Priyanka Kaushik, candidate for the degree of Master of Applied Science in Process Systems Engineering, has presented a thesis titled, *Catalytic Pyrolysis for the Production of Stable Phenol Rich Bio-Oil from Wood Biomass*, in an oral examination held on August 8, 2016. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

Biomass studies over the last two decades shows its use as an alternate source for the production of chemicals and fuels. This can help in reducing our load on the conventional hydrocarbon use and be shared with renewable sources such as forest and agricultural wastes. In Saskatchewan, there is abundant availability of wood waste from the timber industry; hence wood can be used as biomass raw material for the production of bio-chemicals. Pyrolysis is the most promising technology for the conversion of biomass into liquids. In this research, wood pellets obtained from a lumber company were used as the feed for pyrolysis to produce a phenol-rich stable bio-oil. Usually, after the bio-oil production, catalytic cracking is done to produce valuable products. In this research, the aim was to produce phenol-rich bio-oil in single step.

The experiments were carried out in three phases; Phase I: Parametric study, Phase II: optimized conditions and best-suited catalyst for stable phenol rich bio-oil and Phase III: kinetic study of the process.

Experiments were performed in a packed bed reactor under varying temperatures (400, 500, 600°C), acidic catalysts (H-ZSM-5, γ-alumina and silica alumina), feed size (0.71, 0.85, 1, 1.18 and 1.44mm) and catalyst weights (1g and 2g). For the kinetic study, experiments were carried out at varying residence times (0, 30, 60 and 90 minutes).

Products were collected and analyzed in three phases: bio-oil, gas and char. Gas Chromatography - Mass Spectroscopy (GC-MS) and online GC equipment was used to analyze bio-oil and gases respectively. Significant
increase in phenol derivatives is observed with the use of acid catalyst along with the reduction of oxygenates or sugars. The reduction in sugar content shows the stabilization of bio-oil as the amount of free radicals is reduced hence polymerization of undesired products can be avoided thus increasing the bio-oil shelf life. Catalyst acidity, strength and number of acid sites showed a significant effect on yield of phenol derivatives in bio-oil.

Kinetic study of wood catalytic pyrolysis was performed in a batch reactor; component content data was obtained at increasing time intervals and temperatures. The gases were analyzed with the help of GC and carbon content in char was analyzed by sending samples to the Saskatchewan Research Centre (SRC) in Saskatoon. Using the ultimate analysis of wood and carbon in char, carbon conversion was calculated. The rate of reaction can be expressed by a 2 order kinetic model with an activation energy of 17104.04 J/mol and a pre-exponential factor of 0.000567/s.

Statistical analysis was also carried out using the physical and chemical properties of the catalysts. Using MINITAB, a statistical model for the yield of phenol derivatives was determined for 1g and 2g acidic catalysts. The analysis for second resolution interaction model shows the main effect of pore volume, surface area and number of acid site on phenol derivatives yield. Also, interactions of these factors help to understand the effect on phenol yield. The predicted yield from these models and experimental yield gave overall AAD of 7% that shows a good agreement with the model.
ACKNOWLEDGEMENTS

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DEDICATION

THIS WORK IS DEDICATED TO YOU

MAA & PAPA
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NOMENCLATURE AND ABBREVIATIONS

T: Temperature
K: Degree Kelvin
°C: Degree Celsius
AAD: Average Absolute Deviation
%: Percent
A: Collision or Pre-exponential Factor
J: Joule
n: Reaction order
N₂: Nitrogen
g: Gram
OH⁻: Hydroxide ion
mL: Millilitre
mm: Millimetre
t: Reaction time
min: Minutes
mg: Milligram
wt%: Weight Percent
k: Rate constant
i.d: Internal diameter
NLREG: Non-Linear Regression
bar: pressure Unit
H⁺: Hydrogen ion
**H-ZSM-5:** Zeolite catalyst

**GC-MS:** Gas Chromatogram/Mass Spectroscopy

**GC:** Gas Chromatogram

**Ea:** Activation Energy

**R:** Molar gas constant (8.314 J/mol/K)

**Psi:** Pounds per square inch

**Xc:** carbon conversion

**Wci:** weight of the carbon in wood

**Wc:** weight of carbon in pyrolysis char

**FTIR:** Fourier Transformed Infrared Spectroscopy of Bio-oil

**TGA:** Thermo-gravimetric Analysis
CHAPTER 1: INTRODUCTION

1.1 MOTIVATION

To reduce environmental pollution, an economical, clean and eco-friendly option is needed to substitute the conventional chemicals and fuels obtained from fossil reserves. Limited supplies of petrochemicals and fossil fuels gives the motivation to have alternative solutions. Biomass is a renewable source that has got attention because it is environmentally friendly and can meet increasing energy demands. Biomass can produce liquid, solid and gaseous fuels and chemicals and being an organic material feedstock produces net zero carbon emissions (Zhou, Xia, Lin, Tong, & Beltramini, 2011). The biomass and wood in particular can be converted into chemicals through various chemical processes.

Liquid fraction obtained from thermochemical processes is called bio-oil. Bio-oil can satisfy the above-mentioned concerns; this liquid fuel is derived from the biomass materials like municipal wastes, crops, algae, by-products of forests and forest wastes with the help of thermo-chemical processes such as pyrolysis.

Prime interest is to use biomass as feed to produce rich bio-oil that can help derive valuable chemicals, which can be used as alternates for industrial petrochemicals.
1.2 POTENTIAL OF BIOMASS

Biomass is considered to be the third largest energy resource in the world that can help produce low sulfur and low nitrogen fuels and chemicals (Vamvuka, 2003). Lignocellulosic biomass is studied as a renewable feedstock available in abundance and easy availability (Somervile et al., 2010; Taarning et al., 2011). Biomass is composed of mainly three components cellulose, hemicellulose and lignin. Most of the lignocellulosic biomass has about 40-50% cellulose and 25-30% of hemicellulose and lignin each as shown in figure 1.1. Biomass also contains some amount of mineral content that gets converted into ash after the pyrolysis process. Cellulose being the biggest component in biomass, its conversion into valuable chemicals is of vital importance (Somervile et al., 2010; Taarning et al., 2011; Boerjan, Ralph & Baucher, 2003; Shuai & Pan, 2010). The composition and yield of bio-oil depends on the distribution of cellulose, hemicellulose and lignin in the biomass feed (Yang, Kumar, & Huhnke, 2015).
Figure 1.1 Composition of wood
Majority of biomass energy is produced from wood wastes, municipal wastes and agricultural wastes, in that order (Demirbas, 2000b, 2001a, 2004a; Akdeniz et al., 2004). Figure 1.2 shows a typical dry wood analysis approximate composition comprising of 52% carbon, 6% hydrogen, 40% oxygen and nitrogen (around 0.4%) (Demirbas, 2000b, 2001a, 2004a; Balat et al., 2005).

Bio-oil produced from biomass is highly oxygenated and unstable requiring further up-gradation processes. Therefore, production of bio-chemicals such as phenols has better market prospects if the extraction procedures are economical (Connor and Piskorz, 1994).

![Figure 1.2 Elemental composition of wood](image-url)
1.3 SCOPE OF RESEARCH

Over half of Saskatchewan land area is forest. Out of 11.7 million hectares of forest, 5.3 million hectares is productive with an annual allowable cut of 82 thousand hectares (Saskatchewan's Forestry Sector, Government of Saskatchewan 2016) as illustrated by figure 1.3. Having a competitive forest industry, many forest products manufacturing facilities in Saskatchewan use timber. The by-products from the forestry processes can be used as feed for production of bio-oil and further bio-chemicals and fuels.

Figure 1.3 Saskatchewan Forestry Statistics
Summary of products obtained from biomass using various processes is shown in figure 1.4. Pyrolysis process among the various thermochemical processes is a good choice for a higher yield and good quality bio-oil. To produce useful chemicals, bio-oil needs to be upgraded using various processes. One way is to use catalytic cracking of bio-oil. Several methods suggest the use of zeolites for bio-oil up-gradation (Hew, Tamidi, Yusup, Lee, & Ahmad, 2010). Despite having the potential to produce valuable chemicals and fuels; bio-oil has a limitation of high changing viscosity, high water content, presence of large amounts of oxygenates and high acidity (Yang et al., 2015). The presence of free radicals and oxygenates reduces the shelf life of bio-oil leading to polymerization (Oasmaa, Korhonen, & Kuoppala, 2011). Hence, after the pyrolysis process to produce stable and valuable chemical rich bio-oil, multiple step processes are required.

The above-mentioned limitations give motivation for this thesis to study and probe a one-step process for the enhanced yield and quality of stable phenol rich bio-oil using acidic catalysts during the pyrolysis process.
Figure 1.4 Products from thermo-chemical processes from wood
1.4 RESEARCH OBJECTIVES

The aim of this thesis is to study the effect of heterogeneous acidic catalysts for the production of phenol-rich bio-oil pyrolysis process. The study was carried out in three phases. Objectives according to the phases are listed below

Phase I

- Analyze the range of temperature for the production of bio-oil from the wood sample.
- Determine the ideal operating conditions for high yield of bio-oil from wood biomass using pyrolysis.
- Optimize operating conditions (temperature & feed size) for the yield of bio-oil using pyrolysis process in packed bed reactor.

Phase II

- Select heterogeneous acidic catalysts for a higher yield of bio-oil.
- Study the effect of H-ZSM-5, γ-alumina and silica-alumina on the yield of bio-oil.
- Analyze the performance of catalyst on increase in phenol derivatives in bio-oil and decrease in sugar components for a stable bio-oil.
- Study the interrelationship between the catalyst characteristics and phenol derivatives.
- Determine the optimum feed size, temperature and catalyst for kinetic studies.
Phase III

- Perform statistical analysis to study the effect of pore size, lewis to bronsted site ratio, acidity, acid site and acid strength on the yield of phenol derivatives in bio-oil.
- Develop a statistical model using catalyst properties for phenol derivative yield.
- Perform experiments at varying residence time, temperature and catalyst loading for kinetic study in batch reactor using selected catalyst.
- Develop a rate model to understand the kinetics of catalytic pyrolysis for the production of bio-oil from wood biomass.
1.5 THESIS LAYOUT

A brief overview of contents in this thesis are as:

Chapter 1: Introduction discusses purpose, significance and scope of this research. Followed by objectives of this work.

Chapter 2: Literature review, discusses research that has been done until now regarding the biomass conversion processes, mechanism behind it and the catalysis. This chapter discusses bio-oil composition, its significance and importance of phenols from bio-oil.

Chapter 3: Details on the experimental procedures and operating conditions are discussed in this chapter for three phases. Also the catalyst characterization and feed preparations sections are discussed.

Chapter 4: Results from experiments is presented, reviewed and discussed in this chapter.

Chapter 5: This chapter focuses on the catalyst properties for the production of phenol derivatives. Purpose of this chapter is to study the inside of catalysts that can help for synthesizing catalysts in future.

Chapter 6: This chapter discusses the importance, contribution and limitations of this research work.

Chapter 7: Conclusions and recommendations from this research work is discussed.
CHAPTER 2: LITERATURE REVIEW

This chapter will discuss the various processes used for the conversion of biomass into bio-oil for the production of bio-fuels and chemicals. Pyrolysis process will be discussed in details to understand the reaction path for bio-oil production. Followed by the details on composition and applications. For the up-gradation of bio-oil catalytic cracking and acidic catalysts are also discussed.

