

# **Catalytic depolymerization of lignin over HZSM5**

*A thesis Submitted to Indian Institute of Technology Hyderabad In Partial Fulfilment of the Requirements for The Degree of Master of Technology*

By

**VIBIN VARGHEESE**  
CH14MTECH11020

*Under the guidance of*

**Dr. Debaprasad Shee**



Indian Institute of Technology  
Hyderabad

***Department of Chemical Engineering  
Indian Institute of Technology Hyderabad  
June, 2015***

## **DECLARATION**

I declare that this written submission represents my ideas in my own words and where ideas or words of other have been included: I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the institute and can evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.



(SIGNATURE)

VIBIN VARGHEESE  
CH14MTECH11020

## APPROVAL SHEET

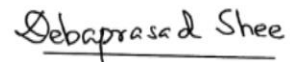
This Thesis entitled "*Catalytic depolymerization of lignin over HZSM5*" by Vibin Vargheese is approved for the degree of Master of Technology from IIT Hyderabad.



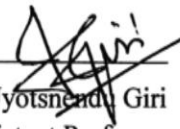
Dr Saptarshi Majumdar  
Associate Professor  
Dept. of Chemical Engineering  
Indian Institute of Technology Hyderabad  
Examiner



Dr. Sunil Kumar Maity  
Associate Professor  
Dept. of Chemical Engineering  
Indian Institute of Technology Hyderabad  
Examiner



Dr. Debaprasad Shee  
Assistant Professor  
Dept. of Chemical Engineering  
Indian Institute of Technology Hyderabad  
Supervisor



Dr. Jyotsnendu Giri  
Assistant Professor  
Dept. of Biomedical Engineering  
Indian Institute of Technology Hyderabad  
Chairman

## **Acknowledgement**

First, I would like to express my deep and sincere gratitude to my adviser Dr. Debaprasad Shee, Asst professor, Indian Institute of Technology, Hyderabad for giving me the opportunity to do this project and providing excellence guidance throughout this research. His sincerity and motivation have deeply inspired me. He has taught me the methodology to carry out the research and to present the research works as clearly as possible. It was a great privilege and honour to work and study under his guidance. I am extremely grateful for what he has offered me.

I would like to thank Dr. Saptarshi Majumdar, Asst Professor, Department of Chemical engineering, Indian Institute of Technology, Hyderabad for his immense support and guidance throughout the execution of this project, his outlook towards the problem and methodology to solve them way really inspiring, more over that I want to thank him for motivating the group all the time.

I would like to extend my sincere thanks to my seniors Deepak Raikwar, PhD. You was always such an caring and helping personality, research was motivating and approachable with your assistance

Moreover I want to thank all my lab mates Suhail Farokhi and Venkata Chandra Sekhar Palla for their assistance during my project.

In the end I want to give my gratitude towards the Department of science and technology for giving us finical aide and support to conduct this research at IIT Hyderabad.

# CONTENTS

ABSTRACT.....	i
LIST OF TABLES.....	iv
LIST OF FIGURES.....	v
1.INTRODUCTION.....	1
2.LITERATURE REVIEW.....	3
2.1 STEAM EXPLOSION.....	3
2.2 ORGANSOLOV PROCESS.....	3
2.3 IONIC LIQUID LIGNIN.....	4
2.4 KRAFT PROCESS and SULPHITE PROCESS.....	4
2.5 ALKALI PRE TREATMENT COUPLED WITH ACID TREATMENT.....	5
2.6 AMMONIA FIBER EXPLOSION .....	5
2.7.1 HYDROTHERMAL DECOMPOSITION .....	6
2.7.2 CoMo SULFIDE-CATALYZED HYDRODEOXYGENATION .....	6
2.7.3 PRODUCTION OF PHENOLS VIA CATALYTIC CRACKING .....	7
2.7.4 EFFECTS OF MESOSTRUCTURED SILICA CATALYSTS .....	7
2.7.5 HZSM-5 CATALYZED ONE-POT SOLVOLYTIC DEPOLYMERIZATION .....	8
2.7.6 SOLID ACID CATALYZED DEPOLYMERIZATION .....	8
2.7.7 FORMIC-ACID-INDUCED DEPOLYMERIZATION .....	9
2.7.8 CONTROLLING THE SELECTIVITY TO CHEMICALS FROM LIGNIN .....	9
2.7.9 THE ROLE OF SHAPE SELECTIVITY .....	10
3. Experimental.....	11
3.1 Materials .....	11
3.2 Reactions .....	11
3.3 Extraction .....	11
4 Product characterization.....	13
4.1 Fourier Transform Infrared Spectroscopy .....	13
4.2 Molecular weight analysis of lignin using viscosity .....	13
5. Results and discussion.....	14
5.1 Parameters and factors.....	14
5.2 Effect of Temperature.....	14
5.3 Effect of catalyst-to-lignin ratio (HZSM-5).....	14
5.4 Effect of NaOH.....	15
5.5 Effect of Si/Al ratio of HZSM-5.....	15
5.6 Effect of hydrogen pressure .....	15
5.7 Effect of heating profile.....	15
5.8 Effect of different solvent.....	18

5.9 Molecular weight of lignin.....	18
5.10 Characterization of lignin and residual lignin.....	19
5.11 Characterization of liquid phase.....	20
5.12 Identification of products.....	21
6. Conclusion.....	22
7. Reference.....	23

## ABSTRACT

The situation around the globe is changing dramatically. There are many factors political and climate change that are affecting the rate of consumption of fossil fuel, Nowadays the consumption of the fossil fuels have reached a critical level which challenges their existence for the consumption of future generation simultaneously having an adverse effect towards the society and our environment. So here we are focusing our interest towards the economical use of Lignin, which is one of the primary by product from bio refinery and paper, and pulp industry, it is composed of complex aromatic compounds. Thus If we are able to break it to monomeric units then these compounds can be utilized as a source of industrial chemical from an bio refinery, reducing our dependence towards the fossil fuel. Here we have studied the catalytic depolymerisation of lignin using HZSM 5 as our catalyst, under different parameters of temperature, pressure and with different solvent like methanol, ethanol, butanol, iso propanol. A detailed analysis of the products was conducted. We have achieved to produce benzene, xylene, catechol, cresol, phenol and guaiacol via our reaction. Simultaneously maintaining more than 95% conversion in most of the reaction, with minimal amount of char formation.

## **LIST OF FIGURE**

Fig1: Major linkages found in lignin polymer

Fig 2: Structure of lignin monomers and basic monomeric units

Fig3: lignin structure and strategies for depolymerization

Fig 4: Product separation scheme

Fig.5: Lignin conversion, monomer yield and char formation at different reaction conditions

Fig.6: Reduced viscosity ( $\eta_{sp}/c$ ) vs concentration of lignin solutions in 0.4% NaOH at 70 °C

Fig.7: FTIR spectra of (A) Pure Lignin and residual lignin (B) without catalyst and (C) with catalyst (HZSM-5)

Fig.8: GC peak for benzene and product sample

Fig.9: GC peaks for pure samples

## **LIST OF TABLE**

Table 1 : Shape selectivity

Table 2: Lignin conversion, monomer yield, char production at different experimental conditions

Table 3: Yields of products under different reaction conditions

Table 4: Effect of different solvent



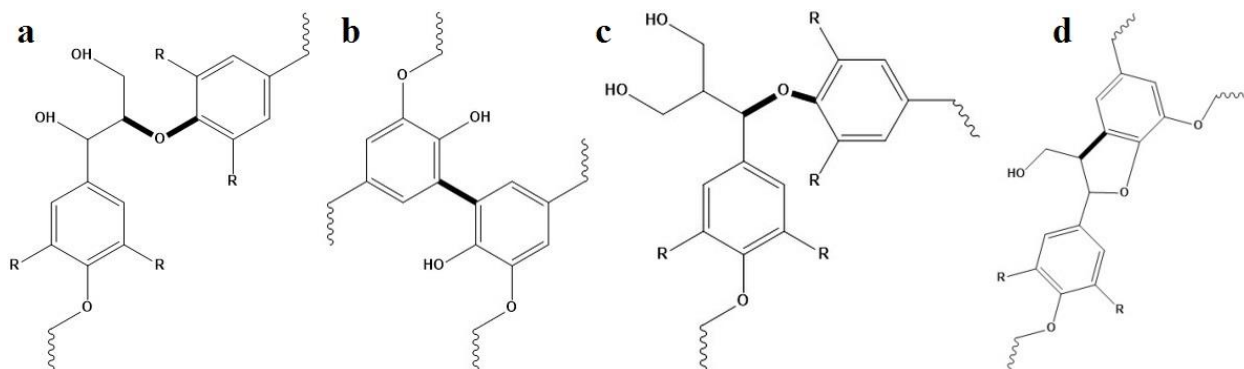
# 1. INTRODUCTION

The current technological and environmental situation around the globe is in a transition state. With the rapid development in the society, due to the industrial revolution coupled with geo political and technological changes has caused adverse impact to the environment. The rate of consumption of the fossil fuels have reached a critical level which challenges there existence for the consumption of future generation. So it's the need of the hour that we have to focus more on the renewable sources of energy. Picking just the slice of this cake, we will be focusing here on the utilization of lignin as a source for value added chemicals. Here we will discuss its origin, chemical structure, and extraction, scope of this study, the current development and our plan of action along with challenges.

