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Fast Pyrolysis of Biomass in a Fluidized Bed for Production of Bio-oil and Upgradation by Ex-situ Catalytic Bed

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Abstract

Production of bio-oil from biomass is now becoming best substitute of fossil fuels in the transportation sector. Pyrolysis is one of the most promising route to produce bio-oil from biomass. However, bio-oil needs to be upgraded due to presence of high percentage of oxygenated compounds. Catalytic fast pyrolysis is a very efficient way to produce and upgrade the bio-oil either it is in-situ or Ex-situ arrangement.

This study presents the experimental investigation of fast pyrolysis of lignocellulosic biomass by ex-situ catalytic upgradation. The whole process consists of four parts: biomass grinding and sieving, pyrolysis, ex-situ fixed bed and vapours quenching. The pyrolysis experiment has been performed with nitrogen with or without catalyst to investigate the yield of different products. The analysis of results shows that higher yield of gas is obtained from catalytic upgradation together with the low yield of oil. The more oxygen was removed into CO and CO₂ from vapours due to more cracking reactions occurred on catalytic bed. The yield of oil was decreased in catalytic experiments, but it has relatively good energy content due to no water in viscous phase and low acid number. The char yield was same for non-catalytic and catalytic experiments.

Sammanfattning

Framställning av bioolja från biomassa är ett av de bästa alternativen som kan ersätta fossila bränslen i transportsektorn. Pyrolys är en av de mest lovande teknologierna för att framställa bioolja från biomassa. Bioolja behöver dock uppgraderas på grund av en hög andel oxygenerade föreningar. Katalytisk snabbpyrolys är en effektiv metod för att producera och uppgradera sådan bioolja, antingen genom in-situ eller ex-situ processuppställning.

Denna studie presenterar en experimentell undersökning av snabbpyrolys av lignocellulosisk biomassa kombinerat med ex-situ katalytisk uppgradering. Processen består av fyra delar: förbereda lämplig partikelstorlek av biomassa, pyrolys, ex-situ fastbädd och kondensering av ångor. Pyrolysexperiment har genomförts med vätgas med och utan katalysator för att undersöka utbytet av olika pyrolysisprodukter. Resultaten visar att en katalytisk uppgradering ger en ökad andel gasprodukt samt ett lågt utbyte av olja. Stor andel syre avlägsnades från oljan som CO och CO₂ genom krackningsreaktioner i den katalytiska bädden. Oljeutbytet var lägre vid katalytiska experiment, men visade ett lovande energivärde pga en minskad andel vatten samt ett lägre syratall. Utbytet av kol var detsamma för katalytiska och icke-katalytiska experiment.

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1. Introduction

Fossil fuel extraction is constantly increasing due to advancement in exploration technologies, but these resources are finite and energy security is becoming a world issue. Furthermore, combustion of fossil fuels results in climate change and accumulation of greenhouse gases (GHG) such as carbon dioxide (CO₂) in the air. Renewable resources provide alternative meanings to reduce the environmental concerns of CO₂ emissions. A major part of fossil fuels is used in sectors such as power, heat and transportation. Fossil fuels are expensive as well as insufficient to meet the future demand. As renewable energy resources provide renewable alternatives to solve the problem of energy and climate change, these technologies are not fully established and require high investments in research and development. Large scale changes are required to replace the petrochemical technologies which are based on fossil fuels. Furthermore, an efficient and effective alternative is required to produce the petroleum-like products with same energy densities [1].

Biomass, especially lignocellulosic, is a popular source of energy due to its availability and non-competitiveness to the food industry. There are many routes to produce bio-oil from biomass based on either thermochemical or biochemical conversion. Gasification and pyrolysis are the most popular technologies to produce bio-oil. Pyrolysis can be used to produce transportation fuel from biomass or waste materials without any major modification in the existing infrastructure of petroleum industry. Pyrolysis has a great potential to play a big part to reduce the reliance on fossil fuels [1].

Pyrolysis has two types, slow pyrolysis employs slow heating rate (below 80 °C/min, residence time 5-30 min) and favors the production of char. Fast pyrolysis typified by fast heating rate (above 100 °C/min, residence time 0.5-5 s) and maximizing the oil yield. Bio-oil is obtained after the immediate quenching of pyrolysis vapors. Fast pyrolysis has highest yield of liquid products and contains most of the energy from biomass feedstock. Bio-oil is composed of highly complex mixture of oxygenated compounds (>300). Among the other conversion routes of biomass into oil, economically fast pyrolysis is the most feasible way to produce liquid fuels.

Bio-oil is relatively unstable, highly viscous, highly acidic and contains a huge number of oxygenated compounds. Bio-oil also has a very high level of water content which lowers the heating value. A high amount of oxygen and water contribute to the main differences between hydrocarbon fossil fuels and bio-oil. Advancement in current technologies of pyrolysis especially fast pyrolysis has resulted in improved bio-oil quality so that it can replace the fossil fuels usage. Pyrolysis oil needs to be upgraded due to presence of oxygenated compounds and water to meet the requirements of fuel. Upgradation of bio-oil to characteristics of conventional fuel requires severe deoxygenation. This can be achieved by catalytic upgrading and hydro treatment. Oxygen can be removed from oil by using specific catalysts and convert oxygenated compound into aromatics [3].

A zeolite catalyst, particularly HZSM-5, is most commonly used for the upgradation of vapors in biomass pyrolysis. Zeolite-based catalysts deoxygenate the pyrolysis vapors with isomerization, dehydration and aromatization reactions. There are two processes to upgrade the vapors in catalytic pyrolysis: in in-situ the upgrading catalyst is placed in the same reactor

while in ex-situ pyrolysis vapors are passed in a separate reactor. Advantages of in-situ catalytic pyrolysis is lower capital cost and of ex-situ process, it separates the catalyst from biomass contaminants. For example, biomass contains small amount of alkali and alkaline earth metal which may deposit on the catalyst during volatilization and affecting its properties. Thus, conversion of biomass-based on lignocellulose into transportation fuel has attracted much attention in recent decades due to catalytic fast pyrolysis. But the main challenge is to develop stable and active catalyst which deals with a large variety of compounds [2]. This report will focus on the fast pyrolysis with ex-situ catalytic up grading of vapors [4].

1.1. Objectives

The main purpose of this thesis work is to experimentally upgrade the pyrolysis vapors by using HZSM-5 as catalyst in a separate fixed bed reactor downstream a pyrolyzer (Ex-situ catalytic pyrolysis). The experiments have been performed with and without catalyst in pyrolysis of lignocellulosic biomass. The pyrolysis products such as gas, liquid and char were analyzed for evaluating the process.

2. Background

2.1. Biomass

Lignocellulosic biomass consists of three main components: cellulose, hemicellulose and lignin. The composition of following components in different type of biomass is given in Table 1. Cellulose and hemicellulose are linked by hydrogen bond, lignin and hemicellulose connected with hydrogen and covalent bonds [6].

Table 1: Composition of different type of biomass based on wt % [7]

	Cellulose	Hemicellulose	Lignin
Hardwood	40-55	24-40	18-25
Softwood	45-50	25-35	25-35
Wheat straw	30	50	15
Corn cobs	45	35	15
Grasses	25-40	35-50	10-30
Switch grass	45	31.4	12

Cellulose and hemicellulose comes from sugar monomers and lignin is dependent on plant specifications. Cellulose is a linear polysaccharide that contains glucose units in a log chain. These glucose units linked by β -1 to 4 glycosidic bond, the most abundant polysaccharide. Cellulose is denoted by $(C_6H_{10}O_5)_n$, where n is a degree of polymerization. Hemicellulose includes pentoses, hexose and xylan and is composed of short chain hetro polysaccharides in branched structure and amorphous in nature. Chemical formula of hemicellulose is $(C_5H_8O_4)_n$, where n is degree of polymerization and ranging 50-200. Lignin is highly branched aromatic polymer that adds strength to the cell wall [6]. Figure 1 illustrates how the three components are combined in a plant.

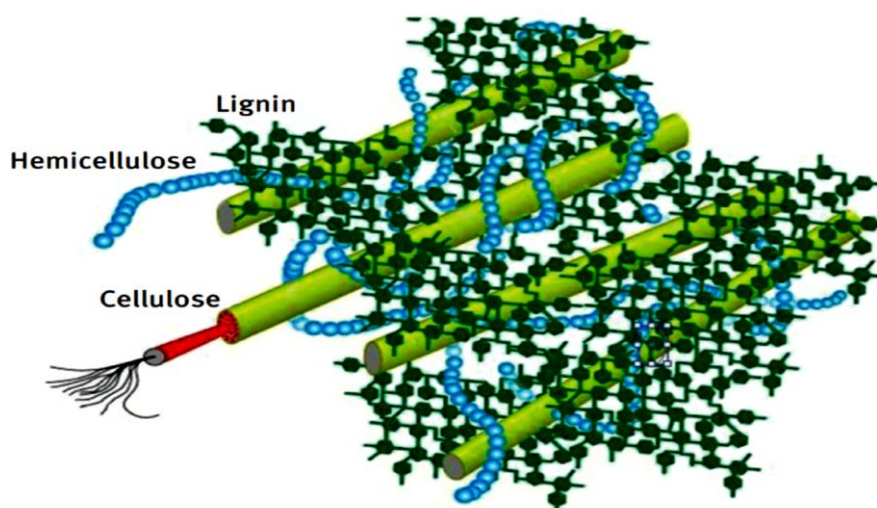


Figure 1: Plant structure [6]

2.2. Pyrolysis

Pyrolysis is conventionally carried at atmospheric pressure in the absence of oxygen with temperature ranging 300-600 °C. There are two types of pyrolysis; slow pyrolysis in which charcoal is the main product by slowly heated to a temperature up to 400 °C. The fast pyrolysis has high temperature around 500 °C followed by rapid cooling and condensation of vapours. The main product is dark brown liquid and it can be use as fuel oil. The interesting feature of pyrolysis is that it can connect the agricultural, forest or wood business to petrochemical processes, preferably by fast pyrolysis, and with different techniques to upgrade the liquid to accomplish the standards of fossil fuel [8].

