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Catalytic Fast Pyrolysis of Whole Field Pennycress Biomass

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CATALYTIC FAST PYROLYSIS OF WHOLE FIELD PENNYCRESS BIOMASS

by

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ABSTRACT

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Utah State University, 2015

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Reports indicate that the worldwide energy consumption and fossil fuel energy production level will have an opposite trend in the coming two decades. The former will continue to increase while the later will decrease. Therefore, additional sources of energy need to be developed. Field pennycress (*Thlaspi, arvense* L.) has been found to be an ideal source of energy because it has prolific yield and has no value as food. We demonstrated conventional and catalytic fast pyrolysis of whole pennycress biomass in a fluidized bed reactor. Characterization studies on field pennycress showed that the biomass had a potential to be converted to energy-rich bio-fuel. Thermogravimetric and kinetic study on field pennycress provided vital information on the degradation behavior of the feedstock. A parametric study was conducted on conventional rapid pyrolysis by using the effects model. The optimum experimental condition that gave maximum liquid yield was found to be at a temperature of 500 °C and a gas flow rate of 24 l/min. The catalysts used for catalytic fast pyrolysis were HZSM-5, a commercial catalyst, and red mud, an alumina industry waste material. The liquid products obtained from pennycress were found to have better qualities compared to a typical lignocellulosic feedstocks pyrolysis bio-oil. The bio-oil from the red

mud catalyzed experiment had almost neutral pH of 6.5 and the pH in the case of HZSM-5 was 5.7. In comparison to bio-oil from conventional rapid pyrolysis, HZSM-5 and red mud reduced the viscosity of the bio-oil by 3 and 5 times, respectively. However, red mud was only found to be effective in improving the higher heating value (HHV) of the bio-oil from 33.18 MJ/kg (dry basis) in conventional pyrolysis to 35.7 MJ/Kg (dry basis). The HHV of HZSM-5 catalyzed bio-oil was 33.63 MJ/kg. The composition of non-condensable gases and the chemical makeup of the bio-oil from the two catalysts were different, suggesting that the reaction pathways could be different. HZSM-5 had higher selectivity for aromatics whereas red mud produced longer aliphatic chains. The bio-oil obtained from red mud catalytic pyrolysis of field pennycress is a promising alternative energy source that could replace petroleum fuels after some upgrading.

(141 pages)

PUBLIC ABSTRACT

Catalytic Pyrolysis of Whole Field Pennycress Biomass

Yonas Afewerki Kidane

To satisfy the energy demand of the ever-increasing world population as well as to prevent environmental pollution arising from the use of fossil fuels, an alternate source of energy has to be developed. Biomass has the potential to provide a renewable energy source that is inexpensive and environmentally friendly. Field pennycress (*Thlaspi arvense* L.), previously considered as a weed, has now been found to be an ideal source of bio-fuel production. The focus of this research was to produce upgraded bio-oil by a process known as catalytic fast pyrolysis. A characterization and a temperature degradation profile study helped to understand that the biomass can be converted to energy-rich bio-oil and also provided information for designing the pyrolysis process. The influence of operational conditions was investigated using suitable experimental design. The optimum reaction condition was found to be at a temperature of 500 °C and a gas flow rate of 24 l/min.

Catalytic fast pyrolysis was demonstrated in a fluidized bed reactor by using HZSM-5, a commercial catalyst, and red mud, which is an industrial waste product. Both catalysts improved the quality of the bio-oil. However, red mud was found to be more effective than HZSM-5. The bio-oil produced from catalytic pyrolysis of red mud had almost a neutral pH, a similar density as water and a heating value of 35.7 MJ/kg (which is equivalent to 89% of petroleum derived heavy fuel oil). In the case of HZSM-5, the pH and heating value of the bio-oil were 5.7 and 33.63 MJ/kg, respectively. The bio-oil obtained from catalytic pyrolysis of field pennycress is predicted to have a vital contribution to the bio-energy sector.

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I dedicate this work to my father, Afewerki Kidane Gebrezgabihier, to my mother Abeba Sium Gebrehawariat, and to all my seven siblings.

Yonas Afewerki Kidane

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CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 Introduction

There is no doubt that an alternate source of energy is needed to satisfy energy demand of the increasing world population. In order to achieve this objective, it is necessary to utilize renewable feedstocks, such as biomass, as the existing source from fossil fuels is limited and non renewable.[1–3] With the upsurge of environmental issues like global warming, alternate sources of energy both cheaper and environmentally friendly have therefore to be developed to address the issue of energy demand and environmental concern.[1–3] Processes like fast pyrolysis of biomass can play a vital role in producing adequate bio-fuel that can compete with existing fossil fuels.[4] Fast pyrolysis is thermal decomposition process in the absence of oxygen with temperature of around 500 ^{o}C (range of 400-600 ^{o}C) at vapor residence time of 1-5 s.[1–6] The focus of this study is on the thermal conversion of biomass into renewable energy.

Pyrolysis has become one of the most promising method for the production of liquid fuel intermediates from biomass.[1–4] The relative yields of gas, liquid and char depend mostly on the residence time and the final temperature.[1–5] In the past three decades, research studies has demonstrated that fast pyrolysis can produce liquid yield as high as 75 wt.% under optimum reaction conditions.[2,3] Even though various studies have been conducted, there is still a challenge in understanding the fundamentals of the science of biomass pyrolysis and a model that can explain the chemistry undergoing.[6] Moreover, if the bio-oil is going to compete with the conventional liquid fuels it must overcome technical and market barriers. Hence, it is imperative to set norms and standards for fast

pyrolysis bio-oils that can serve as a guide line in commercializing and evaluating fast pyrolysis bio-oil.[7] Furthermore, there are issues on how to scale-up bio-fuel infrastructure. If all the above mentioned issues are addressed, it will not be too long to see the promising future of pyrolysis to happen in reality.[8]

1.2 Problem Statement

In order to provide adequate energy supply and to tackle the warning signal in the environment due to excessive emission of greenhouse gases, new energy technologies that are domestic and sustainable need to be developed.[1,6,9] According to Renewable Fuel Standards (RFS, the United States Environmental protection Agency) of 2007, the consumption of renewable transportation fuel will have to be 36 billion gallons of bio-fuel per year by 2022.[9] The plan is to achieve or surpass the biofuel demand and reduce greenhouse gas emission. Therefore, the source of bio-based raw material must be sustainably met to achieve the objectives. Out of the total 36 billion gallons, corn ethanol is estimated to contribute about 15 billion gallons.[9] The remaining 21 billion gallons is expected to come from cellulosic biomass and other advanced bio-fuels. To meet this requirement, there has been a search for collection of cellulosic feed stocks that can be sustainably cultivated on subsidiary lands.[9]

It has been found that pennycress (*Thlasphi arvense* L.) could play a vital role in satisfying feedstock requirement for bio-fuel production.[10] Field pennycress is a member the mustard family and has been previously considered by many as a weed.[11,12] But now, this plant has been found to be one of the ideal sources of bio-fuel.[10–12] *T. arvense* can be grown in temperate regions of the world.[12–14] This plant can potentially produce as high as 840 L/ha oils and 1470 kg/ha press-cake on 16 million hectare of farm land in the USA

Midwest Corn Belt that left fallow during the fall through spring months.[12] Field pennycress has no value as food because it has toxic agent, which is allylthiocyanates (ATC).[15] Thus, field pennycress has no significant use so far. The use of edible crops for energy production has raised a debate in the past years because there is also demand for food production.[16] Hence, using non-food biomass such as pennycress solves the controversy of using food sources in order to get energy.[10,16]

Despite the benefits of being easily storable and transportable form of bio-energy and source valuable chemicals, the problem with pyrolysis oil is that it has unstable, acidic, corrosive, and viscous fuel characteristics.[1–7] These phenomena is caused by their high oxygen content, water content, char and alkali metals in the oils. The presence of these components in bio-oil accelerates secondary reaction during storage. To improve the properties of bio-oil, secondary processing like catalytic-upgrading, hydro-treating, liquid-liquid extraction, and gasification can be applied. However, this increases the operating and capital cost of the process and the yield of upgraded product is not satisfactory.[1–5] Fractional catalytic pyrolysis has been found to be successful to selectively convert biomass into suitable products by using appropriate catalyst.[5] Therefore, it is imperative to conduct a research in one of the ideal source of biomass, field pennycress, and upgrading the quality of bio-oil using mechanisms like catalytic pyrolysis by using a suitable catalyst.

1.3 Objectives

The main objective of this project is to conduct catalytic pyrolysis of whole pennycress biomass feedstock using HZSM-5 and Red mud as catalysts. The specific objectives are to conduct:

i. Characterization, thermogravimetric and kinetic study of whole pennycress biomass.

ii. Parametric study on conventional rapid pyrolysis of pennycress biomass.

iii. Catalytic fast pyrolysis using red mud and HZSM-5

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CHAPTER 2

LITERATURE REVIEW

2.1. An overview of Field Pennycress

2.1.1 Background

Field Pennycress belongs to the family of *Brassicaceae* (Alternatively *Cruciferae*) and genus *Thlaspi.* Its species name is *T. arvense L.*[1] Pennycress is a member of mustard family.[2,3] Other common names for field pennycress are fanweed, frenchweed, stinkweed, wild garlic, mithridate mustard.[1–3] It resembles like field pepper-grass and is noticed by its sour turnip-garlic odor when its leaves are crushed.[2] Pennycress originated in Eurasia (Asia-temperate, Asia-tropical and most part of Europe). And now it grows wide spread as naturalized species in Africa (Algeria, Morocco & South Africa), Australia, Northern Europe, throughout Northern America (USA & Canada) and Southern America (Brazil, Argentina & Chile).[1,3]Pennycress emerged in Canada as early as 1882 while trading of food stuff in prairies by traders and was distributed throughout the USA by 1937.[3]

2.1.2 Growth and Development

Field Pennycress is a winter annual or spring annual plant. The species of pennycress survive the unfavorable winter season as seed or vegetative rosette.[3] The species who overwinter as seed germinate during spring. Those seedlings that germinate in the autumn overwinter as a rosette and begin flowering early in the growing season (i.e. April and early May) and are harvested late May to early June.[3,4] Field pennycress is able to survive to a range of environmental conditions. It can grow in both dry and wet

habitats (exposed knoll to moist valley) and from sea level to an altitude of 2,739 m.[3] The habitat includes crop land, fallow field, gardens, areas along roadside, weedy meadow and waste area. The stem can elongate up to 80 cm on the onset of flowering when the soil is more fertile, deeper and in relative absence of competition.[2,3] Best and McIntyre[3] showed the different growth and development stages as in Figure 2.1.

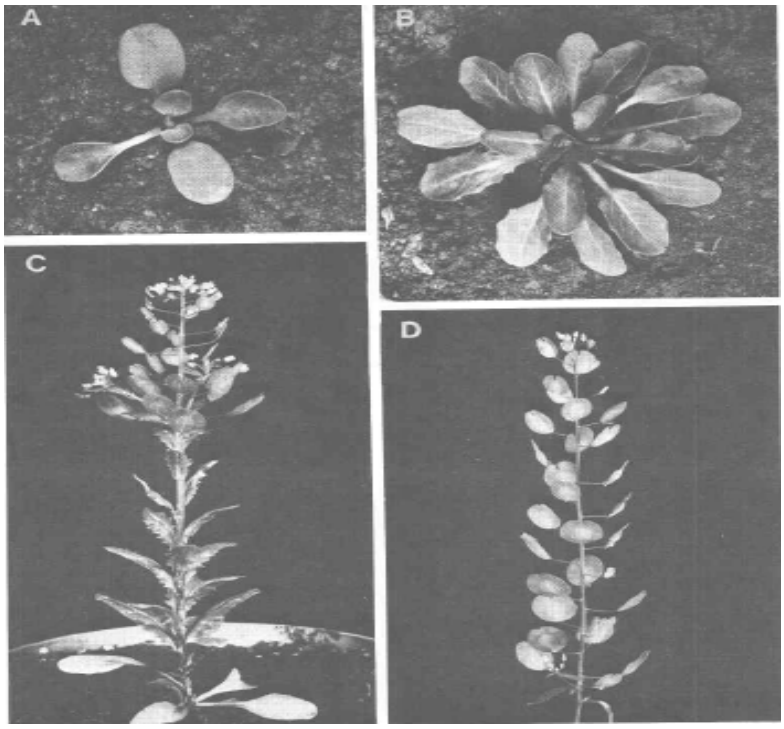

Figure 2.1 Stages in the growth and development of Thlaspi arvense L.(Taken from Best and McIncyre, 1975)[3] A) A young seedling showing the cotyledons and the first four true leaves. (B) A vegetative rosette which had overwintered at this stage (C) The flowering stage. (D) Infloresence with mature seed pods

Germination of seeds takes place in greatest number in early spring. Some seeds also germinate in the fall and may also even germinate during summer if the soil is distributed and there is adequate moisture therein.[3] Field pennycress is generally self-pollinated. Pollination takes place when stamina filament is bent and contacts the introrse

anther with the stigma.[2,3] Field pennycress has early and late flowering forms. This difference is due to a single gene which completely dominates the late flowering.[2,3]

Early flowering (EF) strain grows shorter than late flowering (LF). The early form of pennycress strain flower is between 35 and 65 day whereas that of the late form strain flower after 95-150 days.[5] Hume[5] reported that pennycress had a prolific seed yield with a range of 13,162 ± 842 to 14,914 ± 748 seeds per plant for EF and LF of spring emerging, respectively.[5] Some studies tried to investigate the variation and they reached to the conclusion that vernalization could overcome the strain difference delay in the days to flower.[3,5] Vernalization of seed, when begun after 48 or 96 hr of seed germination at 2 ^{o}C for 6 weeks, appeared to override the late flowering. Even though vernalization can remove the difference in the strains but has no difference in seed dry weight or physical character between strains.[2,3,5]

2.1.3 Poisoning or Harmful Effect of Pennycress

Field Pennycress is considered as agricultural weed. The toxic agent in pennycress is allylthiocyanates (ATC).[2] This component is produced when allylglucosinolate (a glucosinolate) is hydrolyzed (crushed and moistened) and produces the characteristic garlic-like odor. Pennycress taints milk or meat of animal that eats it with unpleasant flavor if there is admixture of its seed and to a lesser extent its leaf.[2] When pennycress is injected in a hay containing 25-100% to pregnant cows, it caused abortion, peeling skin, massive sub-mucosal edema of the wall of stomach and even death.[6] *T. arvense* can also be a host for insects, nematode, fungi and viral pests.[2]

2.1.4 Economic and Environmental Significance of Pennycress

Recent studies about pennycress suggest that it can be one of ideal source for bio-fuel production. Moser et al.[7] demonstrated that the oil from pennycress can be used in bio-diesel production.[7] Bio-diesel has advantage over petroleum because it is domestic and renewable, biodegradable, and has reduced toxicity. Feedstocks such as soybean oil, palm oil and other vegetables have been used as a source for bio-diesel production. However, the use of edible feedstocks for energy production has raised the debate of food versus energy.[7] The cost associated with bio-diesel production is high due to expensive price of vegetable oil.[7] Therefore, it is imperative to investigate alternative sources of energy such as pennycress that does not replace the commodity crop for food use.[8]

Field Pennycress is one of the attractive targets for energy production because of its low cost, minimal agricultural input (such as fertilizers, pesticide, and water), production in off-season, definite growth season and its compatibility with existing farm and structure.[7] *T. arvense* can be grown in temperate regions of the world.[9] This plant can potentially produce as high as 840 L/ha oils and 1470 kg/ha press-cake on 16 million hectare of farm land in the USA Midwest Corn Belt that left fallow during the fall through spring months.[9]

According to recent studies, 1120-2240 kg of seed/ha can be harvested from wild population of *T. arvense*. From this product, approximately liters 600-1200 of oil/ha can be produced.[7] Pennycress has a high oil content with the yield ranging from 20-36%.[7,8] The oil contains a typical triacylglycerol structure and erucic acid (up to 38%) as the major fatty acid component.[7,8] The oil extracted from pennycress has been tested for bio-

diesel production. Moser et al.[7] reported that the bio-diesel met ASTM D6751 specifications. A good quality bio-diesel with excellent low temperature operability and high cetane number (59.8) was obtained.[7]

Apart from being a source of bio-fuel, pennycress has some agronomic advantage. It produces allelopathic compounds, primarily glucosinolates, that can affect growth of weeds.[10] The presence of sinigrin (2-propenyl glucosinolate), which in the presence of water disintegrates into allylthiocyanates, could serve as a valuable bio-fumigant.[10] Johnson et al.[4] reported that pennycress play a good role in the growth of beneficial insects. Since *T. arvense* begins flowering April to early May, it is a good source of food for honey bees and native pollinators, which suffer from lack of food during spring.[4]

Pennycress is also one of the candidates in temporal intensification of land for economic, environmental and ecological strategic planning. Field pennycress can serve as cover crop. Hence it prevents soil erosion during winter. After germination during fall, its leaves grow low to the ground and provides a good vegetative cover to the soil.[4,11] Being a winter annual crop oil seed, pennycress can fit into existing crop rotation cycle with soybean.[4,12] Since pennycress is harvested in May to early June, there will not be an overlap in time in cultivating full season soybean oil in the same land.[4] Research studies reported that growing soybeans after harvesting pennycress has no negative effect on the yield of soybean seed yield.[12] Moreover, it was demonstrated that the growth of soybean after pennycress increased the seed yield than a single cropping season.[4]

Even though it has been successfully demonstrated that pennycress oil could be used as a source for bio-diesel production via standard transesterification procedure[7], additional effort is required to satisfy the energy demand targeted by Renewable Fuel

Standards (RFS2).[13] The target of RFS2 is that by 2022, the consumption of renewable fuel will be 36 billion gallons (bg) of transportation fuel per year. The plan is to achieve or surpass this biofuel demand and reduce greenhouse gas emission by lowering carbon footprint. USDA is working toward the plan in developing reliable bio-fuel source. This objective is also believed to ultimately grow the rural agricultural economy. Corn ethanol and some oilseeds are expected to contribute about 16 bg. The remaining 20 bg has to be obtained from other sources like cellulosic feedstock.[13]

To provide added quantity to the above mentioned bio-fuel demand, fast pyrolysis of the entire value chain of field pennycress seed was conducted. The resultant bio-oil had high carbon, low oxygen, and high energy content.[14] The Recycling of non-condensable gases and light hydrocarbons was applied for fast pyrolysis of while oak, switch grass and pennycress seed press-cake in order to create a reactive gas atmosphere. This process worked well for white oak and switch grass but had less significant deoxygenation effect on pennycress.[15]

Hydrotreating of fast pyrolysis oil from protein-rich pennycress seed press-cake was also conducted to further improve the quality of the bio-oil.[16] Generally the presence of high nitrogen content (4-11%) from the mustard family-derived oil resulted in the deoxygenation effect in the product and produced less acidic bio-oil.[14,16] The reason attributed for this phenomenon is the substitution of oxygen by nitrogen as a result of reactions of nucleophilic organonitrogen with electrophilic oxygenated compounds.[16] However, hydrotreating is important in order to remove heteroatom (O+N+S) so that the bio-oil can be used in the current fuel system directly or with will little modification. Hydrotreating over Ru/C and Pd/C catalysts further deoxygenated the bio-oil and that

over Pt/C was comparatively more effective in hydrodenitrogenation (HDN) than hydrodeoxygenation. All the catalysts were found to be effective for complete hydrodesulfurization.[16]

So far, the focus to use pennycress as the source for biofuel production has been on the oil extracted from the seed and on the residual press-cake after extraction. However, there is no further information on the pyrolysis of whole biomass, which encompasses the stem, leaves and whole seed. As all forms of biomass, pennycress is composed of cellulose, hemicellulose, lignin, extractives, and some inorganic material. Pyrolysis of the whole pennycress biomass can therefore increase the total yield of bio-oil because there will be contribution from both lignocellulosic material and the oil seeds.

Rukavina et al.[17] demonstrated the effect of nitrogen fertilization rate on field pennycress seed yield and oil content. They obtained a biomass and seed yield of 2212 lb/are and 557.3 lb/acre under nitrogen fertilization treatment of 50 lb/acre. When there was no nitrogen treatment the yield was 1175.8 lb/acre and 313.1 l lb/acre for biomass and seed yield, respectively.[17] The harvest index, percentage of seed yield to biomass ratio, is 25.2 and 26.7 for treatment with and without nitrogen, respectively. This shows that the biomass, excluding the seed, is approximately three times higher than the seed yield. Fast pyrolysis of the whole biomass could therefore potentially increase the total yield of bio-oil. However, the quality of bio-oil could be affected by the presence of high percent of lignocellulosic biomass than the oilseed. As mentioned earlier, a typical lignocellulosic bio-oil has a poor quality. To improve the quality of the bio-oil, catalytic fast pyrolysis of whole pennycress biomass was conducted in this work. Hence, this

thesis focused in achieving a higher quantity bio-oil while maintain a better quality as its main objectives.

2.2 Fundamentals of Fast Pyrolysis

The renewable energy from biomass is believed to meet the energy demand of the increasing population and will also have vital contribution to satisfy environmental concern, such as CO_2 emission, over fossil fuel usage.[18] Biomass has potential to provide the only source renewable liquid, gaseous and solid fuels. These can be achieved via thermal, biological and physical processes.[18] The three main types of thermal processes are pyrolysis, combustion and gasification.[18,19] Combustion of biomass has well established commercial application. It has low efficiency (15% for small plant to 30% for large) and also contributed to environmental problems.[18] Gasification has been practiced in the past years but it is relatively expensive compared to fossil fuel based energy and thus has few successful operational units.[18,19]

Pyrolysis is a thermal conversion process in the absence of oxygen, at atmospheric pressure and temperature range of 300-600 °C.[20] It have been practiced for thousands of years to produce charcoal by slowly heating at temperature ranging between 300 & 400 °C, which is known as slow pyrolysis.[19,20] High temperature and longer residence time favors the formation of gas than liquid fuels. This technology is known as gasification.[18–20] Fast pyrolysis is conducted at moderate temperature of around 500 °C and short vapor residence time of approximately 1-5 s.[19–21]

2.2.1 Principles of Fast Pyrolysis

In the past three decades, fast pyrolysis has became an attractive technology that produces high yield of liquid which can be used for energy, chemicals or as an energy carrier. Depending on experimental conditions, the liquid yield may vary from 55-60 wt.% (on a dry feed bases) for grasses to as high 60-75 wt.% (on a dry feed bases) for woody biomass.[19] At optimum reaction condition, there should be minimal cracking to small non-condensable gases and char formation.[20] The main aim of fast pyrolysis is to produce liquid product. The principal features of fast pyrolysis are:[18–20]

- Rapid heat transfer to small biomass particle (<3mm) at high heating rate
- Properly controlled optimum process temperature of around 500 °C (may range from 400-600 °C depending on the type of biomass)
- Short vapor residence time of less than 1-5 s for both decomposing particle and in the equipment before condensation
- Rapid cooling and condensation of vapors produced
- Proper removal of char to avoid secondary cracking of vapors

Almost all types of biomass can be used in fast pyrolysis. So far over 100 different types of biomass are being tested in different parts of the world. The type of biomass includes woody biomass, agricultural waste, energy crops, forestry wastes, sewage sludge and different other wastes.[19] Biomass is mostly composed of hemicellulose, cellulose, lignin, extractives and inorganic materials.[18–22] Each of these components have different composition characteristics. Thermogravimetric analysis (TGA) is used to investigate the pyrolysis temperature range and chemical reaction kinetics.[23] In general, cellulose is 30-100% of biomass and its decomposition starts over

300 °C where the peak is between 320-380°C. Hemicellulose, 12-40% of biomass, start to decompose early at around 220 °C and complete around 400°C. Lignin content in biomass is about 4-35%. Lignin has wide decomposition range starting from 160 °C to as high as 800-900 °C.[20,23,24] Cellulose contributes to the largest proportion of bio-oil whereas hemicelluloses and lignin yield higher amount of gas, tar and char. This is due to the fact that the covalent bond that links lignin and hemicelluloses is difficult to decompose than the hydrogen bond that links cellulose and hemicelluloses.[20] Most lignin goes to char and its composition is similar to that of char.[20]

2.2.2 Process Characteristics of Fast Pyrolysis

In order to improve the performance, product consistency, product characteristics, reliability and scale-up of fast pyrolysis, the following important aspects should be taken into consideration.[20]

2.2.2.1 Feed Preparation

The feed material has to be dried to typically less than 10% moisture content. This will minimize the water in the product liquid and will ultimately improve the quality of bio-oil. If the moisture content is greater than 10%, it may cause phase separation and lowering of heating value.[18–20] Particle size of the feed also affects heat transfer rate. For high biomass heating rate, the size is recommended to be less than 2-3 mm in most reactors such as fluidized and circulating bed reactors.[19,20] However cost of size reduction, in both financial and energy terms, is one of the important factors that has to be quantified and evaluated.[22] Therefore, feed reception, storage, handling, preparation

and treatment are the first stages of the process that need to be considered in any commercial process after ensuring the availability of adequate source of biomass.[19]

2.2.2.2 Heat Transfer and Heat Supply

Heat transfer has significant effect in fast pyrolysis and hence determines the liquid yield and quality.[25] Heat transfer takes place mostly by conduction and convection with some radiation effects.[22] Heat is transferred to biomass by either heating a solid material and / or hot gas. In general biomass has poor thermal conductivity (0.1 W/mK along the grain, 0.05 W/mK across the grain).[22] Therefore in order to produce higher yields of volatile organics (i.e. bio-oil), a higher heating rate is required.[20,25] Heating rate greater than 1000 °C/s is necessary to simulate fast pyrolysis.[25] It is also reported that thin reaction layer can be heated up to 10,000 °C/s but the heat transfer throughout a wood can be lower due to its low thermal conductivity.[22] Hence heat transfer from sand to biomass of about 500 W/m^2K is required with vapor phase residence time of few seconds and smaller particle size in order to get good liquid yield. In laboratory scale fast pyrolysis, the recommended heart transfer and supply could be achieved but in large scale commercial processes it imposes a major design requirement.[19,20,22] In woody biomass fast pyrolysis, char yield is about 15% (on dry feed basis) but the char has about 25% (on dry feed basis) of energy of biomass. And the byproduct gas also has about 5% of energy of biomass (on dry feed basis).[19] About 75% of the energy obtained from char can be enough source of heat for fast pyrolysis. The heat can be transferred by heating surface of reactor, bed material and fluidizing gas.[19]

2.2.2.3 Char Removal

Bio-char removal from pyrolysis vapors and liquid product is important because it can act as vapor cracking catalyst. Its presence in the bio-oil can also catalyze repolymerization reaction that can cause aging. This effect is accompanied by production of water and possibly CO_2.[18–20,26,27] Incomplete char separation in the process may also cause catalyst blockage and engine injector blockage.[20] Cyclones have been used in most times but are not efficient enough in char removal. Hot vapor filter, analogous to hot gas filter, is found to be effective in producing char free bio-oil in recent times.[18,19,26,27] The problem associated with using them is that the char accumulated on the filter cracks the hot vapor and can reduce the liquid yield by about 10-20%. Cleaning the accumulated char/coke on the filter is therefore challenge.[18,26]

2.2.2.4 Liquid Collection

The gaseous products from fast pyrolysis are composed of condensable gases, aerosols and non-condensable gases.[18,19] Capturing the true vapor and aerosols has been one of the major difficulty.[22] In order to avoid secondary reaction, rapid cooling and condensation is required.[18–22] True vapor can be condensed with chilled ethylene-glycol cooled condensers. A series of two condensers with 50-50% mixture of water and ethylene-glycol at temperatures of 10 °C and 4 °C can be used to capture the true vapor.[28]

Aerosols are reported to be effectively captured by electrostatic precipitator (ESP).[18–21,28] Demisters have been used for this purpose but are less effective.[19] Aerosols consist of incompletely depolymerized lignin fraction which seen to exist as liquid with substantial molecular weight.[19] ESP is currently practiced at laboratory and commercial scale.[19] The electrostatic charge induced from ESP impinge (ionize) the aerosols and they

then coalesce as liquid. If a large volume of gas is used for fluidization, it results in low partial pressure of condensable product. This ultimately reduces the amount of collected product, hence should be taken into design consideration.[18,19]

2.2.3 Reactor Configurations

In the past few years, a number of reactor configurations have been developed in order to maintain an optimum reaction condition for fast pyrolysis. A reactor is reported as the heart of entire process and accounts for 10-15% of the total liquid capital cost.[19] A number of reactor configurations have been developed in the past three decades. Three of the main types of reactors will be discussed hereafter.