Lignin comes under the class of lignocellulosic biomass; lignocellulose is one of the most abundant sources of biomass produced from photosynthesis. Annually around 200 billion metric tons of lignocellulosic biomass is produced worldwide. It mainly consists of three major biopolymers cellulose, hemicellulose and lignin. The composition of these biopolymers varies greatly with respect to their plant species, tropical conditions and plant parts. [1]

The main role of lignin is that it acts as glue, which binds the hemicellulose and cellulose together that gives rigidity and strength to the plant. It is an amorphous polymer, which mainly consists of three C6C3 types of monolignols coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. [2] These monolignols are cross linked with each other by various inter-unit linkages such as  $\beta$ -O-4,  $\beta$ - $\beta$ ,  $\beta$ -5,  $\beta$ -1, 5-5, 4-O-5,  $\alpha$ -O-4 etc.[3] Among which the alkyl-aryl ethers linkage  $\beta$ -O-4 and  $\alpha$ -O-4 accounts for about 45-62% and 3-12% respectively.[4] But in general the  $\beta$ -O-4 and 5-5 are the major linkages found in the plants which together accounts for around 70-90% of the linkages.[5]

The average bond dissociation energy of these bonds is as follow  $\beta$ -O-4 [290 kJ mol<sup>-1</sup>],  $\beta$ -5 [530 kJ mol<sup>-1</sup>],  $\beta$ -1 [280 kJ mol<sup>-1</sup>], 5-5 [490 kJ mol<sup>-1</sup>], 4-O-5 [330kJ mol<sup>-1</sup>],  $\alpha$ -O-4 [215 kJ mol<sup>-1</sup>].



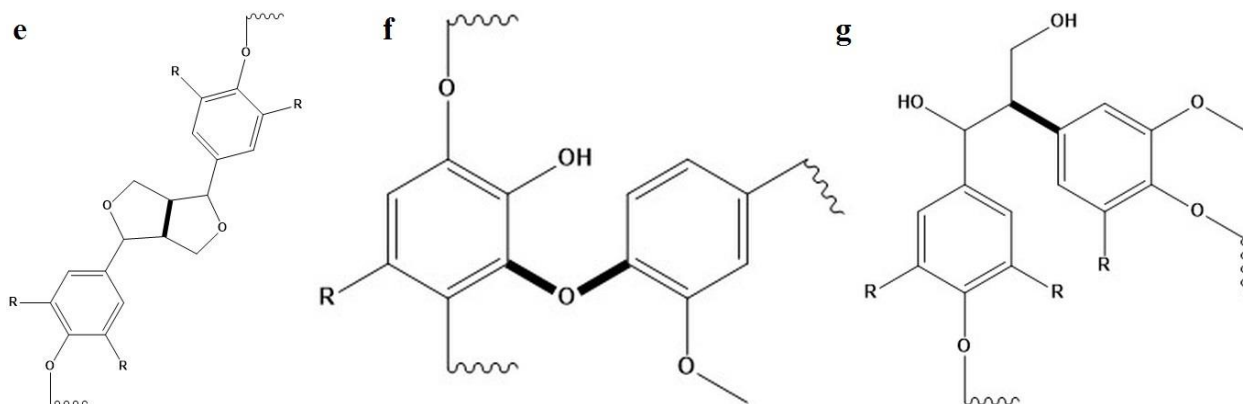


Fig1: Major linkages found in lignin polymer (a)  $\beta$ -O-4, (b) 5-5, (c)  $\alpha$ -O-4, (d)  $\beta$ -5, (e)  $\beta$ - $\beta$ , (f) 4-O-5, (g)  $\beta$ -1

Figure 1 gives us an idea of how the different cross linkages are present in the lignin. In addition, the composition of these three monolignols depends upon the type of plant under consideration like the composition of coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol will be different for soft wood and hard wood. Softwood lignins contain considerably very less amount of sinapyl lignin, which have methoxyl groups at both the C3 and C5. Whereas the hard wood lignin, have a majority of sinapyl alcohol. [6]

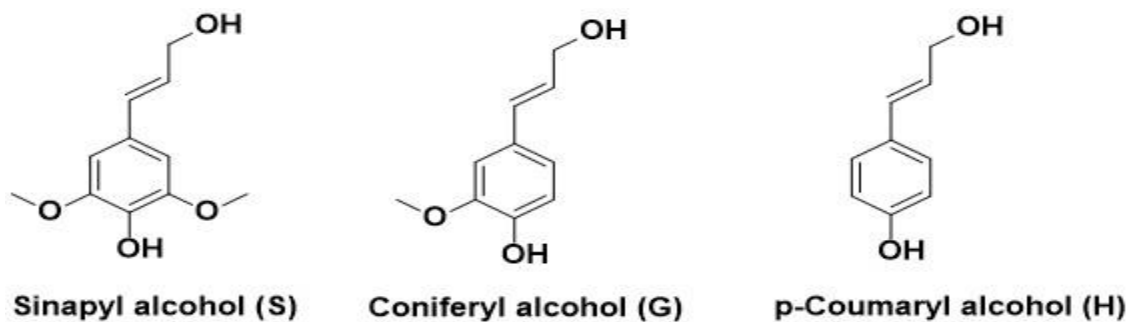


Fig 2: Structure of lignin monomers and basic monomeric units

While the extraction of lignin it is nearly not possible to obtain its natural structure as it is, because due the rigorous chemical and physical condition applied during the extraction process its structure and chemical composition changes extensively.

As we can see from the figure 1 and 2 that lignin is composed of mainly aromatic structure of the class of benzoic and phenolic family. It is the only class of lignocellulosic branch whose basic structure is aromatic. However, until this date the utilization of lignin as a source of aromatic is still a challenge due to its complex structure and linkages. Therefore, here is why researcher around the globe are interested in lignin: 1) access to a large reservoir of aromatic hydrocarbons, 2) by deoxygenation of ethereal oxygen we can easily obtain hydrocarbons, and 3) it is potential

root for nanostructured carbon by the carbonization of lignin in the presence of/or absence of directing templates. [7]

Lignin is one of the main product from bio chemical process, thus if we can find an optimized method for the extraction of valuable chemicals from these lignin, then we can not only reduce the cost of bio fuels like ethanol, but we can also make the society free from the dependence of fossil fuels as most of the chemicals are petrochemical. However, there are prior needs of infrastructure development in this sector.

Further, we will discuss about the different methods for extraction of lignin. Its characterization, properties and the methods used for it is the degradation.

## **2. LITERATURE REVIEW**

### **2.1 STEAM EXPLOSION**

Prior to steam explosion the lignocellulosic biomass is dried in an oven for 16 h and then shredded to a size of 2-5 cm. After that, this raw material is fed to a reactor where it is exposed to steam in the range of 16-34 kg/cm<sup>2</sup> and along with that, a temperature in the range of 200-240 °C is maintained. The resident time for this process varies from 30 s - 20 min. After the completion of reaction time, we open the valve rapidly to atmospheric pressure, which results in the explosive decompression of the material. The sample thus obtained is collected, cooled down and screened into powders. [8]The fibers thus obtained are then subjected to alkaline extration where the steam exploted fibers are mixed with 1.5 mol/L NaOH at 70°C for around 120 min with a wood to liquid ratio of 1:10. The solid residue thus obtained are washed to a newtral pH and then dried to get the exploded fibers. The liquid is neutralized to a pH 4 by addition of sulphuric acid, the precipitates are then isolated by filtration and then dried aroud 40°C to obtain alkaline extractable lignins.[9]

Steam explotion results in the cleave of  $\beta$ -O-4 linkage accompanied by condensation reaction and demethylation of aromatic methoxy groups. Furthermore, the amount of lignin extracted depends upon the reaction time, if we increase the reaction time then there are chances of repolymerisation, but by increasing the water to biomass ration, it will reduce the chance for repolymerisation.

### **2.2 ORGANSOLOV PROCESS**

Prior to the process the biomass may be crushed or milled for loosing the structure, thus a milled wood lignin can be an optimum feed stock. After this the organic solvent is selected according to the requirement, the bio mass is then mixed with the organic solvent and inorganic acid catalyst such as HCL or H<sub>2</sub>SO<sub>4</sub> which helps in rupturing the lignin hemicellulose bonds, the mixture is left for some time (for 24 hr.), then the organic suspension is put in a reactor, which is then heated and pressurized for some time (generally for 30 to 60 min.). After which, during the process the lignin and hemicellulose are dissolved in the organic solvent. The cellulose are

obtained as solids, thus the liquid phase and solid phase are separated using the filtration. The organic solvent is recovered and the black liquor containing lignin is precipitated by dilution (by adding water). Now if the process is taken place at an temperature range of around 185-210°C there is no need for acid addition as the organic acid thus produced from the biomass act as a catalyst for the degradation of lignin-carbohydrate complex.[10][11][12]

The solvents generally used are ethanol, methanol, ethylene glycol, acetone and tetrahydrofurfuryl alcohol. The solvent to feed ration varies from 4:1 to 10:1 (w/w). While the pH is maintained in between 2 to 3.8. During the process the major component cellulose is only partially hydrolyzed and thus remain insoluble where as the hemicellulose is hydrolysed to soluble fraction such as oligosaccharides, monosaccharides, and acetic acid. The acetic acid thus produced lowers the pH of the medium thus promoting the acid catalysed hydrolysis of the other components. As a result lignin breaks down into smaller molecular weight fraction which is soluble in aqueous organic solvent.

The ethanol-acetone solvent mixture gives the highest amount of pulp. Now one of the advantage of this process is that the organic solvent used can be recovered by simple distillation technique and further we don't use any catalyst in this process so it is cost effective.

### **2.3 IONIC LIQUID LIGNIN**

Here the pre-crushed or flour of the biomass is mixed with the preheated ionic liquid and the mixture is then stirred under a desired condition. After the reaction is over the lignin thus dissolved is separated from the undissolved residue and after which it is precipitated upon addition of organic solvents which is then separated by filtration to remove the ionic liquid which is then recycled. The ionic liquids are generally salts in liquid state, whose boiling point is less than 100°C.[13]

Given that the  $pK_a$  values for the reagents are Py 5.14, Mim 7.50, Pyr 11.27, and HAc 4.76. Thus the choice of a correct solvent is necessary. Further more this method is not so popular as the ionic liquids are very expensive and thus they can't be used in a commercial scale.[14]

### **2.4 KRAFT PROCESS and SULPHITE PROCESS**

In kraft process we make use of the white liquor which is a mixture of sodium hydroxide and sodium sulfite. During the process the wood is first treated with steam and then it mixed with white liquor, the liquor breaks the linkage between cellulose and lignin. Now cooking liquor which is a mixture of white liquor, chips in water and weak black liquor is fed to a pressurized reactor. The temperature in the reactor is maintained between 150-180°C with a considerable resident time. After this the black liquor containing lignin is separated from the solid pulp. For the regeneration of white liquor we need to remove the lignin from the black liquor. This can be done by the acid treatment, organosolv and ultrafiltration.[15]

During the sulphite process the  $SO_2$  along with the biomass is added to the autoclave. But the type of reaction that will take place depends upon the amount of  $SO_2$  added during the reaction. So based on the concentration of  $SO_2$  the process can be classified as acid sulfite, bisulfite, neutral sulfite, alkaline sulfite. The acid process have a range of pH 2-3, followed by bisulfate

processes operated at pH range of 3-5, neutral sulfite at a pH range of 6-9 and alkaline sulfite processes have pH range above 11.