In pyrolysis, thermal decomposition of biomass occurs and produces biochar, non-condensable and condensable gases. Fast pyrolysis produces condensable vapours as the main product and slow pyrolysis is more emphasized on the production of char. These processes are done by convection or radiation of heat from the surface of particle and heat penetrated to the particle by conduction. According to conditions of fast pyrolysis, the temperature development within the particle and reaction kinetics influences the decomposition rate and distribution of the product. Aim of the fast pyrolysis is to maximize the yield of bio-oil and it is promoted by rapid heating of biomass. Furthermore, condensable vapors are rapidly removed from reactor to avoid further cracking. It is also necessary to create a short vapor residence time in the equipment before condenser to prevent polymerization and cracking reactions [9].

For the fast degradation of biomass, small particles are needed for the rapid penetration of heat into particle. For the larger particle size, more time is required to penetrate heat into particle, and it will lower the yield of bio-oil. The Yield of bio-oil from wood-based feedstocks in continuous operation on the pilot scale is 60-70 wt% on dry basis. Run the process under proper conditions like temperature, feedstock type, residence time and feedstock parameters to get maximum yield of oil [9].

2.3. Feedstock pre-treatment

- Thermal treatment
- Physical treatment

Pre-treatment of biomass is very important step in order to get a high-quality of bio-oil. Hydrolysis is the pre-treatment step that can be used under acidic, basic or sequential acid/base environment at ambient pressure and conventionally within 25 or 122 °C. There is also inorganic species present in bio-oil that will limit the use of bio oil on commercial bases. For example, alkaline earth metallic (AAEM) and alkali accelerate the ageing of bio-oil during storage which contributes the modification of the physical properties of bio-oil. This will be reduced by washing the biomass in pre-treatment step to remove AAEM. Sometimes biomass contains a huge amount of water that can be problematic in terms of the application of bio-oil. This type of feedstock must be dried before going for pyrolysis. This is called thermal treatment of biomass [10].

The particle size of biomass is a very important parameter to influence the heating rate of solid fuel. The size of a particle controls the rate of drying in pyrolysis, and to what extent this

process will go on. If the size of a particle is greater than the optimal size, it will reduce the yield of liquid oil. Initially in the fast pyrolysis development, it was considered that very small size of particle-like hundred microns needed to enhance the heating rate but later on this was experienced that 2 mm particle size is sufficient to get an efficient heating rate. Particle size distribution of EFB (empty fruit bunches) is given in Table 2 [10].

Table 2: Particle size distribution of EFB [11]

Feedstock particle size μm	Mass fraction	Average ash (wt%)
Less than 250	22	7.44
25-355	30	5.29
355-500	42	4.82
More than 500	6	4.72
Mass average	-	5.39

2.4. Kinetics of pyrolysis

Cellulose, hemicellulose and lignin have different composition and structure and they will break down in different compounds. The pyrolysis can be exothermic or endothermic depending on the temperature of reaction and type of feedstock. For example, in hemicellulose stock, the process is endothermic at a temperature below 450 °C and exothermic above this temperature. The vapour phase of the product needs to condense quickly otherwise it will decompose further.

Figure 2 illustrates the possible reaction pathways for the pyrolysis of biomass with enough rapid heating, the particle of biomass is first decomposed to char (10-15 wt%) and vapours in which permanent gases (CH_4 , CO_2 , CO) and condensable liquids exist. These condensable liquids also include the moisture of biomass and water produced by the decomposition process. Fine particles of char collect with bio oil carried by vapour stream to a condenser and from pyrolysis reactor [9].

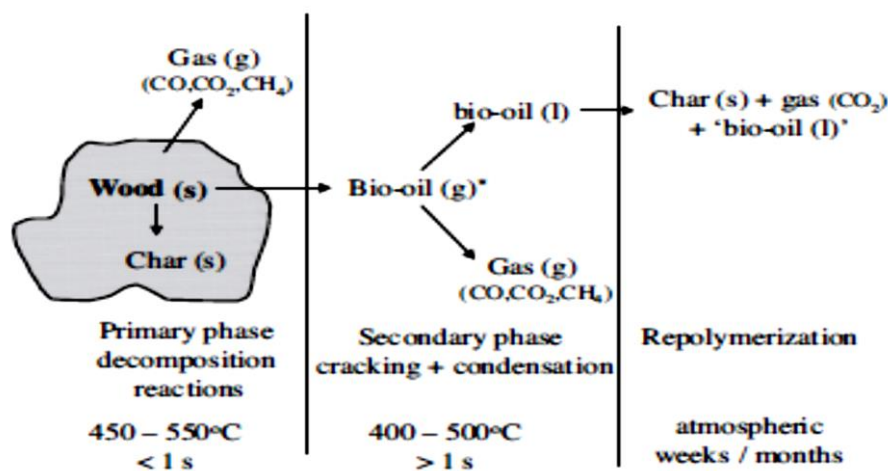


Figure 2: Kinetics of pyrolysis process [9]

2.5. Properties of bio oil

Bio-oil is a reddish-brown dark liquid influenced by chemical composition and presence of fine carbons in the liquid. A more translucent red brown oil can be obtained by hot filtration of vapors owing to removal of fine carbon. Heating value of fast pyrolysis liquid is much higher about 17MJ/Kg with almost 30% water, cannot be easily separated. The bio-oil is composed of oxygenated compounds and very challenging for utilisation due to low heating value, high water content and high number of oxygenated compounds [8]. Typical elementary composition of bio-oil and crude oil is given in Table 3.

Table 3: Elementary composition and properties of bio-oil and crude oil [8][2]

Composition	Bio-oil	Crude oil
Water (wt%)	15–30	0.1
pH	2.8–3.8	—
Density (kg/L)	1.05–1.25	0.86–0.94
Viscosity 50°C (cP)	40–100	180
HHV (MJ/kg)	16–19	44
C (wt%)	55–65	83.86
O (wt%)	28–40	<1
H (wt%)	5–7	11–14
S (wt%)	<0.05	<4
N (wt%)	<0.4	<1
Ash (wt%)	<0.2	0.1
H/C	0.9–1.5	1.5–2.0
O/C	0.3–0.5	~0

The properties of wood-derived bio oil and compositions are given in the above table. The density of bio-oil is much higher than the fuel oil. This viscosity varies from 25 up to 1000cp depend on the lighter components in oil and water. Oil characteristics may change during storage called ageing [2].

The main limitation of bio oil is the presence of a significant amount of water ranging 15-35 wt % and a huge amount of oxygenated compounds present which are the main obstacles in the path of applications. This water content and oxygenated compound reduce the heating value of oil (HHV) as compared to fossil fuel. Biomass should be dried before pyrolysis in order to reduce the water content in the product phase. There must be some careful control of moisture to get the high quality of bio oil [8][2].

2.6. Fast Pyrolysis technology

The important parts of fast pyrolysis for maximum production of oil, are operating temperature around 500 °C, rapid heating of biomass and rapid quenching of vapours. The required conditions are; mainly dry feedstock (less than 10 %), small particles less than 3mm, rapid

quenching at the end of the process and get the yield of bio oil 60-70%, gaseous products 12-15% and char 13-15%. The requirement of energy for the pyrolysis process is depending on the yield of bio oil and feedstock [10]. The yield of produced gas is increased with increasing pyrolysis temperature as shown in Figure 3. The obtained yield of organics is decreased with temperature due to conversion of more oxygenated compounds into gases [8].