2.1 PROCESSES FOR BIOMASS CONVERSION

Biomass conversion processes can be grouped in two categories; thermo-chemical processes and bio-chemical processes. Thermo-chemical process can broadly be divided as i) gasification and ii) liquefaction.

Gasification of biomass is conversion of biomass in gas phase, which produces hydrocarbons by partial oxidation whereas pyrolysis is a process that liquefies biomass in inert atmosphere at high temperatures into bio-oil with high quality that can be used for the production of chemicals and fuels. Gasification decomposes biomass to syngas by controlling the oxygen content. On the other hand, pyrolysis is known as carbonization process, in which one of the product is solid i.e. char (Balat, 2008).

Other thermo-chemical processes are combustion, liquefaction and hydrogenation (Goyal, Seal, & Saxena, 2008). Bio-chemical process for the production of bio-oil is by enzymatic production where enzymes are used to convert biomass into biofuels and chemicals.
2.2 PYROLYSIS PROCESS

Pyrolysis is the best-suited thermo-chemical process for the conversion of biomass to bio-fuels and chemicals. In the absence of air, biomass is thermally broken down into bio-oil, gases and char. Depending on the type of biomass, conversion starts at a high temperature equal to or above 280°C. At different conditions, different proportions of products are formed (Goyal et al., 2008). Depending on the heating rates pyrolysis can be categorized into various processes. Table 2.1 shows different pyrolysis process types depending on the heating rates. The factors affecting the pyrolysis process are temperature, heating rate, reactor configuration, residence time, particle size and pyrolysis environment. (Uzun, Pütün, & Pütün, 2007).

<table>
<thead>
<tr>
<th>PYROLYSIS TECHNOLOGY</th>
<th>Residence Time</th>
<th>Products</th>
<th>Temperature (°C)</th>
<th>Heating Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonization</td>
<td>Days</td>
<td>Charcoal</td>
<td>400</td>
<td>Very Low</td>
</tr>
<tr>
<td>Conventional</td>
<td>5-30 min</td>
<td>Oil, Gas, Char</td>
<td>600</td>
<td>Low</td>
</tr>
<tr>
<td>Fast</td>
<td>0-5-5.0 s</td>
<td>Bio-Oil</td>
<td>650</td>
<td>Very High</td>
</tr>
<tr>
<td>Flash-liquid</td>
<td>&lt; 1s</td>
<td>Bio-Oil</td>
<td>&lt; 650</td>
<td>High</td>
</tr>
<tr>
<td>Flash-gas</td>
<td>&lt; 1s</td>
<td>Chemicals, Gas</td>
<td>&lt; 650</td>
<td>High</td>
</tr>
</tbody>
</table>

Table 2.1 Pyrolysis processes wrt heating rate and residence time (Uzun, Pütün, & Pütün, 2007).
The breakdown of wood produces a large amount of chemical substances, some of which can be used as substitutes for conventional fuels. The processes convert organics into solid, liquid and gas whose compositions are dependent on the process variables and biomass feed (Taylor, Kele, Kaygusuz, & Akgün, n.d.). Thermal degradation of biomass takes place in the following way: Thermal degradation of hemicellulose > of cellulose > of lignin (Chum, 1991; Demirbas, 2000a, 2001a; Demirbas and Arın, 2002). Gani and Naruse explain how cellulose and lignin behave during the pyrolysis process using different biomass. After reaching the pyrolysis temperature the combustibles in the biomass react at two stages. First due to cellulose volatilization mass decreases really quickly followed by slow decrease in mass because of lignin decomposition (Gani & Naruse, 2007). Because lignin is in the bark of biomass, it is harder to decompose than cellulose hence the decrease in mass from lignin is slower. The presence of benzene rings in lignin makes it harder to decompose (Sharma, Wooten, Baliga, Lin1, Chan & Hajaligo, 2004). A study from literature shows biomass with higher cellulose content makes pyrolysis rate faster than the biomass that has higher lignin content (Gani & Naruse, 2007).

The focus of this thesis is to have a higher yield of bio-oil. From literature, it is suggested by Balat (2008) that pyrolysis should take place at a low temperature, high heating rate and short gas residence time. For higher production of char, pyrolysis of biomass should be done at low temperature and low heating rate. To maximize the gas yield, pyrolysis should be carried out at higher temperatures, low heating rate and long gas residence time (Demirbas,
2006). Hence, pyrolysis processes may be conventional, fast pyrolysis or flash pyrolysis depending on the operating conditions. Conventional pyrolysis may also be termed slow pyrolysis with slow heating rate of 5-7 K/min. Fast pyrolysis has rapid heating rate but not as fast as flash pyrolysis where the heating rate is just few seconds or less.

2.3 PYROLYSIS REACTION MECHANISMS

Figure 2.1 shows the reaction pathway for biomass undergoing pyrolysis to produce bio-oil. In the absence of air, biomass is heated and gets converted to volatiles and char then the volatile gas is quickly cooled to bio-oil and gases (Xiu & Shahbazi, 2012).
Figure 2.1 Reaction pathway of pyrolysis process
Another mechanism explained by Demirbas (2003c) states that the reaction is a five-stage process as follows:

i) Loss of moisture and volatiles,

ii) Emission of carbon monoxide and carbon dioxide from the breakdown of hemicellulose,

iii) With the emission of methane and ethane, an exothermic reaction takes place increasing the reaction temperature from 252 °C to 352 °C of biomass,

iv) Heating is required externally to continue the pyrolysis process,

v) Decomposition of biomass takes place completely (Balat, 2008).

Mechanisms of pyrolysis according to the composition of biomass can be explained as follows:

2.3.1 PYROLYSIS MECHANISM OF CELLULOSE

Based on the Broid-Shafizadeh figure 2.2 shows the mechanism of cellulose in pyrolysis (Balat, 2008). Thermal degradation of cellulose lead to gradual degradation, decomposition and charring at lower temperatures along with the rapid vaporization with the formation of levoglucosan on pyrolysis at high temperatures. Depolymerization, hydrolysis, oxidation, dehydration, and decarboxylation are the initial degradation reactions (Demirbas, 2000c).
Figure 2.2 Pyrolysis mechanism of cellulose
2.3.2 PYROLYSIS MECHANISM OF HEMICELLULOSE

Hemicellulose is a complex polysaccharide present in biomass along with cellulose and they are soluble in dilute alkali. Hemicellulose consists of monomeric units along with simple sugar residues like xylan. The degradation of xylan produces water, methanol, formic, acetic, propionic acids, hydroxyl-1-propanone, hydroxyl-1-butanone and 2-furfuraldehyde (Beaumont, 1985).

During pyrolysis reactions, water is formed by dehydration, acetic acid comes from removal of acetyl groups linked to xylose leading to the formation of furfural, formic acid from carboxylic groups and methanol from methoxyl groups (Demirbas, 1998 and Gullu, 2003). Hemicellulose reacts faster than cellulose during heating (Demirbas, 2000c). Hemicellulose has more moisture compared to lignin and has lower softening point than lignin.

2.3.3 PYROLYSIS MECHANISM OF LIGNIN

Guaiacol is chiefly obtained from coniferous wood with the same aromatic nature same as lignin. Yields of charcoal and tar are obtained from lignin of wood (Tang and Eickner, 1968; Wenzl et al., 1970; Adler, 1977; Higuchi, 1990; Demirbas, 1998a). Phenol compounds are derived from lignin after the cracking of the phenyl-propane units of the macromolecule lattice of biomass. The process of pyrolysis produces the most phenols on selective basis. Dehydration reactions thermally degrade the lignin; which is an exothermic reaction (LeVan, 1989).
2.3.4 OVERALL REACTION IN PYROLYSIS PROCESS

Overall changes that occur during pyrolysis is explained below (Bridgwater, 2003; Demirbas, 2004; Mohan et al., 2006) (Taylor et al., n.d.)

- Basic pyrolysis reactions at higher temperature produce volatiles and forms char
- Hot volatiles flow towards the cooler solids resulting in heat transfer between hot volatiles and cooler un-pyrolyzed fuel produced
- Condensation of volatiles takes place in cooler parts followed by secondary reactions that produces tar
- Auto-catalytic pyrolysis reactions continue and simultaneously primary pyrolysis reactions occur.
- There are chances for thermal decomposition, reforming, radical recombination, and dehydration that are function of the processes residence time, temperature and pressure.
2.4 BIO-OIL

Bio-oil produced from biomass has high oxygen content and a low hydrogen carbon (H/C) ratio. The three major groups of compounds in bio-oil are carbonyl compounds, such as acetic acid, acetaldehyde, acetone, hydroxylaldehydes, hydro-xyketones, and carboxylicacids; secondly; sugar-derived compounds for example; furfural, levoglucosan, anhydrosugars compounds; and lastly lignin-derived compounds, mainly comprised of phenols and guaiacols (Stedile, Ender, Meier, Simionatto, & Wiggers, 2015). The presence of oligomers with molecular mass range of 900 to 2500 is also found in significant amounts (Liu, Gu, Kong, & Guo, 2014).

2.4.1 COMPOSITION OF BIO-OIL

Bio-oil obtained from pyrolysis has several organic and inorganic species as listed in table 2.2 (Diebold, 2000; Milne, Elam and Evans,1997):

<table>
<thead>
<tr>
<th>Acids</th>
<th>Formic, acetic, propanoic, hexanoic, benzoic, etc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esters</td>
<td>Methyl formate, methyl propionate, butyrolactone, methyl n-butyrate, velerolactone, etc</td>
</tr>
<tr>
<td>Alcohols</td>
<td>Methanol, ethanol, 2-propene-1-ol, isobutanol, etc</td>
</tr>
<tr>
<td>Ketones</td>
<td>Acetone, 2-butanone, 2-pentanone, 2-cyclopentanone, 2,3 pentenedione, 2-hexanone, cyclo-hexanone, etc</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>Formaldehyde, acetaldehyde, 2-butenal, pentanal, ethanodial, etc</td>
</tr>
<tr>
<td>Phenols</td>
<td>Phenol, methyl substituted phenols</td>
</tr>
</tbody>
</table>

|
## Table 2.2 Composition of Bio-oil (Diebold, 2000; Milne, Elam and Evans, 1997)

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkenes</td>
<td>2-methyl propene, dimethylcyclopentene, alpha pinene, etc</td>
</tr>
<tr>
<td>Aromatics</td>
<td>Benzene, toluene, xylenes, naphthalenes, phenanthrene, fluoranthrene, chrysene, etc</td>
</tr>
<tr>
<td>Nitrogen compounds</td>
<td>Ammonia, methylamine, pyridine, methylpyridine, etc</td>
</tr>
<tr>
<td>Furans</td>
<td>Furan, 2-methyl furan, 2-furanone, furfural, furfural alcohol, etc</td>
</tr>
<tr>
<td>Guaiacols</td>
<td>2-methoxy phenol, 4-methyl guaiacol, ethyl guaiacol, eugenol, etc</td>
</tr>
<tr>
<td>Syringols</td>
<td>Methyl syringol, 4-ethyl syringol, propyl syringol, etc</td>
</tr>
<tr>
<td>Sugars</td>
<td>Levoglucosan, glucose, fructose, D-xylose, D-arabinose, etc</td>
</tr>
<tr>
<td>Miscellaneous oxygenates</td>
<td>Hydroxyacetaldehyde, hydroxyacetone, dimethyl acetal, acetal methyl cyclopentenolone, etc</td>
</tr>
</tbody>
</table>

### 2.4.2 APPLICATION OF BIO-OIL

Comprising of the various chemicals listed in Table 2.2 above, bio-oil can be used in various industries. Some of the uses are:

- Combustion fuel,
- Power generation,
- Chemicals and resins,
- Transportation fuel,
- Liquid smoke,
• Production of anhydro-sugars like levoglucosan,
• Binders for palletizing and briquetting of combustible organic waste materials,
• Preservatives, e.g., wood preservative,
• Adhesives

2.5 HETROGENEOUS ACIDIC CATALYSTS

Catalysts affect the rate of a reaction; the equilibrium composition of reactants and products is determined only by thermodynamics. Difference between heterogeneous catalysts and homogeneous catalysts is by the different material phases within which the reaction takes place. Homogeneous catalysts are in the same phase as reactants and products; most commonly liquid phase and heterogeneous catalysts are present in a different phase, usually solid while the reactants are in a gaseous or liquid phase (Davis & Davis, 2003).