During acid sulfite cooking, lignin and hemicelluloses were dissolved simultaneously. As the cooking time increased at a specific temperature, spent liquor pH had decreased. Longer the cooking time, lower will be the spent liquor pH because during cooking, acetic acid is formed from acetylated polysaccharide of the hemicelluloses. Acetic acid formation enables the hydrolysis for the dissolution of the hemicelluloses and cleavage of lignin carbohydrate bonds. When pulp is cooked for longer time, condensation of lignin on fiber takes place which results in black cook. To deal with the problem of pH regulation we add counter ions that are used as buffer to maintain the pH of the solution .

## **2.5 ALKALI PRE TREATMENT COUPLED WITH ACID TREATMENT**

During alkali pre treatment also known as the soda pulping. The solid is treated with aqueous solution of NaOH with a solid: liquid ratio of around 1:10, at a temperature around 100°C for a duration near around 3 hr. After the completion of process the black liquor containing lignin is filtered out, which having a pH in the range of 12. Which is then treated with acidic solution to reduce the pH to 2-3. It results in the precipitation of lignin, which is then separated using a centrifuge. The property of lignin thus obtained depends up the pH at which it is obtained. Figure 4 shows the colour change associated with black liquor with addition of acid.

## **2.6 AMMONIA FIBER EXPLOSION AND CARBON DIOXIDE EXPLOSION**

Ammonia fiber explosion is a physicochemical process in which the biomass is treated with liquid ammonia at an elevated temperature and pressure, then similar to steam explosion the valve is opened suddenly. The amount of ammonia used is usually 1-2 kg of ammonia per kg of biomass(dry) and the temperature will be around 90°C for around 30 min. The ammonia reacts with the lignin-carbohydrate linkage and results in the degradation of lignin.

Similarly for the case of carbon dioxide explosion, CO<sub>2</sub>, which is at a lower temperature than that of steam explosion, is used. As the CO<sub>2</sub> forms carbonic acid when dissolved in water, the acid thus produced increases the rate of hydrolysis. It is cheaper than steam explosion. [17]



There also many other methods like ozone treatment using O<sub>3</sub>, which is carried at room temperature. Similarly oxidative delignification in which biodegradation could be catalyzed by the peroxidase enzyme with the presence of H<sub>2</sub>O<sub>2</sub> and also ultrafiltration which is a post pretreatment method which uses the ceramic material like TiO<sub>2</sub> to separate lignin from black liquor. Enzymatic treatment is also studied but is not as popular as the enzymes are temperature sensitive, their handling and stability is an issue.

## **2.7 DEGRADATION OF LIGNIN**

Now here we will discuss about the different methods applied for the valorization of lignin. Many researches are going on the field of thermal cracking, hydrolysis, catalytic hydrolysis, Catalytic hydrodeoxygenation, enzymatic degradation etc. However, in a catalytic process many things has to be taken into account as if the acidity of the catalyst, its stability, catalyst cost and more over the porosity and regularity of the pore size plays an important role in the process. The

selective breaking of the cross linkages, without affecting the aromaticity and the removal of oxygen is an important challenge.

### **2.7.1 HYDROTHERMAL DECOMPOSITION [16]**

Here they have used sub and supercritical water, which have a positive effect in the hydrothermal degradation of lignin to phenolic products. In this process, the reaction carried out in a batch reactor where 5g of alkali lignin and 95 g of water used in each run. The temperature for hydrothermolysis varied from 553 to 663k. The reaction performed for different holding time starting from zero min to 120 min.

After the completion of reaction, the liquid fraction separated and characterization of the fraction performed using a GC-MS. Thus in the above process they have concluded that high molecular weight alkali lignin can be successfully degraded into low molecular weight components. The maximum yield of the main products differed with temperature like for guaiacol, catechol, phenol and cresol isomers reached the highest values of approximately 11.23% (553 K, 0 min), 11.11% (653 K, 0 min), 4.21% (663 K, 240 min) and 7 % (663 K, 240 min). Therefore with the variation in the in the temperature the composition of the post-reaction solid residue differed significantly.

But in this process the yield of products are distributed over a large scale an most of them are phenolic compounds. Thus, it is not suitable for our case, where the production of benzene toluene and xylene is our priority.

### **2.7.2 CoMo SULFIDE-CATALYZED HYDRODEOXYGENATION [17]**

Here they have used sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of lignin model compound at 50 bar hydrogen pressure and around 300°C in a dodecane solvent. In many of the studies hydrodeoxygenation of lignin and other bio-chemical process, they have used cobalt and nickel promoted molybdenum catalyst. Due to the lower intrinsic hydrogenation activity, the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst is generally preferred over nickel.

The support Al<sub>2</sub>O<sub>3</sub> consists of acidic sites and these acidic site participate in the guaiacol conversion, in the formation of ring-methylated products as well as formation of heavier products. Researchers have also studied the de-activation of the catalytic sites with ammonia, water and H<sub>2</sub>S. From which we can conclude that the oxygen elimination reaction are poisoned by sulfur and nitrogen containing compounds

Form the above table we can notice that the product depends upon the model compound, as these are model compounds it's difficult make a judgment about the reaction that will take place with the lignin compound. However, it gives us an idea on the pathway of reaction taking place.

Change in the reaction parameter or long reaction time will lead to the coupling of guaiacol or catechol thus, leading to oligomerization. When such a compounds are formed, they cannot be detected by the GC analysis, which results in the mass balance closed to 80-90% in most of the reaction.

It should n=be noted that for the hydrogenation reaction to take place the molecules must be adsorbed flat over the surface of the catalyst, and in order for the ring methylation reaction to take place the aromatic ring must approach the catalyst surface while an forced non-planar co-ordination will hamper methylation

### **2.7.3 PRODUCTION OF PHENOLS VIA CATALYTIC CRACKING [18]**

Here the lignin depolymerized into lower molecular weight liquid products and into its constituent monomers. For this, purpose the hydrolysis carried out using a solid catalyst in a water alcohol mixed solution. The lignin-derived slurry then converted into phenol by catalytic conversion.

Now thus for the depolymerisation the lignin along with silica alumina (Si/Al=2) catalyst, mixed in a solution of water and 1-butanol in an autoclave. The weight ratio of lignin to silica-alumina to solvent was 1:1:30. The reaction carried out at 473-623 K for 0.5-8 hour. After the completion of the reaction, the gaseous product collected with a gas pack and the remaining slurry filtered to get the lignin-derived slurry.

As the targeted chemicals mainly found in the BuOH phase, thus, the catalytic cracking of the BuOH phase was carried out in a fixed bed reactor at 673 K for 2 h, Under atmospheric condition.

It's believed that the hydrolysis of lignin over silica-alumina mainly occurred in the water phase, and thus the extraction of phenolic compound by BuOH phase promoted the reaction.

The conversion of lignin to phenol and aromatics entirely depends upon the solvent used and the reaction parameter like time and temperature. Figure 6 explains the importance of these parameters.

### **2.7.4 EFFECTS OF MESOSTRUCTURED SILICA CATALYSTS [19]**

In this work organosolv lignin, which then purified with alkali treatment was used. The depolymerisation of the lignin studied at several temperature and solvent system with and without the presence of solid catalysts. The catalyst used where NiMo/Al<sub>2</sub>O<sub>3</sub> and mesostructured silica (SBA-15 and MCM-41) and oxide support like ZrO<sub>2</sub>-MCM-41 chosen due to its higher stability.

The catalyst prepared using incipient wet impregnation and the lignin fed to the autoclave, mixed with water or methanol and with or without the presence of catalyst. The reaction temperature maintained from 200-350 for 60 min.

Now after the analysis of the sample, it was found that there was significant decrease in the solid fractions with MCM-41 and SBA-15; the reason can be due to the acidity of mesostructured silica catalysts. The three catalysts MCM-41, SBA-15 and NiMo/Al<sub>2</sub>O<sub>3</sub> all gave similar amount of aqueous fraction. Further, it was concluded that the optimized reaction temperature is 300°C, and changing the reaction solvent from water to methanol/water further increased the yield of syringol.

### **2.7.5 HZSM-5 CATALYZED ONE-POT SOLVOLYTIC DEPOLYMERIZATION [20]**

Solvent-based conversion has reported to reduce the char formation with water and alcohols catalyzed by homogeneous base. The ionic product of high temperature water is three folds, which increase the solubility of organic compounds and the lower dielectric constant, which is favorable for oxygen removal.

Here the process carried out with gaseous hydrogen at elevated temperature and pressure (300 °C and 100 atm), but using methanol, ethanol and propanol is a better alternative for the supply of

hydrogen. In the process 0.1 g lignin, 0.1 g solid catalyst, 1.7 mmol NaOH in 20mL 1:1 water-methanol mixture was used in a autoclave. The Si/Al ratio was 42.

The results show that the products have a mass distribution in the range from 60-1000 m/z in both the catalytic reaction. During the process, the cleavage of  $\beta$ -O-4 linkage in lignin results in the release of monomeric and dimeric products. These linkages then cleaved by High temperature water in the presence of base catalyzed hydrolysis, these depolymerized products further undergo demethoxylation to give phenolic products, which are then hydrogenated to form cyclohexanol, the cyclohexanol then dehydrated to cyclohexene. It can be hydrogenate to form cyclohexane.

It should be noted that the addition of NaOH reduced the char formation, without the presence of NaOH char formed was 19.3 % but its presence reduced it <1%.