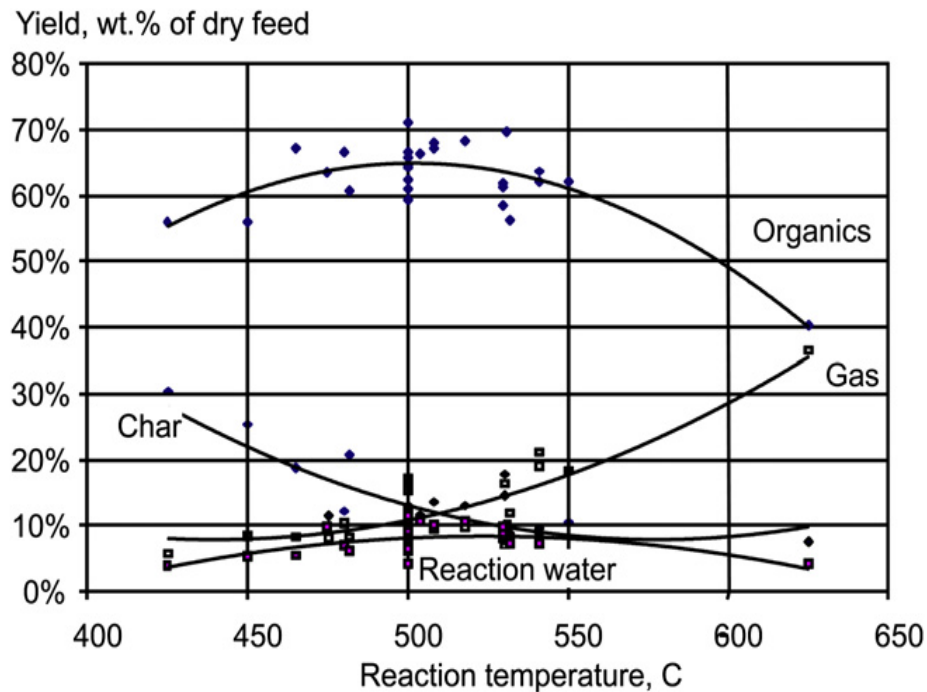


Figure 3: Yields of pyrolysis products with reaction temperatures [8]

Different type of reactor can use in pyrolysis, below is the list of the most commonly used. Further, bubbling and circulating fluidized bed will discuss in detail.

- Entrained flow reactor
- Ablative reactor
- Fixed bed reactor
- Bubbling fluidized bed
- Circulating fluidized bed (CFB)
- Moving grate pyrolysis
- Rotating cone pyrolysis

2.6.1. Bubbling fluidized bed

Bubbling fluidized bed is the most efficient process for rapid heating of biomass. Gas is entered from the bottom through vertically upward in a bed of granular material like sand as shown in Figure 4. It should have enough velocity to make enough bubbling in the fluid. A fluidized bed-reactor has high heat and mass transfer rates in particle, gas and the material used as the bed. Generally, pyrolysis temperature is 500-550 °C in the bed with high yield of oil for 0.5 s residence time (in bed). However, bed systems can operate at lower temperature and longer residence time. All above conditions are very important for pyrolysis in which biomass is quickly heated and then vapors are rapidly released from the reactor. In the fluidized bed, the

bed is heated by either direct heat transfer or indirect. Direct heating is not recommended because flue gases are used to transfer heat, results in lower oil yield due to oxidation of biomass from excess air in flue gases. Furthermore, heat is externally supplied to the bed by indirect heat transfer [10].

Bubbling fluidized bed technology is implemented in the semi and continuous pyrolysis in recent decades. The BFB behave like a boiler in which gas bubbles are rise and burst on the bed surface. These bubbles may contain a small number of particles either sand or biomass. BFB is hydrodynamic- ally stable for smaller particle size ranging 0.5 to 2 mm and inert helium or nitrogen gas used for fluidization [10]. Sand is used as a bed to achieve good heat transfer, temperature control and interrupts the char particles.

Bubbling fluidization bed has very consistent performance with up to 70 to 75 wt % liquid yield. But there is fine char present in the liquid up to 15 wt%, normally depend on the reactor shape and fluidization velocity. To avoid this problem, a cyclone separator is used after the reactor for continuous char separation [11].

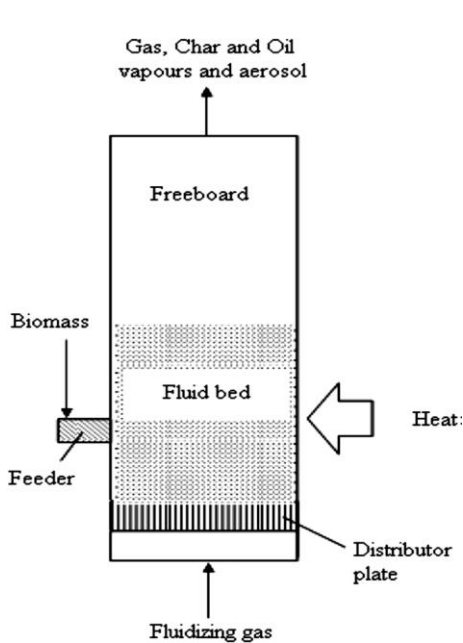


Figure 4: Bubbling fluidized bed [11]

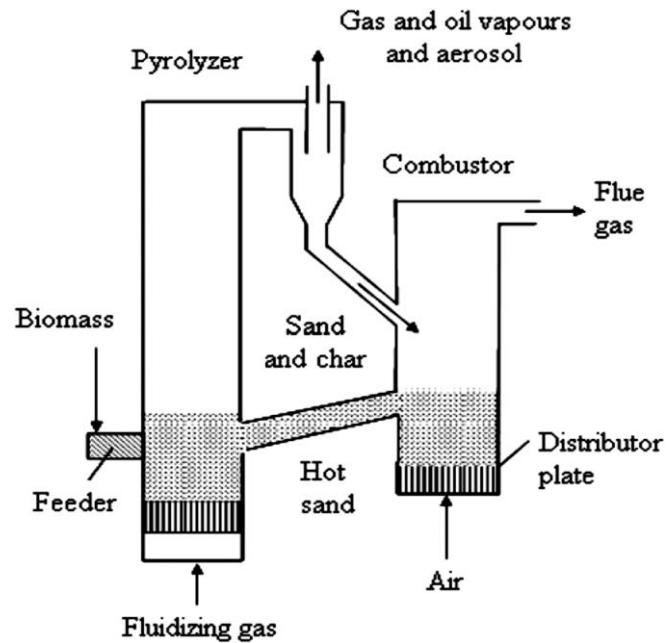


Figure 5: Circulating fluidized bed [11]

2.6.2. Circulating fluidized bed (CFB)

CFB process is different from the BFB in which the amount of the gas used to fluidize the bed is different. In CFB the velocity of the gas is high enough to transport the particles out of bed and then it is recovered by a gas cyclone and get back to the bed. The particle size is much smaller than those used in bubbling bed. The particle will have only 0.5-1.0 s residence time in the high heat transfer zone. This process is more difficult to design as compare to BFB. Biomass and sand are mixed and then entrained in the gas flow, heat is transferred between them and pyrolysis occurs as illustrates in Figure 5. At the exit, there is a cyclone installed in which char and sand particles are separated from the gas vapors and circulate back to the reactor [12].

The working principle of BFB and CFB is a bit different. The main difference is the vapour gas residence time in CFB and BFB. CFB has 0.5 to 1 s vapour residence time and BFB has 2 to 3 s with high energy recovery in CFB [10]. It is noted that in CFB 15 wt % char has been produced which contain 25 % unreacted biomass. This can be used in waste energy recovery unit to provide the process heat in CFB for heating the sand in char combustor. In BFB system biochar and syngas stream is not facilitate for energy recovery but CFB utilizes char and non-condensable gases to make more energy efficient. CFB has rapid elimination of organic gases from biomass material due to short residence time and lead to increase the bio-oil yield [11].

CFB reactor has high particle flux ranging 10-1000 kg/m² and high superficial velocity 2-12 m/s. These conditions were selected to avoid distinct interface between the dense bed and dilute region. However, gas velocities were chosen above the bubbling point. High fluid velocity provided better gas-solid contact due to intense mixing of fluid to produce a better quality of the product (oil, gas). Despite this advantage, CFB systems are more expensive due to high gas velocities and recirculation of solid particles as compare to BFB [11].

The Technology of CFB is comparatively is well established but still, there is some limitation. Erosion of the reactor occurred due to the circulation of particles and operations are relatively complicated [12].

2.7. Effect of operating parameters in continuous BFB and CFB

The operating parameters are particle size, feeding rate, heating rate, temperature and residence time. These parameters are not only responsible to maximize the liquid yield but also improve the efficiency of continuous fast pyrolysis and composition of product quality.

2.7.1. Effect of particle size

Biomass has low heat conductivity which leads to poor heat transfer rate in the bed during the pyrolysis process. The Particle size of feed is a very important parameter to minimize heat transfer problems. Large particle size may contribute to produce more char and less liquid due to decrease in heating rate, reactor hydrodynamics, fluidization properties and solid residence time. Average biomass particle size less than 3 mm is used to attain high heating rate and liquid yield in continuous fast pyrolysis. In the beginning, the 1.3 mm particle size was used with temperature range 470-540 °C with residence time 0.88 s and get maximum yield of oil 54 wt%. Later on, the similar results were observed with particle size 1-2 mm [13]. it is investigated further that if particle size increases from 0.3 to 1.5 mm has significantly decreased the bio-oil yield.

If the particle size greater than 2 mm then it may be responsible to increase the chances of secondary pyrolysis reactions. This may lead to more char and less bio-oil. The literature review showed the particle size around 2mm is necessary to get a high yield of oil [11].

2.7.2. Effect of feeding rate

The feeding rate can affect the heat transfer rate, fluidization behaviour, vapour residence time and secondary reactions. Pyrolytic vapour movement may decrease due to high feeding rate and that will lead the secondary reactions [11].