Three solid zeolite catalysts used in this research are silica-alumina, Y-alumina and H-ZSM-5 having a crystalline porous structure with SiO$_4$ and AlO$_4$. Silica alumina is an amorphous catalyst with silicon and aluminium atoms. The silicon atom is attached to four oxygen atoms and aluminium with three oxygen atoms (Katikaneni et al., 1995). Y- alumina has crystalline structure that is used in petrochemical refinery processes and for alcohol dehydration (Wolverton et al., 2000; Gutierrez et al., 2001; Digne et al., 2004). For ZSM-5 is zeolite catalyst having pentagon of 5- silica- alumina molecules linked to oxygen atoms (Bhatia, 1989). Aluminum content in ZSM-5 helps in catalytic activity, water content and ion exchange capacity (Olson et al., 1981). The ion exchange of cations with H$^+$
and Na\(^+\) forms H-ZSM-5 which is highly selective and has high activity. H-ZSM-5 is more acidic in nature than ZSM-5 as former zeolite has more protons (Furrer, 1988).

## 2.6 CATALYTIC PYROLYSIS

Chemistry behind the catalytic pyrolysis as follows (Carlson, Jae, Lin, Tompsett, & Huber, 2010):

- Cellulose first gets converted to volatile organic, gases and coke
- Volatile organics then undergo dehydration reaction to release water and dehydrated species. Heterogeneous catalyst or homogeneous gas phase, with any of these set-ups these reactions can occur.
- Dehydrated species then go through the pores of the catalyst where these species get converted into aromatics, gases and coke.

### 2.6.1 CATALYTIC CRACKING OF BIO-OIL

Due to the high viscosity, high oxygen content and being thermally unstable direct usage of bio-oil as chemicals or fuel is limited. Hence, there is a need for the up-gradation of bio-oil for various uses, the process for improving the quality of bio-oil are catalytic cracking, hydrogenation and steam reforming (Zhu et al., 2005; Zhang et al., 2006; Guo et al., 2004). Acid catalysts help in extracting phenols and other useful chemicals from biomass giving high selectivity towards aromatics and effective for reducing free radicals (Carlson, Tompsett, Conner, & Huber, 2009). Separation of solid catalyst from products is easier than liquid catalysts and these catalysts can be recycled to give long time activity (Guo et al., 2012).
Catalytic cracking can be performed in an offline or online set-up. In offline catalytic cracking, bio-oil is used directly for up-gradation whereas in online cracking the vapours formed during pyrolysis are used at raw material (Bao et al., 2006; Guo and Yan, 2006; Sharma and Bakhshi, 1993a,b; Hyun et al., 2006; Adam et al., 2006; Nokkosmaki et al., 2000). Hydro treatment followed by hydrocracking can help in converting bio-oil to gasoline with the use of hydrogen. (Babu and Chaurasia, 2002). Twaiq et al. (2003) used palm oil as feed and mesoporous HZSM5 coated with layer of siliceous mesoporous crystalline material MCM-41 as the catalyst for gasoline conversion. Judit et al. (2006) investigated conversion of biomass directly from fast pyrolysis vapours through in situ catalytic cracking increased the hydrocarbon and phenol yields in organic phase with the decrease in acid and carbonyl yield. The catalysts were used to convert vapours from pyrolysis to improved high quality bio-oil (Hew et al., 2010).

Catalytic hydrogenation is the process where bio-oil is hydrotreated under hydrogen pressure of 10-20 MPa. Besides, thermal catalytic cracking is a process where bio-oil is heated in gas phase in the presence of a heterogeneous catalyst at atmospheric pressure without the presence of hydrogen. The drawback of catalytic hydrogenation when compared to thermal catalytic cracking is low bio-oil yield and easy coking which leads to reduced catalyst life (Srinivas, Dalai, & Bakshi 2000; Guo, Zheng, Zhang, & Chen, 2009).

Catalytic cracking also helps with side-by-side deoxygenation and dehydration, decarboxylation, and decarbonylation reactions that happen in the presence of zeolites. ZSM-5, synthetic zeolites were determined to convert
oxygenated organic compounds into hydrocarbons (Chang, Silvestri, 1977; Weiz, Hagg & Rodewald 1979). For methanol to gasoline conversion ZSM-5 is proved to be effective (Chang; 1975) leading to commercialization of the methanol-to-fuels (gasoline) Mobil (French & Czernik, 2010).

2.7 PHENOLIC COMPOUNDS IN BIO-OIL

Amount of lignin in the feed gives phenolic compounds, on heating the lignin component of wood depolymerizes to monomeric and oligomeric phenolic compounds. Depending on the biomass wood can be divided into soft wood and hard wood, soft wood has more of lignin content than hard wood. Because of the lack of syringols with single methoxy group softwoods may yield more reactive phenolics derived liquids compared to guaiacol with two methoxy groups derived from hardwood. Lignin majorly has functional groups of hydroxyl, methoxyl, carbonyl and carboxyl in different proportions and amounts, depending on extraction process and origin (Effendi, Gerhauser, & Bridgwater, 2008).

Depending on the wood particle size, low reactor residence time and moderate pyrolysis temperature the compounds of phenol such as guaiacol, syringol and their alkyl-derivatives are produced (Amen-Chen et al., 2001). At higher pyrolysis temperatures, production of aromatic hydrocarbons increases while the alkylguaiacol and phenolic aldehyde yields are reduced.
2.7.1 SEPARATION TECHNIQUES USED FOR PHENOL SEPARATION

The separation techniques used for bio-oil components are as follows (Kim, 2015):

- Solvent and supercritical fluid extraction: the target components are selectively dissolved in the solvents (solvents include water, alcohol, hydrocarbons, etc.)
- Column chromatography: using silica gel and aluminium oxide as stationary phase, column chromatography is performed and the moving phase is selected by the polarity of bio-oil components to be separated.
- Distillation – mainly steam distillation: in this the steam is introduced in the distillation column to heat bio-oil and decrease its viscosity. By adding to distillation, bio-oil boils at a lower temperature letting the thermal sensitive compounds to be separated with reduced decomposition.

2.7.2 APPLICATION OF PHENOL RICH BIO-OIL

The bio-oil rich in phenols are of importance because the presence of simple phenols has a wide range of applications. These phenols can be used as fine chemicals, pharmaceutical, food processing and resin manufacturing. Phenol resins are used in electronic laminations and wood composite industries as binders.

Bio-oil rich in phenols can be used as a alternate for the petroleum derived phenols in phenolic resins. There are mainly three ways to use the phenols in bio-oil (Sukhbaatar, Steele, & Kim, 2009):
• Phenol rich bio-oil also called pyrolytic lignin, produced after fractionation of bio-oil.

• Pyrolysis oil produced from lignin.

• Whole bio-oil (crude bio-oil)

The importance of phenol rich bio-oil is that it can be synthesized to phenol resins without any fractionation or separation process reducing the steps of processing.
CHAPTER 3: EXPERIMENTAL PROCEDURE

3.1 EXPERIMENTAL PROCEDURE SUMMARY

Experiments were performed in three phases to study the pyrolysis process for phenol rich bio-oil. This chapter gives a detailed description of the experimental set-up, runs, procedures, material used and preparation methods along with the details on catalyst used and operating conditions. This section also describes how product analysis was performed.

3.2 CHEMICALS AND EQUIPMENT

Gases

- Nitrogen (UPG, Praxair)

Equipments

- Weighing Balance, PB8001-S, MonoBloc
- GC-MS (Model 6890/5073, Hewlett-Packard Canada Ltd., Canada)
- Gas Chromatograph (GC-TCD, HP 6890, Agilent Technologies)
- U.S.A standard test sieve, ASTM, E-11 standards, Fisher Scientific

3.3 FEED PREPARATION

Wood pallets were acquired from MLTC Industrial Investments LP; SPF sawmill based in Saskatoon, Saskatchewan, Canada. Wood pallets were made from the shavings of spruce, pine and fir planer (thin pieces of wood obtained when dried lumber is planed smooth before shipping). The wood pallets were then crushed and separated according to size ranges with the help of standard sieves and stored in plastic zip lock bags. Ultimate elemental analysis of wood was carried out in Loring Laboratories, Alberta, Canada, for determining carbon,
hydrogen, nitrogen, sulphur, oxygen, ash and water content. Following table 3.1 shows results of wood pallets used as reactant in pyrolysis process.

<table>
<thead>
<tr>
<th>ULTIMATE ANALYSIS</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>47.47</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.62</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.18</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.01</td>
</tr>
<tr>
<td>Oxygen</td>
<td>40.28</td>
</tr>
<tr>
<td>Ash</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Water</td>
<td>6.43</td>
</tr>
</tbody>
</table>

Table 3.1 Ultimate Analysis of wood

3.4 FEED STOCK

For Phase I, 15 g wood was used and in Phase II and III, 10 g wood was used. For equal distribution of heat, 1mm stainless steel balls were mixed homogeneously with the feed.

3.5 CATALYSTS

Three commercial catalysts: H-ZSM-5, γ-alumina and silica-alumina were used for Phase II –Catalytic Pyrolysis. H-ZSM-5 was purchased from Zibo Yinghe Chemical Company Limited, Zibo City, China. γ-alumina from Zeochem, USA and Silica-alumina from Riogen Inc. New Jersey, USA.

3.5.1 CATALYST CHARACTERIZATION

Catalysts characterization was carried out at Biomedical and Chemical Laboratory, University of Saskatchewan, Canada.
Brunauer-Emmett-Teller (BET) Analysis

Micromeritics ASAP 2020 instrument was used for surface area, pore volume and average pore size measurements. For analysis, the sample was degassed at 200°C under isothermal conditions for 3 hours and adsorption & desorption isotherms were used for result evaluations.