### **2.7.6 SOLID ACID CATALYZED DEPOLYMERIZATION [21]**

For obtaining a better result, it is necessary that we should reduce the diffusion resistance and to obtain this they have used water-methanol 1:5 solvent system, which believed to have a high solubility of lignin near to 100%.

As shown in figure 10, the catalytic performance of various solid acid catalyst used for the depolymerisation of lignin which carried out at 250°C for 30 min was studied and from the observation we can conclude that HUSY, HZSM-5 gave the highest yield. However, for the case of HUSY there are problems related with its stability at high temperature.

It concluded that lignin can be converted below 250°C to aromatic monomers using these solid acid catalyst. Lignin with very high degree of polymerization having a molecular weight of 60kDa was successfully depolymerized to value added chemicals. For the regeneration of catalyst, it has seen that SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> can be effectively reused with slight decrease in the activity after each run.

### **2.7.7 FORMIC-ACID-INDUCED DEPOLYMERIZATION [22]**

Here they have introduced a method in which depolymerisation of oxidized lignin was done in formic acid, that resulted in the 60 % yield of low molecular mass aromatics. The studies have shown that the oxidation of C $\alpha$  alcohol to a ketone facilitates the removal of lignin from cellulose, by promoting the breaking of  $\beta$ -O-4 linkage.

The oxidized lignin was subjected to formic acid/ sodium formate. The reaction temperature was 110°C, and the amount of formic acid added was three equivalent of formate per S/G aromatic sub unit. The formic acid evaporated after 24 hr. and the residue was extracted with ethyl acetate. A soluble fraction of 61.29 wt % of lignin was obtained. The analysis via GC revealed considerable decrease in the molecular mass of the product compared to actual lignin. Over all 52 % of the lignin was converted to aromatics.



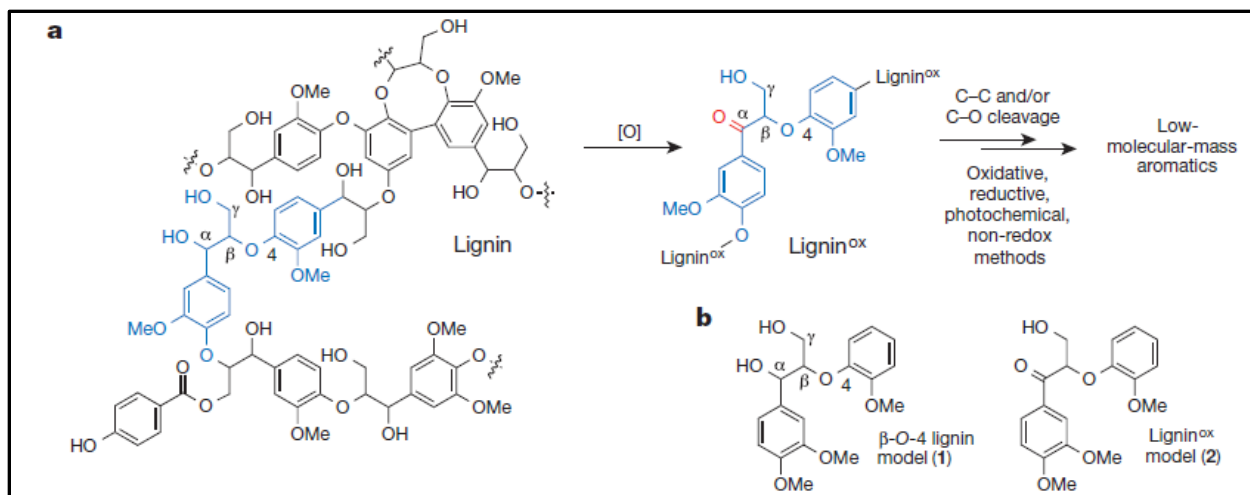


Fig3. lignin structure and strategies for depolymerization.

In figure 11 (a) defines the oxidation of lignin to (b) oxidized lignin. It was seen that for that the case of unoxidized lignin the conversion to aromatic lignin was only 7.2 %.

Their strategy is to first selective oxidation of secondary alcohol to a ketone, which then activates the cleavage of C-C or C-O bond cleavage.

### 2.7.8 CONTROLLING THE SELECTIVITY TO CHEMICALS FROM LIGNIN [23]

Here they have used different catalyst to study their effect for the conversion to aromatics. Like HZSM-5 with different silica to aluminum ratio, sulfated zirconia dispersed on a mesoporous MCM-41, Al-MSU-S. The kinetic diameter of many lignin derivatives is larger than 5.5-5.6 angstrom dimension of HZSM-5; therefore, HZSM-5 limits the mass transfer rates although it has higher acidic sites. Therefore, a mesoporous catalyst that will have large pore size as a result reduced diffusion resistance will be suitable. The Al-MSU-S has acidity as well as hydrothermal stability.

For the experimental setup 0.5 mg of biomass packed with catalyst with a 5:1 weight ratio. The pyrolysis condition is 650°C for 20s

The silica aluminum ratio In HZSM-5 affected the aromatics, SAR 23 and 30 gave the highest aromatic yield. The product yield will significantly improve by altering the pore size of the catalyst. The aromatic and coke formation inn a process is a function of acidity and pore size. Mesoporous catalysts removed the diffusion resistance, but due to the absence of crystalline micropore and the presence of large pores, they were not very selective to aromatic hydrocarbon. Thus, we need to optimize the size and the acidity of catalyst in order to increase the aromatic yield from it.

### 2.7.9 THE ROLE OF SHAPE SELECTIVITY [39]

So far, we have discussed about the different methods employed for the conversion of lignin to aromatic and catalytic conversion is the prior one. Here we will discuss about the importance of the pore size and the shape of catalyst.[24]

The conversion of biomass depends greatly on how the compounds can enter and diffuse through the pores of zeolite, which is determined by the structure and dimension of lignin, thus the pore size strongly influence the process. However, the effective pore size of zeolite depends upon the operating temperature; as 5.6 A to 6.62 at 300°C and can go up to 8.0 to 8.1 A at 650 °C.

**Table 1 Shape selectivity**

Compound	X	Y	Z	Critical Dia
Benzene	7.36	6.702	3.4	6.63
Toulene	8.314	6.701	4.172	6.7
P-xylene	9.085	6.701	4.175	6.63
Ethylbenzene	9.726	7.157	4.175	6.7

Comparing the table 5 and table 6 we can see that the pore size of ZSM-5 is less than the critical diameter of most of the basic aromatic compounds like benzene, toluene. However, we should remember that lignin has three-dimensional complex structure and to break them into smaller units we make use of this catalyst. However, from these data we can suggest that most of the reactions are taking place over the surface and the pores are not exposed. Therefore, we should make use of regular mesoporous acidic catalyst to effectively utilize the catalyst.

There is one alternative of increasing the temperature, but then the deactivation of the catalyst due to coke formation will be an issue. Therefore, we should focus on the development of mesoporous catalysts.

### 3. Experimental

#### 3.1 Materials

The lignin (alkali) was purchased from Sigma–Aldrich Co. (Product number 471003) and was used directly. The reagents used were Methanol (99%, SD Fine Chemicals), Butanol (99%, SD, Ethanol, iso-propanol (99%, SD Fine Chemicals), Fine Chemicals), Ethyl Acetate (99%, SD fine chemicals), Tetrahydrofuran (99.5%, SD fine chemicals), Gallium (III) nitrate hydrate (99.9%, Sigma-Aldrich Co.). The chemicals were used as received. ZSM-5 (CBV-2314 and CBV5524G, Zeolyst International) was purchased in the nominal ammonium cation form. The acidic form, HZSM-5, was prepared by calcination in air for 3 h at 500 °C. Ga/HZSM-5 catalysts were prepared through a wet impregnation technique. Appropriate amount of Gallium (III) nitrate hydrate and HZSM-5 were mixed to obtain 1% loading of Ga with respect to total catalyst. The water was then removed via drying at 110 °C for 6h. The resulting dried catalyst was calcined at 500 °C for 6 h with a ramp rate of 1 °C /min in muffle furnace. Finally, the catalyst was reduced using 10% H<sub>2</sub> balance in nitrogen gas 500 °C for 3 hrs.

#### 3.2 Reactions

The experiments were carried out in a 300-mL stainless steel high pressure batch reactor (Parr Instruments Co., Illinois, USA ) controlled by a temperature controller (Parr 4848). The reactor was loaded with lignin (0.75 g), a mixture of water and organic solvent (volume ratio 1/1, total 90 mL), NaOH (1.17mmol). Solvent like Methanol was used as the source for reductive equivalents via hydrogen transfer. The role of NaOH as a co-catalyst. The amount of catalyst was varied from 1:2 to 1:4 with respect to lignin. Reactions were performed at a temperature of 220- 250 °C. The reactor used to purged with nitrogen 3 to 5 times to expel air and after each reaction the vessel used to cleaned multiple times, The reactor was also pressured with H<sub>2</sub> in

some of the reactions. During the reaction the reactor was stirred using a mechanical stirrer set at desired rpm.. After desired reaction time had elapsed, the reactor was cooled to room temperature and the gases thus produced were purged out, in some cases they were taken to TCD detector for analysis of gaseous product.

### 3.3 Extraction

The liquid product along with suspended catalyst and lignin, from the reactor was acidified with 10% HCl until reaching a pH around 1-2 and stirred for 30 min. This is done to precipitate the unconverted lignin from the liquid solution. The acidified mixture is then filtered with Watmann filter paper to separate water soluble and water insoluble products. The water insoluble products (solids) in the filter paper were dried in vacuum oven at 60 °C for 24 hours. In this stage, the water insoluble products contains catalyst, char, unconverted lignin and trimeric compounds. The catalyst, char, unconverted lignin were separated from water insoluble products by dissolving in ethyl acetate. Unconverted lignin was then separated from catalyst and char by solubilizing subsequently in tetrahydrofuran (THF). The in-soluble were found to be char and catalyst, THF was evaporated to recover the unconverted lignin. The liquid from the first filtration step was mixed with ethyl acetate to extract the organic compounds from the solvent, after mixing the ethyl acetate and water phase will separate out, the ethyl acetate phase is then used for the product analysis in GC , The product separation is shown in Figure 4.