Different biomass feeding rate from 1.6 to 2.7 kg/hr has been used with particle size 0.5 mm of biomass to observe the effect of feeding rate on pyrolysis product [14].

They observed that feeding rate below 1.92 kg/hr has a negligible effect on pyrolysis products. Moreover, increasing the rate from 1.92 kg/hr, the negative effect was observed on tar and biochar yield. However, the feeding rate needs to be retained at a certain level to get suitable products. Figure 6 illustrates the effect of feeding rate on the product at 450 °C temperature.

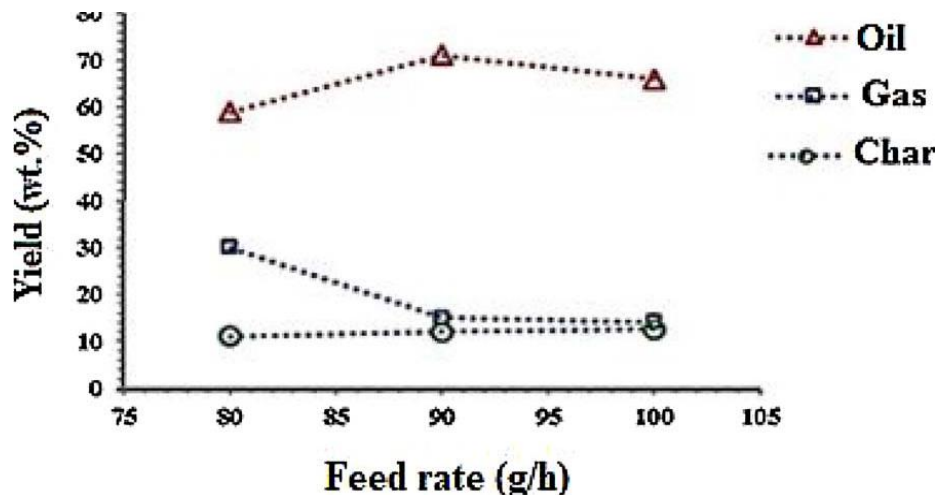


Figure 6: Influence of feeding rate on products yield [17]

2.7.3. Effect of heating rate

The heating rate is a very important parameter for converting biomass to liquid in continuous fast pyrolysis. Fast pyrolysis has higher heating rate 10-200 °C/s, short vapor residence time 0.5 to 1.0 s, fast cooling of vapours to get a high yield of bio-oil up to 75 wt%. Process limitation in heat transfer for fast pyrolysis is associated with the conduction of heat from the reactor to biomass and limitation in mass transfer linked with flow dynamics of biomass in pyrolysis reactor. However, a higher heating rate may be overcome the heat and mass transfer limitations and can bring out bio oil at high temperature [16]. The high heating rate may lead to getting a high yield of liquid and less biochar formation. In literature, heating rates up to 1000 °C/min have been recommended [11].

2.7.4. Effect of temperature

Variations in the product of biomass and the composition depend on the temperature and type of feedstock. At a high temperature greater than 450 °C, pyrolysis reactions modify the product which may reduce the char formation and support higher liquid yields [11]. It was observed that, in continuous fluidized bed reactor, there is reduction in bio-oil yield whereas gas yield increased by increasing temperature from 450 °C to 600 °C. Furthermore, the amount of char decreased from 19.7 to 14.2 wt%. Due to increase in temperature, secondary cracking of pyrolysis vapours increased the gas yield and it will reduce the liquid yield [15].

2.7.5. Effect of vapour residence time

During the pyrolysis process a significant amount of vapors are formed from biomass. These vapors can experience secondary reactions of repolymerization, re-condensation of the char

and thermal cracking, which leads to reduce the yield of bio-oil. Bio-oil yield will be increased if the vapour residence time is short due to the rapid exclusion of gases from the reactor which minimizes the secondary reactions. The main parameters are heating rate, sweeping gas flow rate and reactor pressure to create short vapour residence time. Increasing the high inert fluidizing gas may lead to increase reactor pressure which also reduces the vapour residence time and enhance the liquid yield. Furthermore, the kinetic energy of syngas increases with the heating rate which may also reduce the vapour residence time [16]. There is another possibility to reduce the vapour residence time by run the pyrolysis reactor under vacuum conditions. It is possible to reduce the vapor residence time by reducing the reactor pressure to minimize secondary reactions e.g. rapid quenching on condensation. Furthermore, the type of material (biomass type) is a very important parameter to create short vapour residence time [11].

2.7.6. Effect of inert gas as fluidization medium

During the fast pyrolysis process, the effect of inert gas used as fluidization medium has greater influence to control reactor hydrodynamics in order to get high liquids and gas [15]. Observed the effect of nitrogen as inert fluidization medium with flow rate 12.6 L/min is investigated in fast pyrolysis. It is observed that the yield of bio-oil reduces due to higher gas fluidization. This behaviour showed that the increasing flow rate of fluidization gas aided in swiping out the vapors. Furthermore, this process leads to reduce residence time both in reactor and condenser and resulted in decrease liquid yield [15] [16].

2.8. Bio-oil upgradation

Pyrolysis liquid or bio-oil is a dark brown liquid, composed of a very complex mixture of oxygenated hydrocarbons (HC) with a considerable amount of water. Bio oil has acidic, thermally unstable, corrosive and highly oxygenated characteristics. It has some more critical drawbacks like the low heating value of fuel, high viscosity, and high-water content and its substantial solid content. This water content making this fuel is immiscible with conventional fuel because it cannot be separated. Hence biofuel produced from conventional technologies cannot be suitable as a transportation fuel. The oxygen content ranges 30-55 wt % in bio-oil influence by type of biomass [17].

The acidity of boil oil is also problematic causing the corrosion of materials involved in an acidic environment. Viscosity is also the main issue, especially in pumping applications. In carbonyl compounds like aldehydes and ketones have a major role in aging reactions due to polymerization of oxygenates into oligomers with time and makes it unstable.

The oxygenated compound present in bio-oil and water content limit the use of oil as compared to fossil fuel. There are many ways to upgrade the oil, in which it can meet the characteristics of conventional oil and can be used on a commercial scale. Bio-oil can be upgraded physically, chemically and catalytically [17]. Filtration, solvent addition and emulsions are used to physically upgrade the bio oil into biofuel. In catalytic upgrading, catalyst is used to deoxygenate the liquid as in conventional refining.

Bio oil has good potential to be the feedstock for producing valuable chemicals in the form of hydrocarbon-based products. The main problem in fast pyrolysis is the low yield HC and high

amount of oxygenated compounds. This can be improved by catalytic cracking with deoxygenated capability. Zeolite catalyst is very famous and efficient to convert pyrolysis vapors containing an oxygenated compound to light aromatic hydrocarbons such as toluene, xylene, benzene and naphthalene [10]. Catalytic cracking is causing the coke deposition from 5-10 % on catalyst and increased production of gas. There are two ways to upgrade the bio oil in catalytic cracking [17], further described below.

2.8.1. In-situ catalytic cracking

In-situ catalytic upgrading is the onsite treatment of vapors in the pyrolysis reactor as shown in Figure 7, before condensation. In this system biomass and catalyst injected in the reactor and after pyrolysis process, the catalyst reacts with the vapors to crack the compounds [17]. This reaction induces the cracking to break down the heavy molecules present in the pyrolysis reactor to high-value hydrocarbons and phenols. This system has better technical benefits and lower investment cost as compare to Ex-situ process.

2.8.2. Ex-situ catalytic cracking

Ex-situ catalytic reaction is carried out at the downstream of pyrolysis reactor in a separate reactor consists of fixed bed system. Catalyst filled in a separate column of reactor as shown in Figure 7. This arrangement is very efficient for deoxygenation of vapors, increased the formation of hydrocarbons and deoxygenize the acidic compounds into other compounds like CO, CO₂. But at the same time, this could be problematic on a commercial scale due to continuous regeneration of catalyst and it will increase the cost.[17]. Regeneration of catalyst is the limiting factor for Ex-situ process due to fixed bed arrangement. After few runs catalyst need to be removed from the bed, regenerate it and put it back. Regeneration in In-situ catalytic bed is much easier due to presence of catalyst in the pyrolysis reactor and it will continuously regenerated.

Fluidized systems are prone to catalyst losses and attrition, it is not possible to eliminate but it can modify with different methods of preparations can make catalyst less prone to attrition and more robust. However, small losses can lead to an increase in the cost. This is a key reason why to explore an Ex-situ fixed bed option in order to get the desired results. The main advantage of fluidizing bed in a continuous system is its quick catalyst regeneration. But this is the main limitation for fixed bed setups. To avoid this limitation, Ex-situ fixed bed catalyst design and operations are constrained to avoid conditions that exhibit the rapid catalyst deactivation, especially in terms of coking [18].

The Ex-situ process separates the fast pyrolysis with catalytic vapour upgrading. This configuration minimizes the contact between pyrolysis solid residue (char, ash) and catalyst. Furthermore, it will reduce the effect of coking and increase the life span of the catalyst. However, catalyst performance is improved, and maintenance cost will reduce for the catalytic reactor [19].

