Understanding the depolymerization of lignin into value-added chemicals

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Abstract: Depolymerization of lignin is vital to make lignocellulosics (2G) to bio-ethanol process economically viable. The efforts in our group were undertaken to depolymerize lignins derived from various sources having very high molecular weights (10000-60000 Da) using solid acid and acidic ionic liquids. Also efforts were taken to catalyze this reaction using solid base catalysts. The results were encouraging to see that almost 30-80% yield of organic solvent soluble products with lower molecular weight could be obtained. The detailed analysis of lignins, products and catalysts along with correlations between lignin-product and activity-catalyst property were established.

Keywords: Lignin, Depolymerization, Catalyst.

1. Introduction

Lignin, an only naturally available aromatic polymer has a 3-D amorphous structure consisting of methoxylated phenylpropane structure in general and in particular is made up of three major units; p-coumaryl, coniferyl and sinapyl alcohols connected through numerous linkages such as ≡C-O-C≡ (β-O-4, α-O-4, 4-O-5 etc.) and ≡C-C≡ (β-5, β-1, β-β, etc.).[1-4] Since the amount of these linkages and units show dissimilarities in different lignins, efforts are taken to understand those differences and their effects on depolymerization products. The catalytic depolymerization of lignins would be interesting to carry out with solid and liquid acids along with solid base as catalysts. These catalysts would show several advantages over conventional processes like pyrolysis, gasification, supercritical, homogeneous etc.

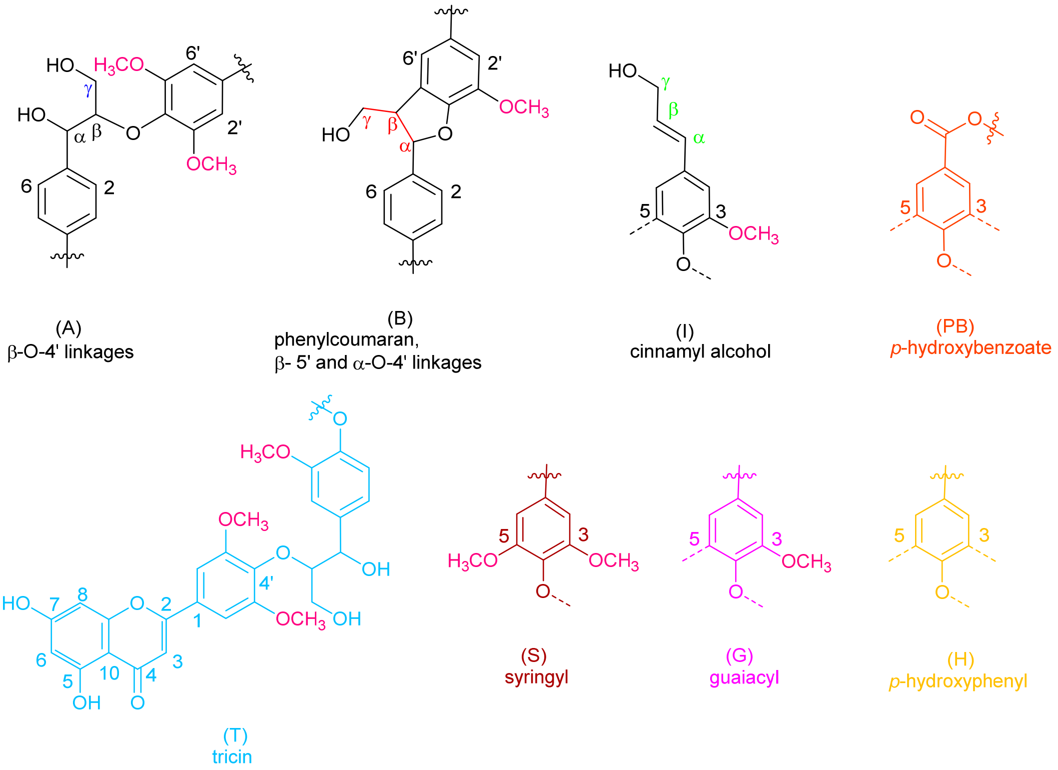
2. Experimental (or Theoretical)

Lignins were purchased commercially and were also isolated in the laboratory. Those were depolymerised in batch mode reactor at 120-250°C for 30 min – 120 min using acidic and basic catalysts. The products were extracted in various organic solvents and identification and quantification of products was done by GC, GC-MS, LC, LC-MS techniques.

3. Results and discussion

By XRD, GPC, MALDI-TOF, TGA and elemental analysis it was found that different lignins have comparable properties on bulk level but, molecular level analysis conducted using UV-Vis, ATR, 1D/2D HSQC/NOSEY NMR techniques disclosed that lignins used in these studies have varying concentrations of G, H, S and T substructures (Figure 1).

The catalytic reactions were done using acidic and basic catalysts and both the types of catalysts could show depolymerisation activity to form organic solvent (THF, DEE, EtoOAc) extracted low molecular weight aromatic products with varying yields (30-80%).[3, 4] However, depending on the reaction conditions employed the product distribution varied. From the GC, GC-MS, LC and LC-MS studies, identification and quantification of the products formed in the reactions were done. Additionally, efforts are taken to correlate the product distribution based on the lignin properties and also change in the functional groups is checked between lignin and products by IR and NMR techniques. The effects of physico-chemical properties of catalysts were also studied in detail on the depolymerisation activity. To understand why catalysts show good activity, interaction studies between catalyst and substrates was undertaken, which throw light on the mechanistic aspects of the reactions.



(A)
β-O-4' linkages

(B)
phenylcoumaran,
β- 5' and α-O-4' linkages

(I)
cinnamyl alcohol

(PB)
p-hydroxybenzoate

(T)
tricin

(S)
syringyl

(G)
guaiacyl

(H)
p-hydroxyphenyl

Figure 1. Different substrcutures present in lignin.

The products were formed with high efficiencies because milder reaction conditions (<250^{o}C) were used compared to earlier known methods like pyrolysis (>300^{o}C), gasification (>500^{o}C), supercritical (>300^{o}C) etc. which essentially give gases as major products along with char and tar formation. The mass balance obtained under our reaction conditions was very high (>90%).

4. Conclusions

It was concluded that lignins obtained from various sources could be depolymerised with high efficiencies by developing environmentally benign method and also under milder conditions than reported earlier. The effects of substructures present in lignin are also seen to be influencing the activity of catalyst..

References

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