The following equations (1-6) were used to calculate the yields:

$$\text{Lignin Conversion (\%)} = 1 - \frac{w(\text{EtoAc insolubles} - \text{Catalyst used})}{w(\text{Initial lignin})} \times 100$$

$$E \text{ (wt\%)} = \frac{w(\text{EtoAc solubles})}{w(\text{Initial lignin})} \times 100$$

$$T \text{ (wt\%)} = \frac{w(\text{THF solubles})}{w(\text{Initial lignin})} \times 100$$

$$C \text{ (wt\%)} = \frac{w(\text{THF Insolubles} - w(\text{Catalyst added}))}{w(\text{Initial lignin})} \times 100$$

$$G \text{ (wt\%)} = 100 - (E + T + C)$$

Where, E = Ethyl acetate soluble products, T = THF soluble products, C = char, G = Gaseous products.

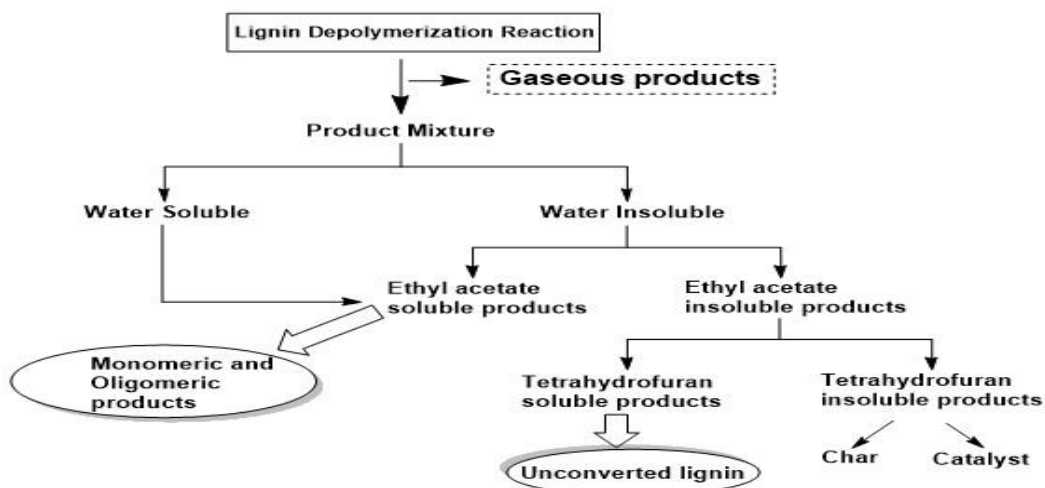


Figure 4: Product separation scheme

#### 4. Product characterization

The organic phase (EtoAc soluble products) containing our products were analyzed quantitatively with an Agilent 7890 GC-FID equipped with HP-5 capillary column (30 m×0.32mm×0.25µm) and nitrogen as a carrier gas. The column was initially kept at 50 °C for 5 min, then was heated at a rate of 10 °C /min to 120 °C, and maintained for another 5 min, then was heated at a rate of 10 °C /min to 280 °C which is maintained for another 8 min. The sample (0.1) was injected with an autosampler in a split mode with a column flow of 1.9 mL/min. In all cases identical methods of extractions and analysis conditions were maintained. For the identification of the products from our sample we used pure compounds like benzene, catechol, phenol, xylene, o-p-cresol and toluene. These pure sample were dissolved in the solvent EtoAC in minute amount, then fed to the GC to find out the corresponding resident time of each of the pure sample, then these data were compared with our product sample to find out which peak correspond to which one.

##### 4.1 Fourier Transform Infrared Spectroscopy

FTIR analyses on lignin and residual lignin were carried out in a transmission mode using a Perkin-Elmer spectrophotometer to get structural information. Pellets were prepared mixing 10 mg of samples in 200 mg of KBr. The range of data acquisition ran from 500 to 4000 cm<sup>-1</sup>.

##### 4.2 Molecular weight analysis of lignin using viscosity

Molecular weight of the lignin was determined using viscosity measurement. The lignin at different concentrations was dissolved in 4% NaOH solution at 70 °C. Then the absolute viscosity of the solution was measured using Brookfield DVII Pro viscometer. In solution, the fractional increase in viscosity due to the presence of macromolecules (solute) is defined as the specific viscosity:

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s}$$

Where  $\eta$  is the absolute viscosity of solution and  $\eta_s$  is the absolute viscosity of solvent. Because the degree of viscosity increase depends on the amount of dissolved material as well as on the molecular size, a more fundamental quantity, the reduced viscosity is defined as:

$$\eta_{red} = \frac{\eta_{sp}}{c}$$

Where  $c$  is the concentration of the solute.

In the limit of infinite dilution,  $\eta_{red}$  characterizes the fractional viscosity increase due to each isolated macromolecule and is known as intrinsic viscosity:

$$[\eta] = \lim_{c \rightarrow 0} \eta_{red}$$

Kuhn-Mark-Houwink-Sakurada equation gives a relation between intrinsic viscosity and molecular weight of the polymer.

$$[\eta] = KM^a$$

The values of the Mark-Houwink parameters  $a$  and  $K$  depends on the particular polymer-solvent system.

## 5. Results and discussion

### 5.1 Parameters and factors

The primary study was done to understand the parameters and factors effecting the lignin conversion. Hence, the experiments were performed in different spectrum to find out the effect of: (i) Si/Al ratio of HZSM-5, (ii) catalyst to lignin ratio, (iii) stirrer speed, and (iv) reaction temperature (v) Effect of metal loading on HZSM-5 (vi) Effect of different solvent.

Our first set of reactions were primarily done with water-methanol mixture, it was to standerdise the reaction condition, temperature and other operating parameters.

### 5.2 Effect of Temperature

A series of experiments were performed at a temperature ranging from 220 °C and 250 °C. With different operating condition, 64% of lignin conversion was obtained with a significant amount of char formation (10.66%) when reaction was performed at 220 °C for 7h without solid catalyst (Entry 1- Table 2). But when the reaction temperature was increased to 250 °C the lignin conversion was increased to 90.66% along with a reduction in char formation (5.33%) (Entry 2 – Table 2). It is clear from the Fig. that the temperature had a significant role to play in the lignin depolymerization reactions.

### 5.3 Effect of catalyst-to-lignin ratio (HZSM-5)

To observe the effect of HZSM-5 in lignin depolymerization reactions, a number of experiments were carried out to optimize the catalyst-to-lignin ratio. The sample was mixed with NaOH (1.17 mmol) to increase the solubility of lignin in the reaction mixture ensuring the lignin molecules thoroughly dispersed in the reaction mixture to reduce the possibility of recombination reactions, besides promoting alkaline hydrolysis of lignin into smaller units. One set of reaction was performed with greater catalyst-to-lignin ratio (1:2) at 220 °C (Entry 4 – Table 2). For this case, a decrease in lignin conversion (83.3%) was observed but there was a remarkable reduction in char formation (<1%). This may be due to hydrodeoxygenation of products by HZSM-5 which minimized the re-polymerization reactions. The main role of the catalyst lies in the rapid stabilization of the primary products generated during lignin decomposition that helps in preventing their re-polymerization. Therefore, the key issue is to ensure a close contact between the catalyst active centers, on the one hand, and the lignin depolymerization intermediates, on the other hand. Therefore, a comparison of the lignin conversion at various catalyst-to-lignin ratios was performed at two reaction temperatures (Fig. 4). An increase in temperature to 250 °C enhanced the lignin conversion and monomer yield sharply to 99.33% and 81.41% respectively at 7h of reaction time with negligible amount of char formation (Entry 5 – Table 2). It was observed that the increase in temperature to 250 °C favored the hydrothermal degradation of lignin both in the presence and absence of catalyst. From an economic point of view our next objective was to reduce the catalyst-lignin-ratio without affecting the lignin conversion and monomer yield. Therefore, another experiment was performed to evaluate the effect of decreasing the catalyst-to-lignin ratio. It was observed that a reduction in catalyst-to-lignin ratio from 1:2 to 1:4 had a significant effect on the gaseous products yield while the lignin conversion was almost same when the reaction was performed at 250 °C. Catalyst-to-lignin ratio that can be considered as an indicator of the proximity of the catalytically active sites and reactants which can be a reason for the increase in gaseous product yield. Therefore, a maximum conversion of 99.66% along with higher monomeric yield of 81.41% respectively was obtained with 1:4 as a catalyst-to-lignin ratio at 250 °C (Entry 6 – Table 1). This experiment was assigned as standard due to significantly higher lignin conversion and monomer yield with lower catalyst-to-lignin ratio. Therefore, the standard condition for lignin depolymerization experiments were 250 °C, 7h of reaction time, 0.75g lignin, 0.1875g catalyst, 1.17 mmol NaOH, and a mixture of water and methanol as solvent (volume ratio 1/1, total 90 mL).