Ex-situ catalytic fast pyrolysis favors the formation of olefins and In-situ process favors the formation of aromatics. However, this behavior linked with the secondary thermal cracking of

primarily produced pyrolysis vapors before catalyst in Ex-situ process; generate small molecules which are easier to be converted into olefins [20].

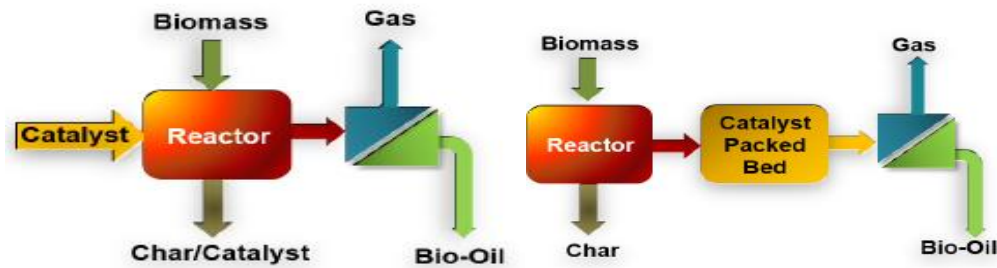


Figure 7: In-situ and ex-situ process [17]

2.9. Catalyst selection

Today the catalytic cracking of pyrolysis vapors is the main key to produce biofuels on a commercial scale. Zeolites exhibit exceptional properties as compared to other catalysts with respect to activity and selectivity. Zeolites have the ability to selectively absorb and transform molecules in their volume. Zeolite has a crystalline aluminosilicate structure linked through oxygen atoms. However, they produce three-dimensional networks. Zeolites were first synthesized in 1965 by Argauer. Furthermore, zeolites are used in the petroleum industry for the upgradation of low-octane components into the gasoline range and the isomerization of linear olefins to higher branched olefins. The main advantage of applying zeolite for biomass pyrolysis is its low cost and knowledge gained over the years. If the zeolites-based catalyst is to be used on an industrial scale for biomass pyrolysis, then it needs to be agglomerated with a binder to get large and more resistant particles. Zeolites-based catalysts exhibit the highest aromatics yield for catalytic fast pyrolysis due to their pore size, low internal pore volume, and structure [22].

Zeolites are the most extensively studied catalysts for pyrolysis processes due to their structure and characteristics. The main problem of using zeolites is their deep cracking and severe production of gas, which decreases the oil yield significantly. They are also deactivated due to coke formation. Deposition of coke on all the catalyst occurred in the conversion of furans, this is an important parameter for the deactivation of catalyst and product distribution. However, it is significant to find out the nature and composition of coked catalyst to investigate the depositing behavior. Thermogravimetric analysis (TGA) is an analytical tool that can be used to find the amount of coke deposition and coke yield [21]. Selective deoxygenation will be performed to control the polyaromatics. Zeolites-based catalysts decrease the concentration of oxygen via deoxygenation reactions like decarbonylation, decarboxylation, and dehydration. They are also reducing the molecular weight of oil via cracking. But on the other hand, they have a relatively small pore size, which leads to a decrease in the organic phase of bio-oil and increased water and gas production by deactivation through coke deposition [17].

The main challenge for catalyst selection is the deoxygenation capability of the material. Oxygen can be eliminated by dehydration, decarbonylation, and decarboxylation with water production, CO_2 and CO . Decarboxylation leads to a decrease in the acidity of oil and

decarbonylation improved the stability of the oil. The best way to calculate the deoxygenation of vapors is through calorific value measurements. As shown in Figure 8, 75 % deoxygenation is done by decarboxylation could lead to higher calorific value as compared to dehydration and decarbonylation [17]. Decarboxylation retain the hydrogen in oil, reduce the oxygen with minimum carbon loss, the heating value will be increased, reduce the water content and aromatics formation.

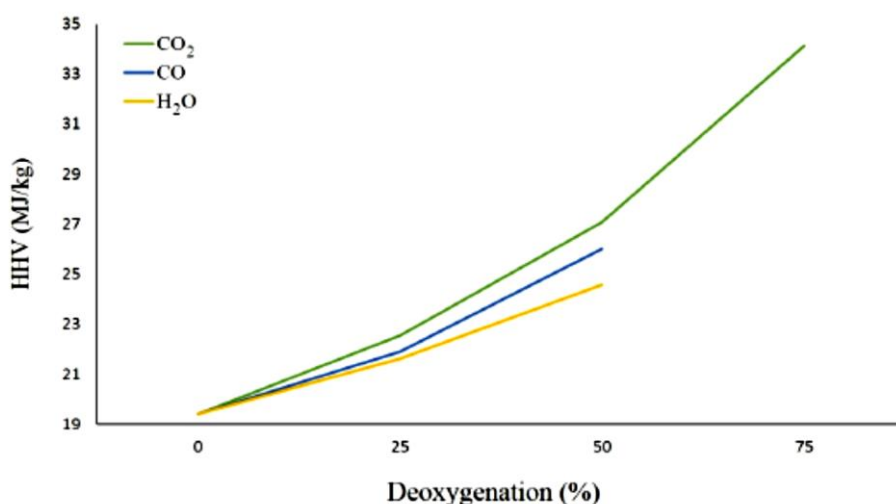


Figure 8: Deoxygenation % with HHV of CO, CO₂, H₂O [17].

2.10. Analytical tools

Upgradation of bio-oil ensures industrial scalability to use on a commercial basis [24]. For the design of the pyrolysis reactor, quantitative information of chemical composition is very important to achieve good efficiency. Comprehensive literature is available on physical and chemical characterization of bio-oil.

Different type of analytical tools can be used to get the analysis data of pyrolysis products. Few of them is discussed below

2.10.1. Micro GC

Gas chromatography is an adaptable separation technique for volatile and thermally stable organic compounds. A variety of detectors has exponentially expanded the dimensions of GC in which mass selective detection is most popular. Two dimensional GC (GC*GC), fast GC and static headspace extraction-GC are prominent techniques. Research in the stationary phase of GC has an attraction for the scientist with ionic liquids having prominent application in the liquid phase and reported in the analysis of biodiesel blends [24].

2.10.2. Mass spectrometric analysis

MS provides structural and elemental composition of the organic molecule. Ionization, sample introduction and analyzers are the key advancements in last two decades [24].

2.10.3. Thermogravimetric Analysis (TGA)

Thermogravimetric techniques utilize the thermal behavior of fossil and biofuels. TGA analyze the thermal stability of material by measuring the thermal decomposition with temperature.

This tool monitors the change in sample mass against temperature or time at a specified rate of heat. Kinetics can be determined by application of Arrhenius equation relate to separate slope of mass degradation and generate valid thermodynamic figures. TGA is a good technique to measure bio oil and coke properties, measured mass losses depending on the volatility of molar masses fraction [24].

3. Methodology

The existing experimental setup in lab at KTH consists of a bubbling fluidized bed reactor. The height of reactor is 95 cm and diameter 7.2 cm. A perforated plate was used at the bottom of reactor for the distribution of hot gas. The holes in the gas distributor has diameter of 1 mm with pitch of 7.1 mm (triangular). Gas is heated before the reactor in the preheater to supply heat in the reactor. Electrically heated elements are also installed around the reactor up to 60 cm height. 800 g silica sand was used as a bed ranging between 250 to 355 μm particle size. A two-stage biomass feeder was used to feed biomass in the reactor in which first feeder is dosing, and second feeder is injecting feeder with high revolution speed (up to 900 rpm). Slightly overpressure is set at the injecting feeder to avoid backward flow of vapors through feeder and hopper. For the char separation after the reactor, a cyclone is used with a nominal cut of 2.5 μm .

Some modifications have been performed in the existing system to upgrade in ex-situ process. As illustrates in Figure 9, a new fixed bed reactor as ex-situ has been designed and installed in the system surrounded by heating elements. HZSM-5 zeolite was used as catalyst and filled in the reactor up to certain height according to weight hour space velocity (WHSV).

