range of 100-200 °C for 1-12 h
- The *in-situ* generated hydrogen was found to be more favourable than external hydrogen for Kraft lignin depolymerization
- A plausible reaction mechanism was proposed based on the products detected

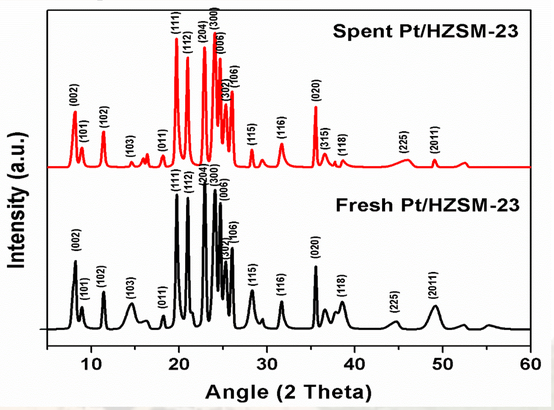


Introduction

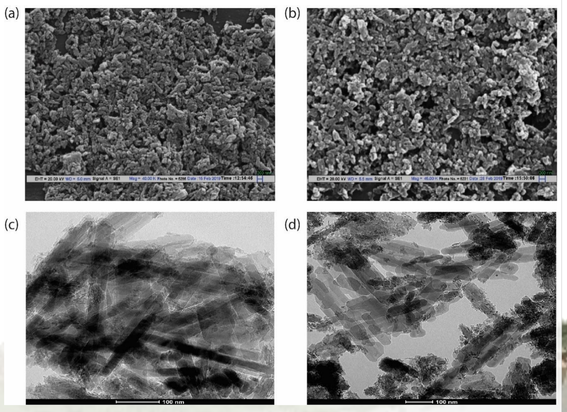
- Burning of fossil fuels causes the emission of green-house gases which is leading to climate change
- Lignocellulosic biomass (LCB) is an interesting renewable alternative feedstock available in abundance
- Several technologies for conversion of cellulose and hemicellulose part of LCB are developed but the third component lignin is highly complex thus making its conversion challenging
- Kraft process is the most widely used process in pulp & paper industry which generates about 78 million metric tons of Kraft lignin (KL) annually which is burned as a low calorific value fuel
- Lignin has a highly complex aromatic structure made of methoxylated phenylpropanoid units linked to each other by C-O-C and C-C linkages
- Most of the studies on lignin conversion are based either on lignin model compounds or organosolv lignin
- Conversion of KL is a challenge owing to its highly condensed structure as compared to the native lignin along with impurities like Na and S which are incorporated during the Kraft process



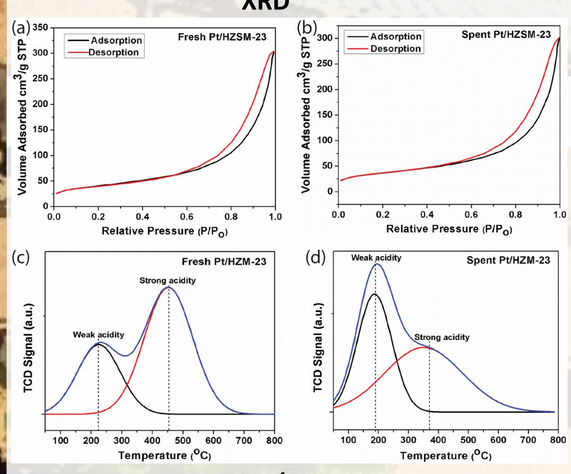
Catalyst Characterization



XRD



SEM/TEM



Nitrogen adsorption/ desorption isotherms

Analysis	Fresh Pt/HZSM-23	Spent Pt/HZSM-23
BET surface area	141.4 m^2/g	129.0 m^2/g
External surface area	119.6 m^2/g	116.9 m^2/g
Micropore area	21.75 m^2/g	12.01 m^2/g
Pore volume	0.01 cm^3/g	0.005 cm^3/g

Ammonia temperature programmed desorption

Analysis	Fresh Pt/HZSM-23	Spent Pt/HZSM-23
Total acidity	2.8 mmol/g	1.9 mmol/g
Weak acidity	0.9 mmol/g	0.9 mmol/g
Strong acidity	1.9 mmol/g	1 mmol/g