2.2.3.1 Bubbling Fluidized Bed Reactors

Bubbling fluidized bed reactor is a reactor where gas is injected upward through a bed fitted with gas distributing plate at sufficient velocity to cause violent mixing of gas and solid. The violent back mixing of the solid material (e.g. sand) results in an emulsion that looks like a fluid.[20] Construction and operation of this type of reactor is simple. Bubbling fluidized bed reactor is found to be efficient in rapid heat transfer and temperature control.[19,20] Heat is transferred directly from the hot solid or indirectly from hot gas.[20] Combustion of char obtained from pyrolysis can serve as a source of heat for the bed or it can be heated by external source.[19] In the early 1980s, University of Waterloo in Canada started working on this type of reactors and it has been commercialized by Canadian Company Dynamotive Corporation. They are also used by many research institutions and universities.[19,20] Though sand or catalyst to biomass heat

transfer can be efficient, the amount of heat that can be transferred to the bed is one of the limiting factors in large scale.[19]

2.2.3.2 Circulating Fluid Bed Reactors

Circulating fluid bed is similar to bubbling fluid bed except that higher gas velocity is used to fluidize the bed. The purpose of using high gas velocity is to move the char and fluidizing media from the reactor through the cyclone to char combustor. The fluidizing media is then directly heated in the combustor by burning the char.[19,20] Careful design in cyclone is necessary because the char is attrited by high gas velocity and may escape from the cyclone and get collected with the bio-oil.[19] Even though circulating fluid bed reactor provide good heat transfer by conduction and convection, a proper control is required on the temperature, heat flux and solid flow match. This makes the process more complicated.[19,20] University of Western Ontario developed this reactor around 1980 and some industrial application is built by Canadian Company Ensyn Technology.[20]

2.2.3.2 Ablative Reactors

Ablative pyrolysis is conducted by pressing biomass on a hot wall surface under pressure to melt the biomass.[19,20] The particle will vaporize as it move away and will produce similar product to that of fluidized bed reactors.[19] The surface can be heated by hot gas that is produced by burning either char and / or gas produced during the reaction.[20] The governing factors for this process are high pressure exerted on particle against hot reactor wall, high relative motion between particle and reactor wall, and reactor wall temperature (less than 600 °C).[19] The advantage of ablative reactors over the

other reactors, such as bubbling & circulating fluid bed, is that there is no particle size requirement as reactions are not limited by heat transfer through the biomass. In addition to that, there is comparatively efficient collection due to the absence of fluidizing gas which is believed to lower the partial pressure of condensable vapors and hence lower the liquid yield.[19]

The major difficulties in ablative pyrolysis are the heat transfer to the ablative surface and contacting feedstock with different morphologies.[20] Aston University built second generation ablative reactor and has been patented.[19] PyTec, German company, is currently involved with the ablative process and has a pilot plant with 250 kg/h in operation.

2.3 Pyrolysis Liquid Bio-oil Properties

Pyrolysis liquid has several names such as pyrolysis oil, bio-oil, bio-crude-oil, bio-fuel-oil, liquid smoke, pyroligneous tar etc.[29] Its color is dark red-brown to almost black liquid. [18–22,29] The color difference is dependent on the presence of micro-carbon and chemical composition of the liquid. Efficient char removal (e.g using hot gas filter) results in red-brown color. The presence of high nitrogen can also generate dark green tinge to the liquid. Under very poor char removal situation, the oil can be almost a black liquid.[19]

2.3.1 Liquid Product Characteristics

Being a degradation product of cellulose, hemicellulose, lignin, extractives and other inorganic, bio-oil is a very complex mixture of oxygenated hydrocarbons.[18–22,29] It has high proportion of water and may also consist some solid char and dissolved alkali

metal from ash.[19] This constitution is one of potential challenges for utilization of bio-oil.[18,19] Since bio-crude-oil is formed by rapid quenching and thus freezing, it is reported that the bio-oil has many reactive species. This is due to the intermediate product of degradation and results in the unstable nature of bio-oil. The breakdown of hydrogen bond that stabilizes the discontinuous phase of holocellulose solution causes aging or instability of bio-oil.[18–20,29]

Generally bio-oil from wood derived biomass has acidic (2.8-3.5 pH), Smoky odor and the vapors can irritate eye.[20] The oil has carboxylic acids (mainly acetic and formic acid) and this contributes to the acidic nature of bio-oil. As a consequence, bio-oil causes corrosion of vessels and pipes; hence it should be used in acid-proof materials like stainless steel or poly-olefins.[19,20,29]

Density of pyrolysis liquid is in the range of 1200-1300 kg/m^3.[30] and viscosity is in from 25 up to 1000 cP (at 40 °C). Viscosity may change with time as a result of aging.[20] Elemental composition for wood derived bio-oil is similar to the biomass with carbon content of about 55-58%, hydrogen in the range 5.5-7%, nitrogen 0.1-0.2%, and oxygen is 35-40%. The ash content can be as low as 0.2 for woody biomass to as high 15 for herbaceous biomass.[18–20,22,30] Due to the presence of high oxygen content, bio-oils are polar in nature and are not miscible with petroleum-derived fuels.[18–20,29] Higher heating value (HHV) is in the range of 16-19 MJ/kg. This value is low because of high percent of water (15-35%) in the bio-oil. The water can either be product of reaction during pyrolysis and / or from moisture content of biomass.[18–20] Although addition of water can lower viscosity but its presence has several complex side effects.[19]

2.3.2 Effect of Ash

The presence of ash in the biomass has great effect on composition and oil yield.[31] The presence of sodium and potassium in bio-oil reduces the organic yield.[32] Alkali metals, which are present in the plant for the purpose of nutrient transfer and growth, can cause secondary cracking of vapors.[19] This can result to degradation of lignocellulosic material to char and gas.[20] It is also reported that the presence of di-ammonium sulfate and di-ammonium phosphate salt on wood resulted in increase of the char and water yield during pyrolysis. Even though the mechanism is not well understood, the removal of these cations has increased depolymerization of anhydyrosugars to levoglucosan (3 wt.% to over 30 wt%).[19] The presence of high percentage of ash can lower the oil yield to below 50 wt.%.[31] Ash can be either reduced in amount or removed from biomass by selection of crop harvesting time and / or washing of biomass with either acid or water. The latter is not economical and may also have an effect on cellulose and hemicellulose.[19] However the catalytic effect of ash needs further investigation so as to exactly know its effect and manage the process accordingly.

2.4 Upgrading Bio-oil

It has been demonstrated that fast pyrolysis can covert biomass into a liquid fuel in an efficient and economically feasible manner.[33] However the presence of hundreds of oxygenated compounds adversely affects the quality of bio-oil.[18–22,33] These compounds contribute to the poor quality of bio-oil such as low heating value, high corrosiveness, high viscosity, high reactivity (instability).[18–22,33] Hence it is problematic to use them for fuel application as they are incompatible with conventional fuels.[34] Post-pyrolysis processing of bio-oil like distillation produced about 35-50 wt.% residual due to the

presence of high amount of non-volatile sugars and oligomeric phenols. This phenomenon is also due to polymerization of reactive species.[33] Therefore it is quite imperative to improve upon the quality of bio-oil by removing oxygen if bio-oil is going to be used as a replacement for diesel and gasoline.[33,35]

Upgrading of bio-oil can be carried out either off-line or during fast pyrolysis by a process known as catalytic fast pyrolysis. The basic principle in both approaches is removal of oxygen with the help of catalyst by hydrotreating and / or catalytic cracking.[33] Secondary processing of bio-oil has been done in the past three decades. The challenges with the process, especially hydrotreating, are high operating and capital cost that is associated with significant catalyst deactivation, expensive catalyst used, high chat/coke formation, lower yield of hydrocarbons, and substantial hydrogen consumption.[21,36] Catalytic fast pyrolysis (CFP), which integrate catalyst in pyrolysis, has attracted the interest of researchers in recent years.

2.4.1 Catalytic Fast Pyrolysis (CFP)

Catalytic fast pyrolysis is an updated pyrolysis approach that converts the biomass to higher quality bio-oil by upgrading the pyrolysis vapors before condensation.[21,33] It is a simple and inexpensive step in which cracking/upgrading of organic vapor intermediates into hydrocarbons or high quality bio-oil takes place via a series of reactions.[37,38] Agblevor et al. demonstrated selective conversion of lignin fraction into phenol, cresols and catechols via fractional catalytic pyrolysis with HZSM-5 as catalyst.[21] In their report, the biomass was fed to the reactor at fixed rate and mixed with catalyst in a fluidized bed reactor. This process is referred to as in-situ catalytic pyrolysis. The process whereby the

catalyst is only contacted with the pyrolysis vapors is called ex-situ catalytic fast pyrolysis.[39]

The sources of the high level of oxygen in bio-oil are oxygenated mixture of carbonyls, carboxyls, phenolics and water.[40] By using a suitable catalyst, the oxygen in these compounds can be rejected in the form CO_2, CO, and H_2O.[21,28,34] The removal of active oxygenates, especially those in carbonyl- and carboxyl-, play a significant role in stabilizing the bio-oil. This will also reduce the demand for hydrogen, if necessary, during further upgrading process.[33] Several factors affect the performance of CFP of biomass. The four pivotal ones are residence time, type of catalyst, heating rate, and reaction temperature.[41]

2.4.2 Cracking Chemistry in CFP

One of the main purposes of CFP is to remove the active oxygenated species such acids, ketones, and aldehydes, thereby have a stable component in bio-oil.[33] The process integrates fast pyrolysis and upgrading of the vapor via catalytic reactions.[21,28,33,34] Even though the reactions are complicated and might occur simultaneously, understanding the cracking chemistry is paramount and several researches have been conducted to define the reaction pathways.

Catalytic cracking of pyrolysis vapor can result in the formation of green aromatics and olefins, which are the building blocks for petrochemical industry. The shape selectivity and acidity of catalyst used were found to be governing factors for efficient reactions. Zeolites can be ideal catalyst for this type of catalytic cracking.[42] The catalytic cracking chemistry involves decarbonylation, decarboxylation, dehydration,

oligomerization, isomerization and dehydrogenation reactions while oxygen is removed in the form of CO_2, CO, and H_2O.[19–21,34,42]

Reactions such as condensation and the Diels-Alder reaction can form aromatics from olefins and dehydrates species.[43] Catalytic studies on thermally stable oxygenates like sorbitol and glycerol resulted in the production of olefins (ethylene, propylene & iso-butene), aromatics, or light paraffins (methane, ethane, and propane).[43] Fractional catalytic pyrolysis is selective process where those with smaller size like carbohydrate are decomposed into gaseous product where as large particles like lignin are cracked (converted) to liquid product as they are large to diffuse into catalyst like HZSM-5.[21]

Lignin derived phenolics can undergo oxygen-aromatic carbon bond cleavage to form phenol/aromatic hydrocarbon or undergo oxygen-alkyl carbon bond cleavage to form benzenediols or benzene-triols. These benzenediols or benzene-triols then undergo hydrodeoxygenation to phenols.[44] Reactions such as aromatization, ketonization/aldol-condensation, hydrodeoxygenation and stem reforming take place during catalytic pyrolysis and result in updated bio-oil that can be either directly used or processed for various applications.[33]

2.4.3 Catalyst for CFP of Lignocellulosic Biomass

A number of catalysts have been used in fluid catalytic cracking, but the discussion will be about the two catalysts that are used in this study.

2.4.3.1 ZSM-5

ZSM-5 is a zeolite type (aluminosilicate) catalyst that is used for a wide range of industrial processes.[45] It is micro-porous material that is used to catalyze fast pyrolysis of

lignocellulosic biomass.[33] Protonated ZSM-5 (HZSM-5) has strong acidity and shape selectivity. These properties give HZSM-5 catalyst the potential to catalyze fast pyrolysis.[33] It has been used for more than two decades and was first commercialized in full-scale by Neste Oy refinery in Naantal, Finland.[45] It is both a very thermally and hydrothermally stable zeolite that can be treated to a temperature as high as 1260 K due to its siliceous nature.[45] Pore size of HZSM-5 can be about 0.55 x 0.56 nm atomic radii (0.62x0.63 normal radii).[33,46] The medium size of catalyst is large enough to fit the reactants inside the pores and covert small molecules like glucose into aromatics.[46] Even though the reaction pathway is complex, the main reaction in catalytic process include; cracking, deoxygenation, decarboxylation, cyclization, aromatization, isomerization, alkylation, disproportionation, oligomerization, and polymerization.[21,47] Compared to non-catalytic pyrolysis, there was a reduction of about 25% in the oxygen content when HZSM-5 was used as catalyst. However, the total liquid yield decreased and there was an increase in gas, water and coke yield.[48]

The acidic site in HZSM-5 catalyst plays a key role in cracking of oxygenates in pyrolysis. The reaction is promoted via carbonium ion mechanism. Bronsted acid is more stronger and is preferred than lewis acid.[49] The ratio of Si/Al of the frame work affects the activity of HZSM-5. Aluminum has major contribution to the acidity of silicate-alumina frame work. Hence, the lower the ratio of Si/Al in the catalyst, the higher the acidity.[33]

2.4.3.2 Red Mud

Red mud is an aluminum industry waste material where aluminum oxide (alumina, Al_2O_3) is produced via the Bayer Process.[50] It is a mixture of mostly metal

oxides such as Fe_2O_3, Al_2O_3, SiO_2, CaO, TiO_2 and Na_2O.[28] The type of ore used and the processing technique determine the amount and composition of red mud generated.[50] It has 20-30% m^2/g specific BET surface area. There is an environmental concern due to the caustic nature of red mud since large amounts are produced.[50,51] Therefore it is both economically and environmentally desirable to use red mud in other value-added industrial application.[50,51]

Red mud is found to have catalytic property in various applications.[50] Even though it can be less active than precious metal or hydro-processing commercial catalyst, the fact still remains that it is a waste material, which is important on the industrial scale.[51] Sushil and Batra,[50] in their thorough review about red mud, mentioned some of the previous successful applications of red mud as catalyst in hydrogenation, liquefaction, hydrodechlorination, and exhaust gas clean-up. They also summarized uses of red mud in water treatment, soil and mine site remediation, production of building & structural material, recovery of metals and treatment of gold ore.[50] In hydrodechlorination of tetrachloroethylene, the active phase of red mud is sulfide form is pyrrhotite, a non-stoichiometric sulfide, which is thermodynamically stable at temperature above 200 °C.[51]

Some studies have been conducted of the use of red mud as catalyst in pyrolysis. Although catalytic pyrolysis is helpful to get upgraded product, the cost of catalyst can be a limiting factor in some application and thus it is crucial to search for cheap catalyst like red mud. [28,50–54] Yanik et al.[52] conducted catalytic degradation and dechlorination of poly (vinyl chloride) (PVC) containing polymer mixture in glass reactor at 430 °C. They found red mud to be more efficient in fixation of evolved HCl and reported that it had no effect on cracking polymers.[52] Marco et al.[53] also tested pyrolysis of plastic waste at

temperature of 400-600 °C and heating rate of 15 °C/min in a semi-batch reactor. They compared HZSM-5, red mud and $AlCl_3$ and found that red mud had the highest liquid yield. They claimed that red mud had significant effect as it produced less viscous oil that does not solidify at room temperature in contrast to the one without catalyst.[53]

Further study was conducted by Lopez et al.[54] in a similar reaction arrangement to that of Marco et al.[53] The purpose was for better understanding of the effect of HZSM-5 and red mud on pyrolysis. They concluded that red mud produced lower viscosity oil, higher amount of gases and great aromatic liquid at temperature of 500 °C. At 440 °C, red mud produced similar liquid to that without catalyst and hence it was better at 500 °C. But HZSM-5 was better than red mud in their studies owing to the fact that it had higher porosity and acid strength.[54]

Yathavan and Agblevor[28] have demonstrated fractional catalytic pyrolysis of Pinyon-Juniper in fluidized bed reactor with red mud and HZSM-5.[28] They found that red mud was better in terms of upgrading as it produced a bio-oil with higher pH, lower viscosity and greater HHV. The reaction pathway of both catalysts was concluded to be different. Red mud rejected oxygen as CO_2, hence decarboxylation was the suggested reaction pathway where as in HZM-5, decarbonylation was proposed due to higher production of CO gas.[28] However it was noted that the main reaction pathway of red mud still requires further investigation.[28]

2.5 Bio-oil Applications

Liquid Bio-oil from fast pyrolysis has considerable advantage of being storable and transportable. It can be used as a source of energy and has a potential to supply a number of valuable chemicals.[55] Byproducts like char and gases can be used as sources of

heat supply for pyrolysis. Hence there is no requirement for an additional heat source. Char can also be used in other application such as fertilizer and activated carbon. Except for the flue gas, there is almost no waste stream in the system.[19] Some of the main application of bio-oil will be discussed below.

2.5.1 Combustion in Boilers and Furnaces

Combustion test on bio-oil shows that they can be used in boilers and furnaces to generate heat and power.[55,56] Although there is problem in flame combustion arising from difference in ignition, viscosity, stability, pH and emission levels, but this problem can be solved with time.[56] Red arrow product pyrolysis plant in Wisconsin used bio-oil to generate heat is one of the examples of commercial application.[55] An attractive option of co-firing of bio-oil with coal has been carried out for commercial production of electricity at Manitowoc Public utilities in Wisconsin, USA.[56] Many tasks have been conducted in Finland by VTT energy in collaboration with Oilon Oy (4 MWth) and by Neste Oy. (2 MW). They proved that bio-oil can be used in boilers and furnace at different combinations of fuel oil to bio-oil ratio.[55] BTG have also tried to replace the fossil fuel by using bio-oil for combustion a standard 250 KW in hot water generation unit.[20] However it is still recommended that the bio-oil needs modification to improve its efficiency.[55]

2.5.2 Combustion in Diesel Engine and Turbines

The potential of bio-oil to be used in the production of electricity is more attractive than process heat because of higher added value. If the difficulty in ignition, corrosiveness and coking problem from bio-oil are improved, they can successfully be

used in diesel engines.[55] Bio-oil may not be used directly in diesel engines because of ignition problem; however they could be efficiently used in pilot-ignited medium speed diesel engines by improving injection nozzles and pyrolysis process[57]. Bio-oil burn rapidly once ignited.[57]

With some modifications, there is a good possibility that bio-oil can be used in gas turbines. Orenda Aerospace Corporation actively worked on the application for gas turbines.[58] They selected a 2.5 MWe class GT2500 engine. They used "silo" type combustion chamber that can be easily modified and optimized for any fuel. Upon testing the engine, they found it had less emission of NO_x and SO_2 but there were higher particulates than in diesel fuel.[58] Hence the fouling problem in gas turbine should be solved for future use.

2.5.3 Transport Fuel

Currently bio-oil is not compatible with the existing transport fuel system but with further upgrading it can be used. The high oxygen content can be removed by hydrotreating and catalytic vapor cracking but the processing cost is high.[55] Blending the bio-oil (10-30%) with hydrocarbon fuel via emulsification with the aid of surfactant proved to be successful. However, cost of surfactant and energy for emulsification is a challenge.[59] Therefore intensive research is required to make the bio-oil a more economically attractive transport fuel.[55]

2.5.4 Chemicals from Bio-oil

Bio-oil as a whole has numerous applications. Bio-oil has hundreds of compounds but so far about 40-50% has been identified with the present technology.[56] Bio-oil can

used as resin for the production of particle or plywood boards when it is mixed with conventional urea-formaldehyde. This property is attributed to higher cross-linking of the lignin derived product.[20] In agricultural lands, it can be used as fertilizer and soil conditioner. Dynamotive Technologies Corporation, Canada, mix bio-oil with lime. This mixture is called BioLime^{TM}. This can help to remove sulfur oxide when injected into flue gas tunnel.[56]

Fraction of bio-oil can be used in wide variety of applications. One of the challenges is how to recover the chemicals in the most economical manner. Liquid smoke or wood flavor is one of the commercial application that has been adopted.[20] Some of the important chemicals that can be obtained from bio-oil are phenolic compound, resin (lignin-derived compounds), sugars (e.g. levoglucosan), hydroxyl-acetaldehyde, calcium carboxylates and furfural derivatives.[19,56]

2.5.5 Biorefinery

A concept of bio-refinery that integrates all the application of bio-oil is proposed by Bridgwater[19] and is shown in figure 2.2.

2.6 Challenges of Biomass Pyrolysis

With all the efforts in making bio-oil as an alternative source of energy, there are certain challenges that should be addressed. These obstacles hinder the commercialization of bio-oil.[60] To convert biomass to liquid fuel it takes place in few seconds and this gives advantage over enzyme catalyzed bio-processes, which take hours or days. However, instability, acidity and complexity of the bio-oil make the process

complicated. Trying to upgrade the oil with catalytic hydrogenation requires additional cost and will make it less competitive compared to the conventional fuels.[18–20,22,33,60]

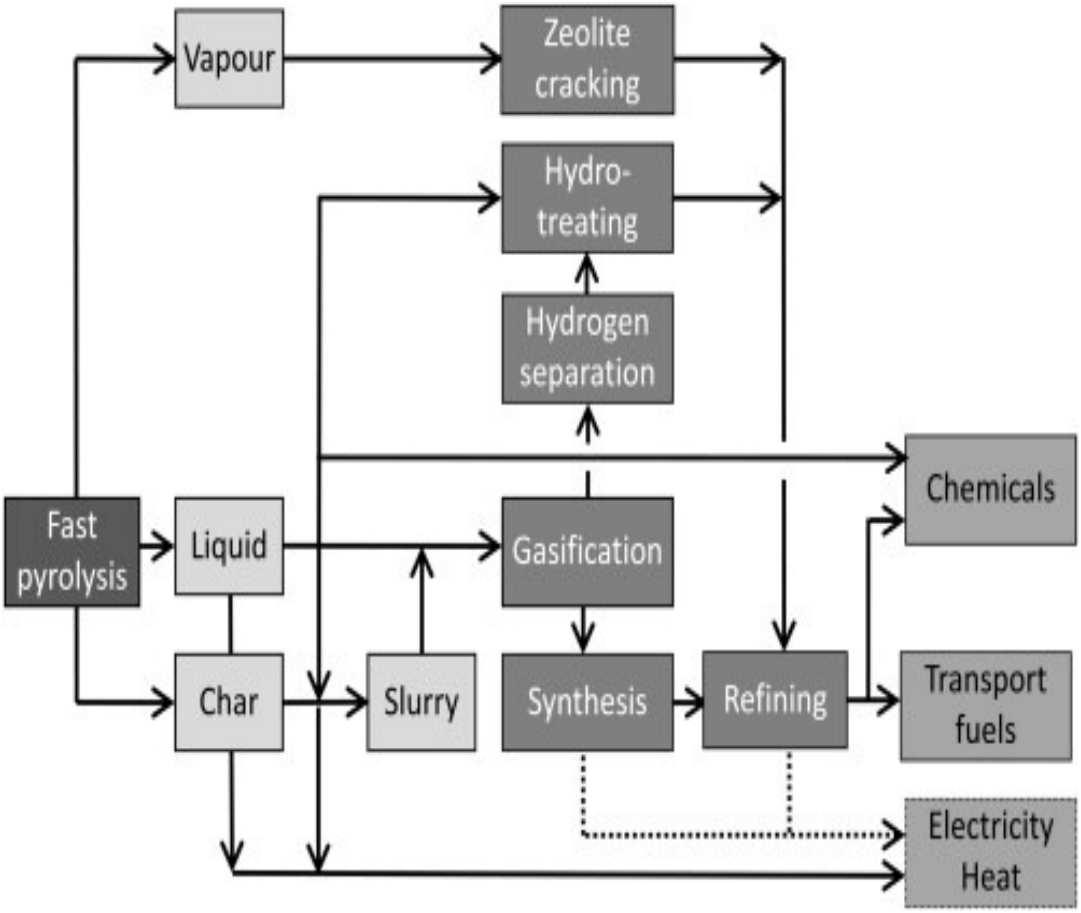

Figure 2.2 Fast pyrolysis based Biorefinery (Adopted from Bridgwater, 2012)[19]

Even though a number of studies have been conducted on pyrolysis of biomass, it still lacks comprehensive understanding of the chemistry and reaction transport model. One of the complexities is the multi-scale nature of biomass.[60] The length of lignocelluloses biomass varies from 10^{-10} to 10^{1} m. This results in variation in degradation and hence challenges in predicting the properties and product distribution.[60] The second complexity is the multiphase nature of pyrolysis. When biomass is heated, it

decomposes into volatile product through intermediate liquid.[61,62] Therefore, it is necessary to know the chemical process occurring within the intermediate liquid in order to understand the potential (elementary) reaction of the functional groups (e.g. many O-H groups). Investigating the process at molecular level with modern technique could reveal the chemistry.[60]

Aerosols ejected from liquid intermediates are analyzed using sily-methylation and Gas Chromatography/Mass Spectrometry (GC/MS).[63] It was found that monomers, dimmers and oligomers exist with similar linkage to parent material (ß-1, 4). This explains that the product is not formed from repolymerization. Simulation of macro-molecules can help predict the chemistry but so far little work has been done.[60,63]

The starting point in modeling could be to understand the formation of products from cellulose which are formed from depolymerization and dehydration reactions.[64] Cellulose contains anhydyrosugars (up to 65%), pyrans (up to 10%) and furans (up to 15%).[60] Studies suggest that transglycosylation or hetrocyclic cleavage results in the formation of levoglucosan but requires confirmation through experiment or computation.[64,65] Natural (inorganic) catalysts in the form ions such as Mg^{2+} and Ca^{2+} exist within the intermediate liquid and change pyrolysis chemistry because they are converted to ash, which is believed to have catalytic effect. They may result in either undesirable cleavage of C-C bond or may play a role in deoxygenation. It is a challenge to examine whether they have desirable or undesirable effects on product distribution.[66]

The formation of char is also another challenge. The three basic mechanisms are repolymerization of gas phase volatile product, polymerization of condensed species and dehydration of polymers.[60] The former mostly takes place in fast pyrolysis. It has been

reported that Aldol-condensation could be one of the mechanisms. This needs further investigation as it could help to know the chemistry of char formation.[60]

Aerosols formation and their effect on bio-oil properties need to be well understood. Previously, it was considered that they are formed by nucleation or condensation of vapors but it was later proposed that aerosols can be formed by thermo-mechanical ejection due to explosive destruction of the biomass.[60,67] Reactive Boiling Ejection (RBE) could be one of the mechanisms that aerosols are produced from intermediate liquids. This idea still remains questionable. Hence, further study is needed to elucidate the process by which aerosols escape the microstructure of biomass.[68] Evaluation of fast pyrolysis based on product yield such as bio-oil, char and gases do not give a good insight about mechanism of the process. In-situ measurement of composition and temperature coupled with thin film pyrolysis and high speed photography could have substantial contribution in providing in-depth understanding of the system.[60,68]

2.7 Norms and Standards

Commercialization of bio-oils requires setting specifications in order to standardize the bio-oil quality. The methodology should be similar to that of the conventional fuels so that it will be easier to compare and contrast with the bio-fuel.[69] Bio-oils have different physical property and chemical composition compared to petroleum-based fuels. Therefore, it is challenging to set up appropriate specifications and standard methods suitable for bio-oil analysis for commercializing them as standard fuel.[69]

The following methods are recommended in determining composition and property of bio-oil:[30,69]

i. Water and Solids (wt %): Karl-Fischer titration is used for water content determination (ASTM E 203). For solid content insoluble's in methanol-dichloromethane solvent.
ii. Kinematic Viscosity (cSt): ASTM D 445 at 40 ^{o}C is used.
iii. CHN (wt %): ASTM D 5291 is used and requires proper homogenization of sample.
iv. Acidity: Total Acid Number (TAN) gives precise value though pH meter can be used.
v. Flash Point: ASTM D 93 is used. The purpose of using this method is not similar to mineral oils (i.e. for ignition) as the water extinguishes the flame. It is mainly used for storage and handling classification.
vi. Pour point: Determined according to ASTM D 97 & used to find the lowest temperature of pumping.