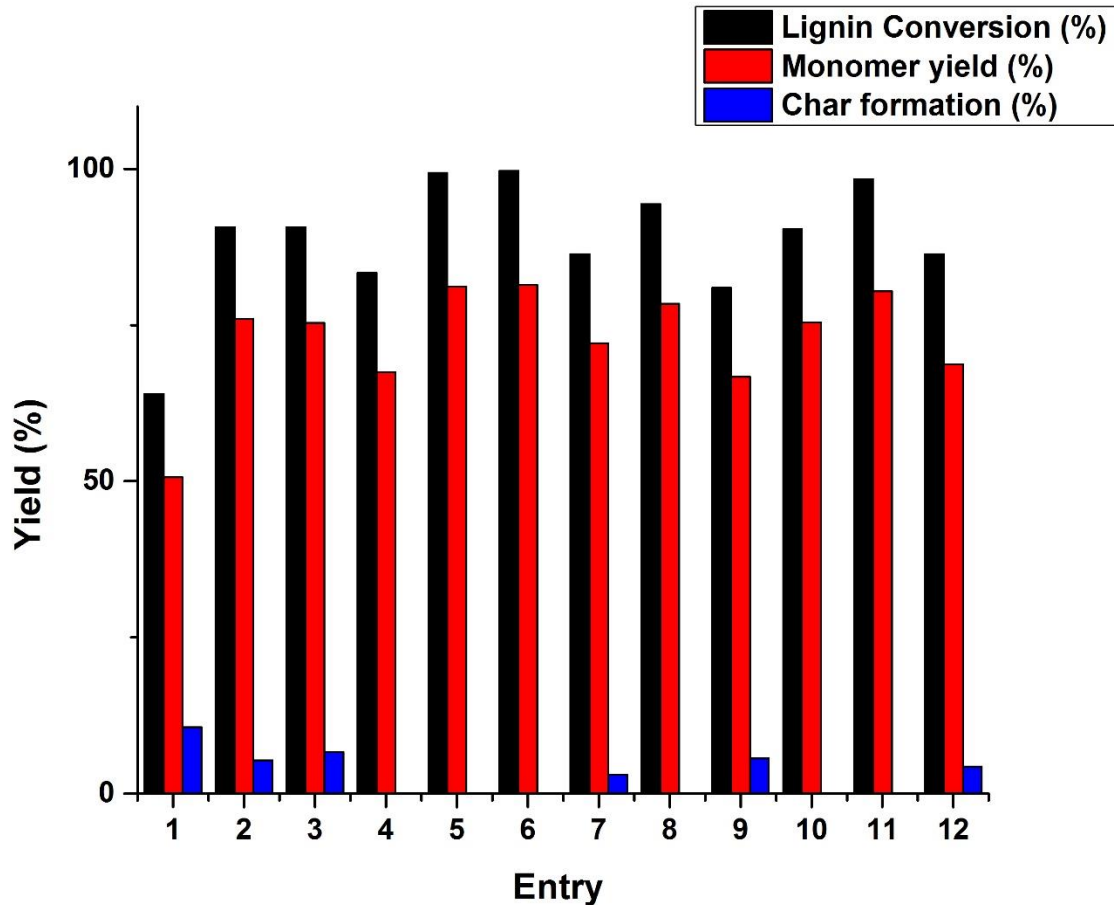


Fig. 5: Lignin conversion, monomer yield and char formation at different reaction conditions

#### 5.4 Effect of NaOH

To determine effect of NaOH another reaction was performed without NaOH and compared with standard (**Fig. 3**). Without NaOH, a significant charring (3%) with reduced lignin conversion and monomer yield of 86.33% and 72.08% respectively was found (Entry 7 – Table 2). It seems that presence of NaOH changes the reaction mechanism favoring the production of monomers. Among the different linkages present in lignin structure,  $\beta$ -O-4 is said to be the first to be cleaved during hydrothermal degradation of lignin. NaOH assists the cleavage of the  $\beta$ -O-4 ether bond heterolytically via the formation of a sodium phenolate derivative and a carbenium ion like transition state, which is instantly neutralized by a hydroxide ion. The sodium cations catalyze the reaction by forming cation adducts with lignin and, thus, polarizing the ether bond

#### 5.5 Effect of Si/Al ratio of HZSM-5

In order to access the Si/Al ratio of HZSM-5 another experiment was performed with higher Si/Al ratio of HZSM-5 i.e. 50 (**Fig. 3**). As the Si/Al ratio of HZSM-5 increased from 23 to 50 (decreased acidity of zeolites), the lignin conversion declined from 99.66 to 90.33 and monomer yield from 81.41% to 78.41% respectively (Entry 8 – Table 2). In another experiments the conditions were different from the standard conditions. In this case, lignin was subjected to

treatment in alkaline solution for 1h then the pH of the solution was adjusted near to 6. Then solid catalyst with Si/A/=50 was added to this reaction mixture for the depolymerization reactions. In this case, lignin conversion and monomer yield reduced to 81% and 66.5% respectively with significant amount of char formation (5.66%) (Entry 9 – Table 2). The results indicated that the catalytic activity of HZSM-5 for the deoxygenation reaction has decreased with the decrease in acidity of the zeolites. The concentration of Bronsted acid sites on the zeolite decreased with an increase in Si/Al ratio, which may be the reason for the observed decrease in lignin conversion and monomer yield.

### 5.6 Effect of hydrogen pressure

Hydrogen pressure was observed to have a negative effect on the lignin conversion as the lignin conversion and monomer yield was decreased to 90.33% and 75.41% respectively (Entry 10 – Table 2).

### 5.7 Effect of heating profile

A set of experiments were conducted to determine the effect of heating profiles of the reaction mixture. The first experiment involved slowly ramping the temperature of reaction from room temperature to 250 °C over a period of 4h and then the temperature was lowered to 220 °C and maintained for 3 hours. In a second experiment, the temperature of the reaction was ramped to 220 °C for 4h and then increased to 250 °C for another 3h (Entry 12 and 13 – Table 2). The lignin conversion and monomer yield was observed to decrease in both the experiments as compared to the standard conditions.

Entry <sup>b</sup>	Solvent Ratio	Catalyst (Si/Al ratio)	Catalyst : Lignin ratio	NaOH (mmol)	Stirrer Speed (rpm)	Temp. (°C)	H2 Pressure	Lignin Conversion (%)	Monomer Yield (wt%)	Gaseous Products (wt%)	Char (wt%)
1	45/45	–	0	1.17	1000	220	–	64	50.66	13.33	10.66
2	45/45	–	0	1.17	1000	250	–	90.66	76	17.33	5.33
3	45/45	–	0	1.17	1500	250	–	90.66	75.33	15.33	6.66
4	45/45	HZSM-5 (23)	1:2	1.17	1000	220	–	83.33	67.5	15.83	–
5	45/45	HZSM-5 (23)	1:2	1.17	1000	250	–	99.33	81.16	18.16	–
6 <sup>a</sup>	45/45	HZSM-5 (23)	1:4	1.17	1000	250	–	99.66	81.41	5.91	–
7	45/45	HZSM-5 (23)	1:4	–	1000	250	–	86.33	72.08	<1%	3
8	45/45	HZSM-5 (50)	1:4	1.17	1000	250	–	94.33	78.41	10.25	–
9 <sup>b</sup>	45/45	HZSM-5 (50)	1:4	1.17	1000	250	–	81	66.75	<1%	5.66
10	45/45	HZSM-5 (23)	1:4	1.17	1000	250	10	90.33	75.41	5.25	<1%
11 <sup>c</sup>	45/45	HZSM-5 (23)	1:4	1.17	1500	220 & 250	–	86.33	68.75	3.91	4.33
12 <sup>d</sup>	45/45	HZSM-5 (23)	1:4	1.17	1500	220 & 250	–	ND	ND	ND	ND

**Table 2: Lignin conversion, monomer yield, char production at different experimental conditions**

<sup>a</sup> Standard condition: Lignin=0.75g, Solvent=90ml, Temperature=250°C, Time=7h

<sup>b</sup> Reaction conditions: Lignin treated with NaOH solution (1.17 mmol) for 1h before depolymerization reaction

<sup>c</sup> Reaction conditions: Lignin=0.75g, Solvent=90ml, Temperature=250 °C for 4h and 220 °C for 3h , Time=7h



Entry	Lower fraction	Middle fraction	Upper fraction
1	31	41	27
2	5	55	40
3	17	45	38
4	35	40	25
5	16	49	35
6	9	54	37
7	3	61	36
8	3	43	54
9	5	62	33
10	5	54	41
11	4	48	48
12	7	44	49
13	4	54	41

**Table 3: Yields of products under different reaction conditions**

### 5.8 Effect of different solvent

To study the effect of conversion of lignin with the introduction of different solvents, we changed the solvent mixtures with ethanol, butanol, isopropanol, 1-propanol. The results were inspiring with all of the solvents as we achieved above 95% conversion and there was a tremendous increase in the yield with respect to the lower fraction. Each run was reproduced to confirm our findings. We got very motivating yield for benzene with Ethanol and isopropanol as we can see from the table below along with 99.66% conversion. But these runs are now in the primary stage of our experiment and we need to find out the mechanism behind these reactions and the role of different solvents. The reaction was performed with the water to solvent ratio of 1:1 and at 240°C with 0.75 gm of lignin loaded along with 0.1875 gm of catalyst and 102 gm of NaOH. The reaction time was 7hr at 1000rpm.

Table 4 Effect of different solvent

Solvent	Lower fracton	Mid fraction	Upper fraction	Conversion(%)
Ethanol	61.68	30.59	7.73	99.6
Butanol	50.93667	48.85667	2.68	85
Isopropanol	65.54667	28.05333	6.4	99.6
propanol	87.495	10.98	1.5	99.6

As we can see from the table there was an tremendous increase in the lower fraction, and the amount of upper fraction has decreased significantly, these lower fraction primary contain benzene, toluene, xylene and cresol whereas mid fraction contain catechol and guaiacol. In the lower fraction the yield of benzene was quite dominating in the case of ethanol, iso-propanol and propanol. We have to analyze and determine the mechanism leading to this result.

### 5.9 Molecular weight of lignin

The molecular weight of the lignin was determined using the Kuhn-Mark-Houwink-Sakurada using the intrinsic viscosity of solution (Fig 6). The Mark-Houwink parameters  $a$  and  $K$  in 4% NaOH solution at 70 °C are 0.23 and 0.4165. The calculated molecular weight calculated was 15604 g/mol.