Fourier Transformed Infrared Spectroscopy (FTIR)

Broker Vertex 70 Model was used for IR measurements with resolution, sample scan time and background scan time were set to 4,16 and 16 respectively. Aperture was set to 6mm with scan velocity to 10kHz and scan was ranged from 4000 to 400cm⁻¹. 0.1g of sample were treated with approximately 25 microliter of pyridine and left for overnight adsorption. After the removal of excess pyridine by heating sample to about 115°C, the samples were examined under FTIR.

Power X-ray Diffraction

BRUKER D8 advanced series II was used to record the XRD patterns from LynxEye Detector. Intensity data was obtained over a scan range of 10-90° with step size of 0.047° with total number of 1707 steps and counting time of 1s. The crystalline phases were identified based on reference data from International Center for Diffraction Data, ICDD.

Temperature Program Desorption (TPD)

Each catalyst was measured using an Autosorb iQ from Quantachrome model with a TCD Detector type for TPD analysis. Initially the sample was exposed to helium while the furnace temperature was increased to 250°C at 20°C/min ramping. Then the temperature was reduced to 50°C after 20 minutes and 3 % of
ammonia in helium gas was flowed for 60 minutes. The gas was then changed to helium, and kept at an isothermal condition at 70°C for 30 minutes.

3.6 OPERATING CONDITIONS

3.6.1 PHASE I & II

The experiments were performed in Packed Bed Tubular Reactor, to study the effect of operating condition on varying temperatures and feed size for pyrolysis of wood with and without catalyst. All the experiments were carried out in inert atmosphere with retention time of 30 minutes after reaching the desired temperature. All experiments were performed at room temperature and atmospheric pressure.

The aim for Phases I and II was to study the ideal and optimized conditions of pyrolysis process with and without catalyst. Along with this the aim of Phase II was to evaluate the performance of the best catalyst for the production of maximum yield of phenol rich bio-oil.

Range of the operating conditions for Phase I are given below:

- Pressure: 1 atm Constant
- Retention time: 30 minutes Constant
- Temperature: 500, 600 and 650°C
- Feed size: (0.7-0.85 mm), (0.85- 1mm), (1- 1.18mm) and (1.18-1.44mm)

Range of the operating conditions for Phase II are given below:

- Feed size: 1.18mm – 1.44mm Constant
- Pressure: 1 atm Constant
- Retention time: 30 minutes Constant
• Catalyst: H-ZSM-5, γ-alumina and silica alumina

• Temperature: 400, 500 and 600°C

• Catalyst amount: 10 and 20 wt%

### 3.6.2 PHASE III KINETIC STUDY

Experiments were performed in CSTR batch reactor, using the best catalyst and feed size determined from Phase I and II for phenol rich bio-oil production, to study the kinetics of pyrolysis process. Experiments were performed by at varying temperatures, catalyst amounts and different retention times. Continuous stirring was done during reaction in inert atmosphere. Range of the operating conditions are given below:

- Feed size: 1.18mm – 1.44mm Constant
- Catalyst: H-ZSM-5 Constant
- Temperature: 400, 440 and 480°C
- Retention time: 0, 30, 60 and 90 minutes
- Catalyst amount: 10 and 20 wt%

### 3.7 EXPERIMENTAL PROCEDURE AND SET-UP

#### 3.7.1 DETERMINATION OF BIO-OIL YIELD RANGE

Every biomass has different temperature range for its decomposition, to determine the temperature range of wood Thermo-gravimetric Analysis (TGA) was carried out. Wood was subjected to a programmed temperature increase in inert atmosphere to give the same condition as pyrolysis process. At atmospheric pressure the weight loss and change in weight due to the decomposition of the wood was studied. TGA runs were performed using Shimadzu TGA-50
instrument connected to a flow controller FC-60A. The applied temperature on wood was 800°C controlled from TA-60WS Collection software. The flow of nitrogen was adjusted at 50 ml/min from the FC-60A flow controller. The heating rate was set up at 10°C/min. Cooling of the furnace was done using an external fan (BLW-50, Shimadzu) purchased alongside with TGA-50 instrument.

Figure 3.1 shows first peak at 90-100°C presenting the removal of moisture. Second peak around 280°C shows the decomposition of biomass and formation of products. Hence, it can be deduced that the range for decomposition of wood is 280°C and above.
Figure 3.1 Thermo-gravimetric analyses for bio-oil yield range
3.7.2 SCHEMATIC DIAGRAM AND EXPERIMENTAL SET-UP

3.7.2.1 EXPERIMENTAL SET-UP PHASE I & II

Figure 3.2 Experimental Set-up (Packed bed tubular reactor)
Figure 3.2 shows the experimental set-up used for Phase I to study optimized conditions and Phase II for selecting the best catalyst for the production of phenol-rich bio-oil. The components of this set-up are as listed below:

- Packed Bed Tubular Reactor (Inconel 0.5" ID, Home-made at UofR)
- Electric Tubular Furnace (ZCP 386, Zesta Engineering Ltd.)
- Two K-type thermocouples (1.6 mm x 18", Zesta Engineering Ltd.)
- Thermal Mass Flow Controller (DFC26, Aalborg Instruments)
- Mass Flow Meter (GFM 17, Aalborg Instruments)
- Gas Chromatograph (GC-TCD, HP 6890, Agilent Technologies)
- Pure Nitrogen Cylinder (UHP 5.0, Praxair)
- Condenser (Water-cooled, Home-made at UofR)
- Collector with ice-cooled jacket (Fabricated, UofS)

### 3.7.2.2 PHASE I & II PROCEDURE

For Phase I and II, 15 and 10 g respectively of wood was charged in the reactor along with 1mm stainless steel balls to help have proper heat conduction. After setting up all the connections, pressure test was conduction before every run to test if there is any gas leak in the system. Next step, was to flow nitrogen through the system for 10 minutes to make sure atmosphere in the reactor is inert.

Reactions were carried out at varying temperatures (400, 500, 600 and 650\(^{0}\)C), feed size (0.7-0.85, 0.85-1, 1-1.18 and 1.18-1.44mm) and catalyst loading of (10 and 20 wt%) at constant atmospheric pressure. While the experiments were running water was continuously passed through the condenser.
to condense the bio-oil vapours and collected in the ice bath collector. Online GC was used to analyze the gases during the experiment.

On reaching the desired temperature, heating was shut down and reactor was left to cool down. Bio-oil was then removed from collector in the measuring cylinder, transferred to vial and stored in the freezer for further analysis. Char was collected from the reactor; stainless steel balls were separated and cleansed for re-use in further experiments. Char was measured and a material balance carried out to determine possible experimental and/or measurement errors.

3.7.3 CATALYTIC PYROLYSIS

The catalyst was loaded to the reactor in two ways namely; mixed and bed.

Mixed - catalyst was mixed homogenously along with the feed

Bed – feed was loaded over the catalyst bed in the reactor.

Similar experimental procedure was followed as above with varying catalyst amount. Results obtained from these two types of catalyst settings in the reactor are further discussed in the next chapter.

3.7.3.1 EXPERIMENTAL SET-UP PHASE III

Figure 3.3 and 3.4 shows the experimental set-up for kinetic runs. Components for this set-up are listed below.

- 500 ml vessel assembly
- Pressure gauge
- Backplate encasement
- Stirrer
- Catalyst basket
Figure 3.3 Experimental set-up (Batch Reactor)
Figure 3.4 Internal Schematic of batch reactor with catalyst gasket
3.7.3.2 PHASE III PROCEDURE

For Phase III Kinetic analysis, 10g feed was weighed and charged in the reactor and H-ZSM-5 catalyst (10 and 20 wt%) was loaded in the catalyst jacket. An autoclave reactor was sealed using a graphite gasket followed by pressure tests to check for gas leaks. Nitrogen was then passed through the system for 10 minutes to ensure an inert atmosphere within the reactor.

Temperature (400, 440, 480°C) was adjusted with the help of a heating controller along with continuous stirring during the reaction. A coolant was passed to prevent the stirrer motor from overheating. On reaching the desired temperature and varying residence times (0, 30, 60 and 90 minutes), the heating was stopped and reactor was left to cool down to room temperature.

On reaching the room temperature, gases were measured with the help of gas flow meter and analyzed with the help of GC. Liquid and char was then removed from reactor and measured. In order to separate char from any traces of bio-oil, it was heated in the furnace at 100°C. Char was then crushed to powder and stored in vials. The samples were sent to the Saskatchewan Research Council, Saskatoon for carbon analysis.

3.8 PRODUCT ANALYSIS

3.8.1 PHASE I AND II

3.8.1.1 LIQUID ANALYSIS

Gas Chromatography- Mass Spectroscopy (GC-MS)

The compounds in bio-oil i.e. phenol derivatives and sugars were measured with a gas chromatograph coupled with a mass selective detector.
(GC-MS). To identify the chemicals present in bio-oil, mass spectroscopy (MS) was used along with the gas chromatograph (GC), for the identification of peaks with best qualitative and quantitative information. From Hewlett-Packard Canada, Ltd., Montreal, Quebec, Canada the GC-MS instrument (model 6890/5073) was obtained. The column HP-35MS (intermediate polarity) with 35% phenylmethylsiloxane with dimensions of 0.25 m thickness x 0.25 mm i.d x 30 cm length obtained from Hewlett-Packard Canada, Ltd., Montreal, Quebec, Canada. Bio-oil sample was injected through auto-sampler injector- model 7683, Hewlett-Packard Canada, Ltd., Montreal, Quebec, Canada. For all samples identical GC-MS operating conditions were applied. All bio-oil samples were diluted 100x in methanol. Method was set to run from 350°C to 300°C at a ramping of 60°C/minute with column flow of 1.5 ml/min and a split ratio of 5:1.

To identify and match the peaks obtained, standards of phenol derivatives and sugars were run through GC using 100, 500 and 1000 times dilutions, giving a range to identify the target compounds.

3.8.1.2 GAS ANALYSIS

Gases of Phase II were analyzed using an online GC/TCD (Agilent 6890) equipped with Hayesep Q and Molecular Sieve A columns. Different gas peaks were studied to identify the presence of carbon dioxide, methane, nitrogen, carbon monoxide and hydrogen.
3.8.2 PHASE III

3.8.2.1 GAS ANALYSIS

The gas product was analyzed using a gas chromatograph (Agilent Technologies 6890) equipped with two columns (Hayesep Q and molecular sieve) and a thermal conductivity detector (TCD). Helium gas was used as the carrier gas in the GC and calibration of GC was done using standard gas mixtures.

3.8.2.2 CHAR ANALYSIS

Char samples were crushed to powder and sent to SRC, Saskatoon for carbon content analysis. A LECO Carbon Sulphur Analyzer was used for total carbon percentage analysis by combusting the samples were combusted in LECO induction furnace in the presence of oxygen. The percentage of carbon is determined from instrument calibration and for quality control after every 20 samples at least once the standard was run.