Feedstock should not have high moisture content. It should not exceed 10%, because increase in moisture content results in multiphase liquid product.[19,66,69] Fast Sartorius MA 45 moisture analyzer and Denver Instrument IR-60 are some of the equipments used.[21,30,69] Standardization of fast pyrolysis bio-oil is under development in ASTM. The specification for bio-fuels for burner application is presented in the table 1. Standardization of turbine and diesel fast pyrolysis fuel is under evaluation.[69]

Table 2.1. Expected parameters for pyrolysis liquid fuel in ASTM burner fuel standard [69]

Property	Test method	Specification	Units
Gross Heat of combustion	D240	15 min	MJ/kg
Water content	E203	30 max	mass %
Pyrolysis solids content	Annex A1	2.5 max	mass %
Kinematic viscosity at 408C	D445	125 max	mm^2/s
Density at 20 ^oC	D4052	1.1–1.3	kg/dm^3
Sulfur content	D4294	0.05 max	mass %
Ash content	D482	0.25 max	mass %
pH	E70-07	Report	-
Flash point	D93 Procedure B	45 min	^oC
Pour point	D97	-9 max	^oC

2.8 Conclusion

Bio-oils from fast pyrolysis have potential to be used as alternate source of energy. They can be used for process heat, electricity and transportation fuel. High value chemicals can also be produced from them.[18–20,22,33] Nevertheless, to commercialize bio-oils, there are several challenges that require intensive research to understand the underlying phenomenon such as reaction pathways and heat transfer. If these issues are addressed, models can be developed to describe the chemistry which will lead to

advanced predictability of the bio-oil that will be produced.[60] Furthermore for bio-oil to be accepted and used as conventional fuels; there should be certain standards on specification and real safety classification.[30,69] In order to achieve the ultimate goal of commercialization, scaling-up bio-fuel infrastructure is also another challenge.[70] Feedstock cultivation, harvesting, processing and transportation systems on the basis of economic, environmental and community goals are important factors that need to be considered for successful commercialization of fast pyrolysis.[19,70]

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CHAPTER 3

CHARACTERIZATION, THERMOGRAVIMETRIC AND KINETIC STUDY OF WHOLE PENNYCRESS BIOMASS

3.1. Abstract

To satisfy the energy demand of modern society and prevent environmental pollution arising from the use of exiting fossil fuels, an alternate source of energy is required. Biomass has the potential to provide a renewable energy source that is inexpensive and environmentally friendly. Field pennycress (*Thlaspi arvense* L.), previously considered as a weed, is now found to be an ideal source of bio-fuel. Thermogravimetric and kinetic studies are important to understand the thermal degradation process, and provide information for designing a pyrolysis process. The goal of this research is to characterize field pennycress and to conduct thermogravimetric and kinetic study of this biomass. Field pennycress biomass was found to decompose between 200 and 450 ^{o}C. Apparent activation energy ranged from 150.19 KJ/mol to 403.89 KJ/mol and pre-exponential factor was between 2.62 x 10^{10} and 1.44 x 10^{29} s^{-1}. Char yields, fixed carbon, and volatile matter content were found to be 24.71 wt %, 12.13 wt %, and 71.11 wt %, respectively. The amount of hexane, ethanol and water extractives present in pennycress were 10.31 wt %, 13.29 wt % and 13.06 wt % on dry weight basis, respectively. The Higher Heating Value (HHV) for pennycress biomass was 19.64 MJ/Kg, as received (22.27 MJ/kg on moisture and ash free-basis).

3.2 Introduction

The increase in the world population and increase in energy consumption with the associated pollution calls for the development of alternative energy resources to meet societal demand.[1] The existing fossil energy resources are limited, non-renewable, and are not geographically uniformly distributed.[2] Furthermore, there is environmental concern over fossil fuel usage due to the emission of about two-thirds of global anthropogenic carbon dioxide, that is a major contributor of global warming.[2–4] Biomass has a potential to provide renewable energy that is environmentally friendly.[1–3] Thermochemical, biological and physical treatment processes can be used for the production of bio-fuel from biomass. The thermochemical process includes combustion, gasification and pyrolysis.[3] The subject of interest in this research is fast pyrolysis. In the past three decades, fast pyrolysis has attracted the attention of many researchers as one of the promising technologies for satisfying the energy demand and in reducing greenhouse gas emission.[1–5]

Fast pyrolysis is a process that converts organic matter such as biomass into liquid fuel by thermochemical degradation in the absence of oxygen. During the process, biomass is rapidly heated at moderate temperature of around 500 ºC (may range from 400-600 ºC) and a short vapor residence time of 1-5 s.[1,4,5] Rapid heating of biomass followed by rapid quenching of the vapors produce the intermediate pyrolysis liquid product.[5] Bio-oil from fast pyrolysis is an easily storable and transportable form of energy compared to solid biomass and has a potential to be a source of valuable chemicals.[5] The byproducts, bio-char and gases, can be used as a source of heat in the

system or can be used for other applications. Hence, there is almost no waste generated during fast pyrolysis of biomass.[4,5]

To satisfy the energy demand of modern society, there has been a search for different types of biomass that can be used as feedstock for bio-energy production. The use of edible feedstocks as an energy source has raised controversial issues.[6] The high price of the feedstock, availability of farmlands and also the increasing demand in food production for human consumption are some of the issues associated with them.[2] Field pennycress (*Thlaspi arvense* L.) is a member the mustard family and it was previously considered by many as a weed. But now, this plant has been found to be one of the ideal sources of bio-fuel.[6,7]

Some of the reasons that make field pennycress an attractive target are: its minimal agricultural input (such as fertilizer, pesticide, and water), low cost, production in off-season, definable growth seasons and compatibility with the existing farmlands.[6,7] Oil extracted from the pennycress seed was tested for bio-diesel production and it met the requirement of the ASTM standard.[6] Fast pyrolysis of field pennycress oilseed, defatted seed cake, and regular seed presscake produced a bio-oil that had high carbon content, low oxygen and high energy content.[8]

As with all forms of biomass, field pennycress is composed of cellulose (a polymer of glucosan), hemicellulose (which is also called polyose), lignin, extractives and inorganic minerals.[4] The content of each component varies with the type of biomass.[4] Cellulose is a linear polymer of ß-1, 4-glycoside linkage, which form the framework of biomass cell walls and support a plant's vertical growth.[4,9] Cellulose is the most abundant organic polymer and constitutes approximately 40- 50% of dry wood.[4] Cellulose is

composed of long chains of thousands of glucose molecules (approximately 5,000-10,000) that are bonded to each other by a long network of hydrogen bonds.[4,9] Cellulose has a mostly crystalline structure with each molecule tightly bound to its neighbor. This makes cellulose to possess a high stiffness. Hence, cellulose molecules are not easily dissolved by common solvents.[4,9] Cellulose can be hydrolyzed to glucose with acid or enzyme but it is insoluble in normal aqueous solutions.[4,10] Thermal degradation of cellulose results in the formation of anhydrocellulose and levoglucosan and it takes place at a temperature range of 315-400 ºC.[4,11,12]

Hemicellulose is a heterogeneous mixture formed by copolymers of monosaccharides such as glucose, galactose, mannose, xylose, arabinose, 4-*O*-methyl glucuronic acid as well as galacturonic acid residues. Hemicellulose is structurally amorphous and branched, and has approximately 150 repeating saccharide monomers.[4,11] Hemicellulose usually accounts for 12-40% of biomass.[10] For instance, sisal, softwood, hardwood and orchard grass have 13%, 28%, 38%, and 40% hemicellulose content, respectively.[10] Unlike cellulose, hemicellulose can be hydrolyzed by a dilute acid or base (such as sodium hydroxide).[12] Hemicellulose decomposes at 220-315 ºC. A maximum weight loss at around 260 ºC was obtained for xylan, which is the most abundant polymer in hardwood.[4,12] During degradation, deacetylation of hemicellulose results in the formation of acetic acid.[4]

Lignin is a complex three-dimensional highly branched polymer of sinapyl, coniferyl and *p*-coumaryl alcohols (phenol propane units).[10,13] The polymer of the propyl-phenol group is bound together by an ether and carbon-carbon linkage.[11] Lignin has no known repeating unit and it is heavily cross-linked.[10,12] It is the main binder for the

agglomeration of fibrous cellulosic components. Lignin has resistance to microbial or fungal destruction and protects cellulosic fibers.[4,12] Lignin is the third major component of biomass and is about 4-35% of lignocellulosic biomass.[4,10]

Lignin is amorphous and possess a number of interlinkages and has high thermal stability.[4,12] Lignin decomposes over a wide temperature range compared to cellulose and hemicellulose which rapidly degrade over a narrow temperature range. The decomposition of lignin starts around 180 ºC and extends to more than 500 ºC.[14–17] Lignin degradation can yield phenols by cleavage of ethers and carbon-carbon linkages.[4] Although decomposition of lignin and hemicellulose starts at lower temperature, the conversion is slow and steady, especially lignin.[17] They are difficult to decompose and mostly yield higher amount of gas, tar, and char whereas cellulose is mostly converted to liquid bio-oil during fast pyrolysis. This is due to the fact the covalent bond found in lignin and hemicellulose is more difficult to decompose than the hydrogen bond that link cellulose and hemicellulose.[17] Lignin and hemicellulose contribute to about 40% and 20% of the char yield of the original sample, respectively.[17]

Organic extractives and inorganic minerals are also components of biomass.[1,4,10–17] Inorganic materials such alkali metals are present in plants for the purpose of nutrient transfer and growth.[5] Different forms of inorganic materials are believed to have catalytic effect on decomposition of the lignocellulosic component in fast pyrolysis.[5,17] This results in the formation of more gases and char.[11,17] Inorganic materials (ash) composition in biomass ranges from less than 1% in softwoods to as high as 15% in herbaceous and agricultural residues.[17,18]

Organic extractives are components of biomass in the form of fats, waxes, proteins, simple sugars, alkaloids, phenolics, pectins, mucilages, gums, resins, terpenes, glycosides, saponins, and essential oils.[4,10] The presence of extractive oil can result in phase separation in bio-oils because bio-oils are mostly immiscible with oils due their polar nature. Proteins in biomass result in an unpleasant and distinct odor of bio-oil due to the presence of a high amount of nitrogen.[17,19] Extractives can be extracted from biomass by either a polar solvent (such as water, methylene chloride or alcohols) or a non-polar solvent (such as hexane or toluene). The uses of extractives in biomass are: as an energy carrier, as intermediates in metabolism and as a defense against microbial and insect attack.[4] Oasmaa et al.[19] reported that the presence of high percent of extractives in forestry residue containing bark and needles result in the reduction of liquid yield from 70-75 wt % to 60-65 wt %. Soft and hardwood may have 1-5% extractives. The presence of bark and needle may increase the extractives content to 4-5 times and 7-8 times, respectively.[19]

Characterization, thermogravimetric and kinetic studies of biomass are important in fast pyrolysis in order to have a better understanding of the process. Biomass characterization such as elemental analysis, higher heating value, ash content, moisture content and extractives content give a good idea about the source of input (solid fuel biomass) and helps to predict the output that can be obtained during fast pyrolysis. Thermogravimetric and kinetic studies are used to investigate the pyrolysis temperature range, degradation characteristics and provide information for designing a pyrolysis process in optimizing the system.[2,4,12,15–17] Therefore the objective of this chapter is to

report data from characterization, thermogravimetric and kinetic analysis of whole pennycress biomass.

3.3 Materials and Methods

3.3.1 Feedstock Preparation

Field pennycress (*Thlaspi arvense* L.) was supplied by Western Illinois University, . The biomass was first air dried by uniformly spreading it on the ground. During drying, the biomass was turned almost every day to ensure uniform drying. The drying process continued for 4 days until the weight change of the biomass in 24 hours was less than 1%, according to ASTM E1757-01.[20] After that the entire biomass, that includes the stem, leaves and seed, was ground using Thomas Model 4 Wiley® mill (Thomas Scientific, Swedesboro, NJ) until all the biomass passed through 1-mm sieve.

3.3.2 Moisture and Ash Content

The moisture content of field pennycress was determined by using infrared moisture analyzer, Denver Instrument IR-60 (Denver Instruments, Bohemia, NY). About 1 g of biomass was spread in a thin even layer in an aluminum pan and was heated at 105 ºC. This was done three times and the average of the three values was recorded as moisture content. The ash content of field pennycress was obtained by following the ASTM E1755-01 standard method.[20] The first step was to properly wash the crucibles with detergent and then drying them in Lindberg Blue M™ LGO oven (Thermo Scientific, Asheville, NC). Three crucibles were first heated to 575 ºC for 3 h. After cooling the crucibles in desiccators to room temperature for approximately 30 minutes,

the weight of each crucible was measured to nearest 0.1 mg. Then the crucibles were reheated for 1 h until the mass of crucibles varied by not more than 0.3 mg.

Approximately 1 g of pennycress feedstock was placed in the 3 crucibles for ash content analysis and was first heated to 250 ºC for 30 minutes to avoid flaming. The temperature was then increased to 575 ºC for 3 h. The weight of the 3 crucibles was recorded to the nearest 0.1 mg after cooling them in desiccators for ~30 minutes. A similar procedure for getting constant weight of the crucibles was then conducted. But the difference in weight of ash produced after heating for 1 h was much more than 0.3 mg. For such cases, ASTM E1755-01 standard method (95% ethanol) recommends to heat the biomass at 575 ºC overnight. After heating the biomass overnight, the stable weigh of the ash produced was finally recorded. The ash content was then determined as follows:

$$\% \, Ash = \frac{(M_{ash} - M_{cont})}{(M_{od} - M_{cont})} \qquad (eq. 3.1)$$

where: % Ash = Mass percent of ash

M_{ash} = Mass of ash and container (crucible), g

M_{cont} = Tare mass of container, g, and

M_{od} = Initial mass of 105 ºC dried sample and container, g.

3.3.3 Extractives

A series of three extraction processes was conducted according to ASTM E1690-08 standard method[20]. First, hexane was used as solvent for extraction, followed by 190-Proof ethanol (and finally de-ionized water. Three Soxhlet extraction thimbles were dried

in oven at 105 ºC over night. After cooling to room temperature in desiccators, the weight of the thimbles was measured. Field pennycress sample was then added to the thimbles. The amount used in each extraction was 17 g, 12 g, and 7 g for hexane, ethanol and de-ionized water extraction, respectively. The same biomass was used in all the three extraction process. Five boiling chips were added to each of the three 500 ml flask and the weight of each flask with chips was determined. About 300 ml of solvent was poured into 3 round bottom flask. After that, 3 soxhlet apparatus were assembled and the thimbles were inserted inside them. The reflux rate was adjusted in such a way that provides four to five solvent exchange rates per hour. The extraction was conducted for about four hours and the 3 samples were transferred to 3 Buchner funnels to remove the residual solvents by vacuum filtration.

The solvent collected in the receiving flask and the one collected by vacuum filtration from each flask was placed on rotary evaporator one by one, at water bath temperature of 45±5 mºC and a using a suitable vacuum pressure. After this procedure, the flask was placed in vacuum oven (75 to 100 torr, which was measured using a pressure gauge) at 40±1 ºC for 24 hr in order to remove all the visible solvents. The flask was then removed and cooled to room temperature in desiccators. Finally the weight of flask was measured. For water extractives, it was difficult to remove the water from the extractives. Hence the amount of water extractives was determined based on the difference in mass of biomass before and after extraction. The percentage of hexane and ethanol extractives was calculated by using the following formula:

$$\%\ of\ Extractvies = \frac{(W_{ef} - W_f)}{(W_s)} \qquad (eq.3.2)$$

where: W_{ef} = Weight of extractives, flask and boiling stones, g

W_f = Weight of flask with boiling stones, g

W_s = Weight of moisture free solid in prepared sample

3.3.4 Elemental Analysis and Higher Heating Value (HHV)

The instrument used for determining the elemental composition of field pennycress was Flash 2000 Organic Elemental Analyzer (Thermo Scientific, Waltham, MA). The elements analyzed were carbon, hydrogen, nitrogen, sulfur, and oxygen content. About 3 mg of sample was used and the analysis was done in triplicate.

The higher heating value (HHV) of the feedstock was obtained using IKA® C2000 Basic Calorimeter (IKA Work Inc., Wilmington, NC). Approximately 0.5 g of sample was used for analysis. To account for the extraneous energy such as the acid that can be produced during combustion, from the sulfur and nitrogen in the biomass, 5 ml of water was added to the decomposition vessel in order to determine the acid produced quantitatively. After combustion, the pennycress biomass with oxygen, the water added was collected and the decomposition vessel was rinsed thoroughly with distilled water. After this action, the acid content was examined by titrating the water solution with sodium carbonate using methyl orange as indicator during titration. The HHV value was then corrected by putting the titer value of sodium carbonate used in titration.

3.3.5 Volatile Matter, Fixed Carbon and Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out using TGA Q500 (TA Instruments, Newcastle, DE). The mass of the prepared field pennycress biomass (<1

mm) used for the analysis was in the range of 17-19 mg. The experiment was conducted at heating rates of 5, 10, 15, and 20 ºC/min from temperatures of 20 ºC to 700 ºC. Nitrogen was used as a carrier gas at a flow rate of 40 ml/min. The data obtained from the TGA was used to estimate the volatile matter, char and fixed carbon content as well as conduct kinetic study. The formulae used for determining the volatile matter and fixed carbon content are:

$$Weight\ loss, wt.\% = A = \frac{(W_i - W_f)}{(W_i)} x\ 100 \qquad (eq. 3.3)$$

where: W_i = Initial weight, g, at 20 ºC

W_f = Final weigh, g, at 700 ºC

Volatile matter content was then determined according to equation 3.4 written below.

Volatile matter (VM), wt %) = A - BM (eq. 3.4)

where: A = Weight loss, wt %, and

BM = Biomass Moisture content of biomass, wt%

Fixed carbon content in field pennycress biomass was calculated after determining the volatile matter, ash and moisture content by using the equation below.

Fixed Carbon (FC), wt % = 100 - (VM + ASH + BM) (eq. 3.5)

where: VM = Volatile matter, wt %

ASH = Ash content, wt % (dry feed basis)

BM = Biomass moisture content, wt %

3.4 Results and Discussion

3.4.1 Characterization of Field Pennycress

The proximate and ultimate analyses of field pennycress are shown in Table 3.1. The results show that field pennycress is a carbon and oxygen element rich material containing a low hydrogen percentage and a high amount of nitrogen. The molar ratio of H/C, O/C, and N/C is 1.65, 0.67, and 0.05, respectively. Therefore, the empirical formula is $CH_{1.65}O_{0.56}N_{0.05}$. The source of nitrogen in field pennycress could be from chlorophyll in the leaves and the proteins present in the oilseed of the biomass. In this study, the entire biomass including the leaves, oilseeds, and the stems was used. Selling et al.[21] reported that pennycress press-cake has 25.8% crude protein when extracted with 0.5 M sodium chloride at 5 ºC. The purity of the crude protein was about 83%. Therefore, the proteins present in the biomass are one possible source of nitrogen in the biomass.

The ash content of field pennycress was 7.11 wt % (dry feed basis). The lowest ash content is found in softwood, which is < 1 wt %, whereas herbaceous biomass can posses up to 15 wt % ash cotent.[18] Boateng et al.[8] reported that the ash content of pennycress seed and defatted press-cake were 6.02 wt % and 12.08 wt %, respectively. Herbaceous plants like milkweed had an ash content as high as 11.20 wt %.[22] The ash content of field pennycress is in the middle range specified for softwoods and herbaceous plants.

Table 3.1 Composition and calorific value of field pennycress feedstock

Component	Whole Pennycress feedstock
Ultimate and HHV Analysis	
Carbon (wt %)	47.92±0.39
Hydrogen (wt %)	6.58±0.16
Oxygen (wt %)	35.51±0.65
Nitrogen (wt %)	2.88±0.18
HHV (MJ/kg)	19.64 (22.27)[a]
Proximate Analysis	
Ash (wt %)	7.11±0.18
Moisture (wt %)	4.70±0.12
Volatile Matter (wt %)	71.11
Fixed Carbon (wt %)	17.08

[a] moisture and ash free value is in parenthesis.

The higher heating value (HHV) of the feedstock as received was 19.64 MJ/kg (22.27 MJ/kg on moisture and ash free-basis). HHV is one of the major quality indexes for any biomass that is considered as fuel source. The HHV of field pennycress shows that it has the potential to be converted to a more energy rich bio-oil with a further densification process like fast pyrolysis. Boateng et al.[8] observed that the lipid content in pennycress seed had an effect in the HHV value. The HHV value were 21.1 MJ/kg and 27.6 MJ/kg (dry and ash free basis) in defatted press-cake and pennycress seed,

respectively. The reason they attributed for this trend was due to the lipids present in the pennycress seed. Hence, due to the presence of oilseed, the HHV in the whole field pennycress is comparatively higher than that of other feedstocks, for example 16.67 MJ/kg for milkweed.[22]

Field pennycress has a high volatile matter (VM) and a low fixed carbon (FC) content of 71.11 wt % and 17.08 wt %, respectively. Determining these parameters is important because it is helpful in evaluating of the product yield in a process such as fast pyrolysis. Moreover, several studies had also tried to develop numerous correlations by using VM, FC and ash content to estimate the HHV, elemental composition and the percent of major components (cellulose, hemicellulose and lignin).[2,12,23] Cordero et al.[23] had derived an equation from multiple linear regressions for estimating the HHV. The two equations they used were:

$$\text{HHV (MJ/kg, dry basis)} = 354.3FC + 170.8VM \qquad \text{(eq. 3.5)}$$

$$\text{HHV (MJ/kg, dry basis)} = 35{,}430 - 183.5VM - 354.3ASH \qquad \text{(eq. 3.6)}$$

Equation 3.6 accounts for the diluting effect of ash on lowering the HHV. Both equation 3.5 and 3.6 were tried to check the applicability of the formula in estimating the HHV of field pennycress obtained from instrumental analysis. The HHV of field pennycress was found to be 18.20 MJ/kg and 19.86 MJ/kg by using eq. 3.5 and 3.6, respectively. The HHV for field pennycress on dry basis was 20.61 MJ/kg (19.64 MJ/kg as received). The deviation from experimental value for eq. 3.5 is negative 11.70 % whereas for eq. 3.6 it is negative 3.62%. Hence equation 3.6 was found to be a better formula for estimating HHV of field pennycress on a dry basis. Determining analytical

parameters require more sophisticated and expensive instruments. Therefore, if the formula derived from linear regression is applicable for a wide variety of biomass, this could save considerable amount of money, time and energy that is wasted in using the sophisticated instruments that require a highly skilled personnel, high capital and operating cost.

The amount of hexane, ethanol and water extractives present in pennycress are 10.31 wt %, 13.29 wt % and 13.06 wt % on dry weight basis, respectively. Hexane extractives include fatty acids and other non-polar extractives.[17,19,24] Field pennycress has an oilseed that contains up to 36 wt % oil, which is rich in triacylglycerol and also contains 27 % crude protein.[25,26] Moser et al.[27] conducted hexane extraction on dried field pennycress seed that had 29 wt % oil content. They found that the primary fatty acid were erucic acid (32.8 wt %), linoleic (22.4 wt %), linolenic (11.8 wt %), oleic acid (11.1 wt %), gondoic acid (8.6 wt %) and nervonic acid (2.9 wt %).

Rukavina et al.[28] obtained a biomass and seed yield of 1,316.9 and 350.7 kg/ha, respectively when the land was not treated with any nitrogen. Therefore the harvest index, which is defined as percent of seed yield to biomass ratio, for field pennycress is about 26.6%. If we consider the oil yield of the seed to be 36 wt %, which is around the maximum, the oil yield from whole pennycress biomass will be ~9.59 wt %. Since in this study the whole pennycress plant was used, the 10.31 wt % hexane extractives obtained is in agreement with the expected oil yield from the biomass.