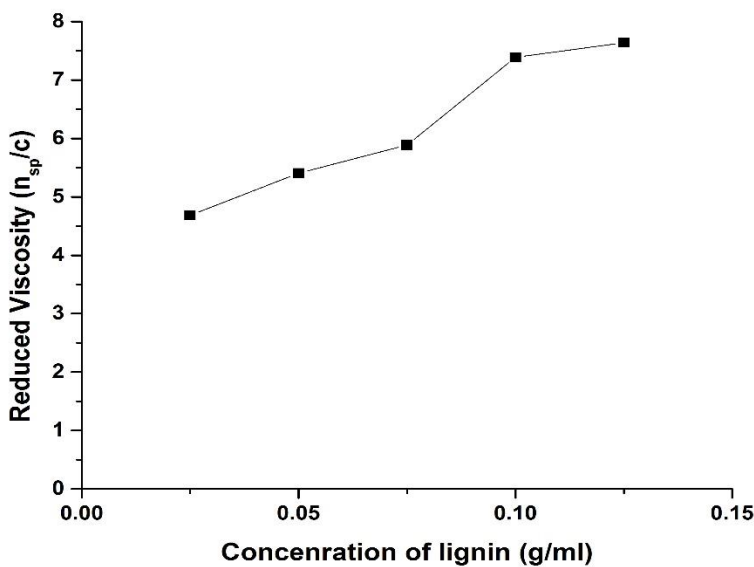


Fig. 6: Reduced viscosity ( $\eta_{sp}/c$ ) vs concentration of lignin solutions in 0.4% NaOH at 70 °C

### 5.10 Characterization of lignin and residual lignin

FTIR analysis was performed to analyze the changes in the functional groups between starting lignin and the residual lignin (THF soluble) occurred during depolymerization experiments. The IR transmittance spectra for initial and residual lignin are shown in **Fig 5 (A)**. The FTIR spectrum of lignin show peaks at 1041  $\text{cm}^{-1}$  for C-O stretching assigned to primary alcohol (guaiacyl C-H ), 1083  $\text{cm}^{-1}$  for C-O of secondary alcohol. Peaks at 1134  $\text{cm}^{-1}$  corresponds to guaiacyl and syringyl C-H stretching vibrations. The peaks at 1217  $\text{cm}^{-1}$  and 1263  $\text{cm}^{-1}$  corresponds to C-O of guaiacyl ring whereas the peak at 1379  $\text{cm}^{-1}$  represents C-O of syringyl ring. The peaks at wavenumber 1421  $\text{cm}^{-1}$  represents C-H in plane deformation with aromatic ring stretching and 1461  $\text{cm}^{-1}$  for C-H deformation (methyl and methylene). The peaks at 1508

$\text{cm}^{-1}$  and  $1596 \text{ cm}^{-1}$  corresponds to aromatic skeletal vibrations and C=O stretching. Broad vibrational band at  $3435 \text{ cm}^{-1}$  are due to hydrogen bonded –OH stretching vibrations.

The FTIR spectra of the THF soluble products (residual lignin) with and without catalyst for the reactions performed at  $220 \text{ }^\circ\text{C}$  are shown in Fig 8 (B) and (C). Increase in intensity of IR band at around  $2900 \text{ cm}^{-1}$  accompanied by signals at  $1461 \text{ cm}^{-1}$  and  $1379 \text{ cm}^{-1}$  and decrease in intensity of signal at  $1508 \text{ cm}^{-1}$  and  $1596 \text{ cm}^{-1}$  indicated the hydrogenation of aromatic rings in the lignin derived products. A very intense peak in residual lignin at  $1703 \text{ cm}^{-1}$  and  $1714 \text{ cm}^{-1}$  with and without catalyst can be assigned to C=O stretching in  $\alpha$  and  $\beta$  unsaturated aldehydes or ketones. With HZSM-5, increased intensity of peaks is observed at around  $1714 \text{ cm}^{-1}$ ,  $2900 \text{ cm}^{-1}$  and  $3469 \text{ cm}^{-1}$  which clearly indicated a higher degree of cleavage in ether linkages and demethylation/demethoxylation reactions that resulted in higher disassembly of lignin into low molecular weight compounds. Hydrogenation reaction also occurred in the case of reactions performed without catalyst but with lesser cleavage of ether linkages and demethylation and demethoxylation reactions.

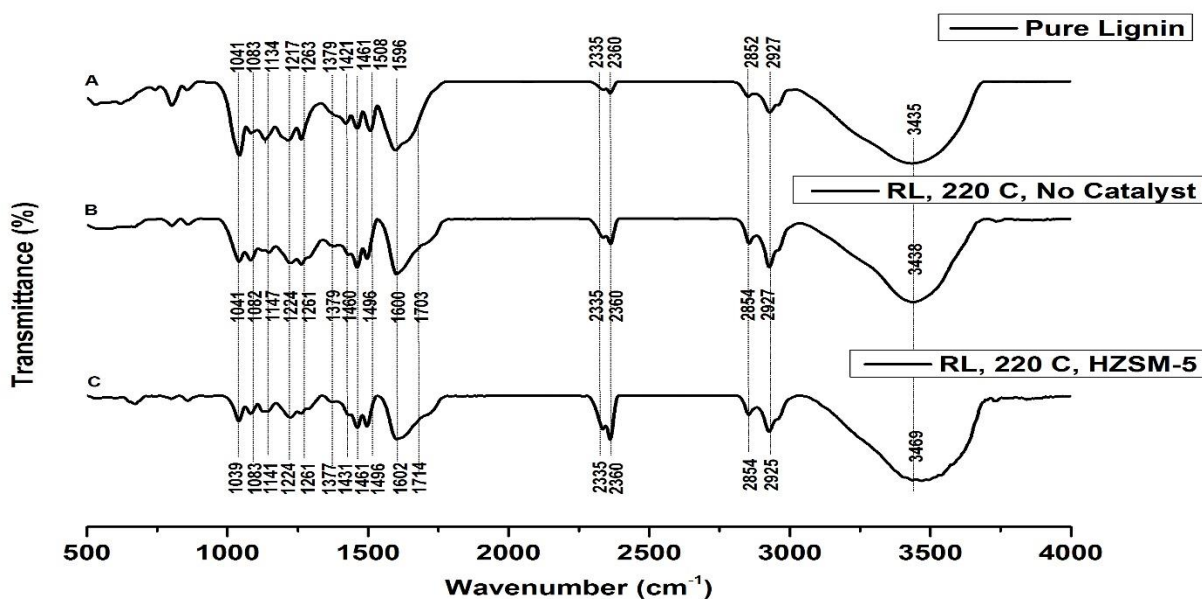


Fig. 7: FTIR spectra of (A) Pure Lignin and residual lignin (B) without catalyst and (C) with catalyst (HZSM-5)

### 5.11 Characterization of liquid phase

The composition of the EtoAc soluble products obtained in catalytic tests was investigated by GC-MS-FID chromatography. The peaks for the different compounds observed in the chromatogram were grouped in three fractions on the basis of retention time (Table 2): (1) lower fraction (less than 4.5 min) (2) middle fraction (4.5 to 10 min) (3) higher fraction (greater than 10 min). It can be clearly observed from Table 2, reactions performed at a lower temperature i.e. 220 °C gives more lower fractions which can be lower molecular weight aromatics (Entry 1 and 2 – Table 2). An increase in the stirrer speed was also found to have a significant positive effect on the production of lower fraction (Entry 3 and 5 – Table 2). The H<sub>2</sub> addition and Ga loading on HZSM-5 had increased the upper fractions (Entry 8 and 11 – Table 2). The main products that are quantified in the lignin depolymerization experiments are benzene, xylene, toluene and catechol.

### 5.12 Identification of products

The identification of products like benzene, xylene, phenol, catechol and cresol. Was done using GC-FID. For this purpose we purchased pure sample of each of these solvents and then they were diluted in Ethyl acetate (solvent). In a general procedure 1 to 2 drops of pure solvent was added, in order to get narrow and intense peak. The GC condition was maintained similar to one that we use for our product analysis.

Hence it is assumed that when the peak of our pure compound will coincide with a peak in our product sample distribution. Then that peak in the product sample will correspond to that compound. For example from the injection off pure benzene, we get our benzene peak at a resident time of 2.09 min as show in fig. 8. Were the green peak correspond to pure benzene and blue peak correspond to our product same, superimposing two peaks we can identify which peak correspond to which product. Similar analysis was done for different pure samples as shown in fig 9.