3.9 CALCULATION EQUATIONS FOR YIELD AND CONVERSION

For the calculation of phenol derivatives yield in bio-oil, the following equation was used.

\[
\text{Yield of } "A" = \frac{\text{ml of } "A"}{\text{gram of wood}} \quad (\text{ml/g}) \tag{3.1}
\]

where:

"A" is the phenol derivatives in liquid phase i.e. bio-oil produced during pyrolysis

A detailed calculation of the products yield is shown in Appendix A.
Carbon conversion of wood was calculated from ultimate analysis of the char remaining at the end of pyrolysis reaction. The conversion was in terms of the amount of carbon remaining with respect to the amount initially present in wood.

\[
\text{Carbon Conversion (Xc)} = \frac{W_{ci} - W_c}{W_{ci}} \quad \text{(3.2)}
\]

Where:

- \(W_{ci}\) = initial weight of carbon in wood before the reaction.
- \(W_c\) = weight of carbon in the char at the end of pyrolysis reaction.
CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 PHASE I - PARAMETRIC STUDY

Experiments were performed using varying size of wood and temperature. Table 4.1 shows observations for the effect of varying feed size (0.71, 0.85 and 1mm) and temperature (500, 600 and 650°C). Each experiment was carried out with nitrogen flow rate of 30 ml/minute; weight of biomass was 15 grams and atmospheric pressure. Reading for the temperature ramping was taken at every 5 minutes and bio-oil was collected in the collector after passing through the condenser. To grasp a better knowledge of this new pyrolysis system, reading of the first drop of bio-oil was also noted. For a better understanding of bio-oil quality density of bio-oil was analyzed by the density meter. Yield percentage of char and bio-oil were noted after every run.

It can be observed from table 4.1, formation of bio-oil starts from 339°C and up till 375°C. From the results it can be seen with the increase in temperature the yield of bio-oil increases but not much of difference can be seen on bio-oil yield at 600 and 650°C.
<table>
<thead>
<tr>
<th>T</th>
<th>FEED SIZE</th>
<th>1st DROP (°C)</th>
<th>Bio-oil (ml)</th>
<th>Char (g)</th>
<th>Bio-oil Density @15°C (gm/cm²)</th>
<th>Yield Char (%)</th>
<th>Yield Bio-oil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C</td>
<td>1 mm</td>
<td>349</td>
<td>5.6</td>
<td>4.22</td>
<td>1.13209</td>
<td>28.13</td>
<td>42.30</td>
</tr>
<tr>
<td></td>
<td>0.85 mm</td>
<td>339</td>
<td>7.0</td>
<td>4.44</td>
<td>1.12460</td>
<td>29.60</td>
<td>52.48</td>
</tr>
<tr>
<td></td>
<td>0.71 mm</td>
<td>342</td>
<td>7.3</td>
<td>4.14</td>
<td>1.12448</td>
<td>28.00</td>
<td>53.97</td>
</tr>
<tr>
<td>600°C</td>
<td>1 mm</td>
<td>369</td>
<td>7.8</td>
<td>3.62</td>
<td>1.12772</td>
<td>24.13</td>
<td>58.64</td>
</tr>
<tr>
<td></td>
<td>0.85 mm</td>
<td>362</td>
<td>7.8</td>
<td>3.55</td>
<td>1.13435</td>
<td>23.66</td>
<td>59.98</td>
</tr>
<tr>
<td></td>
<td>0.71 mm</td>
<td>375</td>
<td>7.7</td>
<td>3.50</td>
<td>1.12289</td>
<td>23.33</td>
<td>57.64</td>
</tr>
<tr>
<td>650°C</td>
<td>1 mm</td>
<td>360</td>
<td>8.0</td>
<td>3.42</td>
<td>1.12412</td>
<td>22.80</td>
<td>59.95</td>
</tr>
<tr>
<td></td>
<td>0.85 mm</td>
<td>365</td>
<td>7.9</td>
<td>3.61</td>
<td>1.12858</td>
<td>24.06</td>
<td>59.43</td>
</tr>
<tr>
<td></td>
<td>0.71 mm</td>
<td>359</td>
<td>8.0</td>
<td>3.38</td>
<td>1.12735</td>
<td>22.53</td>
<td>60.12</td>
</tr>
</tbody>
</table>

Table 4.1 Effect of temperature and feed size on pyrolysis process
Fourier Transformed Infrared Spectroscopy (FTIR) of bio-oil was performed to investigate the presence of various functional groups. Figure 4.1 shows the presence of aliphatic hydrocarbons, phenols, aldehydes, ketones and carbolic acids. According to the observed wave number cm$^{-1}$ each functional group is clubbed in table 4.2.

![Figure 4.1 Fourier Transformed Infrared Spectroscopy of bio-oil](image)
Table 4.2 Functional groups in bio-oil
4.1.1 EFFECT OF CATALYST ON BIO-OIL YIELD

To study the effect of acidic catalyst on bio-oil yield, two catalysts $\gamma$-Al$_2$O$_3$ (gamma-alumina) and H-ZSM-5 were studied. Experiments were carried out at 600°C with nitrogen flow rate of 30ml/minute, feed weight of 10 g and catalyst weight of 1g (10 weight % of feed) with varying feed size range of (1-1.18 and 1.18-1.44mm).

Table 4.3 shows with the presence of catalyst there is an increase in the yield of liquid phase i.e. bio-oil. This means the acidic catalysts are effective in increasing the quantity of bio-oil; hence they should be studied in detail to analyze the effect of catalyst for the production of phenol rich bio-oil.

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>FEED SIZE</th>
<th>BIO-OIL (ml)</th>
<th>CHAR (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without Catalyst</td>
<td>(1.00 – 1.18) mm</td>
<td>5.2</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>(1.18 – 1.44) mm</td>
<td>5.3</td>
<td>2.42</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>(1.00 – 1.18) mm</td>
<td>5.7</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>(1.18 – 1.44) mm</td>
<td>5.5</td>
<td>2.12</td>
</tr>
<tr>
<td>HZSM5</td>
<td>(1.00 – 1.18) mm</td>
<td>5.7</td>
<td>2.10</td>
</tr>
<tr>
<td></td>
<td>(1.18 – 1.44) mm</td>
<td>5.5</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Table 4.3 Observations from effect of acidic catalyst on bio-oil yield
4.1.2 EFFECT OF CATALYST LOADING SYSTEM

Experiments were carried out in two different catalyst-loading systems, to deduce an effective system for the increase in phenol derivatives in bio-oil. Figure 4.2 shows the two systems named as mixed and bed, in mixed system the catalyst was mixed with the wood and in other case the produced bio-oil was made to pass over the catalyst bed. Figure 4.2 clearly shows, the increase in the phenol and furan derivatives, making catalyst bed system a better setting for phenol rich bio-oil.

![Phenol Derivatives](image)

Figure 4.2 Effect of catalyst loading system on phenol derivatives
Figure 4.3 Effect of catalyst loading system on furan derivatives
4.1.3 EFFECT OF CATALYST LOADING SYSTEM ON BIO-OIL COMPONENTS

Following figure 4.4 and 4.5 shows the important components of bio-oil, it is to be noted here Bed catalyst loading system works better for increase in the phenol derivatives. While the phenol derivatives quantity is increased the sugar component i.e. levoglucosan is decreased, this means the presence of free radicals is reducing and a phenol rich bio-oil is being produced. This mechanism is explained as cellulose on heating produce levoglucosan with free radicals and these get polymerized to form solid char or residue but the presence of catalyst stops the free radicals from polymerizing instead it helps them in the formation of phenols. For hemicellulose and lignin, the presence of catalyst helps in enhancing the phenol derivatives and reduction of hydroxyl groups.
Figure 4.4 Bio-oil components in mixed feed catalyst system

Figure 4.5 Bio-oil components in catalyst bed system
4.1.4 EFFECT OF PARTICLE SIZE ON BIO-OIL YIELD

Figure 4.6 shows the effect of feed size on bio-oil yield, experiments are performed at 600\(^{0}\)C with nitrogen flow rate of 30ml/minute. It can be seen from figure with the increase in feed size the bio-oil yield increases, but at 1.18 and 1.44mm the bio-oil yield becomes consistent. Hence, 1.18mm feed size is the optimized feed size for Phase II.

![Figure 4.6 Effect of feed size on bio-oil yield](image)
**4.2 PHASE II - PYROLYSIS OPTIMIZATION**

Experiments for Phase II were performed using three catalysts: \( \gamma-Al_2O_3 \), silica-alumina and H-ZSM-5 with 1g and 2 g of catalyst amounts and varying temperatures (400, 500, 600\(^0\)C). All experiments in this phase were carried out using 1.18mm feed size, 10 g of feed and nitrogen flow rate of 30 ml/minute. Table 4.4 shows the observed values of bio-oil, char and gases obtained from with and without catalyst along with varying parameters.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>400(^0)C</th>
<th>500(^0)C</th>
<th>600(^0)C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without catalyst</td>
<td>55.12</td>
<td>55.9</td>
<td>58.4</td>
</tr>
<tr>
<td>10 wt% ( \gamma-Al_2O_3 )</td>
<td>55.5</td>
<td>56.2</td>
<td>58.8</td>
</tr>
<tr>
<td>16.1</td>
<td>17.5</td>
<td>15.3</td>
<td></td>
</tr>
<tr>
<td>20 wt% ( \gamma-Al_2O_3 )</td>
<td>54.8</td>
<td>55.7</td>
<td>58.1</td>
</tr>
<tr>
<td>28.1</td>
<td>13.9</td>
<td>21.7</td>
<td></td>
</tr>
<tr>
<td>17.6</td>
<td>25</td>
<td>19.2</td>
<td></td>
</tr>
<tr>
<td>10 wt% HZSM5</td>
<td>56.6</td>
<td>56.6</td>
<td>57.5</td>
</tr>
<tr>
<td>28.4</td>
<td>25</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>18</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>20 wt% HZSM5</td>
<td>55</td>
<td>57.1</td>
<td>54.8</td>
</tr>
<tr>
<td>28.4</td>
<td>24.6</td>
<td>22.1</td>
<td></td>
</tr>
<tr>
<td>17.1</td>
<td>19</td>
<td>20.5</td>
<td></td>
</tr>
<tr>
<td>10 wt% Silica Alumina</td>
<td>53.9</td>
<td>56.1</td>
<td>57.1</td>
</tr>
<tr>
<td>30.1</td>
<td>26.8</td>
<td>23.4</td>
<td></td>
</tr>
<tr>
<td>17.2</td>
<td>7.6</td>
<td>19.2</td>
<td></td>
</tr>
<tr>
<td>20 wt% Silica Alumina</td>
<td>52.74</td>
<td>56</td>
<td>56.9</td>
</tr>
<tr>
<td>29</td>
<td>26.6</td>
<td>24.6</td>
<td></td>
</tr>
<tr>
<td>16.5</td>
<td>15.2</td>
<td>22.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4 Bio-oil, char and gas yields from with and without catalytic pyrolysis
4.2.1 OVERALL EFFECT OF DIFFERENT CATALYSTS, TEMPERATURE AND CATALYST AMOUNTS ON BIO-OIL COMPOUNDS

For this section the set of experiments were performed using 1.18 mm of feed at varying temperatures (400, 500 and 600°C) with catalyst amount of 1g and 2 g (10 & 20 wt%) with feed weight of 10 g. The nitrogen flow rate was kept the same as other experiments at 30 ml/min. Following figures 4.7, 4.8 and 4.9 show the effect on phenol derivatives, furan derivatives, sugars and ketones yield in bio-oil. With the increase in temperature a significant increase in phenol derivatives and furan derivatives is observed where as sugar component in bio-oil yield is decreased. All products have the unit of ml/g i.e. yield of component from wood.