Ethanol and water extractives in field pennycress are 13.29 and 13.06 wt %, respectively. Ethanol soluble materials that could be present in field pennycress include chlorophyll and other non-structural components such as tannins and resins.[20,29] Hojilla-

Evangelista et al.[26] reported that the proteins present in pennycress seed are not soluble in ethanol. Water extractives in field pennycress can be inorganic materials, non-structural sugars and proteins.[29] About 22.5 % of protein in the cold-processed cakes was found to be water soluble, according to studies by Hojilla-Evangelista et al.[26]

3.4.2 Thermogravimetric and Differential Thermogravimetric Analysis

The slow pyrolysis thermogravimetric (TG) characteristics of field pennycress in weight percent is shown in Figure 3.1. Thermogravimetric analysis (TGA) was conducted at heating rates of 5, 10, 15, and 20 ºC/min. There was a similar trend of weight loss in all of the four heating rates and the degree of degradation increased with increase in heating rate. From Figure 3.1, it can be seen that the weight loss appeared to be constant at 700 ºC, which is the final temperature. Therefore, the char yield can be estimated the pyrolysis residue. The summary of the weight change at different heating rates is presented in Table 3.2.

Table 3.2 Char yield at final temperature of 700 ºC from TGA weight loss curve

Heating Rate (^oC/min)	Initial Temp. (^oC)	Initial Weight (mg)	Final Temp. (^oC)	Final Weight (mg)	Weight % at Final Temp.
5	20.42	19.38	700	4.69	24.19
10	24.17	17.52	700	4.32	24.69
5	25.5	17.13	700	4.29	25.05
20	22.67	19.02	700	4.74	24.94
				Average Char Yield, wt %	**24.71±0.38**

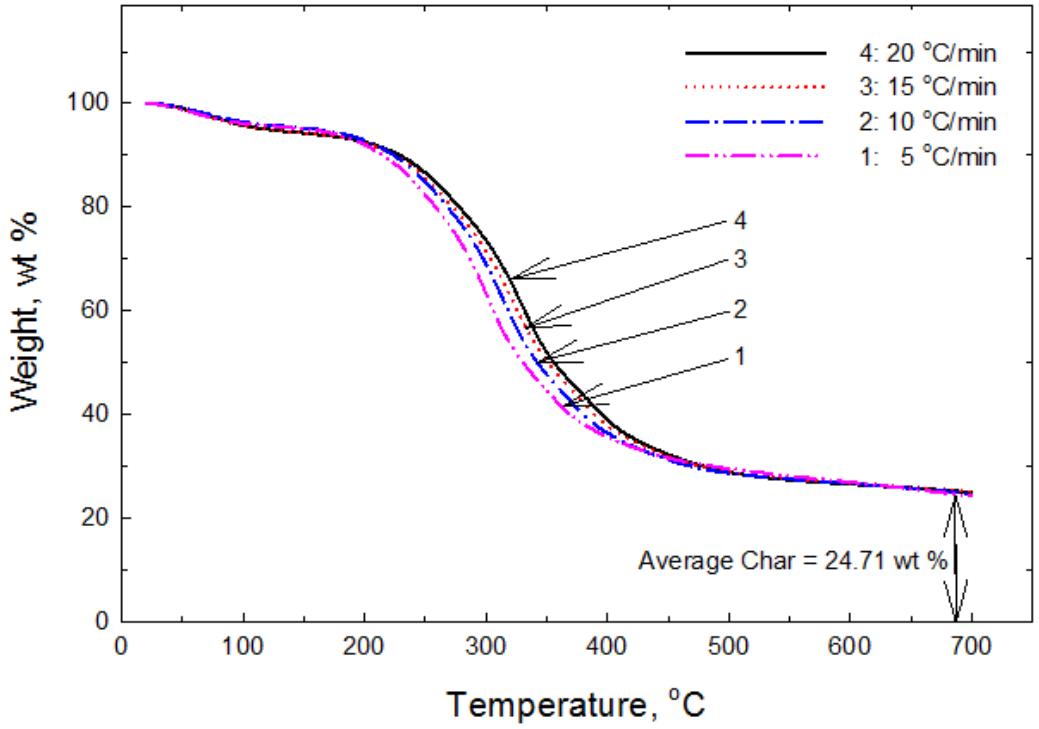

Figure 3.1.Weight loss curves of Field Pennycress at heating rates of 5, 10, 15, and 20 ºC/min

The average char yield for field pennycress was found to be 24.71. The reason for high char content could be due to higher ash content (7.11 wt %) of the pennycress compared to woody biomass. Pennycress press-cake, which is 26.6 wt % oilseed, was found to have a high char yield upon pyrolysis (~35 wt %).[8] Therefore the high char yield can be associated with the combined contribution of the press-cake and the lignocellulosic biomass.

Boateng et al.[8] reported, the char yields of 17.4, 34.2, and 35.1 wt % for the seed, defatted press-cake and press-cake, respectively. Kim and Agblevor[22] also reported that the char yield for milkweed was as high as 24.96 wt % because the biomass had a high inorganic yield (11.2-11.7 wt %). However, char yield as low as 12.6 wt % was obtained

on fractional catalytic pyrolysis of popular wood that had 0.94 % ash content.[30] Raveendran et al.[31] studied the effect of ash on product yield of 12 different types of biomass and found that the demineralization of biomass samples reduced the char yield compared to the one that had inorganic minerals. Ash is believed to have a catalytic effect on the repolymerization reaction and leads to an increase in char yield.[17]

Lignin has also significant contribution on char yield.[17] A recent study on catalytic pyrolysis of Pinion-Juniper showed that the presence of bark, which had high lignin and ash content had negative effect on the product yield and resulted in a high char yield of 22.49 wt %.[32] Therefore, the presence of high ash and lignin contents have an effect on high char yield. Though the effect of ash requires further investigation,[17] from what is reported in previous research, it is plausible to say that ash content could have a role in the high char yield of the pennycress.

Figure 3.2 shows the TGA and differential thermogravimetric (DTG) of field pennycress that are compiled together for all heating rates. Biomass conversion, X, is defined as: [2,22]

$$X = \frac{(W_o - W)}{(W_o - W_\infty)} \qquad (eq. 3.7)$$

where: W_o = The initial mass of the sample at room temperature, mg

W = Mass of pyrolyzed sample, mg

W_∞ = Mass of pyrolyzed sample, mg

In the TGA curve, conversion (X), is plotted versus temperature. At all the heating rates (5-20 ^oC/min), initially, there was a loss of moisture starting at about 45-50

^{o}C. The phenomenon continued up to ~120-130 ^{o}C. Drying of biomass at temperature above 100 ^{o}C occurs due to loss of water bound by surface tension in the capillaries of the ground particles of the feedstock.[33] During the entire pyrolysis process, there was a high amount of weight loss until ~450 ^{o}C and from than onwards the decomposition became very slow or almost constant. Therefore, it can be inferred that the major weight loss of field pennycress took place between 200 and 450 ^{o}C.

The nature of the TGA curve in combination with DTG peaks gives a clear indication of the number of stages associated with thermal degradation. The weight loss due to the volatiles (including moisture) from field pennycress had four different stages. As mentioned earlier, the first peak at temperatures less than 200 ^{o}C is due to the volatilization of moisture in the feedstock.[16,22,33] The second shoulder at a temperature range of 200-260 ^{o}C for heating rate of 5 ^{o}C/min (may extend up to 280 ^{o}C for 20 ^{o}C/min) is attributed to the decomposition of hemicellulose. There was a similar observation by Kim and Agblevor[22] for hemicellulose degradation at a temperature range of 220-280 ^{o}C. The difference in the total degradation at the four heating rates (5-20 ^{o}C/min) is due to the difference in thermal energy and residence time of the vapors. Thus, with an increase in heating rate, there is a higher rate of volatilization because of high level of heat transfer to the biomass and shorter residence time of vapors.[33,34]

The pyrolysis of cellulose followed after hemicellulose degradation. In the DTG curve, there was a clear peak at 300 ^{o}C and 323 ^{o}C for 5 ^{o}C/min and 20 ^{o}C/min heating rates, respectively. A degradation temperature range of 240-350 ^{o}C was reported for cellulose[4] which is in agreement with what was obtained in the current study. The peak after the one from cellulose was attributed to the decomposition of oilseeds in the

feedstock. As it has been discussed in extraction result, the whole pennycress biomass had about 10.31 wt % hexane extractives which are mostly lipids .[26] The oil present in the oilseed is rich in triglycerides. The oilseed also has considerable amounts of proteins.[25,26].Studies report that the decomposition temperature of triglycerides and proteins could take place in the range of 320 to 450 ^{o}C and 405 to 415 ^{o}C, respectively.[16,35,36] This finding could be a possible answer for the degradation profile observed in this study. Lignin degrades in a broad temperature range. Its decomposition starts at about 180 ^{o}C and extends to more than 500 ^{o}C.[14–17,22,33] The long tail at the end of the DTG is therefore attributed to the degradation of lignin.

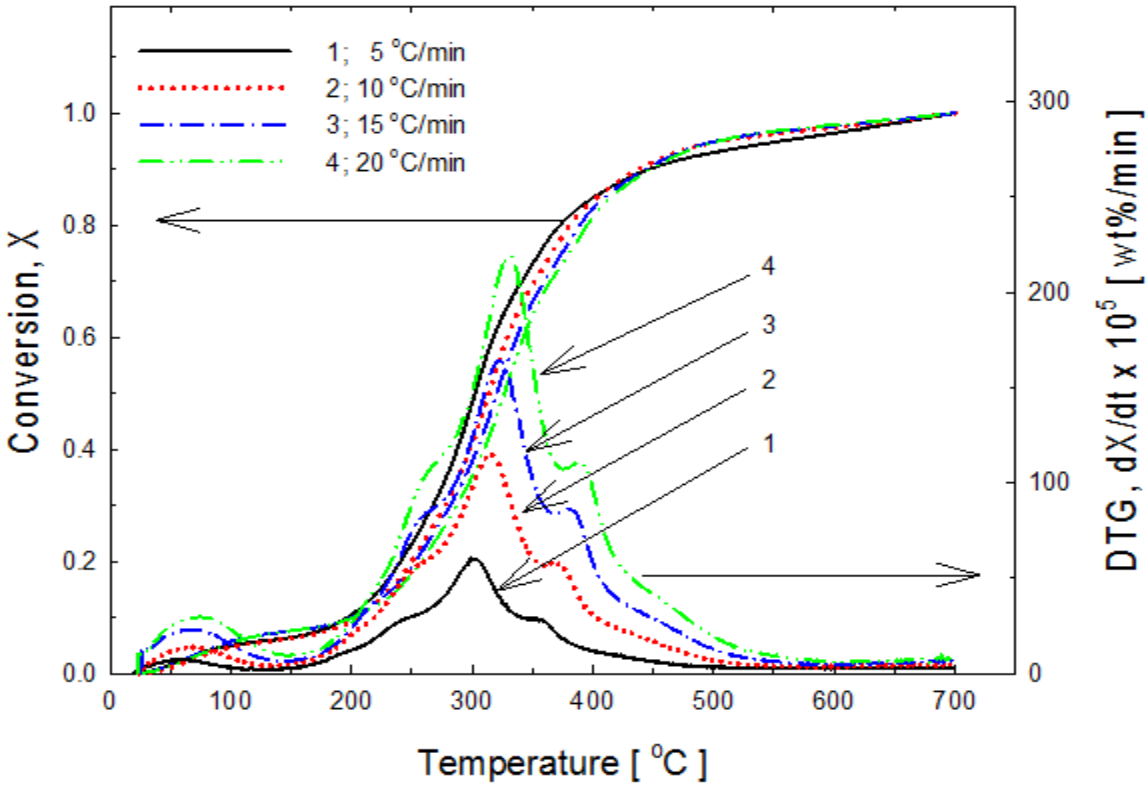

Figure 3.2 Thermogravimetric and differential thermogravimetric of field pennycress in nitrogen atmosphere at heating rate of 5, 10, 15 and 20 ^{o}C/min

3.4.3 Kinetic Parameters of Field Pennycress

To determine the kinetic parameters such as activation energy (E) and pre-exponential factor, differential method was used as proposed by similar studies.[16,22,37] The thermogravimetric data was used to conduct kinetic study. In thermal decomposition, the rate of conversion (dx/dt) is expressed by:

$$\frac{dX}{dt} = k\,f(X) \qquad (eq.\ 3.8)$$

where: K = reaction rate constant

f(X) = function of conversion independent of temperature

The temperature dependence of the reaction rate constant (k) can be determined according to the Arrhenius equation.

$$k = A\exp\left(-\frac{E}{RT}\right) \qquad (eq.\ 3.9)$$

where: A = pre-exponential factor

E = activation Energy

R = universal gas constant

T = absolute temperature (in Kelvin)

A function of conversion independent of temperature, f(X), is expressed as:

$$f(X) = (1-X)^n \qquad (eq.\ 3.10)$$

where: n = reaction order

Therefore, equation (3.8) can be expressed by using the parameters from equation (3.9) and (3.10) as follows:

$$\frac{dX}{dt} = A\exp\left(-\frac{E}{RT}\right).(1-X)^n \qquad (eq.\ 3.11)$$

Taking natural logarithm on both sides of equation (3.11) will give the equation written below:

$$\ln\left(\frac{dX}{dt}\right) = \ln\left[A\cdot(1-X)^n\right] - \frac{E}{R}\cdot\frac{1}{T} \qquad (eq.\ 3.12)$$

From equation (3.12), plotting ln (dX/dt) on the Y-axis versus (1/T) on the X-axis, at the four heating rates (5, 10, 15 and 20 ^{o}C/min) by using the same degree of conversion, X (%), gives four points, which upon connecting form a straight line. The slope of the straight line is (-E/R) and the intercept will be ln [A (1-X) ^{n}]. For example, at 50% conversion, the temperatures at 5, 10, 15 and 20 °C/min heating rates were 302.47, 313.99, 320.89 and 327.13 °C, respectively. Hence the value for [1/T, (K^{-1})] for these temperatures, according to their order, will be 1.7377×10^{-3}, 1.7036×10^{-3}, 1.6838×10^{-3} and 1.6663×10^{-3}. And the corresponding ln (dX/dt) values are -7.4145, -6.7720, -6.4124, and -6.1325, respectively. After plotting the pairs of points for ln (dX/dt) and (1/T), the slope of the line, (E/R), was found to be -18,064.75. Taking the value of universal gas constant to be 8.314 J g $mole^{-1}$ K^{-1}, the activation energy (E) for 50% conversion was 150.19 KJ/mol.

The X-intercept, which is ln [A (1-X) ^{n}], for this example was 23.99. As per to logarithmic rule, the equation can be written as:

$$\ln\left(A\cdot(1-X)^n\right) = \ln A + n\cdot\ln(1-X) \qquad (eq.\ 3.13)\ )$$

The reaction order (n) was considered to be fixed at 0, 1, and 2. Therefore, the pre-exponential factor (A) for 50% conversion (X=0.5) at the 0^{th}, 1^{st}, and 2^{nd} reaction order was found to be $2.62x10^{10}$, $5.23x10^{10}$ and $1.05x10^{11}$, respectively. Following the same approach, the activation energy and pre-exponential factors for 15, 20, 30, 40, 50, 60, 70, 80, and 85% conversion was calculated in this study. Figure 3.3 shows the plot of the straight line for all the nine conversion percentage used.

Figure 3.4 shows the trend of apparent activation energy at the 9 selected conversion values. The lowest activation energy was found to be 150.19 KJ/mol at 50% conversion whereas the highest was 403.89 KJ/mol at 85% conversion. In the TGA curve, the major conversion took place until 80%. The main peaks in the DTG curve were below 400 °C. In Figure 3.4, there was no significant increase in activation energy before 80% conversion, but there was a rapid increase afterwards. The activation energy increased from 265.86 to 403.89 KJ/mol and this could be attributed to devolatilization reaction of char after the main reaction.[38] A similar trend was observed in pre-exponential factors. Table 3.3 shows summary of the calculated of kinetic parameters for the pyrolysis of field pennycress. From 15-80% conversion, the range was between 10^{10} to 10^{13} s^{-1}. However, the values of pre-exponential factor was as high as 10^{19} s^{-1} and it further increased to 10^{29} s^{-1} at 85% conversion. The overall range of pre-exponential factor for conversions between 15% and 85% was from $2.62x10^{10}$ to $1.44x10^{29}$ s^{-1}.

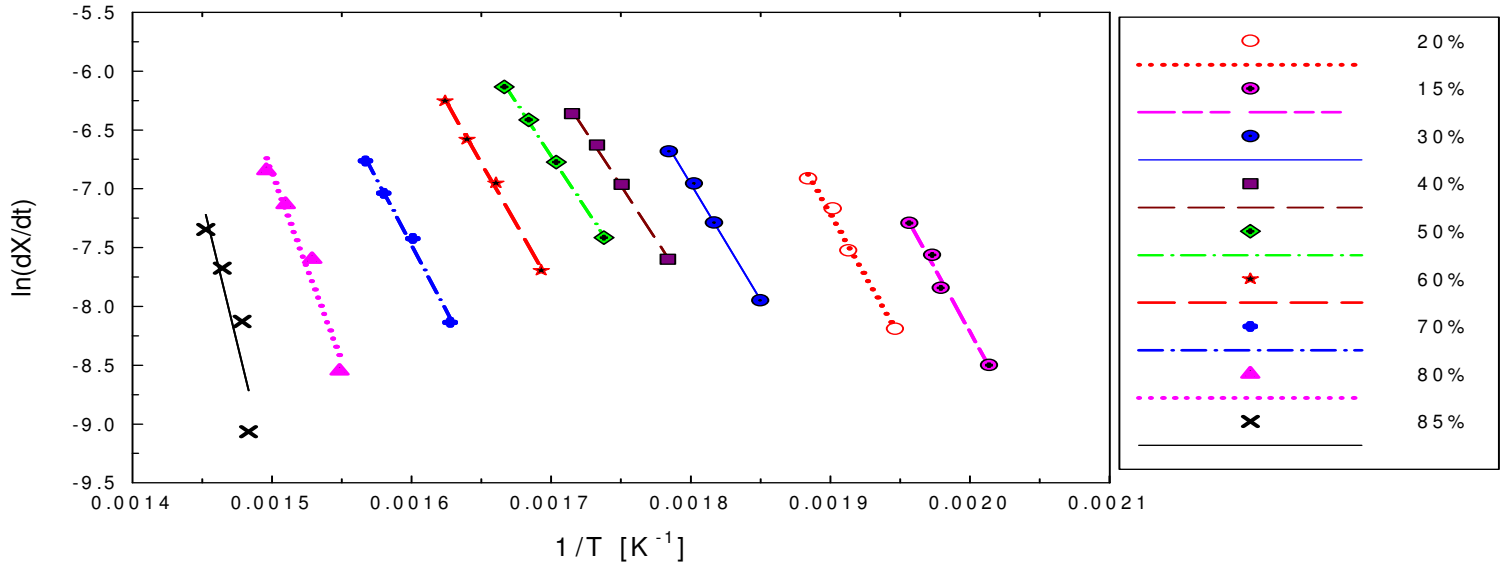

Figure 3.3 Application of equation 3.12 for calculating activation energy and pre-exponential factor at heating rates of 5, 10, 15, and 20 ^{o}C/min and conversion values ranging from 15-85%

Table 3.3 Calculated kinetic parameters for the pyrolysis of pennycress Biomass

		Conversion (%)								
		15	20	30	40	50	60	70	80	85
E_a (KJ/mol)		178.20	174.78	163.82	151.24	150.19	172.67	186.52	265.86	403.89
	n									
	0^{th}	$1.12x10^{15}$	$1.63x10^{14}$	$2.40\ x10^{12}$	$6.28\ x10^{10}$	$2.62\ x10^{10}$	$8.66\ x10^{11}$	$2.20\ x13^{12}$	$7.04\ x10^{17}$	$3.23\ x10^{27}$
$A(s^{-1})$	1^{st}	$1.31\ x10^{15}$	$2.04x10^{14}$	$3.43\ x10^{12}$	$1.05\ x10^{11}$	$5.23\ x10^{10}$	$2.16\ x10^{12}$	$7.32\ x10^{12}$	$3.52\ x10^{18}$	$2.15\ x10^{28}$
	2^{nd}	$1.55\ x10^{15}$	$2.55x10^{14}$	$4.91\ x10^{12}$	$1.74\ x10^{11}$	$1.05\ x10^{11}$	$5.41\ x10^{12}$	$2.44\ x10^{13}$	$1.76\ x10^{19}$	$1.44\ x10^{29}$

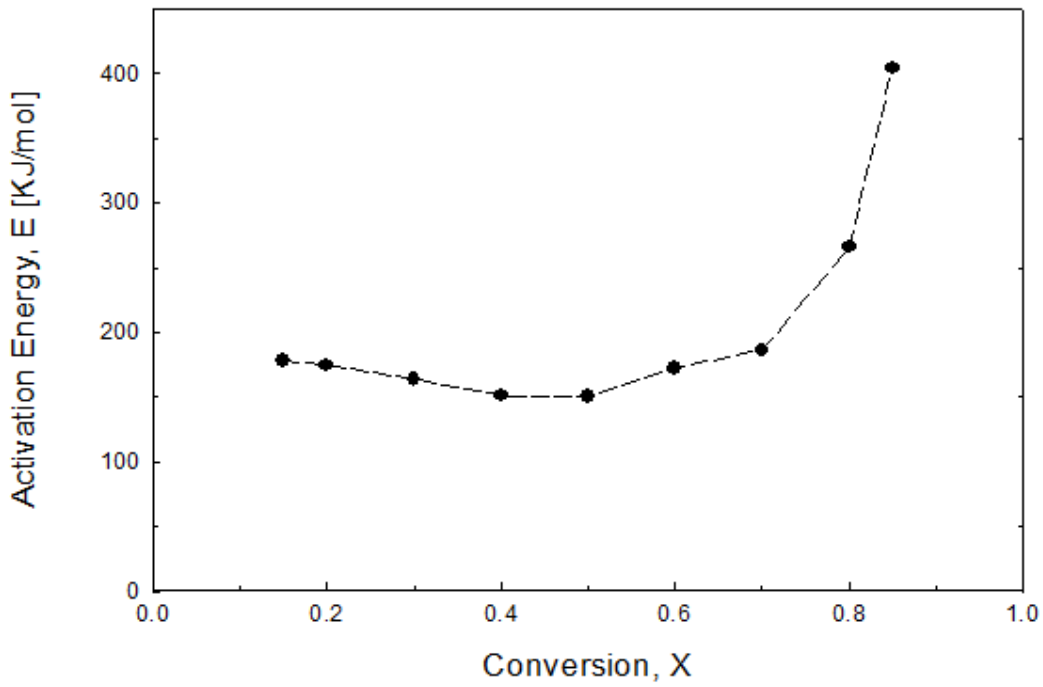

Figure 3.4 Calculated activation energies of field pennycress at different conversions(15-85%)

3.5 Conclusion

In this study, the composition of field pennycress was analyzed and its thermal behavior was investigated. The characterization of the biomass showed that field pennycress had high volatile content and HHV, making it an interesting feedstock for energy production. Field pennycress has an oilseed, which upon hexane extraction yielded about 10.31 wt % of the biomass. This could possibly contribute to the higher calorific value of the biomass obtained in this study compared to other types of biomass.

On carrying out TGA on field pennycress, important differences were observed as the heating rate increased from 5 to 20 °C/min and at temperatures ranging from room temperature to 700 °C. The experimental result in this work indicated that the major decomposition takes place between 200-450 °C and the whole

biomass pyrolysis can be divided into five stages. Below 200 °C, there was moisture evolution and this process was followed by a second shoulder at temperature range of 200-280 °C that was attributed to decomposition of hemicellulose. The third one with clear peak at 300 and 323 °C for 5 °C/min and 20 °C/min heating rate was assigned to decomposition of cellulose. For the oilseed in pennycress, which had considerable amount of oil and proteins, degradation appeared after cellulose at temperature range of 340 °C to 415 °C. The last one with long tail was claimed to be for lignin decomposition. This process started at about 180 °C and extended to more than 500 °C. Kinetic study of field pennycress revealed that the value of activation energy rapidly increased after 80% conversion. This could be due to devolatilization of char after the main reaction. The characterization of the biomass showed that field pennycress is an attractive source of thermal energy production. Field pennycress has the potential to be converted to a more energy rich bio-oil with a further densification process such as fast pyrolysis.

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CHAPTER 4

EFFECT OF OPERATING CONDITIONS ON PRODUCT YIELDS OF CONVENTIONAL RAPID PYROLYSIS OF WHOLE PENNYCRESS BIOMASS

4.1 Abstract

Reports indicate that the worldwide energy consumption and fossil fuel energy production levels will have an opposite trend in the coming two decades. The former will continue to increase and the later will decrease. Therefore, additional sources of energy need to be developed. Field pennycress (*Thlaspi, arvense* L.) has been found to be an ideal source of energy because it has a prolific yield and has no value as food. We demonstrated conventional rapid pyrolysis of whole pennycress biomass in a fluidized bed reactor. The influence of operational conditions was also examined using a suitable experimental design. The operational variables were temperature (400-500 ^{o}C) and nitrogen gas flow rate (16-32 l/min). The highest liquid yield was found to be 54.06 wt % at a temperature of 500 ^{o}C and a gas flow rate of 24 l/min. Char yield was in the range of 22.81 - 30.31 wt % and gas yield was between 19.41-36.13 wt %. The liquid products had better qualities compared to other lignocellulosic feedstocks. The aqueous phase and bio-oil had a higher pH value of 5.61 and 5.16, respectively. The calorific value of the bio-oil was found to be 32.59 MJ/kg (33.18 MJ/kg on dry basis), which is higher than most lignocellulosic bio-oils However, the viscosity of bio-oil was high (1862 cP). The bio-oil obtained from field pennycress was found to be a promising alternative energy source that could compete with exiting petroleum fuels after some upgrading.

4.2 Introduction

The worldwide energy consumption is projected to increase by about 47% in the coming two decades.[1] However, the existing source of energy; fossil fuel is finite and the growth in its production level is predicted to cease by 2025.[2] The production level will then decrease continuously and may halt in few more decades.[2] Therefore, there will be an opposite trend between energy consumption and production levels. Additional sources of energy must be developed to meet the energy demand. The use of fossil fuels leads to many complications. One of them is global warming.[2] According to International Energy Agency (IEA) projections, in order obtain a 50% reduction in greenhouse gas emission by 2050, bio-energy production has to increase by a four-fold.[3]

To achieve this vision, energy production from biomass has to increase to around 150 EJ/yr (EJ=10^{18}J), which is more than 20% of the world's primary energy demand. Bio-energy has the potential to satisfy from 10% to more than 60% of world primary energy demand.[2–4] Therefore, utilizing biomass as a source of energy can alleviate these environmental problems and satisfy the societal energy demands.