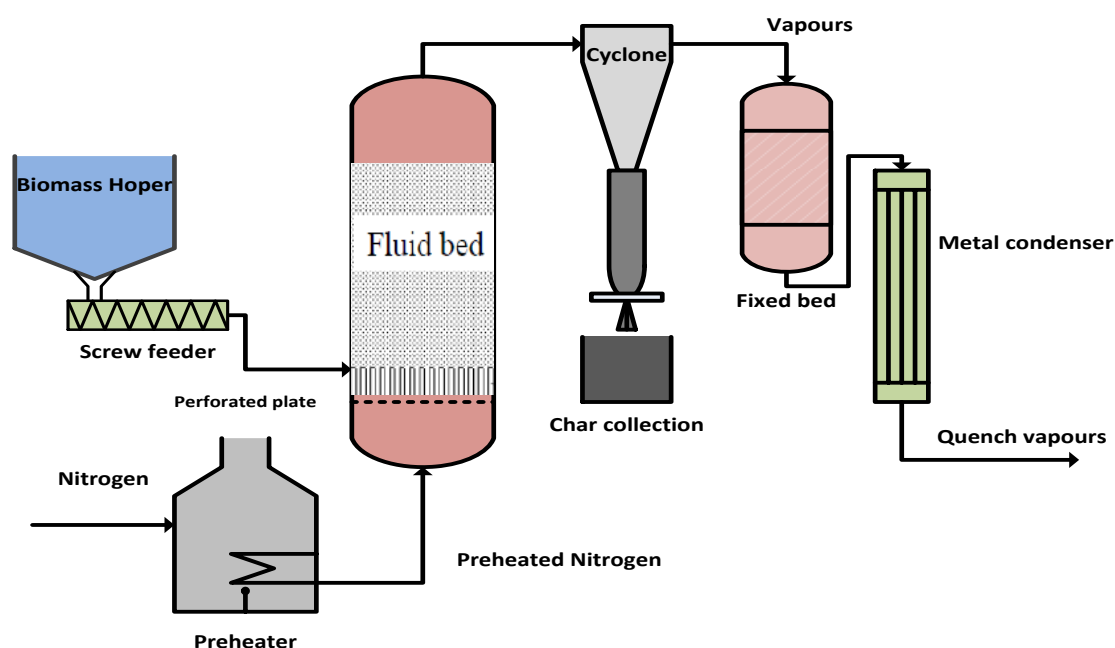


Figure 9: Process diagram of pyrolysis with ex-situ catalytic upgradation

For the quenching of vapours and liquid collection a new condensation system was installed for efficient cooling of vapours as shown in the figure below. A metallic condensation tube is attached with 3 glass bowls and 10 glass tubes in series with circulation of cooling liquid (propane) to cool down the condensable vapours as shown in Figure 10.

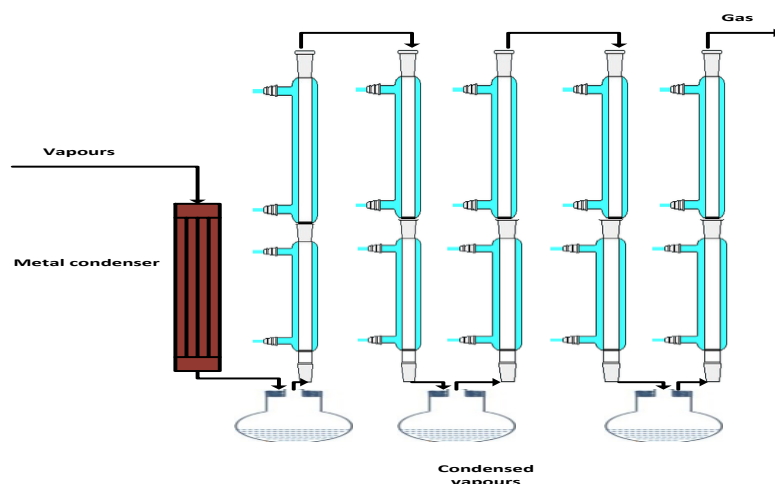


Figure 10: Condensation system to cool down vapours

3.1. Experimental procedure

All the pyrolysis experiments were investigated for three different biomass feeding rate 250g/hr, 379g/hr and 500g/hr with same temperatures. Nitrogen was used as fluidizing medium and heat up the system at 19 NL/min flow rate according to fluidization point and nominal velocity. N₂ was preheated in the preheater and then entered in the reactor at the bottom of reactor. Char has been separated in the cyclone, removed manually after every 15 minutes and cleaned vapours entered in the Ex-situ fixed bed reactor. There was one mesh present at the top of fixed bed in order to further clean the vapours from ash and char before going through the catalyst. Fixed bed reactor was filled with 650 g of catalyst and run twice for each feedstock rate. After two runs, catalyst was replaced with new one due to coke deposition and deactivation. After the fixed bed, a metallic heat exchanger is used to cool down the gases followed by 10 glass tubes for efficient quenching. The whole pyrolysis experiment was run for 5 hr at 1 bar pressure.

3.2. Experimental plan

Total 8 cases have been investigated in which case 1, 4 and 7 were reference test for each feeding rate without catalyst to determine the effect of catalyst on gas and liquid yield. Three different weight hour space velocity (WHSV) has been investigated for each feeding rate.

Table 4: Plan for experimentation

	Feeding rate	Catalyst	Non catalyst	WHSV
Case 1	250		X	0.384
Case 2	250	X		0.384
Case 3	250	X		0.384
Case 4	379		X	0.583
Case 5	379	X		0.583
Case 6	379	X		0.583
Case 7	500		X	0.769
Case 8	500	X		0.769

3.3. Experimental parameters

The temperature of fluidized bed was 500 °C for fast pyrolysis. Ex-situ fixed bed temperature was set to 600 °C. For the complete removal of coke from catalyst, lower deactivation temperature is preferable with least effect on zeolite. Hence 600 °C temperature was chosen for the fixed bed.

3.4. Biomass

The lignocellulosic biomass in terms of softwood sawdust was used as raw material with particle size of 1-1.4 mm. The composition of biomass on wet basis is shown in following table.

Table 5: Composition of biomass on wet basis (weight %)

Proximate Analysis:	
Moisture wt.%	6.2
Ash wt.%	0.24
Volatile matter wt.%	84.4
Fixed carbon wt.%	9.16
HHV MJ/kg	20.093
Ultimate analysis:	
C	50.5
H	6.2
O	43.0
N	<0.11
Metals	
S	<0.011
Cl	<0.010

3.5. Gas analysis

Agilent 490 micro GC has been used for gas analysis. The micro GC contains four columns and thermal conductivity detectors. These detectors can detect, and it is calibrated for O₂, N₂, CH₄, CO, CO₂, H₂S, H₂, He, C₂H₂, C₂H₄, and C₂H₆ gases.

3.6. Liquid analysis

Water content and TAN number of pyrolysis oil was determined by Karl Fischer titration and TAN titration by Mettler Toledo AB. Some drops of oil are diluted in an appropriate solvent normally methanol is used, and the mixture is titrated with alkaline KOH. Pyrolysis oil is very acidic in nature, contains organic acids like acetic acid and formic acids which results acidic liquid with 2 to 3 PH value. Acidity of bio oil leads to corrosiveness which requires some upgradation process. Furthermore, some specific construction material is used in storage vessel to avoid damages due to acidity [25].

GC/MS was used to analyse the liquid products (Agilent 7890A GC coupled with Agilent 5975C MS) and the column is VF-1701ms (0.25um) with 60m length. The program was set as started at 40°C as holding time for 2 minutes, then heat to 250°C by 4°C/min heating rate and followed by stable temperature for 30 minutes. Some samples of oil were also sent to external laboratory to get elemental composition of oil.

3.7. Catalyst preparation

First zeolite HZSM-5 catalyst was calcined in the oven at 600 °C with circulation of air to reduce the moisture and other compounds. The temperature in oven was set as 10 degree/min from 120°C to 600°C, stay 15h at 600°C and then cool it down. According to WHSV, 650 g of catalyst was filled in the reactor. Bulk density of the catalyst is 0.629 g/cm³. Particle density was calculated by weight to volume ratio of one particle. Porosity of calcined catalyst is obtained 88% by using the following equation.

$$Porosity \% = 1 - \frac{Bulk\ density}{Particle\ density} \quad (1)$$

4. Results & Discussions

4.1. Liquid analysis

4.1.1. Two phase mixture

Pyrolysis oil is a mixture of a non-aqueous (viscous) and aqueous phase. Oxygenated organic compounds with low molecular weight are present in the aqueous phase and non-aqueous phase consists of high molecular-weight non-polar oxygenated compounds, monocyclic aromatics and polycyclic aromatic hydrocarbons [25].

The liquid products from the non-catalytic experiments have only single-phase mixture. The colour of the liquid oil is dark brown. As shown in Figure 11, the catalytic experiments produced two-phase liquids which were separated by gravity in a glass tube and the sedimentation of the heavy (non-polar) phase. One phase is aqueous and soluble in water due to polar molecules. The non-polar generates the thick viscous phase (oil) which is insoluble in water. Bio-oil can face aging during storage which leads to increase the viscosity of liquid [24]. This happens due to mainly condensation reactions occurring in the oil [25]. After the experiment, collected bio-oil placed in the refrigerator to cool and in minimum exposure to sun light. These steps were suppressing the aging process in oil.

Catalytic: Aqueous, viscous Non catalytic: Viscous



Figure 11: Pyrolysis oil from catalytic and non-catalytic experiments.

4.1.2. Water content

Water content of single-phase bio oil is approximately 15 to 30 wt %. However, water content of aqueous phase in two phase bio oil can be high as 80 wt %. Water found in the oil is mainly derived from moisture content of feed, water production during reactions of pyrolysis, secondary cracking reactions due to catalyst and bio oil storage. The bio oil characteristics are affected due to presence of water both in positive and negative way. Bio oil is thermally and chemically less stable as compared to fossil fuels due to high percentage of oxygenated compounds. The instability in bio oil occurred as increased in viscosity with time, particularly in ageing. High water content can reduce the viscosity of oil and help to stabilize [26]. High percentage of water has adverse impact on the heating value. If the pyrolysis occurred with drying of feedstock, it will increase the heating value (MJ/kg) as compared to non-dry feedstock [27].