Results from these experiments are explained parameter wise in next segment.

Figure 4.7 Effect of catalyst on phenol derivatives in bio-oil
Figure 4.8 Effect of catalyst on furan derivatives in bio-oil

Figure 4.9 Effect of catalyst on sugar components in bio-oil
4.2.2 EFFECT OF CATALYST TYPE ON PHENOL YIELD

Using 1.18mm feed size at 600°C, catalyst amount of 1g and feed weight of 10g the yield of phenol derivatives and sugar content is compared. Figure 4.10 and 4.11 shows the effect of different acidic catalyst on the phenol derivative and sugar yields. It can be seen that H-ZSM-5 gives the maximum yield of phenol derivatives and a big drop in sugar yield. It can be concluded that H-ZSM-5 helps in reducing the free radicals and oxygenates in bio-oil making it a better quality and stable phenol rich bio-oil.

![Phenol Derivatives](image)

Figure 4.10 Effect of different acidic catalyst on the phenol derivative
Figure 4.11 Effect of different acidic catalyst on sugar components
4.2.3 EFFECT OF TEMPERATURE ON PHENOL DERIVATIVES

Using 1g of H-ZSM-5 with 10g of feed the experiments were carried out at 400, 500 and 600°C. It can be seen from figure 4.12 phenol derivative yield increases with the increase in phenols. This is because with the increase in temperature more of cracking takes place and more olefins, paraffins and phenols are formed whereas at lower temperature dehydration takes place and ultimately isomerisation of hydrocarbons.

![Figure 4.12 Effect of temperature on phenol derivatives](image)

0.02 0.04 0.06 0.08 0.1 0.12 0.14 0.16 0.18

Phenol Derivatives ml/gm

0 0.02 0.04 0.06 0.08 0.1 0.12 0.14 0.16 0.18

Phenol Derivatives ml/gm

0 0.02 0.04 0.06 0.08 0.1 0.12 0.14 0.16 0.18

Phenol Derivatives ml/gm

400 500 600

Temperature °C

Figure 4.12 Effect of temperature on phenol derivatives
4.2.4 EFFECT OF CATALYST ACIDITY ON PHENOL DERIVATIVES

To study the effect of catalyst acidity the experiments were performed at 600°C with three catalysts having varying acidity content. Acidity in the catalysts show the presence of strong acid in the catalyst i.e. the number of H⁺ ions in acid. Figure 4.13 shows the increase in the acidity helps in increasing the phenol derivative yields. It can be reckoned, the increase in the acidity of the catalyst helps in reducing oxygenate and donating H⁺ ions for the formation of phenol derivatives.

Figure 4.13 Effect of catalyst acidity on phenol derivatives
4.2.5 EFFECT OF ACID STRENGTH ON PHENOL DERIVATIVES

Acid strength is calculated by dividing bronsted to lewis site ratio to the acid sites. Experiments carried out at 600°C temperature with 1.18mm feed size with 1g of catalyst show the effect of acid strength on phenol derivative yield. Figure 4.14 shows with the increase in acid strength the phenol derivative yield increases, that because the number of acid site are more so the reactants attach more for reaction and the acid strength helps in losing the H⁺ ions as to make bio-oil more stable with increase in phenols.

Figure 4.14 Effect of acid strength on phenol derivatives
4.2.6 EFFECT OF SURFACE AREA ON PHENOL DERIVATIVES

To study the effect of surface area experiments were carried out at 600°C with feed size of 1.18mm and 1 g of catalyst. Figure 4.15 shows with the increase in surface area the phenol derivative yield decreases this can be due to the deposition of tar over the pores of the catalyst hindering the reaction to take place (Lappas, 2015)

![Figure 4.15 Effect of surface area on phenol derivatives](image)

4.2.6 EFFECT OF CATALYST WEIGHT ON PHENOL DERIVATIVES

Figure 4.16 shows the effect of catalyst weight on the yield of phenol derivatives. It is observed that with the increase in the catalyst weight phenol derivative amount increases the phenol yield and later decreases it. This is because with higher amount of catalyst the gas yield is increasing instead, literature suggests
with higher catalyst weights pressurized system can help in forming more vapors hence help in obtaining higher yield of liquid less of gases.

![Figure 4.16 Effect of catalyst weight on Phenol derivatives](image)

**4.2.6 OVERALL MASS BALANCE**

Liquid, solid and gas phases of all the experiments were analyzed to check if the whole system closes. From the data retrieved during the experiments the overall mass balance was calculated. During the pyrolysis process wood is decomposed into bio-oil, char and gases. Equation shows the error of \( \pm 2.414 \) for this catalytic pyrolysis system.

**Wood – Bio-oil – Char – Gases = +/-2.414 error**
4.3 PHASE III- KINETIC STUDY

Experiments were performed in a batch reactor with the optimum weight of 10 g wood, selected catalyst H-ZSM-5 with catalyst amount of 2 g at temperatures 400, 440 and 480°C and at residence time of 0, 30, 60 and 90 minutes. Pressure was kept constant at atmospheric pressure. The conversion of carbon was calculated from the char samples that were sent to SRC, Saskatoon for total carbon analysis.

WOOD $\rightarrow$ CHAR + BIO-OIL + GAS \hspace{1cm} (4.1)

The carbon conversion was calculated by

$$(X_c) = \frac{W_{ci} - W_c}{W_{ci}}$$ \hspace{1cm} (4.2)

where; $X_c$ is carbon conversion of wood

$W_{ci}$ weight of carbon in wood

$W_c$ weight of carbon in char

Residence time was considered on reaching the desired temperature and holding it for the time needed after which the heating of the system was stopped. Graph was plotted for carbon conversion against the four residence times. Figure 4.15 shows three lines representing different temperatures and carbon conversions. The slope of each line was calculated by differentiating the equations of each temperature using OriginLab software and WolframAlpha computational knowledge engine. Table 4.5 shows the experimental rate, temperature and conversion for kinetic studies.
Figure 4.17 Carbon conversion versus time at different temperatures
<table>
<thead>
<tr>
<th>EXPERIMENTAL RATE dXc/dt</th>
<th>TEMPERATURE (K)</th>
<th>CARBON CONVERSION Xc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000012485</td>
<td>673</td>
<td>0.34111227</td>
</tr>
<tr>
<td>0.000011192</td>
<td>673</td>
<td>0.362477415</td>
</tr>
<tr>
<td>0.000009588</td>
<td>673</td>
<td>0.381243531</td>
</tr>
<tr>
<td>0.000007709</td>
<td>673</td>
<td>0.396882487</td>
</tr>
<tr>
<td>0.000018069</td>
<td>713</td>
<td>0.350179289</td>
</tr>
<tr>
<td>0.000013490</td>
<td>713</td>
<td>0.378738766</td>
</tr>
<tr>
<td>0.000007815</td>
<td>713</td>
<td>0.398006534</td>
</tr>
<tr>
<td>0.000001483</td>
<td>713</td>
<td>0.40638885</td>
</tr>
<tr>
<td>0.000016535</td>
<td>753</td>
<td>0.375791805</td>
</tr>
<tr>
<td>0.000012078</td>
<td>753</td>
<td>0.401696892</td>
</tr>
<tr>
<td>0.000006757</td>
<td>753</td>
<td>0.418755031</td>
</tr>
<tr>
<td>0.000000938</td>
<td>753</td>
<td>0.425727795</td>
</tr>
</tbody>
</table>

Table 4.5 Experimental rate, temperature & conversion (Kinetic Data)
4.3.1 POWER LAW MODEL

The kinetic modeling was performed using an empirical model to fit the kinetic data. The reaction rate for the batch reactor is (Levenspiel, 1999):

\[-rA = \frac{dXc}{dt} = k(1-Xc)^n\]  \hspace{1cm} (4.3)

The rate constant can be written as

\[k = A \ e^{-E/RT}\]  \hspace{1cm} (4.4)

where

A = pre exponential factor (or collision factor)

E = activation energy (J/mol)

T= reaction temperature (K)

R = gas constant (8.314 J/mol K)

The final rate equation can be obtained by the substitution of the rate parameters in the rate equation

\[dXA/dt = A \ e^{-E/RT} (1 – XA)^n\]  \hspace{1cm} (4.5)

4.3.2 KINETIC VALUES AND PARITY CHART

An empirical kinetic model was used for the carbon conversion and data observed for kinetics. Using NLREG software the kinetic parameters A,E and n were regressed. H-ZSM-5 being the most effective catalyst for the production of phenol derivatives from wood gave activation energy of and pre-exponential factor. The obtained values were substituted in the rate model to get predicted data. Figure 4.16 shows experimental rate was plotted against the predicted rate and using the parity plot the AAD% of model was calculated to be 16%.

\[\text{AAD\%} = \frac{(\text{Experimental rate} – \text{predicted rate}) \times 100}{\text{Experimental rate}}\]  \hspace{1cm} (4.6)
Rate model is as follows: Pre-exponential Factor

\[ -r = \frac{dX_c}{dt} = 0.000567e^{-17104.04/RT}(1-X_c)^2 \quad (4.7) \]

Pre-exponential Factor, \( A = 0.000567 \text{ s}^{-1} \)

Activation Energy, \( E = 17104.04 \text{ J/mol} \)

Order of reaction, \( n = 2 \)

Figure 4.18 Parity plot: predicted conversion vs experimental conversion

Table 4.6 shows the comparison of activation energy and pre-exponential factor of this work with literature. It is seen from this table that the activation energy of this work lies in the range of the other activation energies for biomass.
<table>
<thead>
<tr>
<th>Source</th>
<th>Catalyst</th>
<th>Carbon %</th>
<th>Pre-exponential Factor (min(^{-1}))</th>
<th>Activation Energy (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S Poddar, S De and R Chowdhury (2015)</td>
<td>Without</td>
<td>49.79</td>
<td>0.156609</td>
<td>24742</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>49.79</td>
<td>0.1072</td>
<td>16769</td>
</tr>
<tr>
<td></td>
<td>KCl</td>
<td>49.79</td>
<td>0.0189</td>
<td>13502</td>
</tr>
<tr>
<td></td>
<td>ZnO</td>
<td>49.79</td>
<td>0.5071</td>
<td>14392</td>
</tr>
<tr>
<td>This work</td>
<td>HZSM5</td>
<td>47.47</td>
<td>0.000567</td>
<td>17104</td>
</tr>
</tbody>
</table>

Table 4.6 Comparison of activation energy and pre-exponential factor for biomass

Figure 4.19 Literature values vs present work Activation Energy values
CHAPTER 5: STATISTICAL ANALYSIS

The purpose of the statistical analysis of the catalysts used is to understand the effect and significance of each catalyst property on the phenol rich bio-oil production. Data obtained at temperatures (400, 500 and 600°C) and phenol derivative yields were used to study the performance of this system. Table 5.1 lists the surface area, pore volume, pore size, bronsted to lewis ratio and silica to alumina ratio values of the three catalysts used.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (ml/g)</th>
<th>Avg. pore size (nm)</th>
<th>Bronsted to Lewis ratio</th>
<th>Silica to Alumina ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>414.102</td>
<td>0.29</td>
<td>4.55</td>
<td>0.67</td>
<td>0</td>
</tr>
<tr>
<td>HZSM5</td>
<td>381.45</td>
<td>0.47</td>
<td>3.12</td>
<td>1.4</td>
<td>56</td>
</tr>
<tr>
<td>Silica alumina</td>
<td>613.45</td>
<td>0.79</td>
<td>5.79</td>
<td>0.32</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Table 5.1 Catalyst properties