The US biofuel industry has been working to meet the minimum requirement of the Renewable Fuel Standard (RFS2).[5] The target of RFS2 is that by 2022, the consumption of renewable fuels for national transportation has to be 36 billion gallons per year. The goal of the plan is to meet the energy demands and to reduce greenhouse gas emissions. The usage of bio-fuels that meet the minimum threshold life cycle of greenhouse gas (which ranges from 20-60% threshold reduction), will help achieve this purpose.[5] The USDA is currently working on developing bio-fuel sources that can meet these requirement.[6] This blueprint is believed will enrich the rural agricultural economy. Corn ethanol and some oilseeds are predicted to

contribute about 15 billion gallons of the 36 billion gallons per year. The remaining 21 billion gallons has to be obtained from other sources such as cellulosic feedstocks and other advanced bio-fuels.[6]

Field pennycress (*Thlaspi arvense* L.) has been found to be one of the attractive targets for bio-energy production and can contribute significantly to meeting the requirement of RFS2.[7,8] Field Pennycress belongs to the family of Brassicaceae (mustard family).[9] Pennycress originated in Eurasia and now grows widely as a naturalized species throughout the temperate regions of the world.[9] Field pennycress is a winter or overwintering annual plant. The seedlings that germinate in autumn overwinter as rosette, with leaves of up to 15cm diameter.[10–12] Pennycress is an ideal source for bio-fuel production because of its minimal agricultural input requirement, prolific seed yield, production in off-season, definite growth season, and compatibility with existing farms.[7]

According to recent studies, 1120-2240 kg of seed/ha can be harvested from a wild population of *T. arvense.* From this product, approximately 600-1200 liters of oil/ha can be produced.[7] The oil extracted from pennycress was tested for bio-diesel production and yielded a bio-diesel that meets the ASTM D6751 specification.[7] Feedstocks such as soybean oil, palm oil and vegetable oil also have been used as a source of bio-diesel production. However, the use of edible feedstock for energy production has raised the debate regarding usage of food as energy source. Therefore, it is important to investigate alternative sources of energy such as pennycress that don't compete with the commodity crops used for food.[7,13]

The research that has been conducted so far about pennycress as a source of fuel focused on the oilseed of field pennycress.[7,8,14,15] Boateng et al.[8] reported that fast pyrolysis of pennycress oilseed, defatted presscake and regular presscake produced a

good quality bio-oil that had a high carbon, low oxygen, and high energy content. Hydrotreating of fast pyrolysis oil was also carried out to further improve the quality of bio-oil. The catalyst used (Ru/C, Pd/C and Pt/C) were found to be effective in hydrodeoxygenation, hydrodenitrogenation, and hydrodesulfurization.

As noted earlier, the attention has only been given to the oil extracted from the seed and on the residual press-cake after extraction. However, there is no further information on the pyrolysis of whole biomass, which encompasses the stem, leaves and whole seed. The biomass and seed yield of pennycress were 1,316.9 kg/ha and 350.7 kg/ha, respectively.[16] Fast pyrolysis of the whole pennycress biomass can therefore increase the total yield of bio-oil because there will be a contribution from both lignocellulosic materials and the oil seeds.

In the past three decades, fast pyrolysis has become an attractive technology that produces a high yield of liquid, which can be used for energy, chemicals or utilized as an energy carrier.[17,18] Fast pyrolysis is a thermal conversion process at a temperature range of 400-600 ^{o}C, in the absence of oxygen, and at an atmospheric pressure.[17–22] The main aim of fast pyrolysis is to produce a liquid products of good quality. This can be achieved when there is rapid heat transfer to biomass particles (preferably <1mm in size), rapid cooling and condensation of the vapors produced, and proper removal of the char.[18] Therefore, it is important to select an optimum reaction condition than can give the maximum liquid yield.

Almost all forms of biomass are composed of different percentages of cellulose, hemicellulose, lignin, extractives, and inorganic materials.[21,23] In fast pyrolysis, temperature and vapor residence time are one of the key reaction conditions that govern the product yield.[18,21,24] Vapor residence time is defined as the empty reactor volume divided by the inlet gas flow rate at the operating condition.[22,24]

Therefore, it is important to determine the optimum reaction conditions than can produce maximum liquid yield during fast pyrolysis.

The goal of this research is to investigate the effect of temperature and vapor residence time on product yield of conventional rapid pyrolysis of field pennycress. The experiments were conducted at five different temperatures of 400, 425, 450, 475 and 500 ^{o}C, and a nitrogen gas flow rate of 16, 24 and 32 l/min. From these different combinations of temperate and gas flow rate, an experiment that gives the maximum liquid yield was selected by using parametric study.

4.3 Materials and Methods

4.3.1 Feedstock

Field pennycress (*Thlaspi arvense* L.) was supplied by Western Illinois University (Macomb, IL). The preparation of the feedstock was described in detail in Chapter 3, section 3.3.1.

4.3.2 Fast Pyrolysis of Whole Field Pennycress Biomass

Fast pyrolysis experiments were conducted using a bench scale fluidized bed reactor unit located in USTAR BioInnovations Center 620 at the thermochemical laboratory (Logan, UT). Figure 4.1 shows the schematic diagram of the pyrolysis unit. The experimental plant consists of mainly a feeder, a fluidized bed reactor, hot gas filter (HGF), two sets of condensers, electrostatic precipitator (ESP), coalescing filter and gas chromatograph (GC).

The prepared pennycress biomass was filled into the hopper batch wise and conveyed into the reactor by a twin-screw feeder from Brabender Technology (Ontario, Canada). In order to facilitate the entry of the biomass into the reactor, nitrogen was used as a sweep gas. Once the biomass moved into the entrainment

compartment by the feeder, the nitrogen entrained the biomass down into the reactor through a sloping pipeline. This pipeline was cooled by water in order to avoid pyrolysis in the hot tube that could block the tube . The feed rate of the biomass was set to approximately 100 g/h, which corresponds to a weight hourly space velocity of 1 h^{-1}.

A 5.08 cm schedule 40 stainless steel pipe fluidized bed reactor was used to conduct the experiment. The total height of the reactor was 50.8 cm, where about 14 cm of this height was used as a pre-heating zone. This zone heated the fluidizing gas before the gas entered into the reactor bed. The reactor bed was equipped with 100 µm pours gas distributing plate. Nitrogen was used as a fluidizing gas. The nitrogen flow rate was controlled by a mass flow controller. The bubbling fluid bed medium was sand with an average diameter of 249.56 µm. The minimum fluidization velocity was determined experimentally using a glass reactor and was found to be 8 l/min. The gas flow rate used during the experiment was 16, 24, and 32 l/min at room temperature (2, 3 and 4 times the minimum fluidization velocity), which corresponds to an apparent vapor residence time of 1.6, 1.2 and 1.0 s, respectively.

To account for the change in the gas flow rate with increase in temperature during reaction conditions, an ideal gas equation ($P_1V_1/T_1 = P_2V_2/T_2$) was used to obtain the desired flow rate at the reaction temperature. For instance, in order to obtain a flow rate of 32 l/min at 500 ^oC reaction temperature, the nitrogen flow rate supplied at room temperature was 12.13 l/min. About 8 l/min of nitrogen was used as sweep gas for moving the biomass into the reactor and this value was added to fluidizing gas flow rate while calculating the vapor residence time.

The reactor was heated by an electrical furnace with three heating zones (Thermcraft Incorporated, Winston-Salem, NC). The temperature in the reactor was

controlled by K-thermocouples inserted into the thermal well of the reactor. The temperature of the bed zone was one the reaction variables. This parameter was set to a fixed value during each experiment. The temperatures used during the experiment were 400,425, 450, 475 and 500 ^{o}C. The temperature was maintained to the desired value by using LabVIEW software. The temperature above the bed of the reactor was kept lower than the reaction temperature in order to avoid secondary vapor cracking. During the experiment, a stable reaction temperature was achieved by initially heating the reactor for about 1 h. Both fluidizing and sweep gas valves were opened 10-15 minute before the start of the experiment so that the possible fluctuation in reaction temperature that may occur by introduction of the gases could be avoided by adjusting the heating temperature of the furnace. Each experiment was conducted for 2 h.

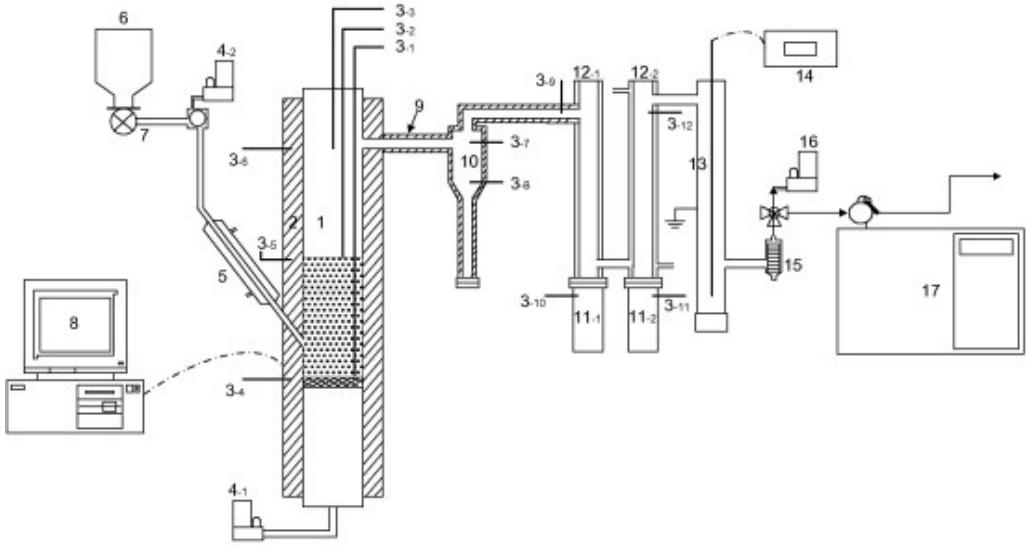

Figure 4.1 Schematic diagram of bubbling fluidized bed reactor

When the temperature inside the reactor was maintained at the desired reaction temperature, the twin-screw feeder was then switched on. Once the biomass entered to the reactor, they decomposed rapidly by the back mixing of the hot fluidizing sand and exited the reactor in 1-1.6 seconds (depending on the gas flow rate). A hot gas filter (HGF) equipped with a 10 μm filter element was connected to the reactor to separate the bio-char leaving the the reactor along with the vapors that were produced by fast pyrolysis. The temperature of the HGF was maintained approximately 330 ^{o}C. This unit was also controlled by the LabVIEW software. To prevent the condensation of vapors in the pipeline, insulation tapes were used to cover the pipeline that connected the reactor and HGF.

The liquid recovery system was placed after the HGF. The condensable vapors were collected in two condensers connected in series. A 50-50% mixture of ethylene glycol and water was used as a coolant in the cooling system (HAAKE A82, Berlin, Germany). Thermocouples were connected to the condensers to check the temperature within them. The temperatures observed were from -10 to 0 ^{o}C. The non-condensable gases and aerosols further moved to the electrostatic precipitator (ESP). The aerosols were captured by the electrostatic charge induced by the ESP, which was maintained at 18-20 kV. The remaining gases were passed through coalescing filter equipped with 0.01 μm filter element (Norgren Express, Littleton, CO). The filtering step was performed to ensure that there will not be any oil escaping from the system. The escaping of bio-oil may affect the mass balance and effect the online GC.

The clean non-condensable gases, comprising of permanent and light hydrocarbon gases, were analyzed online using SRI 8610C gas chromatograph (GC), multi-gas # 3 configuration (SRI Instruments, Torrance, CA). The GC was equipped with both a flame ionization detector (FID) and a thermal conductivity detector

(TCD). A Molecular Sieve 13X column was used to separate hydrogen, methane, and carbon monoxide whereas a HayeSep D column was used to separate for C_2-C_6 hydrocarbons. Argon gas was used as a carrier gas for the gas analysis.

The liquid, bio-char and gas yield were calculated gravimetrically by weighing the parts of the pyrolysis unit. The weight of the reactor, HGF, 1st and 2nd condensers and coalescing filter were determined before and after each experiment. Bio-char yield was obtained by the difference in weight of reactor and HGF before and after pyrolysis. The percentage of the char yield was calculated by dividing the total char weight by the total biomass dry weight, which was fed during the experiment. The liquid yield was divided into aqueous and bio-oil yield. The aqueous phase that contained high percent of water was collected in the vessel (reservoir) of the 1st condenser. The rest of the oil that was collected in the inside cooler wall and the one that stick to the 1st condenser wall was considered as bio-oil yield. The bio-oil yield was the sum of the oil collected in the 1st condenser, 2nd condenser, ESP and coalescing filter. The gas yield was calculated by difference.

4.3.3 Liquid Product Analysis

The pH of the bio-oil and the aqueous phase was measured at ambient temperature using a pH meter and a probe (Mettler Seven Easy S20 pH meter, Mettler-Toledo AG, Switzerland). First, the instrument was calibrated with 3 standard buffer solutions, in pH order of 7, 4, and 10. The pH of each sample was then read in triplicate and the average of the 3 values was then calculated.

In order to determine the organic fraction of the total liquid produced, the moisture content of the bio-oil and the aqueous phase were determined. The analytical instrument used to measure the moisture content was KF Titrino 701 (Metrohm AG, Herisau, Switzerland). Karl fisher titration was conducted with HYDRANAL®-

Composite 5 as titrant and methanol as solvent. After conditioning 50 ml of methanol, the titer value of pure de-ionized water was determined. The instrument was then calibrated with de-ionized water. If the reading of the moisture content for the de-ionized water was between 99-101%, then the samples were analyzed for moisture content. A 5 ml syringe was used to inject approximately 12-22 mg of sample. The average of three moisture content reading was then calculated. The organic yield was calculated by the sum of organic fraction of the bio-oil and the aqueous phase.

The viscosity of the ESP oil was determined using a BROOKFIELD DV-II + Pro viscometer (Brookfield Engineering, Middleboro, MA). The instrument was first calibrated with a N415 viscosity standard at 40 ^{o}C. About 6 ml of standard was placed into a sample container and a similar amount of the standard was also used during the viscosity measurement of the sample. The spindle (SC4-18) was then lowered slowly to commence. The speed selected was within the range of 1-10 rpm. The measurement was carried out for each speed until the viscosity reading became constant and the percentage (torque) was in the range of 10-90%. The average of the last three close values was taken. However, if the last three values were not close, the last reading around 90% torque was recorded as the reading for the viscosity. The higher heating value (HHV) of the feedstock was measured by using IKA® C2000 Basic Calorimeter, which was described in detail in Chapter 3, section 3.3.4

4.3.4 Experimental Design

Statistical analysis was performed to determine the effect of operating condition on the total liquid yield. This was performed using the general linear model (GLM). The software used for the analysis was SAS® OnDemand for Academics, release 3.2 (Enterprise Edition, Cary, NC). Data were subject to analysis with completely randomized 3x5 factorial design. As described earlier, the two factors of

interest were temperature and gas flow rate (corresponding to vapor residence time). The levels of temperature used were 400, 425, 450, 475 and 500 ^{o}C. Three levels of gas flow rate with value of 16, 24 and 32 L/min were used. A total number of 19 experiments were selected in this study.

The Effects model was used for the factorial design. The model is expressed as:

$$Y_{ijk} = \mu + A_i + B_j + AB_{ij} + \mathcal{E}_{ijk} \qquad \text{eq. 4.1}$$

$$i = 1, 2, 3, 4, 5 \qquad j = 1, 2, 3 \qquad k = 1\text{-}3$$

where: Y_{ijk} = the percent of liquid yield for k^{th} experimental unit in temperature level " i " and flow rate level " j ".

μ = Overall (grand) mean

A_i = Mean effect of temperature level " i "

B_j = Mean effect of gas flow rate level " j "

AB_{ij} = Interaction effect of temperature and gas flow rate

$\mathcal{E}_{ijk}$ = Random error associated with observation

The statistical analysis of the experimental results was done using analysis of variance (ANOVA) on a 95% confidence interval. The ANOVA analysis of the effects model was used to find the statistical significant term. The null hypothesis, which states that there is no effect in the factors used in total liquid yield, was rejected when the p-value was less than 0.05.

4.4 Results and Discussions

Fast pyrolysis of whole pennycress biomass was conducted at a temperature range of 400-500 ^{o}C. This temperature range was selected from the thermogravimetric and differential thermogravimetric study which was conducted in Chapter 3. The major decomposition of field pennycress biomass took place between 200 and 450 ^{o}C. Since there was still some decomposition of biomass up to 500 ^{o}C, the experimental temperature was extended to 500 ^{o}C.

The gas flow rate used in this study was obtained from the minimum fluidization velocity of the fluidized bed material, which was sand. Figure 4.2 shows a plot of pressure drop versus gas velocity (in this case nitrogen). The pressure drop then increased up to a certain level but once it reached the maximum value (423.30 N/m^2), the pressure drop then remained almost constant. The point at which the pressure drop reached its maximum value is called the minimum fluidization velocity (U_{mf}). The pressure drop remained constant past the U_{mf}. The pressure drop remained constant because the increase in voidage results in the decrease in pressure drop to static pressure of the bed. Hence, the pressure drop across the bed is equal to the weight of the bed per unit cross-sectional area.[25,26]

From Figure 4.2, the U_{mf} was found to be 6.58 cm/s (8 l/min). The gas flow rates that were used in this study were two times, three times and four times the minimum fluidization velocity. Therefore 16, 24 and 32 l/min nitrogen flow rates were used which is equivalent to the vapor residence times of 1.6, 1.2 and 1.0 s. A short vapor residence time that is less than 2 s is desirable for a higher liquid yield.[18] The apparent vapor residence times were selected based on this criterion.

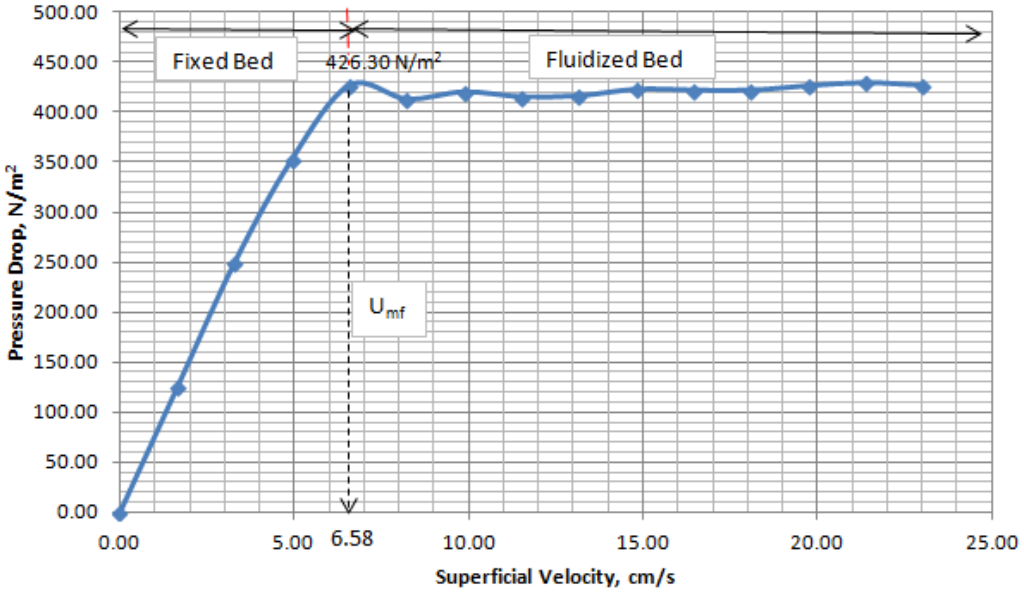

Figure 4.2: Pressure drop versus gas velocity for a bed of sand particle (avg. dia. 249.56 µm) with the down arrow indicating the minimum fluidization velocity (U_{mf})

Mass balance was conducted for each of the selected experiments. Table 4.1 summarizes the liquid, char and gas yields for each experiment. The liquid yield was divided into organic and water yield. The total liquid yield ranged from 40.85 to 55.21 wt % and the total organic yield was between 25.17 and 40.82 wt %. The highest liquid yield was achieved at 500 ^{o}C with a 24 l/min gas flow rate. The organic yield at this reaction condition was 40.85 wt %. This organic yield was also the highest recorded yield from all the experiments. The gas yield at this reaction condition was also the lowest; hence most of the produced vapors were condensed into liquid. This factor accounted for the highest liquid yield. The total liquid yield that could be obtained from fast pyrolysis varies from biomass to biomass. Depending on experimental conditions, the liquid yield could be in the range of 55-60 wt. % (on a dry feed bases) for grasses and could also be as high as 60-75 wt.% (on a dry feed

bases) for woody biomass.[18] Field pennycress, being a herbaceous plant, the highest liquid yield was found to be in a similar range as yields obtained from grasses.

Table 4.1. Product distribution of fast pyrolysis of whole pennycress biomass

S.N.	Experiment Condition			Product Yield (Dry Basis)				
	Temp. (oC)	Umf	Fluid. Med.	Liquid (%)			Char (Wt. %)	Gas (Wt. %)
				Organic	Water	Total		
1	400	2	Sand	27.22	15.42	42.65	28.62	28.74
2	425	2	Sand	30.63	13.09	43.72	27.82	28.46
3	450	2	Sand	31.78	16.08	47.86	27.66	24.48
4	475	2	Sand	30.35	15.27	45.62	25.09	29.29
5	500	2	Sand	28.7	16.27	44.97	25.63	29.4
6	400	3	Sand	31.69	13.78	45.47	30.31	24.22
7	400	3	Sand	30.66	15.04	45.7	27.05	27.25
8	425	3	Sand	28.05	12.8	40.85	27.23	31.91
9	450	3	Sand	29.32	18.18	47.5	24.85	27.65
10	450	3	Sand	32.47	15.75	48.23	24.91	26.87
11	450	3	Sand	36.46	14.91	51.37	26.33	22.3
12	475	3	Sand	31.1	11.79	42.89	23.74	33.36
13	475	3	Sand	35.38	12.44	47.83	25.7	26.48
14	500	3	Sand	37.92	16.79	54.71	23.28	22.01
15	500	3	Sand	40.82	14.39	55.21	25.38	19.41
16	500	3	Sand	36.85	15.4	52.26	24.81	22.93
17	400	4	Sand	25.17	17.23	42.4	25.15	32.44
18	450	4	Sand	29.79	11.57	41.36	24.51	34.13
19	500	4	Sand	26.4	14.66	41.06	22.81	36.13

The presence of ash in a biomass also has a great effect on the composition of bio-oil. Ash could have a catalytic effect during pyrolysis and the presence of considerable amount of ash could lower the total liquid yield.[18,21,23,27] Field pennycress biomass has an ash content of 7.11 wt %. Fast pyrolysis of alfalfa stems that had an ash content of 8.28 wt % for early bud and 5.51 wt % for biomass at the full flowered stage produced a liquid yield of 45% and 53 %, respectively.[28] Fast pyrolysis of milkweed (a herbaceous plant) that had an ash content of 11.2 wt %, produced a total liquid yield in the range of 40.74 - 44.19 wt % when it was pyrolyzed at temperature range of 425-550 ^{o}C.[29] Even in the case of woody biomass, fast pyrolysis of Pinion-Juniper bark, which had an ash content of 6.56 wt % yielded 47.49 wt % liquid product.[30] Therefore, the presence of 7.11 wt % ash content in field pennycress biomass could also possibly contributed to lower liquid yield (55.21 wt %) compared to the total liquid yields obtained from woody biomass (i.e. 60-75 %).

The lowest char yield obtained was 22.81 and was achieved at 500 ^{o}C with a gas flow rate of 32 l/min. This char yield was already predicted from the thermogravimetric analysis (TGA) in Chapter 2. This yield was lower than the result obtained from TGA, which was 24.71 wt % at a temperature of 700 ^{o}C. Since TGA is slow pyrolysis process, there could be repolymerization of the vapors into char due to the longer residence time,[18,21] hence the char yield would be little higher. Therefore, at the mentioned experimental condition, the char yield was lower because the gases did not have enough time to repolymerize due to the short vapor residence time (~1 s). However, this short hot vapor residence time resulted in the highest gas yield of 36.13 wt % at the already mentioned experimental condition.

The highest char yield was found to be 30.31 wt % at the pyrolysis temperature of 400 ^{o}C and the flow rate of 24 l/min. Since the temperature is lower

than the decomposition temperature range of the biomass, the high char yield could be due to the remaining biomass constituents that were not fully decomposed. The summary of the product yield of all the experiments conducted is presented in Table 4.2.

Table 4.2. Experimental summary of product yield of fast pyrolysis of whole pennycress

	Product Yield (Dry Basis)				
	Liquid (wt %)			Char	Gas
	Organic	Water	Total liquid	(Wt. %)	(Wt. %)
Maximum	40.82	18.18	55.21	30.31	36.13
Minimum	25.17	11.57	40.85	22.81	19.41
Average	31.62	14.78	46.40	25.84	27.76
STDEV[a]	4.16	1.83	4.43	1.9	4.53

[a] Standard deviation

4.4.1 Analysis of Variance

4.4.1.1 Liquid Yield

The analysis of variance (ANOVA) results shown in Table 4.3 were used to evaluate the statistical significance of the liquid product yield. The null hypothesis was, there were no difference in the liquid yield at the different experimental conditions used (i.e. combination of temperature and gas flow rate). From the ANOVA table 4.3., the P-value for the model was 0.0163. Since the P-value for the model is less than 0.05, the null hypothesis is rejected. Therefore, there is a difference

in at least two of the experimental conditions used in the production of the total liquid yield.

Table 4.3. ANOVA result for total liquid yield

Source	DF	Sum of Square	Mean Square	F-Value	P > F	Significance
Model	12	327.07	27.26	6.37	0.0163	Significant
GFR[a]	2	121.73	60.87	14.23	0.0053	Significant
Temp[b]	4	124.84	31.21	7.29	0.0173	Significant
GFR*Temp	6	80.50	13.42	3.14	0.0950	Not significant

[a] Gas Flow Rate [b] Temperature

The R^2 value for the model was 0.93. This explains that 93% of the variation in the liquid yield was explained by the model. This is therefore a good indicator that the variability among the experimental conditions is well explained. However, this conclusion can only be valid if the model assumptions are met. Therefore, the assumptions for constant variance and normality of error term were tested in order to justify whether the conclusion drawn was valid or not. The test for the assumptions is explained in the following paragraphs.

Based on the residual versus predicted plot of Figure 4.3 (A), it can be inferred that there was no trend among the residuals. If joining the plots results in the shape of a megaphone, it is one indicator of a non-constant variance. But in this case such a shape was not observed. This implies that the assumption for constant variance in the error term was satisfied. To further support this assumption, a numerical check was

performed using Leven's homegenity test of variance (HOV). The null hypothesis was, there was constant variance in error terms. The P-value for Leven's test was found to be 0.5184. Hence, there is no sufficient evidence to reject the null hypotheis. Hence, it can be concluded that the assumption for constant variance is justified.