BET/NH_3-TPD

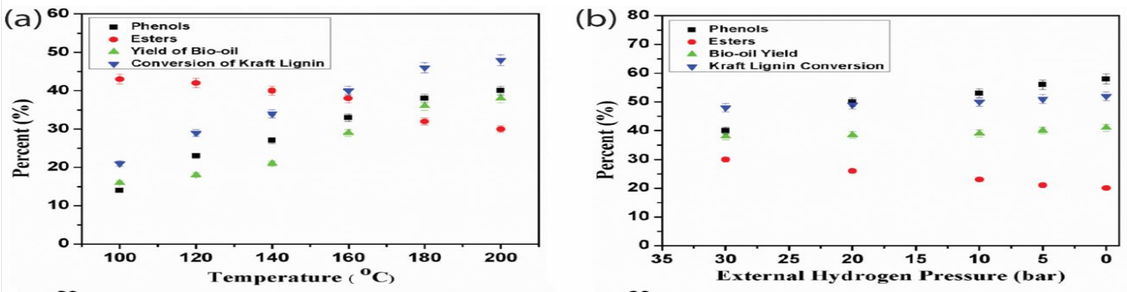
Conclusions

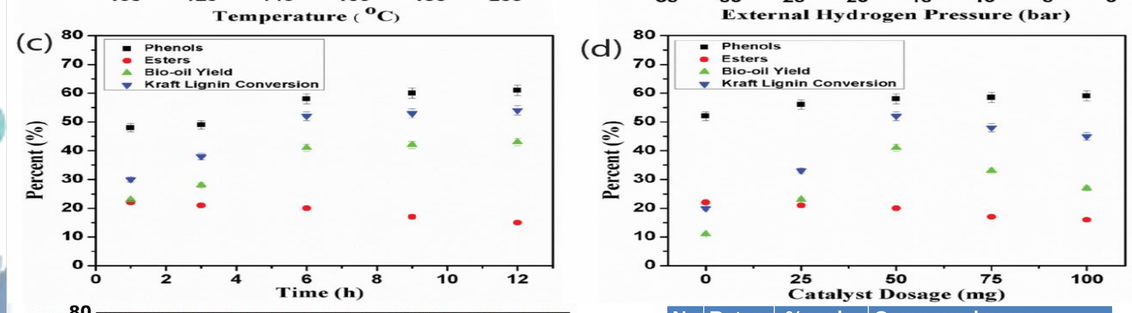
- Kraft Lignin was successfully converted into substituted phenols and aromatics having several applications
- Reductive depolymerization of Kraft Lignin using Pt/HZSM-23 catalyst led to a conversion of 52 wt% and a bio-oil yield of 41 wt% under optimum reaction conditions (200 °C, 6h)
- Mesoporous structure of Pt/HZSM-23 facilitated the transfer of large molecules derived from Kraft Lignin
- *In-situ* hydrogen generated from methanol was found to be more active than external hydrogen for the hydrogenation/hydrogenolysis of Kraft Lignin

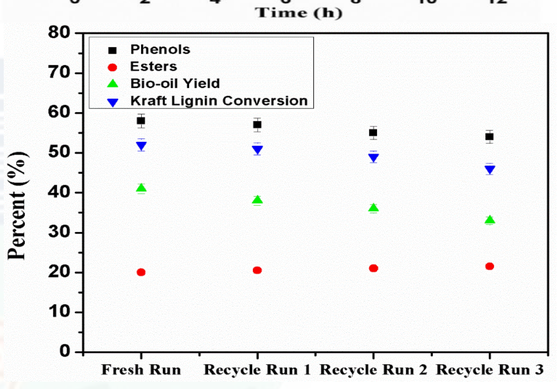
Industrial Significance

- **Successful conversion of Kraft Lignin will be a game changer for pulp & paper industry for efficient utilization of lignin to generate more revenue by getting rid of waste lignin and producing chemicals such as aromatics and phenols for applications as precursors in various industries like food, fragrance, pharmaceuticals, personal care, diesel fuel additives**
- **Lignin conversion technology can also be a crucial step for biorefineries, sugar mills and other agro residue conversion plants as lignin is the toughest to convert, thus often left as waste.**