5.1 EFFECT OF PHYSICAL AND CHEMICAL PROPERTIES OF CATALYSTS

For the three catalysts, properties and experimental data observations are used to model for statistics of catalyst performance was analyzed. Table 5.2 shows the factors affecting the phenol derivatives yield; PV/SA is the effect of catalyst pore volume and surface area (physical), effect of acid sites and bronsted to lewis ratio.
<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction Temperature (in °C)</th>
<th>PV/PS</th>
<th>Surface Area</th>
<th>Acid Site</th>
<th>B/L Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>0.1364</td>
<td>613.45</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>0.0637</td>
<td>414.1</td>
<td>0.428</td>
<td>0.67</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>0.01506</td>
<td>381.45</td>
<td>0.52</td>
<td>1.4</td>
</tr>
<tr>
<td>4</td>
<td>500</td>
<td>0.1364</td>
<td>613.45</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>0.0637</td>
<td>414.1</td>
<td>0.428</td>
<td>0.67</td>
</tr>
<tr>
<td>6</td>
<td>500</td>
<td>0.01506</td>
<td>381.45</td>
<td>0.52</td>
<td>1.4</td>
</tr>
<tr>
<td>7</td>
<td>400</td>
<td>0.1364</td>
<td>613.45</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>8</td>
<td>400</td>
<td>0.0637</td>
<td>414.1</td>
<td>0.428</td>
<td>0.67</td>
</tr>
<tr>
<td>9</td>
<td>400</td>
<td>0.01506</td>
<td>381.45</td>
<td>0.52</td>
<td>1.4</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>0.1364</td>
<td>613.45</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>11</td>
<td>600</td>
<td>0.0637</td>
<td>414.1</td>
<td>0.428</td>
<td>0.67</td>
</tr>
<tr>
<td>12</td>
<td>600</td>
<td>0.01506</td>
<td>381.45</td>
<td>0.52</td>
<td>1.4</td>
</tr>
<tr>
<td>13</td>
<td>500</td>
<td>0.1364</td>
<td>613.45</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>14</td>
<td>500</td>
<td>0.0637</td>
<td>414.1</td>
<td>0.428</td>
<td>0.67</td>
</tr>
<tr>
<td>15</td>
<td>500</td>
<td>0.01506</td>
<td>381.45</td>
<td>0.52</td>
<td>1.4</td>
</tr>
<tr>
<td>16</td>
<td>400</td>
<td>0.1364</td>
<td>613.45</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>17</td>
<td>400</td>
<td>0.0637</td>
<td>414.1</td>
<td>0.428</td>
<td>0.67</td>
</tr>
<tr>
<td>18</td>
<td>400</td>
<td>0.01506</td>
<td>381.45</td>
<td>0.52</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 5.2 Effect of physico-chemical properties on yield
5.2 MINITAB MODEL

Using MINITAB, models for combined catalyst amounts were developed.

Model for temperature, catalyst weight vs acid site, acid ratio, surface area and pore volume/pore site respectively.

Regression equation Coded
Yield = 0.12375 + 0.01625 T + 0.00125 CW + 0.01125 AS + 0.00375 T*CW + 0.00875 T*AS + 0.00375 CW*AS  \hspace{1cm} (5.1)

Regression equation Uncoded
Yield = 0.5568 - 0.000874 T - 0.1142 CW - 0.972 AS + 0.000075 T*CW + 0.001944 T*AS + 0.1667 CW*AS \hspace{1cm} (5.2)
Yield = 0.1647 - 0.000089 T - 0.0469 CW - 0.0810 R + 0.000075 T*CW + 0.000162 T*R + 0.01389 CW*R \hspace{1cm} (5.3)
Yield = -0.0926 + 0.000425 T - 0.0028 CW + 0.000377 SA + 0.000075 T*CW - 0.000001 T*SA - 0.000065 CW*SA \hspace{1cm} (5.4)
Yield = -0.742 + 0.001724 T + 0.1085 CW + 5.833 PV/PS + 0.000075 T*CW - 0.01167 T*PV/PS - 1.000 CW*PV/PS \hspace{1cm} (5.5)

where:

T: temperature

CW: catalyst weight

PV/PS: pore volume/ pore size

AS: number of acid sites

R: Bronsted to Lewis ratio

Figure 5.1 shows factors taken into consideration i.e. temperature, catalyst weight and acid sites. Figure shows, only temperature is most effective factor for
increasing the phenol yield followed by acid site. The trend shows, on increasing
the number of acid sites the yield of phenol derivatives might increase.

Equation 5.1, 5.2, 5.3, 5.4 and 5.5 show Coded equation and uncoded equations
for acid sites, acid ratio, surface area and pore volume/pore size respectively.
 follows the graph and regression coefficients values in the table where as the
uncoded equation is the simplified equation Minitab produces where the exact
value can be substituted and calculated.

Minitab uses coded units to do the analysis. Coded units compares the size of
the coefficients (on a common scale) to determine which factor has the largest
impact on the response. If a design is analyzed in uncoded (or natural) units, it
might no longer be orthogonal, hence the values of coefficient is not in the same
trend as the model equation.

For this reason the coded equation for various factors (acid sites, ratio, surface
area & PV/PS) will not change but the uncoded equation has changed slightly.

Another, important number is VIF. VIF number should be less than 5 and the
results here gives the value of 1 that means the results produced are
trustworthy.
Figure 5.1 Factors effecting Phenol derivatives yield for temperature, catalyst weight and acid sites

Figure 5.2 and 5.3 show the main effects and interaction factors affecting the yield of phenol derivatives respectively. It can be seen from the graph with the increase in temperature the phenol derivative yields are increasing and the catalyst weight it is decreasing. The number of acid sites shows with the increase on acid site the yield of phenol derivatives is increasing. Trend with other factors such as acid site ratio, pore volume/pore size and surface area are similar, the plots for these are attached in the Appendix F. Figure 5.3 shows the interactions at three temperature 400, 500 and 600 °C, catalyst weight of 1 and 2 g and acid site at three values of 0.428, 0.43 and 0.52. As the lines cross for temperature and catalyst weight and temperature with acid sites it means these factors are interacting.
Figure 5.2 Main factors effecting on phenol derivatives

Figure 5.3 Interaction plot for phenol derivative yield.
Table 5.3 shows the values for experimental and predicted yield for considering acid sites, temperature and catalyst weight in consideration. Average absolute deviation of this model was determined. The overall AAD for the set of data was observed to be 2%. This shows a good match with the experimental data obtained.

$$\text{AAD\%} = \frac{(\text{Experimental rate} - \text{predicted rate}) \times 100}{\text{Experimental rate}}$$  (5.5)

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction Temperature (in °C)</th>
<th>Catalyst weight (g)</th>
<th>Acid Site</th>
<th>Phenol Derivatives (Experimental)</th>
<th>Phenol Derivatives (Predicted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>1</td>
<td>0.43</td>
<td>0.120</td>
<td>0.118473</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>1</td>
<td>0.52</td>
<td>0.131</td>
<td>0.150972</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>1</td>
<td>0.43</td>
<td>0.156</td>
<td>0.111089</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
<td>1</td>
<td>0.52</td>
<td>0.116</td>
<td>0.108596</td>
</tr>
<tr>
<td>5</td>
<td>600</td>
<td>2</td>
<td>0.43</td>
<td>0.127</td>
<td>0.120954</td>
</tr>
<tr>
<td>6</td>
<td>600</td>
<td>2</td>
<td>0.52</td>
<td>0.133</td>
<td>0.168456</td>
</tr>
<tr>
<td>7</td>
<td>400</td>
<td>2</td>
<td>0.43</td>
<td>0.111</td>
<td>0.09857</td>
</tr>
<tr>
<td>8</td>
<td>400</td>
<td>2</td>
<td>0.52</td>
<td>0.123</td>
<td>0.11108</td>
</tr>
</tbody>
</table>

Table 5.3 Predicted versus experimental yield, Statistical Analysis
Figure 5.4 Parity plot of experimental versus predicted conversion
CHAPTER 6: APPLICATIONS, CONTRIBUTIONS & LIMITATIONS OF THIS RESEARCH

In this chapter, the applications, contributions and limitations of this research work i.e. catalytic pyrolysis of wood is discussed.

6.1 APPLICATIONS

• By-products from woods and forestry can be used for the production of more valuable products.

• Stable bio-oil with reduced free radicals can be produced, giving a solution to the problem for storing bio-oil.

• Phenol rich bio-oil can be used as a feed in Petrochemical Industry.

• The presence of various phenols, shows the presence of many essential chemicals used in various industries like food, resin and boiler fuels.

6.2 CONTRIBUTIONS

• This research sheds light on the operating conditions for the catalytic process of pyrolysis.

• Unconventional one step process is studied to avoid the multiple steps for the production of stable phenols

• Varying catalyst properties are studied in detail that will help in synthesizing catalyst with suitable properties for the production of valuable chemicals.

• Statistical analysis of catalysts is studied that will help in synthesizing and selecting the catalyst properties effective for producing phenol derivatives.
6.3 LIMITATIONS

- Tailored catalyst needs to be synthesized for increasing the yield and to do the statistical analysis on various parameters. As commercial catalyst was used yield could not be measured at different varying properties of catalyst.

- As wood has a complex structure, specific chemical reaction is needed to depict wood, for better kinetic studies.
CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The following conclusions can be made from this research:

- Ideal temperature for wood pyrolysis with and without catalyst was 600°C. At lower temperatures, bio-oil conversion was less because at lower temperature volatiles condense to form tar and char.

- Catalyst bed loading is the best method for catalytic pyrolysis as the phenol derivatives yield increases when catalyst gets in contact with bio-oil.

- Optimum feed size for pyrolysis reaction for this set-up is 1.18mm, at smaller feed size conversion is lesser and with larger feed size the conversion remains constant. So for better mass transfer smaller particle size that gives maximum yield is selected.

- H-ZSM-5 is considered to the best catalyst for phenol derivatives, having higher acid strength and acidity. Because of these factors, the presence free radicals and oxygenates components in bio-oil is reduced making bio-oil more stable and with higher shelf life.

- Kinetic model for the experiments performed by using the empirical rate model is \( -r_c = \frac{dX_c}{dt} = 0.000567e^{-17104.04 / RT}(1-X_c)^2 \) with order of reaction 2.

- Statistical analysis shows the most effecting factors of catalyst on phenol derivative yields are pore volume, surface area, number of acid sites and temperature.
• Second resolution interaction model shows the main and interacting factors for the increase in phenol derivatives.

7.2 RECOMMENDATIONS

Following recommendations are summarized:

• As the results show a significant effect of acidity, acid sites and acid strength, a catalyst needs to be synthesized with higher acid strength and acidity.

• H-ZSM-5 gives the best performance, so it is recommended the new synthesized catalyst should have similar properties.

• As bio-oil is a complex mixture of compounds, to study kinetics for particular product components experiments and analysis should be carried out at composition level.

• Effect of pressure needs to be studied to analyze the effect of yield and reaction rate for kinetics.