Water content of non-catalytic experiment for low, medium and high feed rate was around 30 to 40 wt% as shown in Figure 12. The aqueous phase of catalytic experiments has high water

content above 80 wt %. After carefully separating the oil phases of catalytic experiments, there is no water in the viscous phase.

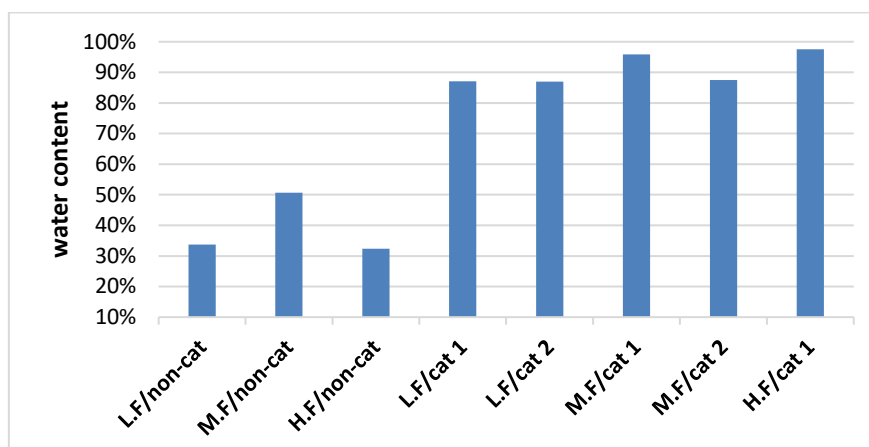


Figure 12: Water content of bio oil from non-catalytic and catalytic experiments.

4.1.3. TAN number

TAN (total acid number) test is performed in order to determine the acid concentration in oil. Oxygen content of bio oil is between 35-40% and contained oxygenated compounds. High content of oxygen in oil lowers the energy density of bio oil. Bio oil contains organic acids such as formic and acetic acid results high TAN number [25]. After catalytic upgradation of the system, acidity of bio oil was reduced. It could be based on the production of CO₂ during catalytic upgrading [28].

TAN number of non-catalytic oil products has relatively high as compared to catalytic products. Aqueous phase of catalytic experiments, acidity was up to 20 and it has almost negligible amount in non-aqueous phase, as illustrates in Table 6.

Table 6: Acid number of boil oil from catalytic and non-catalytic experiments.

Non catalytic					
	L. feed	M. Feed	H. Feed		
Total acid number (TAN)	51.19	68.58	52.67		
Catalytic/Aqueous					
	L. Feed	L. Feed. R	M. Feed	M. Feed. R	H. Feed
Total acid number (TAN)	6.20	8.19	9.24	21.50	7.576
Catalytic/viscous					
	L. Feed	L. Feed. R	M. Feed.	M. Feed. R	H. Feed
Total acid number (TAN)	3.985	8.061	0	14.69	0

4.2. Gas Analysis

Gas analysis has been performed with Micro GC. Catalytic experiments produced more gas as compared to non-catalytic, because more cracking reactions occurred in the presence of zeolite HZSM-5.

The gases produced from catalytic experiments are mainly CO, CO₂ and H₂. The remaining gases are smaller hydrocarbons from C₁ to C₂. As can be seen in Figure 13, the yield of CO and CO₂ is increasing for catalytic experiments. The catalyst accelerates the oil cracking and produces more gas due to generation of non-condensable molecules. During the cracking process more oxygenated compounds in oil is converted into CO and CO₂ which leads to increase the amount of CO and CO₂ in the gas phase [28].

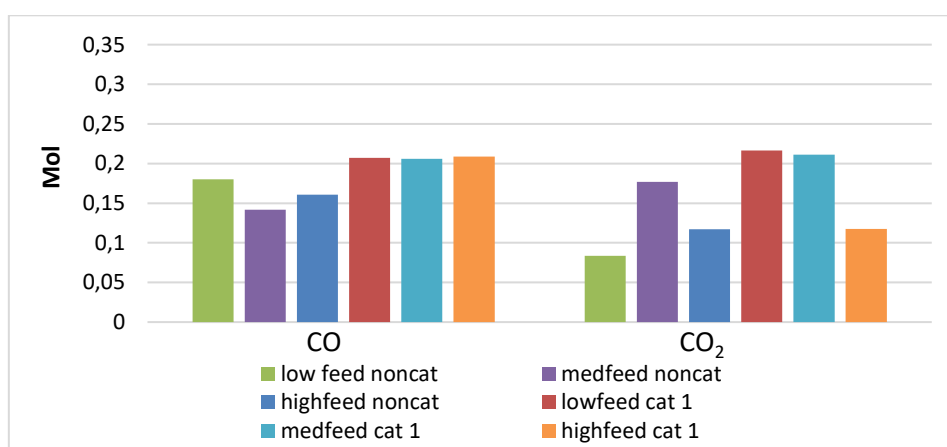


Figure 13: Production of CO and CO₂ in gas phase

The following figure illustrates the yield of gaseous hydrocarbons for catalytic and non-catalytic experiments. As can be seen in Figure 14, catalytic experiment results in higher production of hydrocarbons. Production of CH₄ and C₂H₄ in gas phase is increasing with the feed flow rate.

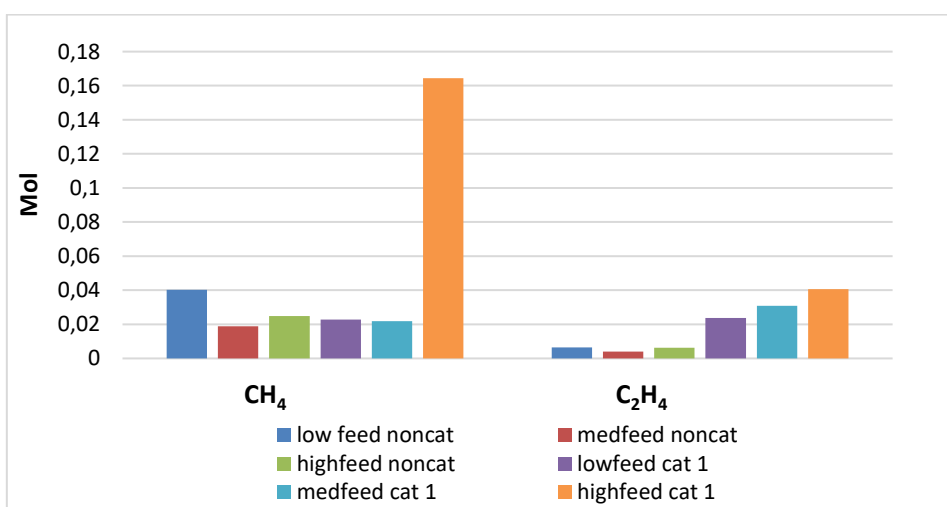


Figure 14: Mols of HC in catalytic and non-catalytic experiments.

4.3. TGA

Coked and non-coked catalyst was investigated for TGA behaviour. There were mainly two aspects, magnitude of catalyst regeneration at different intervals of temperature and the coke yield on each deactivated catalyst. The following figure illustrates the TGA curves for coked catalyst with temperature. Temperature range for TGA curve was 50 to 850 °C. At the start of TGA of a sample, moisture was removed at 120 °C. After 120 °C sample was heated to 850 °C.

