Experimental Study of Biomass Pyrolysis in a Fluidized Bed Reactor: Effect of Biomass Blending and *In-situ* Catalysis

by

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Abstract

Lignocellulosic biomass has been recognized worldwide as a renewable resource of energy for the production of liquid biofuels due to its low cost and abundance. Several routes to convert biomass to biofuels have been studied extensively, but they are limited by the multiple conversion steps and high cost of processing required, which makes it difficult to implement them on a large scale. Fast pyrolysis is a promising technology to convert biomass to hydrocarbons. Fast pyrolysis has several advantages such as short residence time, moderate temperature (400 to 600 °C) and its ability to convert biomass to liquid fuel in a single step with high yield. However, some of the properties of the liquid product from fast pyrolysis such as high acidity, high oxygen content, high viscosity and low heating value are impediments to the development of this technology. High acidity renders the liquid to be corrosive, while high viscosity and low stability make it unattractive as a fuel and practical application of bio-oil suffers due to these properties. A brief review of the background information of this study, including the factors affecting pyrolysis, properties of bio-oil and various upgrading techniques, is summarized in Chapter 2.

A fluidized bed reactor based experimental setup was designed and fabricated for this study which had an overall goal of investigating different techniques to improve the physical and chemical properties of bio-oil obtained from fast pyrolysis of biomass. This goal was achieved by carrying out two specific objectives. The first objective was to identify the optimum residence time and process temperature for fast pyrolysis of southern pine, followed by evaluating the effect of blended biomass feedstocks (southern pine and switchgrass) to understand their impact on the quality of bio-oil obtained from fast pyrolysis (Chapter 3). From this study, it was observed that blending switchgrass with southern pine improved the pH and viscosity of the bio-oil, but there was no significant effect on the heating value of the bio-oil. However, bio-oil produced with greater amounts of switchgrass than pine resulted in a clearly phase separated bio-oil.

In the second objective, basic catalysts (MgO, CaO) and acidic catalyst (ZSM-5) were incorporated in the fluidized bed reactor as *in-situ* catalysts to upgrade pyrolysis vapors (Chapter 4). The performance of each catalyst was evaluated based on the quality of bio-oil obtained, when compared to control experiments using inert bed material (quartz sand). CaO was found to be effective in reducing the acidic components in bio-oil, resulting in improvements to the total acid number (88.9 to 46.6) and pH (2.39 to 3.98) of the bio-oil produced. While the catalytic activity of MgO was observed to be minimal, ZSM-5 proved to be the most effective in deoxygenating bio-oil although it had a disadvantage of significantly reduced liquid yield. The stability of the bio-oils produced was compared by performing accelerated aging tests and it was observed that bio-oil produced through *in-situ* catalysis by CaO was the most stable when compared to the control and other bio-oils tested in this study.

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1. Introduction

1.1. Rationale

The major drive for the development of renewable energy technologies is due to concerns about climate change and limited reserves of non-renewable fossil fuels to meet our energy needs. The consumption rate of fossil fuels is much greater than the rate at which it is being regenerated, hence the need for alternative forms of energy. Biomass is one of the solutions to these problems primarily due to its carbon neutral nature since the carbon dioxide released into the atmosphere during combustion is offset by the consumption of CO_2 by plants through photosynthesis during their growth. Among multiple pathways for conversion of biomass into useful forms of energy, fast pyrolysis is considered as the most promising technique for producing liquid fuels from biomass. It is a thermal decomposition process in which biomass is converted in the absence of oxygen to produce bio-char, non-condensable gases and liquid product – bio-oil. Bio-oil has the potential to be used in many applications such as for heat generation, transportation and as a feedstock for the selective production of value added chemicals. However, a major disadvantage that has hindered the use of bio-oil is its high oxygen content, which results in low energy density of the liquid. Some of the negative physical and chemical properties such as high acidity, high viscosity, low stability are also caused by this high oxygen content. Therefore, there is a need to develop processes that can improve these properties and ultimately make bio-oil more attractive as a potential fuel.