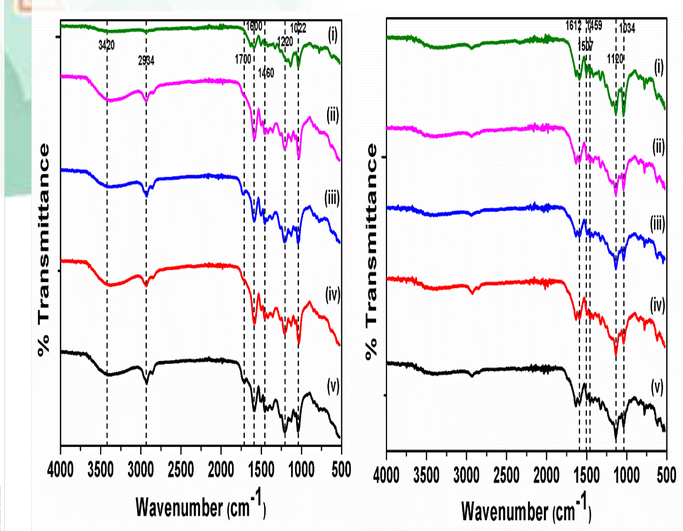
Results







No	Retention time (min)	%peak area of GC-MS chromatogram	Compound name
a	6.45	11.45	Phenol, 2-methoxy-
b	8.86	1.95	Phenol, 2-methoxy-4-methyl-
c	11.02	4.14	Phenol, 4-ethyl-2-methoxy-
d	11.97	1.73	2-methoxy-4-vinylphenol
e	14.31	4.79	Benzaldehyde, 4-hydroxy-3-methoxy
f	15.43	1.65	Phenol, 2-methoxy-4-(1-propenyl)-
g	16.48	3.96	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-
h	17.13	3.1	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester
i	17.83	6.62	Benzene, 4-butyl-1,2-dimethoxy-
j	18.74	5.95	Ethanone,2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-
k	20.33	6.42	Benzenepropanol, 4-hydroxy-3-methoxy-
l	25.95	3.08	Hexadecanoic acid, methyl ester
m	29.11	2.01	9,12-Octadecadienoic acid (Z,Z)-methyl ester
n	29.29	4.89	9-Octadecenoic acid, methyl ester, (E)-
o	29.74	1.55	Octadecanoic acid, methyl ester
p	32.64	1.97	Methyl-12-hydroxy-9 octadecenoate
q	33.43	2.86	Methyl dehydroabietate
r	34.22	1.96	Methyl abietate

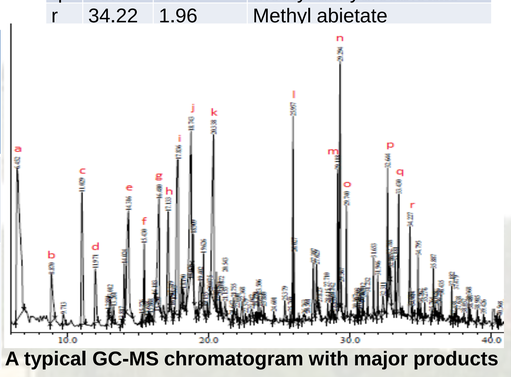


FTIR of liquid product

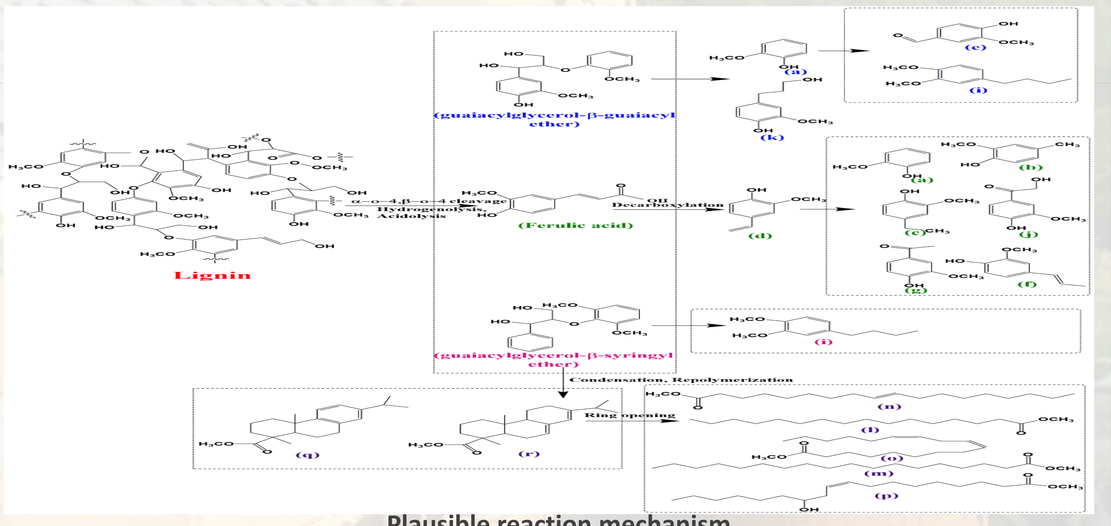
Frequency (cm^{-1})	Type of vibration/ compound
1220 and 3420	–OH groups of phenols
1460 and 2934	C-H stretching in alkanes (aliphatic esters)
1022	–OCH_3 of methoxy substituted phenols
1460 and 1600	C=C stretching in the aromatics

FTIR of solid product

Frequency (cm^{-1})	Type of vibration/ compound
1034 and 1120	C-O-C ether bond
1459, 1507 and 1612	aromatic nuclei of benzene structure



A typical GC-MS chromatogram with major products



Plausible reaction mechanism

References

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Acknowledgement

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