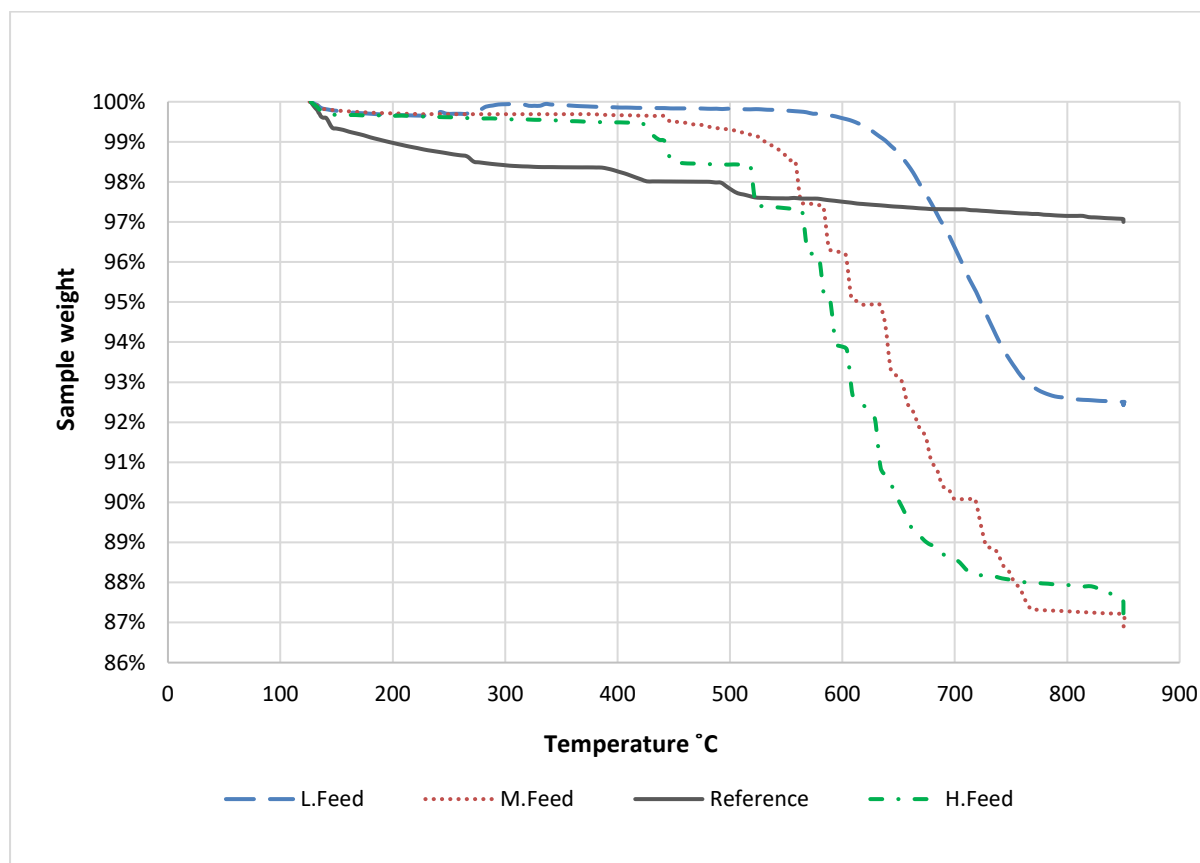


Figure 15: TGA curves

In the figure, the non-coked catalyst (reference) contains significant amount of moisture as compared to coked catalyst and the curve flattens out after the first point indicating that there is no mass loss. This is happened because of surface and pore volume of coked catalyst occupied by coke, which subdue the absorption of water in catalyst. The reference zeolite is fresh and non-coked; hence it will absorb more water. After the removal of moisture content in coked catalyst, there is another clear weight loss due to removal of coke [28].

Coke yield for all the catalyst illustrates in Figure 16. The results of coke from low, medium and high feed experiments demonstrate that coke deposition on catalyst is increasing with the weight hour space velocity.

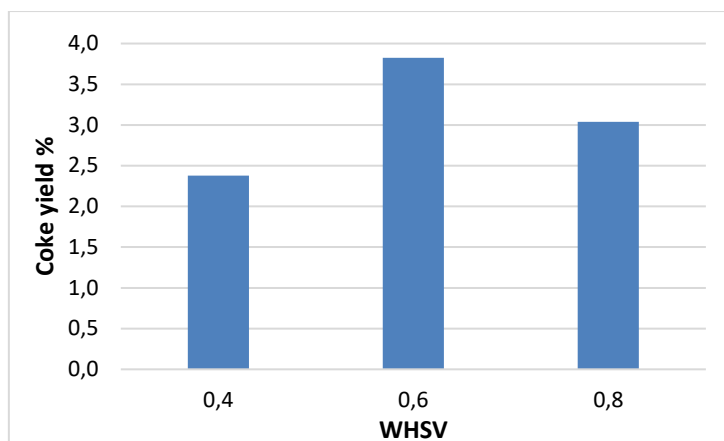


Figure 16: Coke yield with WHSV

4.4. Product distribution

Influence of catalyst on pyrolysis products such as char oil and gas is shown in Figure 17. The distributions of these products for catalytic and non-catalytic experiments have been investigated. The char yield is around 17% and it is almost same in all experiments either it is catalytic or non-catalytic. The yield of oil is much higher for non-catalytic experiments as compared to catalytic. The oil yield decreases from non-catalytic to catalytic and gas yield is increasing due to removal of oxygen as CO and CO₂. HZSM-5 as catalyst was accelerated the bio oil cracking into smaller components and produced more gas. The yield of oil was decreased for catalytic experiments, but the energy content of oil will be better due to removal of oxygenated compounds like acids [28][29].

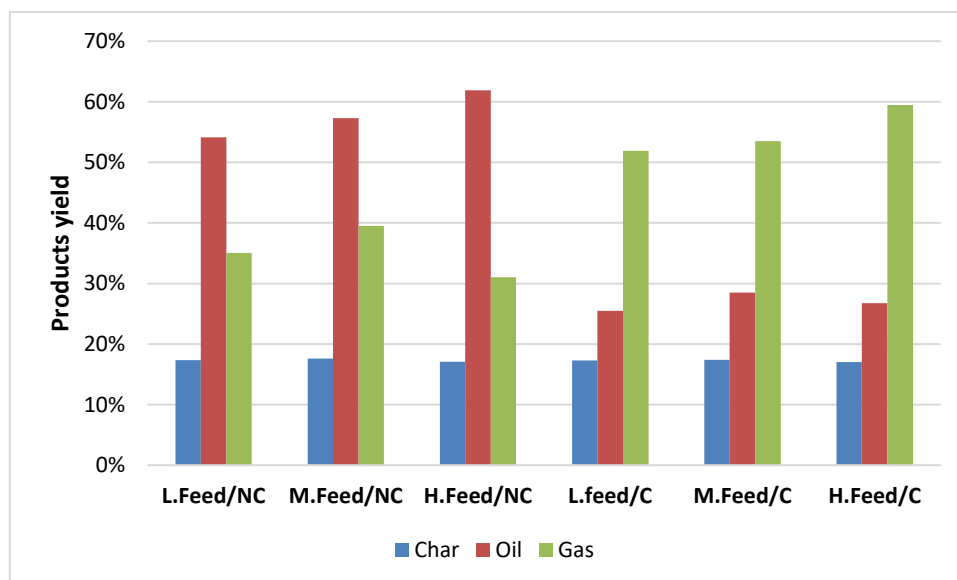


Figure 17: Products yield based on wt %

Elemental composition of oil is clearly showing that the carbon and hydrogen content of oil are very low in aqueous phase, but it is high in viscous phase because more hydrocarbons was produced. Furthermore, oxygen content is much low in catalytic experiments as compared to non-catalytic one as shown in Table 7. This is happened due to deoxygenation of oil vapours.

Table 7: Elemental composition of oil from catalytic and non-catalytic experiments in all phases

Elemental composition of oil on dry wt % basis								
	NCL	NCH	CLAQ	CMAQ	CHAQ	CLVISC	CMVISC	CHVISC
C	37.6	47.2	4.4	2.4	1.3	70.9	76.9	79.3
H	4.52	4.24	1.03	0.57	0.01	6.8	6.6	6.9
O	23.67	16.35	7.36	4.82	0.58	22	16.3	13.6
N	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1
S	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ash	0.064	0.02	0.006	0.003	<0.001			
Σ	65.8	67.8	12.8	7.8	1.9	99.7	99.8	99.8

4.5. Ethical and social aspects

One of the main reasons to produce biofuels is to decrease the greenhouse gas emissions and to reduce the effects of global warming. Production of biofuels especially from crops, created unintended impacts on land, water resources and biodiversity. Agricultural crops can be used to produce bio-oil but then another debate is started: is it ethical for human basics right, e.g food? Biomass is a huge spectrum in which we can use any type of waste feedstock. For example, we can use forest waste, agricultural waste, saw mill waste, garden waste etc. Pyrolysis oil from biomass could reduce the global warming without creating the impact on agricultural land. Pyrolysis is flexible technology and can be run with any type of waste material.

The experiments are based on saw dust biomass which is waste from saw mill and it will be available in future in terms of sustainability. The produced bio-oil can replace fossil fuels to lower the greenhouse gas emissions and global warming. Pyrolysis oil could fit in the existing infrastructure of petroleum industry with small modifications.

This pyrolysis technique is a good way to generate liquid fuels from wood based lignocellulosic biomass. It will ease the energy shortage problem in transportation sector and to provide better usage of waste.

5. Conclusion

In this study, a concept of catalytic pyrolysis is presented in detail with Ex-situ modifications. Lignocellulosic biomass was fed in a bubbling fluidized bed at 500 °C followed by fixed bed Ex-situ reactor at 600 °C. Whole experimental plan was divided into 2 parts, non-catalytic and catalytic. Both parts run for 3 different feedstock rates. Derived oil, char and gas were analysed based on the yields and chemical composition.

Non-catalytic experiments produced single phase viscous liquid which has relatively high water content and TAN number. Catalytic runs generated two phase mixture of oil, aqueous phase and viscous phase. Aqueous phase contains high water content as compared to viscous phase but both have relatively low TAN number. No significant difference in yields of char was observed for both cases. Derived liquids from non-catalytic runs comparatively have high yield as compared to gas. It was observed that gas yield from catalytic experiments relatively high as compared to liquids due to more deoxygenation of vapours into CO, CO₂. Coke deposition on the catalyst was increased with the feed flow rate and affects the activity of catalyst. One catalyst was used for two runs, then replaced it with the new catalyst. Overall, the catalytic and non-catalytic experiments have significant difference in products yield. Catalytic fixed bed reactor reduced the oxygen content of vapours and the acid number. Upgradation of pyrolysis vapours by Ex-situ technology is an interesting alternative to deoxygenise the pyrolysis vapours and increased the carbon value with reduction of water content.

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