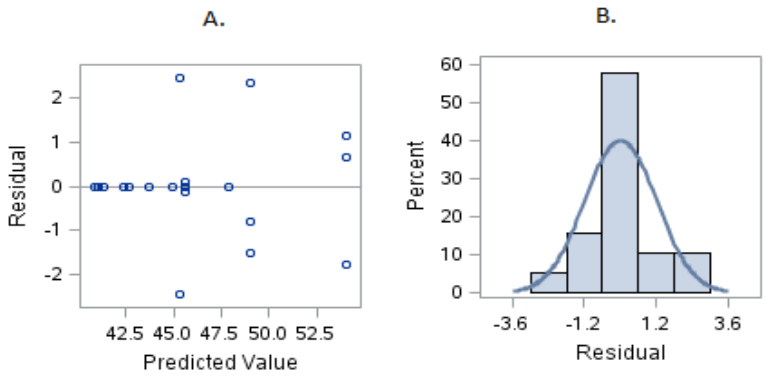

Figure 4.3 Assessing key assumptions using figures A) residual versus predicted plot(For checking constant variance B) Normality distribution

From the plot for normal distribution, Figure 4.3. (B), it can be deduced that it followed the normal distribution curve. There was no clear sign of of the curve being skewed. Hence , it can be inferred that the assumption for normality was not violated. From the two figures hat were used for assessing the violation of the key assumptions, it can be inferred that the key assumption for constant variance and normal distribution were satisfied. Therefore, the conclusion drwan for the model is valid. Hence there is a significant difference in at least two experimental conditions in the prodcution of total liquid yield.

The conclusion drawn from the main model did not clearly categorize which of the two factors had an effect on the liquid yield. The effects model was used to evaluate the effect of each factor and to identify if there was an interaction effect. From the ANOVA results in Table 4.3, the P-value for both gas flow rate (GFR) and

temperature (Temp) were found to be 0.0053 and 0.0173, respectively. Therefore, since the P-value is less than 0.05, there is sufficient evidence to reject the null hypothesis. Both Temp and GFR had effect on the total liquid yield. However, they did not have interaction effect because the P-value was 0.095, which is greater than 0.05.

The next question that needs to be addressed relates to which of the experimental combinations gave a significantly different total liquid yield. The purpose of this parametric study was to identify an experimental condition that produced maximum liquid yield. Multiple comparison procedure (MCP) was conducted for pair-wise comparison of the experimental condition. TUKEY grouping was used for the POSTHOC comparison because we were interested in all possible pair-wise comparisons.. Table 4.4 shows the TUKEY comparison.

According to the TUKEY-KRAMAR grouping, the least square means (LS-means) with the same letter are not significantly different from others. Therefore, the experimental condition at 500 ^{o}C and a gas flow rate of 24 l/min was significantly different from the other combination of the factor levels. This was due to that fact that it did not share the same letters (only has letter "A") with any other experimental conditions. This means that it was significantly different from other pairs of reaction conditions. Therefore, the experimental condition at 500 ^{o}C and a gas flow rate of 24 l/min was selected because it gave the highest liquid yield and was also significantly different from the other conditions.

To examine the quality of the field pennycress bio-oil, the pH, higher heating value (HHV) and viscosity of the bio-oil are presented in Table 4.5. The pH of the aqueous phase and bio-oil were found to be 5.16 and 5.61, respectively. One of the challenges with fast pyrolysis bio-oils is their acidic and unstable nature. Generally

bio-oil from wood, grass and other conventional lignocellulosic derived biomass havean acidic pH that is in the range of 2.8 to 3.8.[21,23,31] The bio-oil has carboxylic acids (mainly acetic and formic acid) and this contributes to the acidic nature of the bio-oil. As a consequence, bio-oil causes corrosion of vessels and pipes.[18,21,31] However, the bio-oil obtained from field pennycress bio-oil had a pH of 5.61 for the aqueous phase and 5.16 for the bio-oil collected from electrostatic precipitator (ESP).

Table 4.4 Tukey-Kramer comparison lines for least square means of GFR*Temp

Letters		Liquid Yield LSMEAN	GFR[a]	Temp[b]	LSMEAN Number
A		54.06	24	500	10
B	A	49.033	24	450	8
B	A	47.86	16	450	3
B	A	45.62	16	475	4
B	A	45.59	24	400	6
B	A	45.36	24	475	9
B	A	44.97	16	500	5
B	A	43.72	16	425	2
B	A	42.65	16	400	1
B	A	42.40	32	400	11
B		41.36	32	450	12
B		41.06	32	500	13
B		40.85	24	425	7

[a] Gas Flow Rate [b] Temperature

Studies on pyrolysis of pennycress oilseed, defatted presscake and regular presscake reported that the aqueous phase had a pH value between 6.5 and 8.9.[8] The reason they attributed for this unusually high pH value was due the presence of high organic nitrogen content derived from the decomposition of proteins present in the

oilseeds. These basic compounds were suggested to have a neutralizing effect on organic acids. This group of researchers also claimed that the ash present in the biomass, which was rich in calcium, phosphorous and potassium, had a catalytic effect in converting some aldehydes to alcohols that was believed to contribute to stable oil with high pH.[8]

Field pennycress has an oilseed that contains up to 36 wt % oil, which is rich in triacylglycerol and also contains 27 % crude protein.[13,32] In the current study, the whole biomass including the stem, leaves and seed were used. As stated earlier, the harvest index, which is defined as percent of seed yield to biomass ratio, for field pennycress, is about 26.6%.[16] Therefore, the proteins present could possibly have a role for the higher pH value of the liquid product.

Table 4.5 Physicochemical properties of pyrolysis bio-oil of field pennycress

Experimental Condition			pH		Viscosity @ 40 °C (cP)	Density (g/cm^3)	HHV[b] (MJ/Kg)
Temp. (°C)	N_2 flow Rate (l/min)	Fluidizing Medium	Aqueous	Bio-oil			
500	24	Sand	5.61±0.11	5.16±0.12	1826 ± 29[c]	1.04±0.01	32.59±0.33 (33.18)[a]

[a] dry basis value is in parenthesis [b] Higher Heating Value [c] = the bio-oil is gel-like at room temperature

The higher heating value (HHV) for the ESP bio-oil of field pennycress was found to be 32.59 MJ/kg (33.18 MJ/kg on dry basis). This HHV is comparatively higher than the one obtained from other lignocellulosic biomass and is about 82% of the energy content of heavy fuel petroleum oil.[33] The lipids and the proteins present in

the pennycress seed could have a substantial role for the higher calorific value obtained in the current study. Mullen et al.[34] investigated the effect of degradation of protein in fast pyrolysis bio-oil. They found out that there was a high percentage of nitrogen in the bio-oil compared to the biomass's nitrogen content whereas oxygen percentage was lower. This resulted in bio-oil with a higher HHV value. The reason they attributed to their finding was that there was a substitution of oxygen by nitrogen due to the reaction of the nucleophilic amine and electrophilic organo-oxygen species. This chemical reaction resulted in rejection of oxygen as water.[34,35] Therefore, this replacement reaction could have a similar effect in the current study. This effect coupled with the presence of lipids in the oilseed could have resulted in increasing calorific value of field pennycress bio-oil.

The bio-oil had a strong unpleasant smell due the presence of nitrogen compounds from the proteins present. The density of the bio-oil was similar to the density of water. The bio-oil had a high viscosity of 1826 cP. The viscosity of wood derived biomass is in the range of 25-1000 cP, but the bio-oil of field pennycress was higher than wood derived bio-oil. Proteins had a higher conversion efficiency into bio-oil than carbohydrates or lignin.[36] Therefore, the protein present in bio-oil could probably be the reason for this high viscosity of the bio-oil. This could negatively affect the transport and pumping of the bio-oil during a commercial application processes. Upgrading of the bio-oil by a process like catalytic pyrolysis could however improve the properties of the bio-oil.

4.5 Conclusion

Experiments were carried out to investigate the product distribution of the conventional rapid pyrolysis of whole pennycress biomass in a fluidized bed reactor. The influence of operational conditions, temperature and nitrogen gas flow rate, was

studied using an experimental design. By using appropriate software, it was possible to validate experimental models, which explain the trend in the pyrolysis product yield within the intervals of the operational variables studied.

The total liquid yield was influenced by both temperature and gas flow rate. However, there was no interaction effect among these two factors. According to the statistical model, a significantly highest liquid yield of 54.06 wt % was obtained for reaction temperature of500 ^{o}C and nitrogen gas flow rate of 24 L/min. At this experimental condition, the highest organic yield and the lowest gas yield of 40.82 wt % and 19.41 wt % were obtained, respectively. The maximum and minimum char yields were found to be 30.31 wt % and 22.81 wt %, respectively. The highest gas yield recorded was 36.13 wt %.

The physicochemical analysis of the selected experimental condition showed that the bio-oil had better qualities compared to other lignocellulosic bio-oils. The field pennycress pyrolysis liquid had a high pH value 5.61 and 5.16 for the aqueous phase and the bio-oil, respectively. This is an interesting finding because the acidic nature of lignocellulosic bio-oil has thus far posed a major challenge for the pyrolysis industry. The calorific value of bio-oil was also unusually higher than lignocellulosic bio-oils. It was found to be 32.59 MJ/Kg (33.18 MJ/kg on dry basis), which is approximately 82% of the energy content of heavy fuel petroleum oil. However, the high viscosity value (1826 cP) of the bio-oil will require a further upgrading if the bio-oil to be used as transport fuel. The bio-oil obtained from field pennycress was found to be a promising alternative energy source that could compete with exiting petroleum fuels after some upgrading.

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CHAPTER 5

CATALYTIC PYROLYSIS OF WHOLE PENNYCRESS BIOMASS USING HZSM-5 AND RED MUD AS CATALYST

5.1 Abstract

It has been demonstrated that fast pyrolysis converts biomass into a liquid fuel in an efficient and economical manner. However, the presences of hundreds of oxygenate compounds results in the poor quality of bio-oil. The purpose of this research was to produce an upgraded bio-oil by the catalytic pyrolysis of field pennycress in a fluidized bed reactor. The catalysts used were HZSM-5 and red mud. The liquid products were found to have better qualities compared to non-catalytic lignocellulosic feedstock pyrolysis bio-oils. The bio-oil from red mud catalyzed process had almost neutral pH of 6.5 and in the case of HZSM-5, the pH of the bio-oil was 5.7. In comparison to bio-oil from conventional rapid pyrolysis, HZSM-5 and red mud reduced the viscosity of the bio-oil by 3 and 5 times, respectively. However, red mud was also found to be effective in improving the higher heating value (HHV) of the bio-oil from 33.18 MJ/kg (dry basis) in conventional pyrolysis to 35.7 MJ/Kg (dry basis). The HHV of HZSM-5 catalyzed bio-oil was 33.63MJ/kg. The composition of non-condensable gases and the chemical makeup of the bio-oil from the two catalysts were different, suggesting that the reaction pathways could be different. From the NMR analysis, HZSM-5 had higher selectivity for aromatics whereas red mud produced longer aliphatic chains. The potential of the bio-oils produced from catalytic pyrolysis was found to be to be promising.

5.2 Introduction

Biomass is being studied worldwide as a feedstock for renewable liquid biofuels because of its low cost and its availability as a primary component of biosphere.[1] One of the major challenges in using biomass as a liquid fuel is due to the fact that an economical process has not yet been developed.[1] Several methods has been proposed and studied to convert biomass into liquid fuels.[2] Biological processes such as enzymatic conversion of biomass involve multiple steps and also require longer period of time in getting the desired products.[2,3] Fast Pyrolysis, however, has the an advantage over the other methods because the thermal degradation process takes place in a single reactor at short residence times (1-2 s) and intermediate temperature (400-600 ^{o}C), followed by rapid cooling.[3–5]

It has been demonstrated that fast pyrolysis can covert biomass into a liquid fuel in an efficient and economically feasible manner.[6] However the presence of hundreds of oxygenate compounds adversely affect the quality of bio-oil.[3–7] These compounds contribute to the poor quality of bio-oil such as low heating value, high corrosiveness, high viscosity, high reactivity (instability).[3–8] Hence, it is problematic to use them for fuel application as they are incompatible with conventional fuels.[9] Post-pyrolysis processing of bio-oil like distillation produced about 35-50 wt % residuals due to the presence of high amount of non-volatile sugars and oligomeric phenols. This phenomenon is also due to polymerization of reactive species.[6] Therefore, it is imperative to improve upon the quality of bio-oil by removing oxygen if bio-oil is going to be used as a replacement for diesel and gasoline.[6,10]

Upgrading of bio-oil can be carried out either off-line or during fast pyrolysis by a process known as catalytic fast pyrolysis. The basic principle in both approaches is removal of oxygen with the help of a catalyst by hydrotreating and / or catalytic

cracking.[6] Secondary processing of bio-oil has been done in the past three decades. The challenges with the process, especially hydrotreating, are high operating and capital cost that is associated with significant catalyst deactivation, expensive catalyst used, high char/coke formation, lower yield of hydrocarbons, and substantial hydrogen consumption.[11,12] Catalytic fast pyrolysis (CFP), which integrate catalyst in pyrolysis, has attracted the interest of researchers in recent years.

Catalytic fast pyrolysis (CFP) is an updated pyrolysis approach that converts the biomass to higher quality bio-oil by upgrading the pyrolysis vapors before condensation. [6,12] It is a simple and inexpensive step in which cracking/upgrading of organic vapor intermediates into hydrocarbons or high quality bio-oil takes place via a series of reactions. [13,14] Agblevor et al.[12] demonstrated selective conversion of lignin fraction into phenol, cresols and catechols via fractional catalytic pyrolysis with HZSM-5 as catalyst. In their report, the biomass was fed into the reactor at fixed rate and mixed with a catalyst in a fluidized bed reactor. This process is referred to as an in-situ catalytic pyrolysis. The process whereby the catalyst is only contacted with the pyrolysis vapors is called ex-situ catalytic fast pyrolysis.[15]

The sources of the high level of oxygen in bio-oil are oxygenated mixture of carbonyls, carboxyls, phenolics and water.[16] One of the main purposes of CFP is to remove the active oxygenated species such acids, ketones, and aldehydes, thereby have a stable component in bio-oil.[6] By using a suitable catalyst, the oxygen in these compounds can be rejected in the form CO_2, CO, and H_2O.[9,12,17] The removal of active oxygenates, especially those in carbonyl- and carboxyl-, play a significant role in stabilizing the bio-oil. This will also reduce the demand for hydrogen, if necessary, during further upgrading processes.[6] Several factors affect the performance of CFP of biomass. The four pivotal ones are residence time, type of catalyst, heating rate and

reaction temperature.[18] The process integrates fast pyrolysis and upgrading of the vapor via catalytic reactions.[6,9,12,17] Even though the reactions are complicated and might occur simultaneously, understanding the cracking chemistry is paramount and several researches have been conducted to define the reaction pathways.[6]

The catalytic cracking chemistry involves decarbonylation, decarboxylation, dehydration, oligomerization, isomerization and dehydrogenation reactions while oxygen is removed in the form of CO_2, CO, and H_2O.[4,5,9,12,19] Fractional catalytic pyrolysis is selective process whereby biomass components with smaller size like carbohydrate are decomposed into gaseous product whereas large particles like lignin are cracked (converted) to liquid product since they are too large to diffuse into catalyst like HZSM-5.[12]

A number of catalysts have been used in fluid catalytic cracking. The catalysts of interest in this study were ZSM-5 and red mud. ZSM-5 is a zeolite type (aluminosilicate) catalyst that is used for a wide range of industrial processes.[20] It is micro-porous material that is used to catalyze fast pyrolysis of lignocellulosic biomass.[6] Protonated ZSM-5 (HZSM-5) has strong acidity and shape selectivity. These properties give HZSM-5 catalyst the potential to catalyze fast pyrolysis reactions.[6] It has been used for more than two decades and was first commercialized in full-scale by Neste Oy refinery in Naantal, Finland.[20] It is both a very thermally and hydrothermally stable zeolite that can be treated to a temperature as high as 1260 K due to its siliceous nature.[20] Pore size of HZSM-5 can be about 0.55 x 0.56 nm atomic radii (0.62x0.63 normal radii).[6,21] The medium size of the catalyst is large enough to fit the reactants inside the pores and covert small molecules like glucose into aromatics.[21]

Even though the reaction pathway is complex, the main reactions in catalytic process include; cracking, deoxygenation, decarboxylation, cyclization, aromatization, isomerization, alkylation, disproportionation, oligomerization, and polymerization.[12,22] Compared to non-catalytic pyrolysis, there was a reduction of about 25% in the oxygen content when HZSM-5 was used as catalyst. However, the total liquid yield decreased and there was an increase in gas, water and coke yield.[23] The acidic site in HZSM-5 catalyst plays a key role in cracking of oxygenates in pyrolysis. The reaction is promoted via carbonium ion mechanism. Bronsted acid is more stronger and is preferred than lewis acid.[24] The ratio of Si/Al of the frame work affects the activity of HZSM-5. Aluminum has a major contribution to the acidity of silicate-alumina frame work. Hence, the lower the ratio of Si/Al in the catalyst, the higher the acidity.[6]

Red mud is an aluminum industry waste material where aluminum oxide (alumina, Al_2O_3) is produced via Bayer Process.[25] It is a mixture of mostly metal oxides such as Fe_2O_3, Al_2O_3, SiO_2, CaO, TiO_2 and Na_2O.[17] The type of ore used and the processing technique determines the amount and composition of red mud generated.[25] It has 20-30% m^2/g specific BET surface area.[25] Since large quantities of red mud are produced, there is an environmental concern due to the caustic nature of red mud.[25,26] Therefore it is both economically and environmentally desirable to used red mud in other value-adding industrial applications.

Red mud is found to have catalytic property in various applications.[25] Sushil and Batra[25], in their thorough review about red mud, mentioned some of the previous successful studies of red mud as catalyst in hydrogenation, liquefaction, hydrodechlorination, and exhaust gas clean-up. They also summarized uses of red

mud in water treatment, soil and mine site remediation, production of building and structural material, recovery of metals and treatment of gold ore.

Some studies have been conducted on the use of red mud as catalyst in pyrolysis. Yanik et al.[27] conducted catalytic degradation and dechlorination of poly (vinyl chloride) (PVC) containing polymer mixtures and found that red mud to be more efficient in fixation of evolved HCl and reported that it had no effect on cracking polymers.[27] De Marco et al.[28] also tested the pyrolysis of plastic waste at temperatures of 400-600 °C and heating rate of 15 °C/min in a semi-batch reactor. They claimed that red mud had a significant effect on the reactions as it produced less viscous oil that does not solidify at room temperature in contrast to the experiments in which no catalysts were employed. However, they did not observe the effect on carbon number of the red mud catalyzed oils.[28]

Further study was conducted by Lopez et al.[29] in a similar reaction arrangement to that of De Marco et al.[28] The purpose was for a better understanding on the effect of HZSM-5 and red mud on pyrolysis. They concluded that red mud produced lower viscosity oil, higher amount of gases and great aromatic liquids at temperature of 500 °C. At 440 °C, red mud produced similar liquid to that without catalyst.[29] Yathavan and Agblevor[17] demonstrated fractional catalytic pyrolysis of Pinyon-Juniper in a fluidized bed reactor with red mud and HZSM-5. They found that red mud was better in terms of upgrading as it produced a bio-oil with higher pH, lower viscosity and greater HHV.

Although catalytic pyrolysis is helpful in obtaining upgraded products, the cost of catalyst can be a limiting factor in some application. Thus, it is crucial to search for cheap catalyst like red mud.[17,25–29] In the previous chapter, we demonstrated the conventional rapid pyrolysis of whole pennycress biomass. The bio-

oil obtained from fast pyrolysis had comparatively better quality than other lignocellulosic bio-oils in terms of pH and calorific value, but it had high viscosity value. In this regard, the bio-oil will require further upgrading process in order to compete with petroleum fuels. We report, herein, catalytic pyrolysis of whole field pennycress biomass for higher value products.

5.3 Materials and Methods

5.3.1 Feedstock Preparation and Moisture Content

Field pennycress (*Thlaspi arvense* L.) was cultivated by researchers at Western Illinois University and was sent directly after harvest. The wet biomass was first dried at ambient laboratory condition by uniformly spreading it on the ground for 5 days. The whole biomass was then ground using Thomas-Wiley Laboratory Mill, model 4 (Thomas Scientific, Swedesboro, NJ). The ground biomass was ground to pass through a 1 mm sieve. In each experiment, the moisture content of the biomass was determined by using an infrared moisture analyzer, Denver Instruments IR-60 (Bohemia, NY).

5.3.2 Catalysts

The catalysts used in the study were ZSM-5 and red mud. ZSM-5 catalyst was obtained from a commercial supplier, BASF Catalyst LLC (Iselin, NJ). The catalyst was sieved to 125-180 μm before use. In order to obtain H^+ZSM-5, the catalyst was calcined for 5 hours at 500 $^{\circ}$C in a muffler furnace, Lindberg Blue M^{TM} LGO (Thermo Scientific, Asheville, NC). The red mud catalyst was provided by Sherwin Alumina Company, LLC (Gregory, TX). The red mud was first dried at ambient laboratory conditions and then ground to pass 125-180 μm sieve. Yathavan and Agblevor[17] characterized red mud in their study on catalytic pyrolysis of Pinion Juniper. They

reported the X-ray diffraction (XRD), X-ray florescence (XRF) and Brunauer-Emmett-Teller (BET) surface area analysis. According to their report, the red mud was composed of Fe_2O_3 (53.98 wt %), Al_2O_3 (13.53 wt %), SiO_2 (8.91 wt %), CaO (8.87 wt %), TiO_2 (6.18 wt %) and Na_2O (5.83 wt %).[17] The same red mud was used in this current study.

5.3.3 Fluidized Bed Pyrolysis

A 2 inch schedule 40 stainless steel pipe fluidized bed reactor was used to conduct the catalytic fast pyrolysis. The total height of the reactor was 50.8 cm; about 14 cm of this height was used as pre-heating zone. A detailed description of the entire process was reported in Chapter 4, section 4.3.2 and was also explained by Kim and Agblevor,[30] hence it will not be repeated here. The experimental plant consisted of mainly a twin-screw feeder, a fluidized bed reactor, a hot gas filter (HGF), two sets of condensers, an electrostatic precipitator (ESP), a coalescing filter, a gas totalizer and a gas chromatograph (GC).

In conventional fast pyrolysis, sand was used as fluidizing medium. However, red mud and HZSM-5 catalysts were used as fluidizing medium in the catalytic fast pyrolysis. The minimum fluidization velocity was determined for both catalysts by using a cold glass reactor that had similar dimensions to the fluidized bed reactor. In order to investigate the effect of catalyst on product yield and quality of bio-oil, the same operational conditions selected based on the parametric study, from Chapter 4, was used. The catalytic pyrolysis experiments were thus conducted at 500 $^{\circ}$C with nitrogen flow rate of three times the minimum fluidization velocity (7.29 L/min). The feed rate was approximately 100 g/h, which corresponds to the weight hourly space velocity of 1 h^{-1} and kept constant during each run. The experiments were conducted for 2 h and in triplicates.

5.3.4 Liquid Product Analysis

The details of the analysis for pH, moisture content, viscosity, ultimate composition and higher heating value (HHV) were discussed in Chapter 4, section 4.3.3. The pH of the liquid product was measured using a pH meter and a probe (Mettler Seven Easy S20 pH meter, Mettler-Toledo AG, Switzerland). The viscosity of the bio-oil was determined using two instruments depending on the quantity of bio-oil collected. When the bio-oil collected after an experiment was not enough, the viscosity was determined by using a BROOKFIELD DV-II + Pro viscometer (Brookfield Engineering, Middleboro, MA). The second viscometer used was Anton Paar Stabinger Viscometer ^{TM} SVM 3000 (Anton paar USA Inc., Ashland, VA). The Stabinger viscometer does not only measure the dynamic viscosity, unlike the Brookfield Viscometer, but it also provides the kinematic viscosity and density of the bio-oil.

The catalytic pyrolysis oil's water content was determined by Karl Fisher titration using methanol as solvent and HYDRANAL$^{®}$-Composite 5 as titrant. The instrument used was KF Titrino 701, Metrohm AG (Herisau, Switzerland). Ultimate analysis (C, H, N and S) of the bio-oils was conducted using Thermo Scientific Flash 2000 CHNS/O organic elemental analyzer (Thermo Scientific, Waltham, MA). Approximately 2.5-3 mg of bio-oil sample was oxidized with a catalyst through combustion and further reduced to produce gases under a high temperature reactor chamber. The gases were then analyzed using gas chromatograph (GC) equipped with TCD detector. Oxygen content was however determined by difference after accounting for the C, H, N and S. The higher heating value (HHV) of the bio-oil was determined using IKA$^{®}$ C2000 Basic Calorimeter (IKA Work Inc., Wilmington, NC).

The chemical characterization of the bio-oil was performed using Nuclear Magnetic Resonance (NMR) spectrometry. The proton and ^{13}C NMR spectrum of the bio-oils was analyzed on a Joel ECX-300 (Joel Ltd., Japan), which is located at the Department of Chemistry and Biochemistry in Utah State University. About 0.2 g of bio-oil was dissolved in deuterated chloroform (1.2 g) and approximately 0.5 g was placed into 5 ml NMR tube. The NMR spectrometer had field strength of 300 MHz and was operated at an observing frequency and a pulse width of 75.57 MHz of 4.92 μs, respectively. The acquisition time was 1.38 s and the relaxation delay was set at 2 s. The sweep width was set at 23.67 KHz and a total of 4000 scans were made for a total measurement time of 3.75 h.

5.4 Results and Discussions

Catalytic fast pyrolysis of whole field pennycress biomass was conducted at 500 °C and gas flow rate of three times the minimum fluidization velocity, which is 7.29 l/min. This experimental condition was selected because it was found to be an optimum condition that gives the highest liquid yield from the parametric study conducted in Chapter 4. The minimum fluidization velocity of both catalysts (red mud and HZSM-5) was determined experimentally in a similar way to that of sand, which was explained in Chapter 4. The point where the pressure drop reached its maximum corresponded to the minimum fluidization velocity (U_{mf}). From Figure 5.1, both red mud and HZSM-5 were found have the same U_{mf} of 2 cm/s (2.43 l/min). The gas flow rate used in the study was three times the U_{mf} that is 7.29 l/min. The equivalent residence time for the red mud and HZSM-5 were 5.1 and 4.7 seconds, respectively.