1.2. Research Objectives

The overall goal of this research was to investigate techniques to reduce the oxygen content in bio-oil and improve some of the negative properties of bio-oil. This goal was divided into two specific objectives:

1.2.1. Fast pyrolysis of biomass: influence of operating conditions and pyrolysis of biomass blends

This study was initially focused on identifying the optimal conditions of process temperature and residence time to produce maximum bio-oil yield in fast pyrolysis of southern pine. At the optimum conditions identified, the effect of blending two different types of biomass – southern pine and switchgrass - was studied at different ratios. The effect of blending was evaluated based on physical and chemical characterization techniques, as described in Figure 1.1.

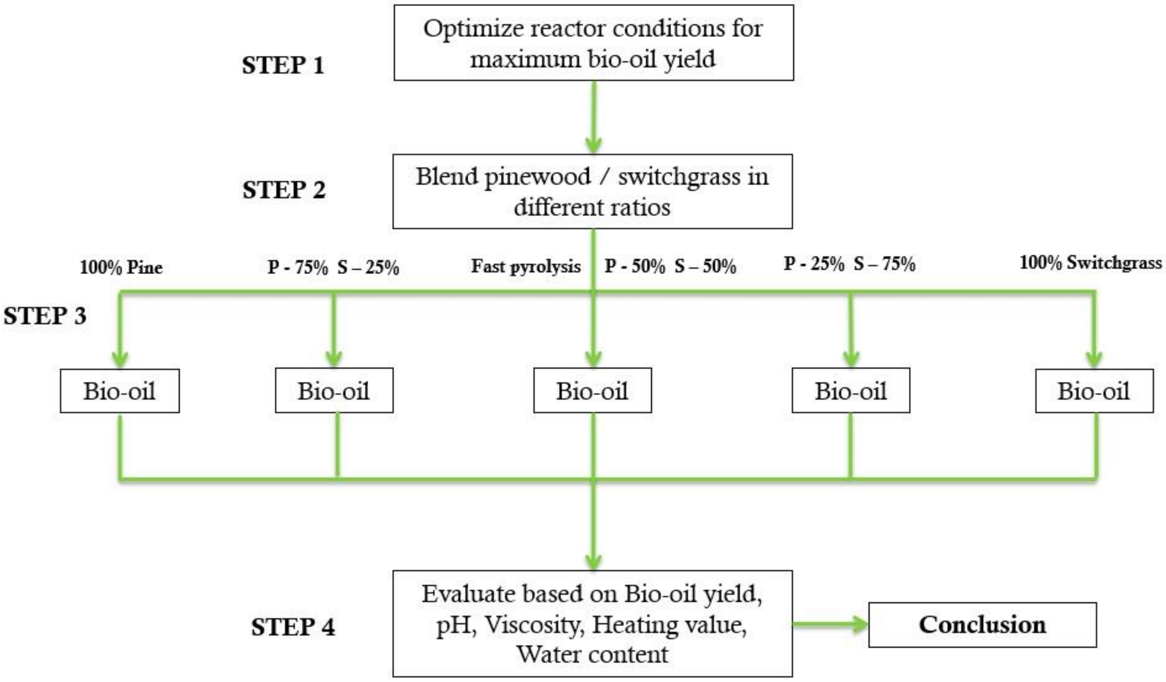

Figure 1.1. Experimental scheme for objective 1

1.2.2. Physical and chemical properties and accelerated aging test of bio-oil produced from *in-situ* catalytic pyrolysis in a bench-scale fluidized bed reactor

This study was performed to investigate the effect of using MgO, CaO and ZSM-5 as *in-situ* catalysts during catalytic pyrolysis of biomass, to identify the catalyst that improves the acidity, viscosity and oxygen content of bio-oil. The performance of these catalysts was evaluated against bio-oil produced in non-catalytic experiments and accelerated aging test was performed to compare the relative stability of the bio-oil produced. The experimental scheme for this objective is described in Figure 1.2.