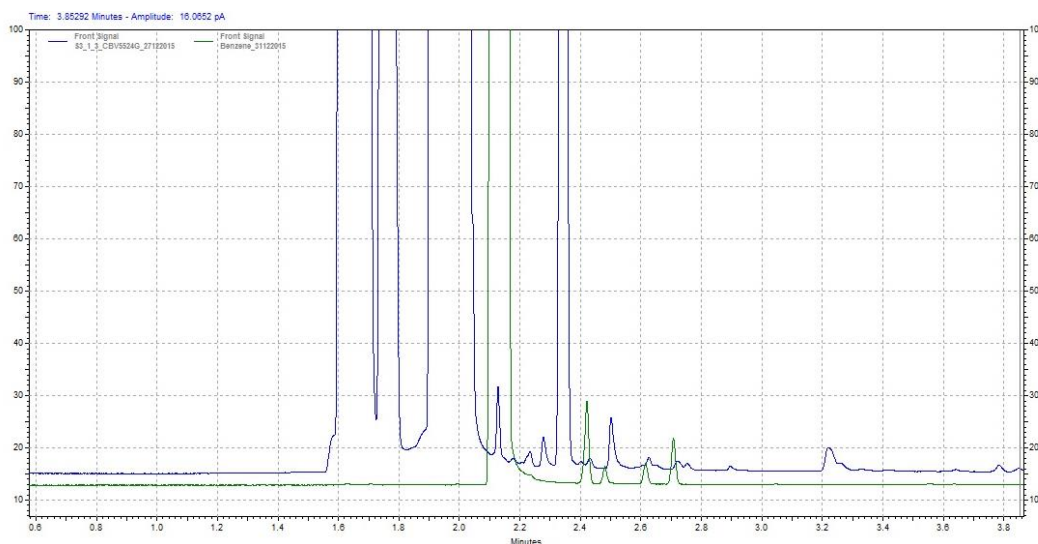


Fig8. GC peak for benzene and product sample

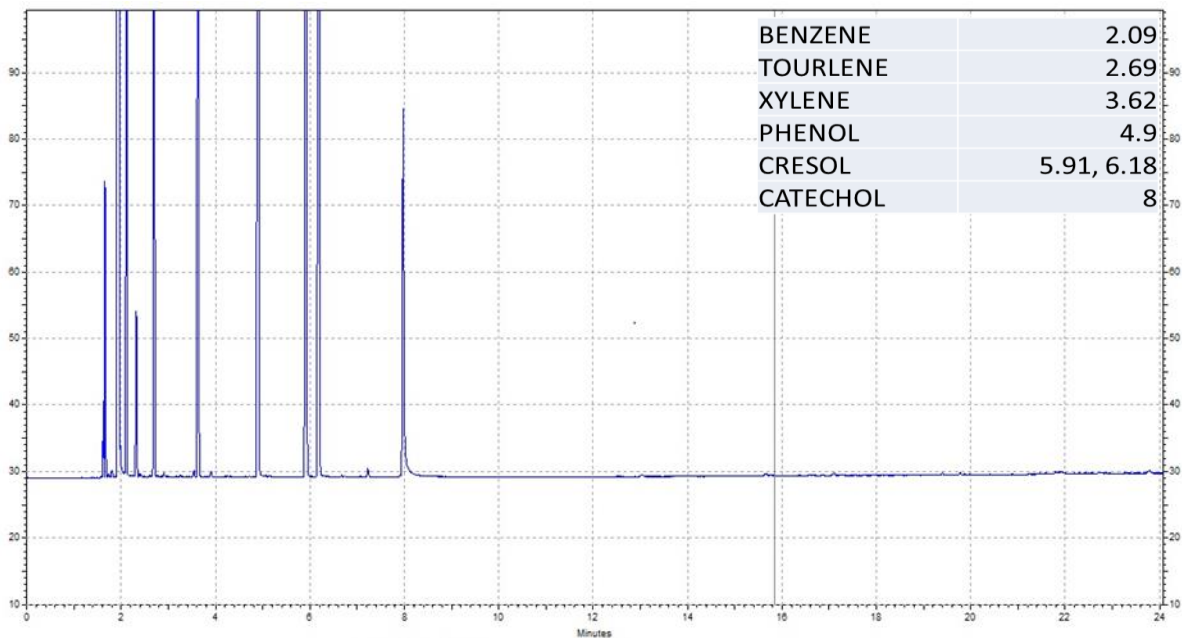


Fig 9. GC peaks for pure samples

## 6. Conclusion

The lignin conversion was observed to be high (>90%), except for the conditions when either temperature was 220 °C (Entry 1 – Table 1 ) or when reaction was performed at 220 °C for 3h and then increased to 250 °C for 4h (Entry 12 – Table 1) and either when reaction was performed at 220 °C in the absence of catalyst (Entry 2 – Table 1) or when the reaction was performed at 250 °C in the absence of NaOH (Entry 9 – Table 1 ). HZSM-5 and Ga doped HZSM-5 were found to be effective in depolymerization of lignin via hydrodeoxygenation and enhanced hydrogenation of depolymerized products. A synergistic behaviour of NaOH is observed during the lignin depolymerization studies. Without NaOH, in the presence of HZSM-5 the conversion of lignin was reduced to 86.3%. The H<sup>+</sup> and OH<sup>-</sup> ions form the self-ionization of water at high temperature with small amount of NaOH (1.17mmol) was successfully utilized for the effective depolymerization of lignin (99.33%) with HZSM-5 catalyst at 250 °C by cleavage of ether linkages in lignin. A water:methanol along with water:ethanol, water:butanol, water:propanol mixture is an effective solvent for lignin depolymerization. One of the challenging issues with water:methanol was lower yield of lower fraction, which was then overcome by the use of other water:solvent mixtures, thus providing an adequate amount of lower fraction with good conversion, reduced char formation and selectivity towards compounds like benzene also char formation due to recondensation reactions have been overcome in this study.

## 7. Reference

- [1] A. García, A. Toledano, L. Serrano, I. Egüés, M. González, F. Marín, and J. Labidi, "Characterization of lignins obtained by selective precipitation," *Sep. Purif. Technol.*, vol. 68, no. 2, pp. 193–198, 2009.
- [2] J.-Y. Kim, J. Park, H. Hwang, J. K. Kim, I. K. Song, and J. W. Choi, "Catalytic depolymerization of lignin macromolecule to alkylated phenols over various metal catalysts in supercritical tert-butanol," *J. Anal. Appl. Pyrolysis*, vol. 113, pp. 99–106, 2015.
- [3] J. Y. Kim, E. J. Shin, I. Y. Eom, K. Won, Y. H. Kim, D. Choi, I. G. Choi, and J. W. Choi, "Structural features of lignin macromolecules extracted with ionic liquid from poplar wood," *Bioresour. Technol.*, vol. 102, no. 19, pp. 9020–9025, 2011.
- [4] N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. T. Liu, and Y. Kou, "Selective degradation of wood lignin over noble-metal catalysts in a two-step process," *ChemSusChem*, vol. 1, no. 7, pp. 626–629, 2008.
- [5] M. Zaheer and R. Kempe, "Catalytic hydrogenolysis of aryl ethers: A key step in lignin valorization to valuable chemicals," *ACS Catal.*, vol. 5, no. 3, pp. 1675–1684, 2015.
- [6] A. P. Dodd, J. F. Kadla, and S. K. Straus, "Characterization of fractions obtained from two industrial softwood kraft lignins," *ACS Sustain. Chem. Eng.*, vol. 3, no. 1, pp. 103–110, 2015.
- [7] S. Dutta, K. C.-W. Wu, and B. Saha, "Emerging strategies for breaking the 3D amorphous network of lignin," *Catal. Sci. Technol.*, vol. 4, no. 11, pp. 3785–3799, 2014.
- [8] Y. G. Sun, Y. L. Ma, L. Q. Wang, F. Z. Wang, Q. Q. Wu, and G. Y. Pan, "Physicochemical properties of corn stalk after treatment using steam explosion coupled with acid or alkali," *Carbohydr. Polym.*, vol. 117, pp. 486–493, 2015.
- [9] X. F. Sun, F. Xu, R. C. Sun, Y. X. Wang, P. Fowler, and M. S. Baird, "Characteristics of degraded lignins obtained from steam exploded wheat straw," *Polym. Degrad. Stab.*, vol. 86, no. 2, pp. 245–256, 2004.
- [10] X. Zhao, K. Cheng, and D. Liu, "Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis," *Appl. Microbiol. Biotechnol.*, vol. 82, no. 5, pp. 815–827, 2009.
- [11] J. Quesada-Medina, F. J. Lopez-Cremades, and P. Olivares-Carrillo, "Organosolv extraction of lignin from hydrolyzed almond shells and application of the  $\alpha$ -value theory," *Bioresour. Technol.*, vol. 101, no. 21, pp. 8252–8260, 2010.
- [12] P. Kumar, D. M. Barrett, M. J. Delwiche, and P. Stroeve, "Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production," *Ind. Eng. Chem. Res.*, vol. 48, no. 8, pp. 3713–3729, 2009.
- [13] A. Pinkert, D. F. Goeke, K. N. Marsh, and S. Pang, "Extracting wood lignin without dissolving or degrading cellulose: investigations on the use of food additive-derived ionic liquids," *Green Chem.*, vol. 13, no. 11, p. 3124, 2011.
- [14] E. C. Achinivu, R. M. Howard, G. Li, H. Gracz, and W. a Henderson, "Lignin extraction from biomass with protic ionic liquids," *Green Chem.*, vol. 0, no. 0, pp. 1–6, 2014.
- [15] A. V. Maldhure and J. D. Ekhe, "Pyrolysis of purified kraft lignin in the presence of  $AlCl_3$  and  $ZnCl_2$ ," *J. Environ. Chem. Eng.*, vol. 1, no. 4, pp. 844–849, 2013.
- [16] H. Piñkowska, P. Wolak, and A. Złocińska, "Hydrothermal decomposition of alkali lignin in sub- and supercritical water," *Chem. Eng. J.*, vol. 187, pp. 410–414, 2012.
- [17] A. L. Jongerius, R. Jastrzebski, P. C. A. Bruijninx, and B. M. Weckhuysen, "CoMo sulfide-catalyzed hydrodeoxygenation of lignin model compounds: An extended reaction network for the conversion of monomeric and dimeric substrates," *J. Catal.*, vol. 285, no. 1, pp. 315–323, 2012.
- [18] T. Yoshikawa, T. Yagi, S. Shinohara, T. Fukunaga, Y. Nakasaka, T. Tago, and T. Masuda,

- "Production of phenols from lignin via depolymerization and catalytic cracking," *Fuel Process. Technol.*, vol. 108, pp. 69–75, 2013.
- [19] T. Klamrassamee, N. Laosiripojana, D. Cronin, L. Moghaddam, Z. Zhang, and W. O. S. Doherty, "Effects of mesostructured silica catalysts on the depolymerization of organosolv lignin fractionated from woody eucalyptus," *Bioresour. Technol.*, vol. 180, pp. 222–229, 2015.
- [20] S. K. Singh and J. D. Ekhe, "Towards effective lignin conversion: HZSM-5 catalyzed one-pot solvolytic depolymerization/hydrodeoxygenation of lignin into value added compounds," *RSC Adv.*, vol. 4, no. 53, p. 27971, 2014.
- [21] a. K. Deepa and P. L. Dhepe, "Solid acid catalyzed depolymerization of lignin into value added aromatic monomers," *RSC Adv.*, vol. 4, no. 25, p. 12625, 2014.
- [22] A. Rahimi, A. Ulbrich, J. J. Coon, and S. S. Stahl, "Formic-acid-induced depolymerization of oxidized lignin to aromatics," *Nature*, vol. 515, no. 7526, pp. 249–252, 2014.
- [23] S. Kelkar, C. M. Saffron, K. Andreassi, Z. Li, A. Murkute, D. J. Miller, T. J. Pinnavaia, and R. M. Kriegel, "A survey of catalysts for aromatics from fast pyrolysis of biomass," *Appl. Catal. B Environ.*, vol. 174–175, pp. 85–95, 2015.
- [24] Y. Yu, X. Li, L. Su, Y. Zhang, Y. Wang, and H. Zhang, "The role of shape selectivity in catalytic fast pyrolysis of lignin with zeolite catalysts," *Appl. Catal. A Gen.*, vol. 447–448, pp. 115–123, 2012.