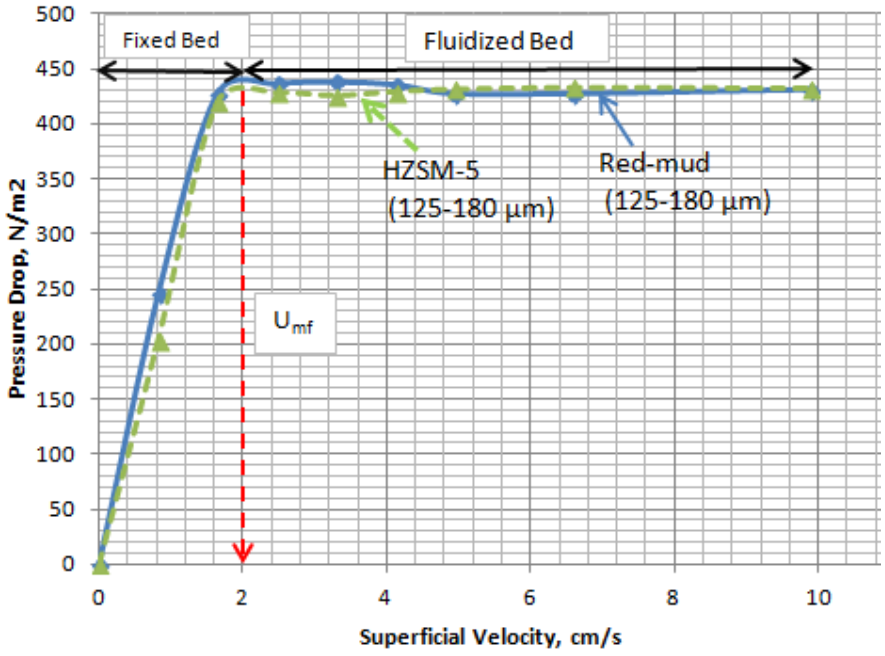

Figure 5.1: Pressure drop versus gas velocity for a bed of HZSM-5 and Red mud catalysts with the down arrow indicating the minimum fluidization velocity (U_{mf})

5.4.1 Product Distribution

The total liquid, char and non-condensable gas yields from conventional and catalytic pyrolysis of whole field pennycress biomass are presented in Table 5.1. The moisture content of the total liquid produced (i.e. aqueous phase and bio-oil) was determined to differentiate between organic and water yields. The analysis of product distribution helped in comparing of the fast pyrolysis products originating from the different fluidizing medium used. An average liquid yield of 54.06 ± 1.58 wt % was obtained for the non-catalytic experiments, which was higher than the liquid yields from the catalytic experiments. The char yield was almost the same in all the three experiments. Opposite trends were observed in the gas yields, the gas yield was higher in the catalytic pyrolysis whereas the gas yield was lower in the conventional rapid pyrolysis. This suggested that the catalytic experiments, which were aimed for oxygen removal, rejected the oxygen in the bio-oil in the form gases. The water yield

was also different in all the three experimental conditions. HZSM-5 catalyzed experiments favored the production of water than those of red mud. Studies on red mud reported that, the magnetite in red mud could be converted to hematite under the presence hydrogen.[17] This reaction releases water; hence this could be one of the sources of excess water in red mud catalytic pyrolysis product. Since red mud is a heterogeneous catalyst,[17] one could not conclusively pinpoint about the undergoing chemical reaction without further investigation about the catalyst. Compared to HZSM-5 (refer Table 5.1 and Table 5.2), red mud rejects oxygen mostly as CO_2 and less as water. This could possibly attribute for the higher percent of hydrogen in red mud than HZSM-5.[17] The difference in product of both catalysts indicates that they had different reaction pathways.

Table 5.1 Product yield distribution of catalytic and non-catalytic fast pyrolysis of whole field pennycress biomass

Pyrolysis medium	Product distribution (wt %, dry basis)				
	Total liquid	Organic liquid	Water	Char	Gas
Sand (non-catalytic)	54.06 ± 1.58	38.53 ± 2.05	15.53 ± 1.21	24.49 ± 1.09	21.45 ± 1.83
HZSM-5	47.13 ± 0.56	23.01 ± 1.06	25.19 ± 0.99	24.87 ± 0.82	29.02 ± 0.40
Red mud	43.71 ± 0.56	22.41 ± 1.06	21.30 ± 0.95	24.53 ± 0.12	31.65 ± 0.91

Figure 5.2 and Table 5.2 shows the effect of the fluidizing medium on gas composition. The gas yield and composition was different in all the three experimental conditions. HZSM-5 produced more carbon monoxide and hydrocarbon

gases. The carbon dioxide and hydrogen yield were highest in red mud catalyzed experiments compared to HZMS-5. The thermal degradation process using sand produced high amount of carbon dioxide. The difference in the product yield, therefore, indicated that the ongoing chemical reactions are not the same. Further scrutiny of the reactions is required before suggesting the probable reaction pathways. To further explain this variation in the yields observed, the composition of the liquid products was therefore analyzed.

Table 5.2 Effect of catalytic and non-catalytic pyrolysis on gas yield

Type of Gas	Sand		HZSM-5		Red mud	
	Gas Yield Mol%	Gas Selectivity (Mol%)	Gas Yield Mol%	Gas Selectivity (Mol%)	Gas Yield Mol%	Gas Selectivity (Mol%)
Methane	0.08±0.03	5.07±0.66	0.23±0.13	9.25±0.49	0.23±0.12	6.35±0.47
CO	0.32±0.05	20.67±0.65	0.97±0.41	30.27±1.68	0.63±0.30	18.03±0.56
CO_2	0.87±0.07	60.07±0.32	1.31±0.43	38.55±1.24	1.75±0.35	49.64±2.21
H_2	0.14±0.09	9.63±0.01	0.32±0.04	9.30±0.36	0.66±0.33	20.62±1.71
Ethylene	0.01	0.78±0.07	0.07±0.02	1.93±0.25	0.03±0.01	0.96
Ethane	0.01	0.90±0.09	0.05±0.01	0.82	0.04±0.02	0.99±0.04
Propylene	0.01	0.62±0.01	0.10±0.05	2.82±0.15	0.03±0.02	0.78±0.09
Propane	0.004	0.26±0.03	-	-	0.02±0.01	0.28±0.01
1-Butene	0.004	0.28±0.03	0.18	5.20±0.28	0.01	0.35±0.01
Butane	0.001	0.06	0.03±0.02	0.84±0.04	0.01±0.01	0.18±0.07
1-Pentene	-	-	0.02±0.02	0.69±0.03	0.01	0.23±0.01
Pentane	0.002	0.14±0.01	0.03±0.03	1.01±0.14	-	-
1-Hexene	0.002	0.15±0.05	0.02±0.01	0.87±0.17	0.01	0.20±0.04
Hexane	-	-	-	-	-	-
Total	1.46±0.02	100	3.33±0.16	100	3.42±0.14	100

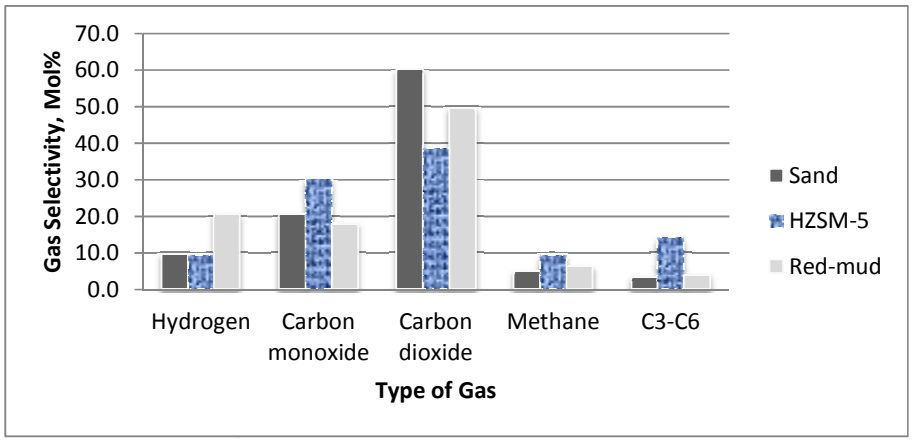

Figure 5.2 Effect of catalytic and non-catalytic fast pyrolysis of pennycress on Gas Yield

5.4.2 Properties of Catalytic and Non-catalytic fast pyrolysis bio-oils

The physicochemical properties of catalytic and non-catalytic fast pyrolysis bio-oils from electrostatic precipitator (ESP) are presented in Table 5.3. The moisture content of the ESP bio-oil ranged between 1.15-1.79 wt %. The water content of typical lignocellulosic bio-oils was reported to be in the range of 15-35 wt %.[4,7,31] The water content of the ESP bio-oil was very low in the current study because there was efficient condensation of water in the two condensers, which were cooled by 50-50% mixture of water and ethylene-glycol. The increase in the water content in bio-oil has a side effect on the liquid oils.[4] Some of these effect include lowering of the heating value and phase separation of the liquid oils.[4] Therefore, it is important to keep the water content as low as possible by using a good condensation system as well as using a properly dried biomass (less than 10% moisture content).[4,5]

The ESP captures more than 80 wt % of the total organic fraction of the pyrolysis liquid, hence it was used as the representative of the pennycress bio-oil. The bio-oil had a dark brown color with an unpleasant smell. This smell is due to the

presence of a considerable amount of nitrogen in the bio-oil (3.04-3.73 wt %). The presence of nitrogen could also have some negative effects such as catalyst poisoning during the upgrading process and emission of NO_x in combustion.[4] The mixture of bio-oil and lime, which is known as BioLime™, could help in reduction of nitrogen oxides when injected into flue gas tunnel.[32]The removal of nitrogen by such kind of process could therefore be helpful in protecting the environment from the release of poisonous NO_x and hence it can have a significant role in future commercialization of field pennycress bio-oils.

Table 5.3 Physicochemical properties of fast pyrolysis bio-oils of whole field pennycress

Property		Sand	HZSM-5	Red mud
Water Content (wt %)		1.79 ± 0.34	1.26 ± 0.3	1.15 ± 0.15
pH	Aqueous phase	5.61 ± 0.11	6.2 ± 0.23	8.86 ± 0.2
	Bio-oil	5.16 ± 0.12	5.67 ± 0.22	6.5 ± 0.14
Density (g/cm^3)		1.04 ± 0.01	ND[a]	1.01
Dynamic Viscosity (cP)		1825.5 ± 38.89[b]	604.75 ± 7.99	336.99 ± 5.78
Carbon Content (wt %)		69.8 ± 0.17	72.23 ± 0.22	75.33 ± 0.22
Hydrogen Content (wt %)		9.03 ± 0.02	8.21 ± 0.13	9.65 ± 0.03
Nitrogen Content (wt %)		3.04 ± 0.07	3.53 ± 0.07	3.73 ± 0.03
Oxygen Content (wt %)*		18.13 ± 0.19	16.03 ± 0.3	11.29 ± 0.26
Higher Heating Value (MJ/kg)		32.59 ± 0.33 (33.18)[d]	33.27 (33.63)[d]	35.29 ± 0.03 (35.7)[d]

* Oxygen is calculated by difference [d] dry basis values are in parenthesis [a] = Not Determined [b] = the bio-oil is gel-like at room temperature

The density of the bio-oil was found to be 1.04 g/cm^3 for the conventional pyrolysis bio-oil and 1.01 g/cm^3 for red mud catalyzed bio-oil. These density values are similar to the density of water. A typical wood derived pyrolysis bio-oil has a density of value around1.2 g/cm^3 and for petroleum derived light fuel oil, it is 0.85 g/cm^3. It is important to note that the lower density value of pennycress bio-oil will help in the ease with pumping the bio-oil in comparison to wood derived bio-oils.

The catalytic pyrolysis resulted in reduction in the viscosity of the bio-oil. Compared to bio-oil from conventional rapid pyrolysis, HZSM-5 and red mud reduced the viscosity of the bio-oil by 3 and more than 5 times, respectively. A similar finding was obtained in catalytic pyrolysis of pinion-juniper using HZSM-5 and red mud.[17] In their report, HZSM-5 and red mud produced a bio-oil with approximately 3 and 7 times less viscous oil than the oil obtained from conventional fast pyrolysis. The difference in viscosity among the pyrolysis catalyzed oils was due to higher degree of cracking of red mud than HZSM-5. As shown in Table 5.2, red mud produced a higher amount of gases and lower liquid yield than HZSM-5. Therefore, the reason for reduction in viscosity could possibly be attributed to catalytic cracking of the higher molecular weight pyrolysis vapors.

There was an improvement in the pH of the pennycress pyrolysis derived bio-oils. It is worth mentioning that thermal pyrolysis using sand had also produced a bio-oil with higher pH (5.16-5.61) than other conventional pyrolysis lignocellulosic bio-oil, which is in the range of 2.8 to 3.8.[32] Fast pyrolysis of pennycress oilseed, defatted presscake and regular presscake produced an aqueous phase liquid that had a pH value between 6.5 and 8.9.[33] However, the pH of the aqueous phase and the bio-oil derived from thermal degradation of pennycress biomass was 5.61 and 5.16, respectively. Compared to pennycress seed bio-oil, the pH of whole pennycress

biomass was lower due to the fact that the entire biomass, that includes the leaves, stem and seeds, was used in the current study; hence the lignocellulosic portion of the biomass could result in the lowering the pH. But the pH of the bio-oil from pennycress is still higher than the normal range from other lignocellulosic feedstocks.

The presence of organic nitrogen in the pyrolysis liquid could produce a bio-oil with high pH value.[32] Pennycress seed with 4.3 wt % nitrogen yielded an aqueous phase with pH 6.4 whereas defatted pennycress press-cake that had 6.93 wt % nitrogen content resulted in a pH value of 8.9.[33] Therefore with the increase in nitrogen content, the pH value increased. The decomposition of the proteins (27%, moisture and oil free basis)[34] present in the oilseeds of field pennycress was the source of nitrogen. The basic nitrogen containing compounds that originate from the decomposition of proteins were suggested to have a neutralizing effect on the organic acids (formic, acetic, propanoic, and others).[33] The whole field pennycress feedstock had 2.88 wt % nitrogen content and the bio-oil from the thermal degradation had 3.04 wt % nitrogen. Hence, the presence of nitrogen could possibly contribute to the increase in the pH value. But the pH value was not as high as the pH of the liquid product from pennycress seed and press-cakes because the whole field pennycress had a lower nitrogen content compared to them.

Catalytic pyrolysis of field pennycress further improved the pH of the bio-oil. The pH of the aqueous phase and the bio-oil from HZSM-5 catalyzed experiments were 6.2 and 5.67, respectively. For red mud catalyzed experiments, the pH for the aqueous phase was as high as 8.86 and the bio-oil had a pH of 6.5. Therefore, the catalysts were effective in upgrading in terms of pH. Taking nitrogen content as reference, there seem to be an obvious trend. With the increase in nitrogen content, the pH value increased. Especially red mud produced almost a neutral pH bio-oil,

which is among the highest reported pH values so far for aqueous phase of pyrolysis liquid product from lignocellulosic biomass feedstocks. It is noteworthy that this pH is similar to those of aqueous phase of pennycress press-cake because the whole field pennycress had about 73.4 wt % lignocellulose feedstock content. If proteins are considered as major contributor to the higher pH, this could possibly serve as indicator that the fate of most protein degradation product it in the bio-oil from catalytic pyrolysis of the whole field pennycress was comparatively higher when red mud was used as catalyst. This is an important finding because the acidic pH of the lignocellulosic feedstock derived bio-oils was one of the major challenges in affecting storage, stability and handling of bio-oil.[4,5,35,36] Therefore, field pennycress pyrolysis bio-oil could suitably be used for fuel application.

The higher heating value (HHV) of the conventional pyrolysis ESP bio-oil was found to be 32.59 MJ/kg (33.18 MJ/kg, dry basis). In general, the HHV of typical bio-oils is about half of conventional petroleum fuels (42-44 MJ/kg).[4,32] This is because of the oxygen content (35-40%) of the bio-oil.[4,7,32,36] The oxygen and water content of pennycress bio-oil (Table 5.3) were far below the range in most lignocellulosic bio-oil.[37] Therefore, the HHV value is much higher in the whole field pennycress bio-oil. The presence of extractives and organic nitrogen containing proteins could affect the higher calorific value obtained.

The carbon and hydrogen content could also best explain the HHV difference because the HHV value is dependent on them.[30,38] A typical bio-oil has a carbon and hydrogen content of 55-58% and 5.5-7%, respectively. But the bio-oils from thermal degradation of field pennycress had a high carbon content of 69.8% and hydrogen content of 9.03%. Hence, that is why the pennycress bio-oil had high calorific value.

The HHV value of the ESP bio-oil increased in the catalytic pyrolysis process compared to the value from conventional fast pyrolysis. The HHV for the HZSM-5 catalyzed experiment was 33.27 MJ/kg (33.63 MJ/kg, dry basis). This increase in HHV was not significantly higher than the one obtained in fast pyrolysis. However, when red mud was used as catalyst, there was a considerable increase in HHV. The bio-oil had a HHV as high as 35.29 MJ/kg (35.7 MJ/kg, dry basis). The HHV for petroleum derived heavy fuel oil is 40 MJ/kg.[7] Hence the bio-oil had 89.25% energy content of the heavy fuel oils. Therefore, when red mud was used as fluidizing medium, the energy content of the bio-oil improved from 82.95 to 89.25% of the heavy fuel oil. The increase in the HHV of the bio-oil can be simply explained by looking the elemental composition of the bio-oils. Red mud catalyzed experiment had higher carbon and hydrogen content than HZSM-5 catalyzed ones. Moreover, the oxygen content, which contributes to the lower HHV, was lower in red mud than in HZSM-5 catalyzed experiments.

In Table 5.2 (and recall also figure 5.2), HZSM-5 produced the highest mole percent of carbon monoxide (CO) and hydrocarbons than red mud. In the case of red mud, oxygen was mostly rejected as carbon dioxide (CO_2). Therefore, the rejection of oxygen as CO_2 in the case of red mud had preeminence over CO production because two oxygen atoms are removed with one carbon, hence less carbon was consumed for rejection of oxygen. In addition to that, HZSM-5 catalytic pyrolysis produced more hydrocarbons gases, which cause additional hydrogen and carbon loss for the bio-oil. The loss of more hydrogen and carbon as C_2-C_6 hydrocarbon gases could possibly have an effect to the reduction of hydrogen and oxygen in the HZSM-5 catalyzed bio-oil. Therefore, this reason could explain why HZSM-5 had lower HHV value than red mud catalytic pyrolysis bio-oils. Moreover, the gas yield could be helpful in

proposing the reaction pathways. Yathavan and Agblevor[17] suggested that the release of high level of CO in HZSM-5 catalytic pyrolysis could be due to the dominance of decarbonylation reaction. The production of high amount CO_2 in the case of red mud was attributed to decarboxylation reaction being a dominant pathway.[17] This reaction pathways could probably have taken place in the current study

Chemical characterization of the electrostatic precipitator (ESP) bio-oil was conducted in order to have a better understanding of the chemical reaction and chemical makeup of the bio-oil. Two nuclear magnetic resonance (NMR) spectroscopy, ^{1}H and ^{13}C, were performed. The analysis of the spectra regions was done according to Mullen et al.,[39,40] who characterized a similar type of bio-oil. The proton NMR spectra of the bio-oils are presented in Figures 5.3, 5.4 and 5.5. The

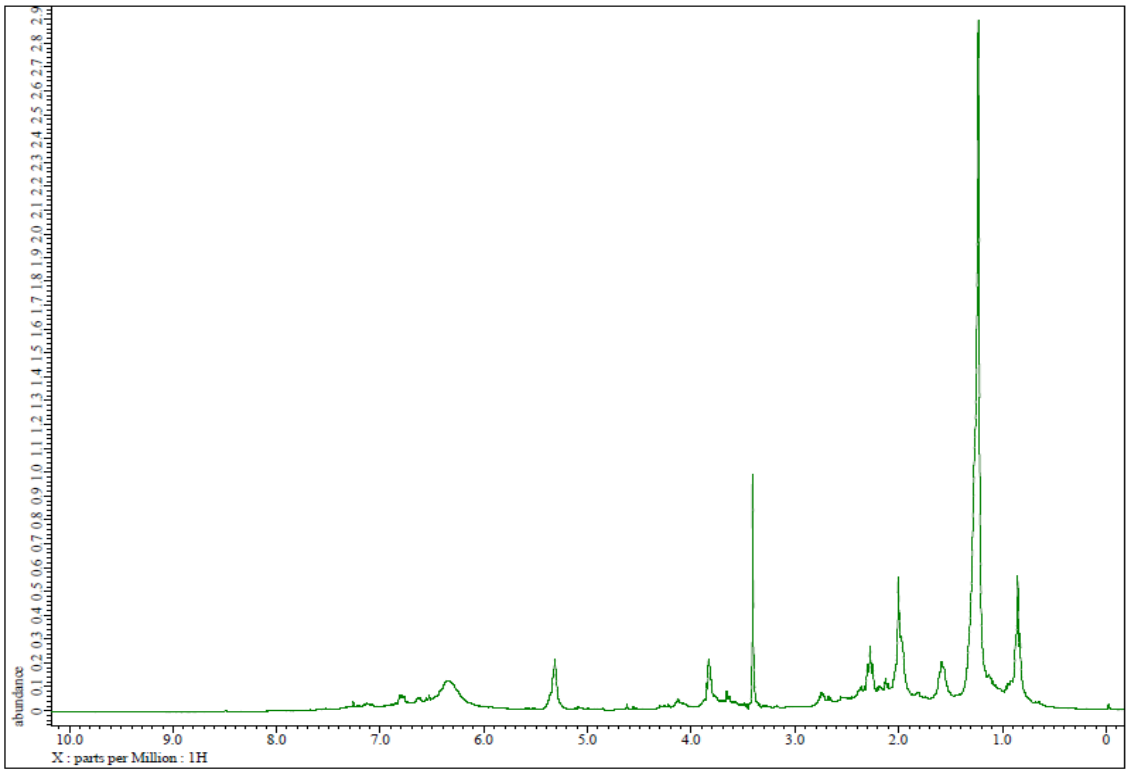

Figure 5.3 ^{1}H NMR spectra of field pennycress bio-oil from conventional fast pyrolysis

difference in intensities and height of the abundance peak were used for the comparison of the amount the catalytic and non-catalytic bio-oils.

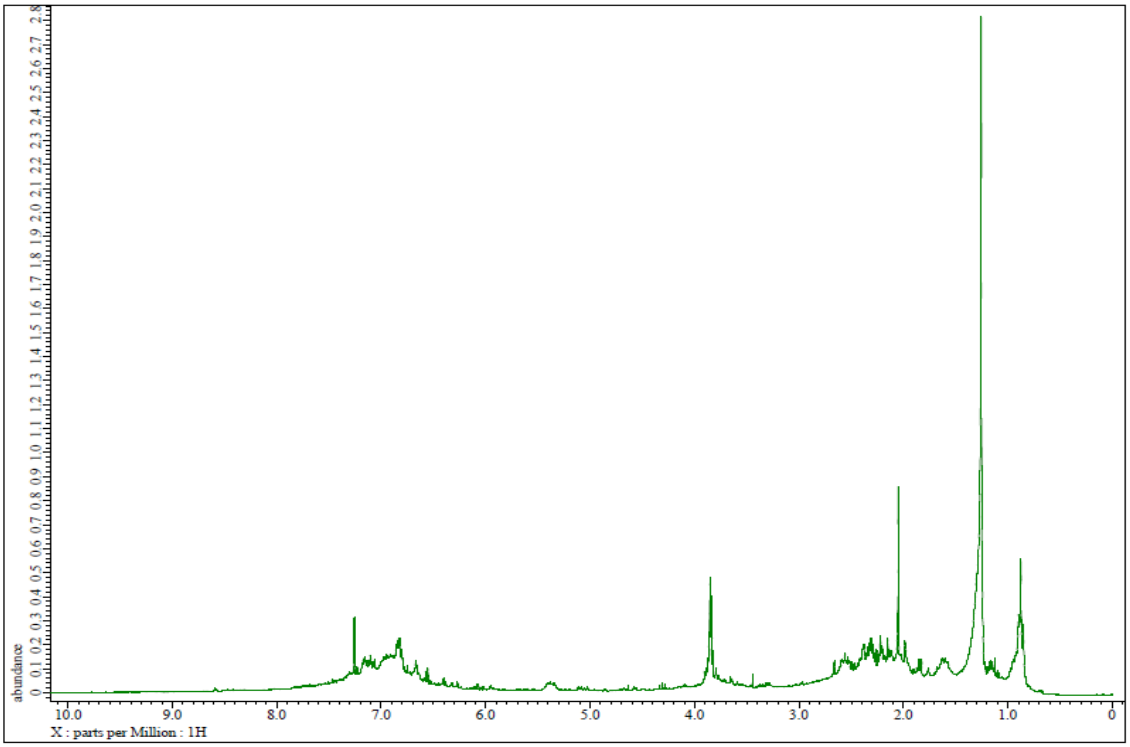

Figure 5.4 ^{1}H NMR spectra of field pennycress catalytic pyrolysis bio-oil using HZSM-5

Figures 5.3, 5.4 and 5.5 (^{1}H NMR spectra) shows the prominence of aliphatic protons (alkanes) from 0.5 to 1.5 ppm. The strong signal observed in this region suggests that they are rich in aliphatic alkyl chains. The chemical shift at 1.3 ppm was the highest of all the peaks. When the three types of bio-oils were compared, red mud had the largest peak. This could possibly be associated with the reason that red mud catalyzed bio-oil had highest energy content. The proton between 1.5 - 3.0 ppm were due to aliphatic carbon atoms that may be bonded to C=C (aromatic or olefinic) or may be bonded to heteroatom.[40] There was slight difference in the intensity of the signal from 1.5 to 3 ppm in the bio-oils. The protons from HZSM-5 catalyzed bio-oils

appeared at a high level and were denser. Therefore, HZSM-5 produced a bio-oil that was rich with these protons. The chemical shift for protons in the 0.5 - 3 ppm had a big role in the energy content of the bio-oils.[40]

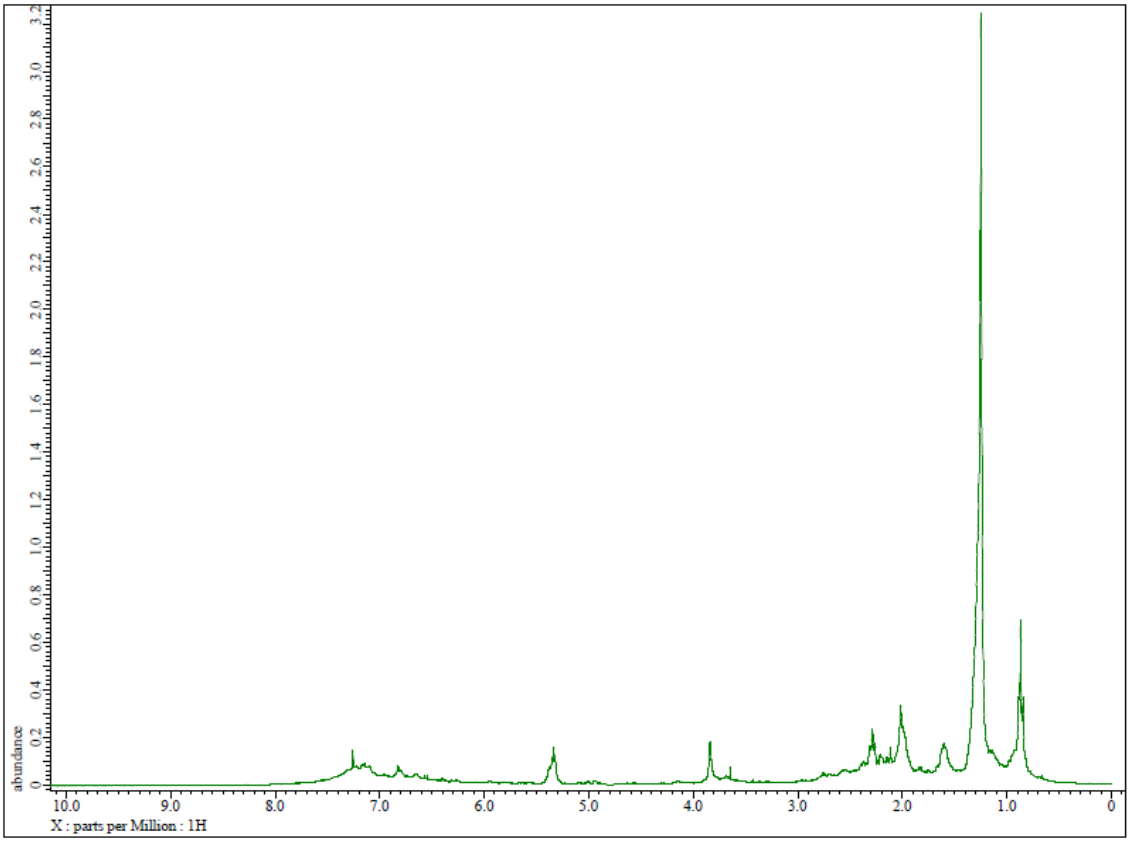

Figure 5.5 ^{1}H NMR spectra of field pennycress catalytic pyrolysis bio-oil using red mud

The proton chemical shift next to an aliphatic alcohol or amines was between 3.0 - 4.4 ppm while those between 4.4 - 6.0 ppm were due to the presence of methoxy, carbohydrates or phenolics-OH (methoxy phenols).[39,40] From Figures 5.3, 5.4 and 5.5, the trend of the degree of prominence of the compounds in the range 3 - 6 ppm was sand > HZSM-5 > red mud. Mullen et al.[39] suggested that this range could indicate the presence of a heteroatom. This trend was found to be consistent with the elemental

analysis of which the amount of oxygen was the highest in Sand, decreased in HZSM-5 and was the lowest in red mud.