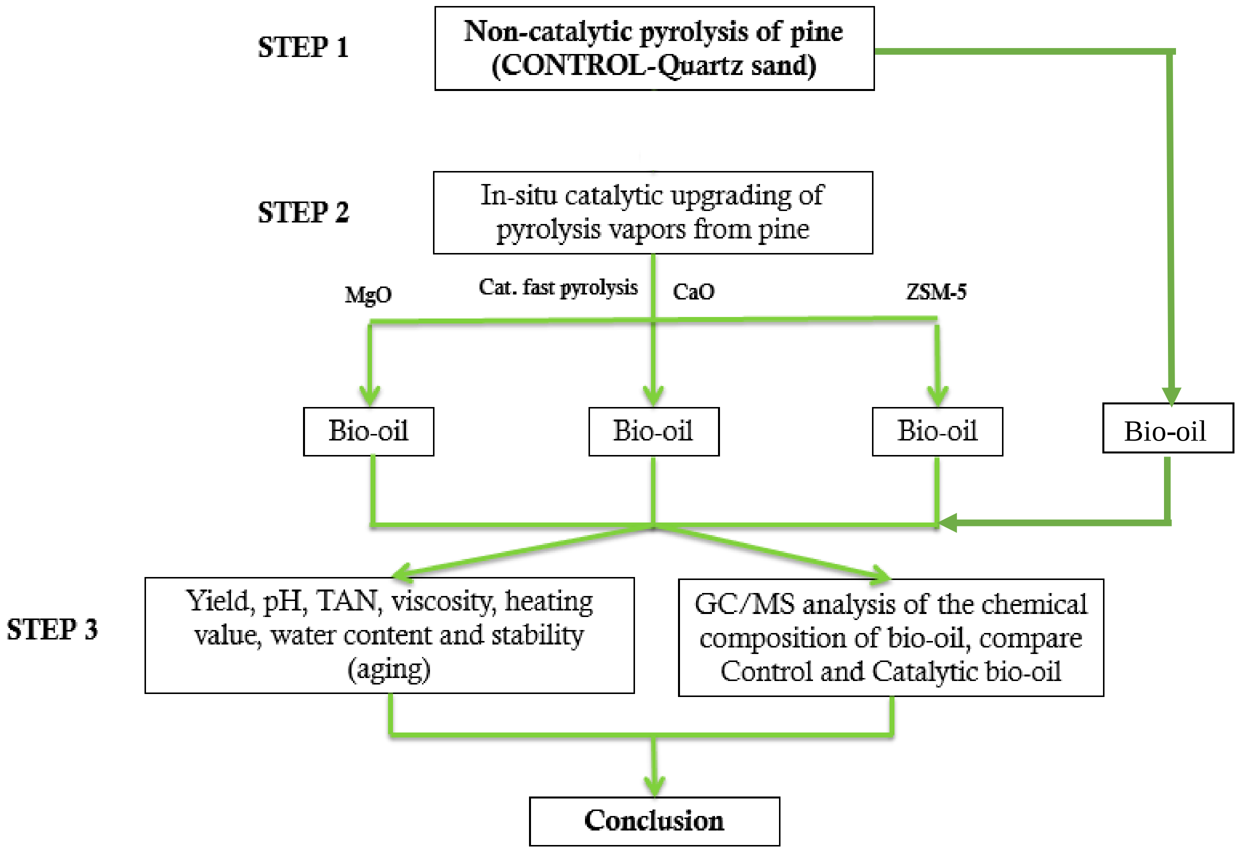

Figure 1.2. Experimental scheme for objective 2

2. Literature Review

2.1. Introduction

Increasing energy demand and the need for environmental conservation are the two major challenges facing our society in the 21st century, which have been thrust into the limelight in the last decade as we push towards finding a cost-effective and carbon neutral alternative. Fossil fuels have been the major source of transportation fuels for over a century but a significant increase in population has led to an accelerated consumption of the resource, particularly petroleum (Figure 2.1). The use of these fossil fuels along with coal has also resulted in an increase in concentration of the greenhouse gases, which adversely affect the environment by contributing to global warming. These factors have resulted in an increased emphasis on research to develop renewable fuels that could replace fossil fuels while also reducing the carbon footprint [1]. The increased interest in renewable technologies has also led to the development of solar, hydroelectric, wind and geothermal power plants that could potentially substitute for fossil based energy [2]. However, we still require hydrocarbons for manufacturing chemicals, fuel oil, lubricating oil and hydraulic fluids [3]. Biomass is well recognized as a sustainable and renewable source capable of yielding petroleum like products for liquid fuels and for conversion into chemicals, which can meet the energy demand without having adverse effects on the environment [4]. It is an excellent renewable feedstock because it is abundant and inexpensive [5]. According to a recent study by the USDA, resources in the US land alone are capable of producing a sustainable supply of biomass to replace at least 30% of the petroleum consumption of the country [6].