• Experiments need to be performed with varying feed size and mixing speeds to ensure the absence of heat and mass transfer limitations to obtain intrinsic kinetic data.

• Design of experiments need to be analysed after obtaining the best operating conditions to minimize the number of experiments for parametric studies.
REFERENCES:


http://doi.org/10.1021/ed043pA758.1


Furrer, R.M., Master’s (Thesis), (1988). Direct Conversion of Plant Tall Oils and De-pitche Tall Oil to Fuels and Chemicals Using HZSM-5 Catalyst, University of Saskatchewan.


pyrolysis vapours in fixed bed reactors using mesoporous materials.


http://doi.org/10.1016/j.biortech.2014.08.121


http://doi.org/10.1016/j.micromeso.2013.08.037


http://doi.org/10.1016/j.rser.2015.04.080


http://doi.org/10.1080/15567030903330652


http://doi.org/10.1021/ef060171a


APPENDIX A: LABORATORY SAFETY OPERATION PROCEDURE

For safety precautions during the experiments adequate trainings and precautions were taken.

• **Training undertaken**

  WHIMS- Workplace Hazardous Material Information System

  H₂S Training and Radiation Safety Training

• **Personnel Protective Equipment Used**

  Safety goggles

  Lab coats

  Gloves and closed shoes

• **CHEMICALS**

  -All chemicals were labelled properly and flammable chemicals were stored in designated storage cupboard. All chemicals were labelled and stored properly.

  -Gas cylinders were transported and stored rightly. All cylinders were secured to a wall or bench and capped well when not in use.

  -Neat and clean workplace was always ensured to avoid any hazard.
APPENDIX B: EXPERIMENTAL DATA SETS

Following raw data was collected for bio-oil, char and gases for Phase II experiments.

**Data for Bio-oil**

<table>
<thead>
<tr>
<th></th>
<th>400°C</th>
<th>500°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without Catalyst</td>
<td>5.512</td>
<td>5.622</td>
<td>5.859</td>
</tr>
<tr>
<td>1g Gamma Alumina</td>
<td>5.555</td>
<td>5.75</td>
<td>5.692</td>
</tr>
<tr>
<td>2g Gamma Alumina</td>
<td>5.481</td>
<td>5.702</td>
<td>5.933</td>
</tr>
<tr>
<td>1g HZSM5</td>
<td>5.453</td>
<td>5.679</td>
<td>5.77</td>
</tr>
<tr>
<td>2g HZSM5</td>
<td>5.401</td>
<td>5.733</td>
<td>5.6</td>
</tr>
<tr>
<td>1g Silica Alumina</td>
<td>5.389</td>
<td>5.609</td>
<td>5.705</td>
</tr>
<tr>
<td>2gSilica Alumina</td>
<td>5.274</td>
<td>5.6</td>
<td>5.685</td>
</tr>
</tbody>
</table>
## Data for char

<table>
<thead>
<tr>
<th></th>
<th>400°C</th>
<th>500°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without Catalyst</td>
<td>2.84</td>
<td>2.62</td>
<td>2.39</td>
</tr>
<tr>
<td>1g Gamma Alumina</td>
<td>2.89</td>
<td>2.61</td>
<td>2.23</td>
</tr>
<tr>
<td>2g Gamma Alumina</td>
<td>2.81</td>
<td>2.39</td>
<td>2.18</td>
</tr>
<tr>
<td>1g HZSM5</td>
<td>2.85</td>
<td>2.51</td>
<td>2.31</td>
</tr>
<tr>
<td>2g HZSM5</td>
<td>2.85</td>
<td>2.47</td>
<td>2.22</td>
</tr>
<tr>
<td>1g Silica Alumina</td>
<td>3.01</td>
<td>2.68</td>
<td>2.34</td>
</tr>
<tr>
<td>2g Silica Alumina</td>
<td></td>
<td>2.66</td>
<td>2.46</td>
</tr>
</tbody>
</table>

## Data for gases

<table>
<thead>
<tr>
<th></th>
<th>400°C</th>
<th>500°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without Catalyst</td>
<td>1.559979804</td>
<td>1.73200498</td>
<td>1.309125993</td>
</tr>
<tr>
<td>1g Gamma Alumina</td>
<td>1.605167805</td>
<td>1.408092038</td>
<td>1.81339435</td>
</tr>
<tr>
<td>2g Gamma Alumina</td>
<td>1.768334159</td>
<td>1.856522622</td>
<td>1.185608892</td>
</tr>
<tr>
<td>1g HZSM5</td>
<td>1.598375531</td>
<td>1.885879587</td>
<td>2.359806847</td>
</tr>
<tr>
<td>2g HZSM5</td>
<td>2.155991585</td>
<td>1.981398215</td>
<td>2.212525444</td>
</tr>
<tr>
<td>1g Silica Alumina</td>
<td>1.718794044</td>
<td>0.768022522</td>
<td>1.91874349</td>
</tr>
<tr>
<td>2g Silica Alumina</td>
<td>1.646104222</td>
<td>1.516333549</td>
<td>2.272256667</td>
</tr>
</tbody>
</table>
APPENDIX C: SAMPLE RESULT – GASES (2g Silica Alumina, 400°C)
Sample- BIO-OIL components GC-MS (2g Silica Alumina, 400°C)

<table>
<thead>
<tr>
<th>Component</th>
<th>Retention Time</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>1.672</td>
<td>5.28%</td>
</tr>
<tr>
<td>Acetaldehyde hydroxy</td>
<td>1.801</td>
<td>0.99%</td>
</tr>
<tr>
<td>2-propanone-1-hydroxy</td>
<td>2.313</td>
<td>2.09%</td>
</tr>
<tr>
<td>2 propanone-1-3dihydroxy</td>
<td>2.646</td>
<td>1.90%</td>
</tr>
<tr>
<td>Furan2-methyl</td>
<td>3.073</td>
<td>0.96%</td>
</tr>
<tr>
<td>Glycine, methyl ester</td>
<td>4.022</td>
<td>0.59%</td>
</tr>
<tr>
<td>Furfural &amp; 3-furaldehyde</td>
<td>4.309</td>
<td>0.57%</td>
</tr>
<tr>
<td>1,2-cyclopentanedione</td>
<td>4.718</td>
<td>0.97%</td>
</tr>
<tr>
<td>2-furancarboxylaldehyde, 5methyl)-</td>
<td>5.454</td>
<td>0.35%</td>
</tr>
<tr>
<td>2-cyclopenten-1-one, 2-hydroxy-3 methyl</td>
<td>6.617</td>
<td>0.84%</td>
</tr>
<tr>
<td>Phenol, 2-methoxy</td>
<td>8.989</td>
<td>0.72%</td>
</tr>
<tr>
<td>Phenol, 4-ethyl-2-methoxy</td>
<td>10.31</td>
<td>1.13%</td>
</tr>
<tr>
<td>Phenol, 4-ethyl-2-methoxy</td>
<td>12.139</td>
<td>0.57%</td>
</tr>
<tr>
<td>Phenol, 4-ethyl-2-methoxy</td>
<td>12.219</td>
<td>0.68%</td>
</tr>
<tr>
<td>2-Methoxy-4-vinylphenol</td>
<td>14.226</td>
<td>1.37%</td>
</tr>
<tr>
<td>Phenol, 2-methoxy-4-(1-propenyl)</td>
<td>14.59</td>
<td>0.94%</td>
</tr>
<tr>
<td>Phenol, 4-ethyl-2-methoxy</td>
<td>15.818</td>
<td>0.53%</td>
</tr>
<tr>
<td>Phenol, 2-methoxy-4-(1-propenyl)</td>
<td>18.831</td>
<td>1.06%</td>
</tr>
<tr>
<td>D-Allose</td>
<td>21.424</td>
<td>0.55%</td>
</tr>
<tr>
<td></td>
<td>39.68</td>
<td>0.43%</td>
</tr>
</tbody>
</table>
APPENDIX D: CALCULATION SAMPLE FOR KINETIC STUDY

Autoclave- Batch Reactor

- Elemental analysis of wood and Char
- Carbon conversion (Xc)= \(\frac{(W_{c\ of\ wood} - W_{c\ of\ char})}{W_{c\ of\ wood}}\)
- Plot conversion vs time graph for each temperature
- Calculate reaction rate (slope dXc/dt) at each point
- Using software regress the data which gives order of reaction, activation energy, pre-exponential factor and rate constant

\[ k = A \, e^{-\frac{E}{RT}} \]

- Validate against experimental results

SAMPLE CALCULATION- REACTION RATES

Rate of reaction for fitting curve equation

At 440°C:

\[ Y = 0.0000000001*RT^2 + 0.000009*RT + 0.4 \]

Differentiating the above equation gives slope i.e. rate.

\[ \frac{dXc}{dt} = (0.0000000001*RT^2) + 0.000009 \]

where: RT is the retention time of the reaction used and Y is the carbon conversion.
## APPENDIX E: CARBON CONTENT RESULTS FROM SRC, SASKATOON

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>C (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA1/B</td>
<td>2.43</td>
</tr>
<tr>
<td>KX0-4 016-115-1</td>
<td>79.21</td>
</tr>
<tr>
<td>KX0-2 016-115-2</td>
<td>80.66</td>
</tr>
<tr>
<td>KX0-3 016-115-3</td>
<td>80.92</td>
</tr>
<tr>
<td>KX0-4 016-115-4</td>
<td>81.11</td>
</tr>
<tr>
<td>KX0-5 016-115-5</td>
<td>83.89</td>
</tr>
<tr>
<td>KX0-4 016-115-6</td>
<td>89.43</td>
</tr>
<tr>
<td>KX0-7 016-115-7</td>
<td>84.80</td>
</tr>
<tr>
<td>KX0-4 016-115-8</td>
<td>84.00</td>
</tr>
<tr>
<td>KX0-9 016-115-9</td>
<td>84.46</td>
</tr>
<tr>
<td>KX0-10 016-115-10</td>
<td>86.49</td>
</tr>
<tr>
<td>KX0-11 016-115-11</td>
<td>86.57</td>
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<tr>
<td>KX0-12 016-115-12</td>
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<td>74.45</td>
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<td>77.21</td>
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<td>79.70</td>
</tr>
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<td>79.78</td>
</tr>
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<td>79.36</td>
</tr>
<tr>
<td>KX0-8 016-115-18</td>
<td>82.49</td>
</tr>
<tr>
<td>KX0-9 016-115-19</td>
<td>83.35</td>
</tr>
<tr>
<td>MA1/B</td>
<td>2.48</td>
</tr>
<tr>
<td>KX0-30 016-115-20</td>
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<tr>
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<td>95.03</td>
</tr>
<tr>
<td>KX0-23 016-115-23</td>
<td>84.12</td>
</tr>
<tr>
<td>KX0-34 016-115-24</td>
<td>98.35</td>
</tr>
<tr>
<td>KX0-24 016-115-24 R</td>
<td>86.40</td>
</tr>
</tbody>
</table>

*Carbon: a 5 g pulp is analyzed in a Leco SC140C/5 C analyzer for Carbon. The standard is MA1/B.*
Pareto Chart of the Standardized Effects
(response is Y, α = 0.05)

Main Effects Plot for Y
Fitted Means