The protons between 6-8.5 ppm were aromatic protons in benzenoids and in N-heterocyclics.[39–41] The order of the abundance and intensity in this range was HZMS-5 > sand > red mud. This suggests that HZSM-5 produced a high amount of aromatics. Studies show that HZSM-5 produced high amount of aromatics.[9,19] This is in agreement with our experimental result. A study on the different energy crops and agricultural feedstock also revealed that the aromatic protons in this region do not correlate with the energy content of the bio-oil.[40] This finding is consistent with the current study because even though HZSM-5 appeared to have a higher aromatic yield, the HHV was similar to that of sand. The low level of signal for red mud could

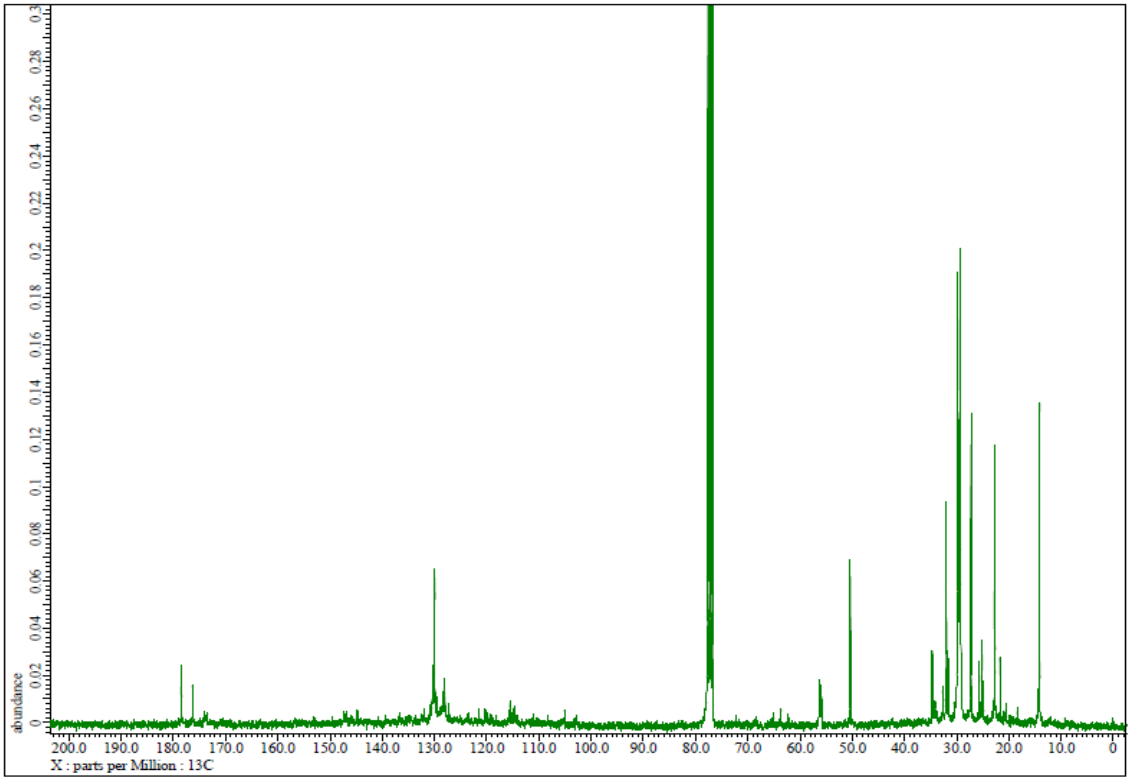

Figure 5.6 ^{13}C NMR spectra of field pennycress bio-oil from conventional fast pyrolysis

possibly be due to the hydrogenation of the aromatic ring to saturated hydrocarbons.[39] However; this proposed reaction requires further investigation. The signal beyond 8.5 (9.5-10.1 ppm) was attributed to aldehydes. Carboxylic acids may also show up, but both of them were not detected in all the bio-oils. The higher pH of the bio-oils could therefore be due to the absence of these compounds.

To further investigate the chemical makeup of the bio-oil, ^{13}C NMR analysis was conducted. Six regions were selected during the characterization process. The ^{13}C NMR spectrum of the bio-oils in Figure 5.6, 5.7 and 5.8 was classified as signals between 0 and 28 ppm (short chainaliphatics), 28-55 ppm (long and branched chain aliphatics), 55-95 ppm (alcohols, ethers, phenolic methoxys, and carbohydrate sugars), 95-165 ppm (aromatics including hetero aromatics), 165-180 ppm (esters, amides, carboxylic acids), and 180-215 ppm (ketones and aldehydes).[39,40]

The most prominent resonance is all the three types of bio-oils occurred in the second region (28-55 ppm), specifically from 28-36 ppm. This appeared to indicate the presence of very long aliphatic chains. The difference in the higher heating value (HHV) of the bio-oil could possibly be attributed to their difference in the aliphatic chain in this region.[2,36,40] Red mud had the highest signal than HZSM-5 and sand at approximately 30 ppm. Even though oxygen is the most important factor for HHV, the fact that red mud had highest signal at this region could serve as an additional reason for having highest HHV value. Both HZSM-5 and sand had similar levels of resonance and their HHV was slightly different. The next spectral region having intense and diversified peak was in the range of 0-28 ppm. Mullen et al.[39] assigned these peaks this region to the isolated methyl and methylene aliphatic groups. The order of the magnitude of the peaks at this up field region was red mud > Sand > HZSM-5.

The production of high amount of aromatics by HZSM-5, which was also observed in ^{1}H NMR, was again confirmed in the 95-165 ppm signal. The relatively strong resonance at 132 ppm could probably be due to the carbon in benzenoids structures or in nitrogen heterocyclics.[41] In contrast to ^{13}C NMR of typical lignocellulosic bio-oils,[12,17,40] there were very few peaks in the range of 55-95 ppm. These signals were assigned to carbon with oxygen atom attached to it.

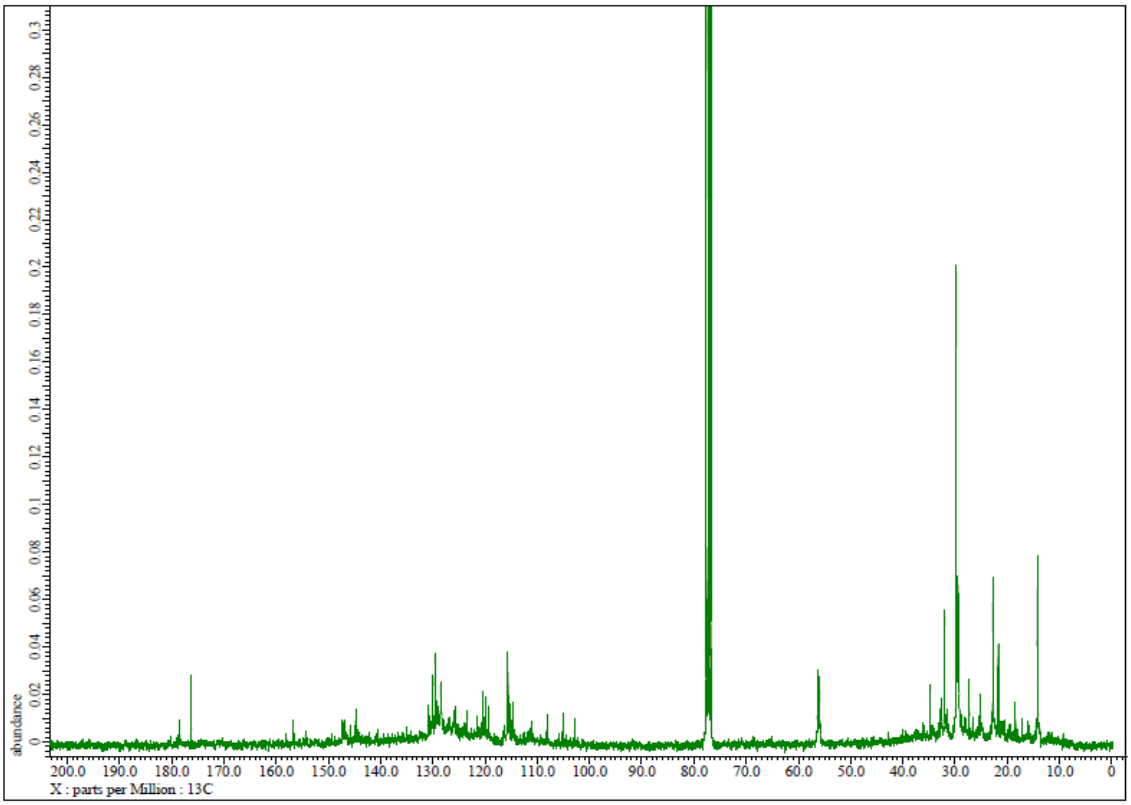

Figure 5.7 ^{13}C NMR spectra of field pennycress catalytic pyrolysis bio-oil using HZSM-5

Yathavan and Agblevor[17] assigned the signal from 55-57 ppm to methoxyl group in lignin. This peak was observed in this study, but the demethoxylation reaction was not clearly observed in the ^{13}C NMR spectrum. However, there was a decrease and / or disappearance in the resonance of the peaks in both catalytic bio-

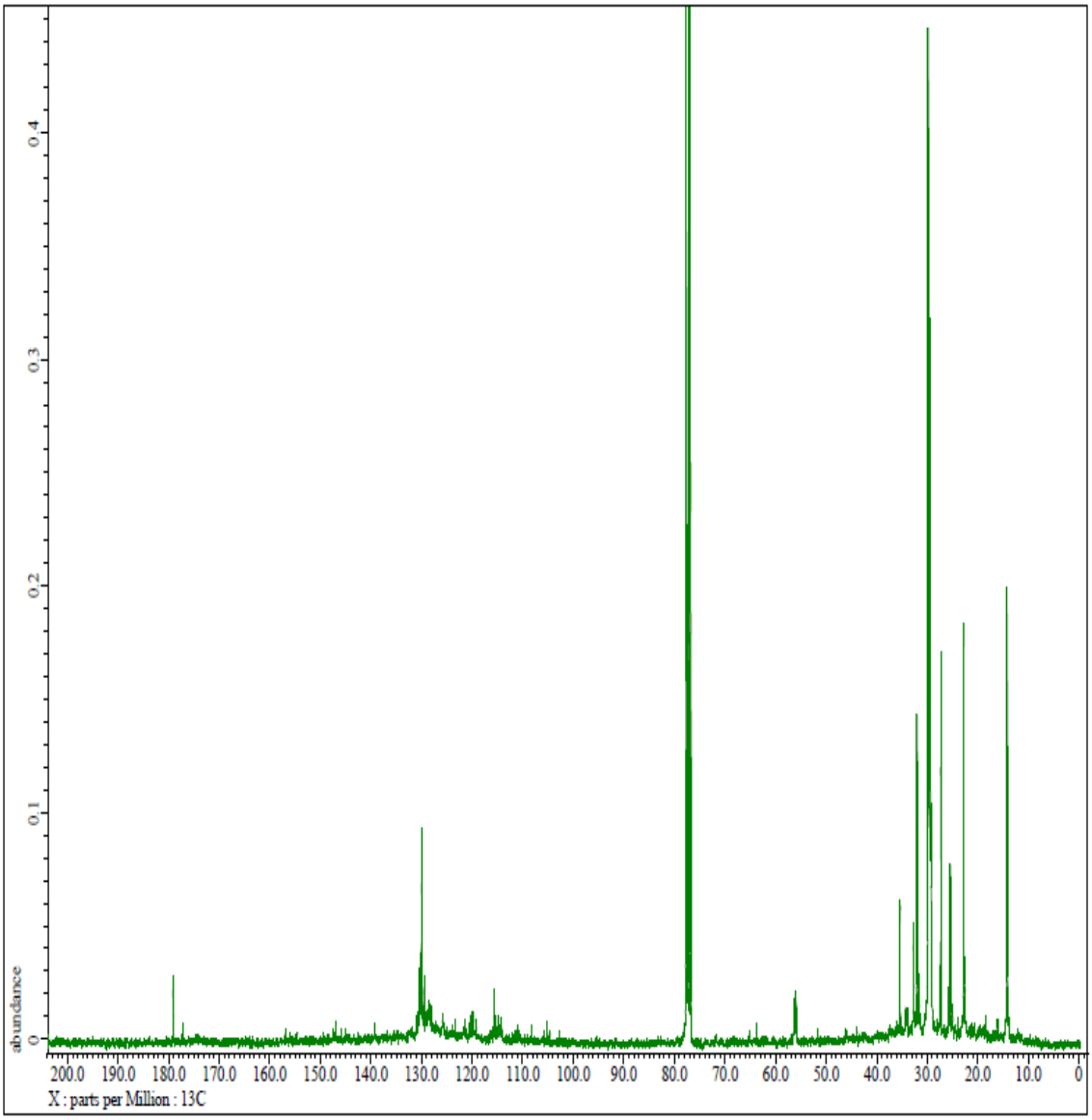

Figure 5.8 ^{13}C NMR spectra of field pennycress catalytic pyrolysis bio-oil using red mud

oils. This indicates that there was deoxygenation of the methoxyl group. A typical bio-oil consists of 35-40% oxygen content.[36] However, in the case of field pennycress the oxygen content was 18.13, 16.03, and 11.29 for sand, HZSM-5 and red mud, respectively. Therefore, these low values of oxygen content were consistent with the observations in the ^{1}H NMR and ^{13}C NMR spectrum because they showed less

intensity and magnitude of peaks at the regions where oxygenated compounds were supposed to resonate. The catalytic effect was also observed with red mud being the most efficient in deoxygenation followed by HZSM-5. The deoxygenation process by a catalyst could take place by cracking carbohydrates and alcohols.[9]

The resonance in the downfield region of 165-180 ppm was attributed to amides, acids or esters. From Figure 5.6, 5.7 and 5.8., it is evident that the appearance of small and handful signals shows that the bio-oils were less acidic. The pH of the bio-oils was 5.16, 5.67, and 6.5 for sand, HZMS-5 and red mud, respectively. A similar trend was observed because there was a decrease in the intensity of the peaks in the order of sand > HZSM-5 > red mud. There was no observable signal in the extreme downfield region (180-215 ppm). This explains that there was no detectable level of aldehydes, which is in agreement with ^{1}H NMR spectrum. Boateng et al.[33] also had also a similar finding. They reported that the absence of aldehydes contributed to the unusual stability of the bio-oil because aldehydes are known to be active compounds that can accelerate aging.

From ^{13}C NMR and ^{1}H NMR spectra, it was evident that the catalyst produced less oxygenated compounds, especially red mud. The presence of the low level of undesirable oxygenates and the production of more aliphatics and aromatics compounds could therefore be the possible reason for the high energy content, less acidity and lower viscosity of the catalytic bio-oils.[9,12,17,39,40] In this study, red mud was found to be more effective than HZSM-5 in upgrading the field pennycress bio-oil. As stated earlier in this chapter, red mud is a waste product from alumina industry. The disposal of high quantities red mud could cause a potential threat to the environment due to its caustic nature.[25,26] Hence, utilizing red mud as catalyst gives much value to this waste product both environmentally and economically. The use of

this inexpensive catalyst, red mud, is hence believed to save significant amount allocated to operation cost during catalytic pyrolysis.

It is worth mentioning that red mud can be regenerated after use for several times and will still maintain its catalytic activity. The catalyst was regenerated in a muffle furnace for 5 hours at 550 °C. The regenerated red mud was then used to conduct the duplication of the red mud catalytic experiments. There was no significant difference between the results obtained from the duplications with regenerated red mud. In this research, we demonstrated a simple and inexpensive upgrading process that produces good quality bio-oil. We didn't observe the many shortfalls of other bio-oil upgrading process, such as hydrotreating, are known for. Reports indicate that the drawbacks related to post-pyrolysis upgrading process include significant catalyst deactivation, expensive catalyst used, high char/coke formation, lower yield of hydrocarbons, and substantial hydrogen consumption.[11,12]

Our achievement in this study was not only limited to demonstrating that red mud can be used as catalyst but the discovery that the whole field pennycress biomass can be used a feedstock in pyrolysis. Some studies were conducted on the use of field pennycress as a source of energy, but the focus on the use of pennycress seed.[33,37,39,42] It has not been reported in published literature on the use of whole field pennycress biomass as a feedstock for bio-energy. The pennycress seed accounts for 26.6% of the entire biomass. According to agronomic studies on field pennycress, harvesting 1,316.9 kg/ha of field biomass yielded 350.7 v of oilseed.[43] Therefore, the product that can be obtained from one fourth of the plant matter could not have considerable contribution towards global energy demand. However, by using the whole biomass, we can utilize the remaining 73.4% of the lignocellulosic biomass. A higher quantity and a better quality bio-oil were produced, which were at least as good as the bio-oil

yield obtained from the experiments on pennycress seed. Therefore the finding of this study was remarkable.

The organic yield obtained from fast pyrolysis of the pennycress seed was 57.1 wt %.[33] This is equivalent to 15.19 wt % of the whole biomass if we consider the seed yield to be 26.6%. In our study, the highest and the lowest organic yield were 38.53 (for conventional pyrolysis) to 22.41 wt % (for red mud catalytic pyrolysis). From the results mentioned, it is apparent that the result obtained in the current study is significantly higher than the pennycress seed. Quantitatively speaking, compared to the yield obtained in the current study, there was an increase in the organic yield by about 45%. The higher heating value (HHV) of the bio-oil from pennycress seed was 34.7 MJ/kg, which was lower than the one obtained from the value obtained from our study (i.e. 35.7 MJ/kg). The ESP bio-oil of the red mud catalyzed bio-oil from our study was a pH of 6.5, but the pH of pennycress seed was not reported. Since the pH of the red mud bio-oil was almost neutral, it can be considered as an ideal bio-oil in terms of pH. The aqueous phase for pennycress oilseed[33] and red mud catalytic oil were 6.4 and 8.7, respectively. The elemental composition of pennycress press-cake had also low carbon and hydrogen content and high oxygen content with lower HHV of 32 MJ/kg.[37] Therefore, the catalytic pyrolysis of whole pennycress biomass produced a bio-oil which was competent both qualitatively and quantitatively.

The bio-oil obtained from field pennycress, which is considered as a weed, is expected to have a vital contribution to the bio-energy sector in particular and global energy demand in general. *T. arvense* can be grown in temperate regions of the world.[44–46] This plant can potentially produce as high as 840 L/ha oils and 1470 kg/ha press-cake on 16 million hectare of farm land in the USA Midwest Corn Belt that is left fallow during the fall through spring months.[44] Therefore, it is an attractive

investment from the stand point of commercializing field pennycress as feedstock to satisfy world energy demand.

In this research, we produced a valuable product from two materials that were considered as a waste. Field pennycress biomass is considered as a weed and red mud is an industrial waste.[25,44] The use of two waste materials to produce a good quality bio-oil could therefore bring this research to the forefront. In contrast to typical lignocellulosic bio-oils, the bio-oil from red mud catalytic pyrolysis may not require excessive amount of hydrogen to upgrade it to hydrocarbon fuel. Therefore the potential of the bio-oil to be used as an alternate source of energy is very high.

5.5 Conclusion

Catalytic fast pyrolysis of whole field pennycress biomass was demonstrated in a fluidized bed reactor at 500 °C. Compared to conventional rapid pyrolysis of field pennycress, the use of red mud and HZSM-5 as catalysts improved the quality of the bio- oil. The pH, higher heating value and density of the bio-oil were also significantly different from a typical lignocellulosic feedstock bio-oil. Red mud was found to be more effective in upgrading the bio-oil than HZSM-5 catalyst. The bio-oil from red mud catalytic pyrolysis had almost neutral pH of 6.5, density of 1.01 g/cm^3 (almost the same as water), a higher heating value of 35.7 MJ/kg (dry basis). The pH and HHV for HZSM-5 were 5.67 and 33.65 MJ/kg, respectively. Moreover, red mud reduced the viscosity of the bio-oil by more than 5 times while the decrease in viscosity was by 3 folds when HZSM-5 was used as catalyst. The composition of non-condensable gases and the chemical make-up of the bio-oils were different, suggesting that the reaction pathways for the catalysts were different. From the NMR analysis, HZSM-5 had higher selectivity for aromatics compounds and red mud produced longer aliphatic chains.

The bio-oil obtained from field pennycress, which is considered as a weed, is expected to have a vital contribution to the bio-energy sector in particular and global energy demand in general. The fact that field pennycress can be grown in temperate regions of the world and has also prolific seed yield makes the study more feasible and sustainable for future commercializing. The use of field pennycress as a feedstock and red mud as catalyst, which are both considered as waste material, to produce such a bio-oil is really remarkable. Further upgrading of the bio-oil to hydrocarbon fuels is predicted to have minimal requirement owing to the fact that the bio-oil had very low oxygen content. Therefore, the results obtained in this study can be considered a remarkable achievement in the catalytic pyrolysis technology.

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CHAPTER 6

SUMMARY

To satisfy the energy demand of modern society and prevent environmental pollution arising from the use of exiting fossil fuels, an alternate source of energy is required. Biomass has the potential to provide renewable energy source that is inexpensive and environmentally friendly by the process such as fast pyrolysis. Field Pennycress (*Thlaspi arvense L.*), previously considered as a weed, is found to be an ideal source for energy production. The purpose of this research is to produce an upgraded bio-oil by the catalytic pyrolysis of field pennycress biomass in a fluidized bed reactor. The specific objectives are to conduct:

i. Characterization, thermogravimetric and kinetic study of whole pennycress
ii. Parametric study on conventional rapid pyrolysis of pennycress biomass.
iii. Catalytic pyrolysis using red mud and HZSM-5

The characterization of the biomass showed that field pennycress had high volatile content and Higher Heating Value (HHV), making it an interesting feedstock for energy production. Thermogravimetric and kinetic study on field pennycress provided vital information on the degradation behavior of the feedstock. Important differences were observed as the heating rate increased from 5 to 20 °C/min and at temperatures ranging from room temperature to 700 °C. The experimental result in this work indicated that the major decomposition takes place between 200-450 °C and the whole biomass pyrolysis can be divided into five stages. Kinetic study of field pennycress revealed that the value of activation energy rapidly increased after 80% conversion.

A parametric study was conducted on conventional rapid pyrolysis by using the effects model. The influence of operational conditions, temperature and nitrogen

gas flow rate, was studied. The total liquid yield was influenced by both temperature and gas flow rate. However, there was no interaction effect among these two factors. According to the statistical model, a significantly highest liquid yield of 54.06 wt % was obtained for reaction temperature of 500 ^{o}C and nitrogen gas flow rate of 24 L/min. At this experimental condition, the organic yield and the gas yield were 40.82 wt % and 19.41 wt %, respectively.

Catalytic fast pyrolysis of whole field pennycress biomass was demonstrated in a fluidized bed reactor at 500 °C and nitrogen gas flow rate of 24 L/min. Compared to conventional rapid pyrolysis of field pennycress, the use of red mud and HZSM-5 as catalysts improved the quality of the bio- oil. The bio-oil from the red mud catalyzed experiment had almost neutral pH of 6.5 and the pH in the case of HZSM-5 was 5.7. In comparison to bio-oil from conventional rapid pyrolysis, HZSM-5 and red mud reduced the viscosity of the bio-oil by 3 and 5 times, respectively. Red mud was also found to be effective in improving the higher heating value (HHV) of the bio-oil from 33.18 MJ/kg (dry basis) in conventional pyrolysis to 35.7 MJ/Kg (dry basis). The HHV of HZSM-5 catalyzed bio-oil was 33.63 MJ/kg.

The composition of non-condensable gases and the chemical makeup of the bio-oil from the two catalysts were different, suggesting that the reaction pathways could be different. HZSM-5 had higher selectivity for aromatics whereas red mud produced longer aliphatic chains. The use of field pennycress as a feedstock and red mud as catalyst, which are both considered as waste material, to produce such a bio-oil is really remarkable. The bio-oil obtained from red mud catalytic pyrolysis of field pennycress is a promising alternative energy source that could replace petroleum fuels after some upgrading.