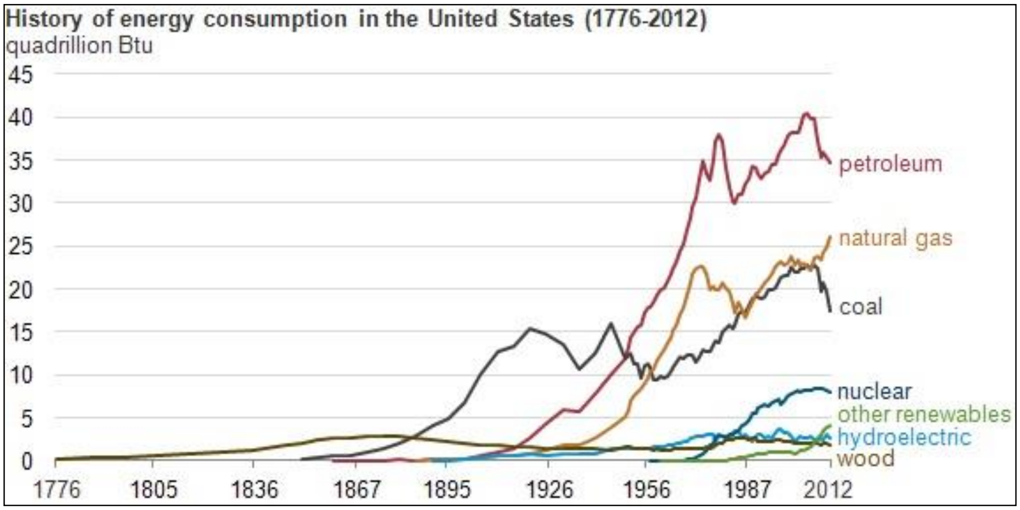

Figure 2.1. History of energy consumption in the United States from 1776-2012

In 2010, the worldwide production of biofuels reached 28 billion gallons, increasing by 17% from 2009. Biofuels also provided 2.7% of the world's transportation fuel, which is predicted to increase by 2030 to 5% according to an assessment by the world energy outlook [7]. In the US, production of bio-fuels has been dominated by first generation feedstock, i.e., sugar, oil crops, and starch to fuels. The most common pathway adopted is the fermentation of corn sugars to produce ethanol. However, this has resulted in a high demand for arable land needed for cultivating first generation feedstock which has caused a competition between food and energy requirements. It has also contributed indirectly to the rise in food prices and thus brings into focus the need to favor production of biofuels from non-edible feedstock to avoid the food vs fuel debate [8]. For example, ethanol from corn and sugarcane have been used extensively in the US and Brazil, respectively. Approximately 30% of the energy need of Brazil is met through fermentation of sugarcane to produce ethanol [9]. However, they have a major drawback since it requires high nutrition input and is a major food crop for human consumption [10]. In comparison, energy crops such as switchgrass, miscanthus, bermuda grass and sorghum which can easily be cultivated with a high yield are promising alternatives to using these food crops since they require low nutrients/fertilizers, consume low water and can grow in different climatic conditions [11]. Agricultural residues and municipal solid wastes such as wheat straw, corn stover, peanut hulls, bagasse, rice husk, paper, wood and yard trimmings can be used extensively for biofuel production. Ideally, an energy crop should have a few desired characteristics, such as high yield, low cost of production, low nutrient requirement and low moisture content, which would reduce the energy required to dry the feedstock.

2.2. Biomass and Biofuels

Biomass can be defined as a heterogeneous material derived from plants or animals available on a renewable basis. It includes wood and agricultural crops, herbaceous and woody energy crops, municipal organic wastes as well as manure [12]. It is comprised of cellulose, hemicellulose, lignin, alkali metals and some extractives whose composition vary from softwoods to hardwoods [13]. Figure 2.2 shows the structure of biomass components: cellulose, hemicellulose and lignin. The largest component which constitutes about 40-60 wt% of biomass is cellulose, with hemicellulose usually about 20-40% and lignin constituting 20-30 wt% [6]. However, the exact proportion of these components in biomass is highly variable from one biomass type to another.

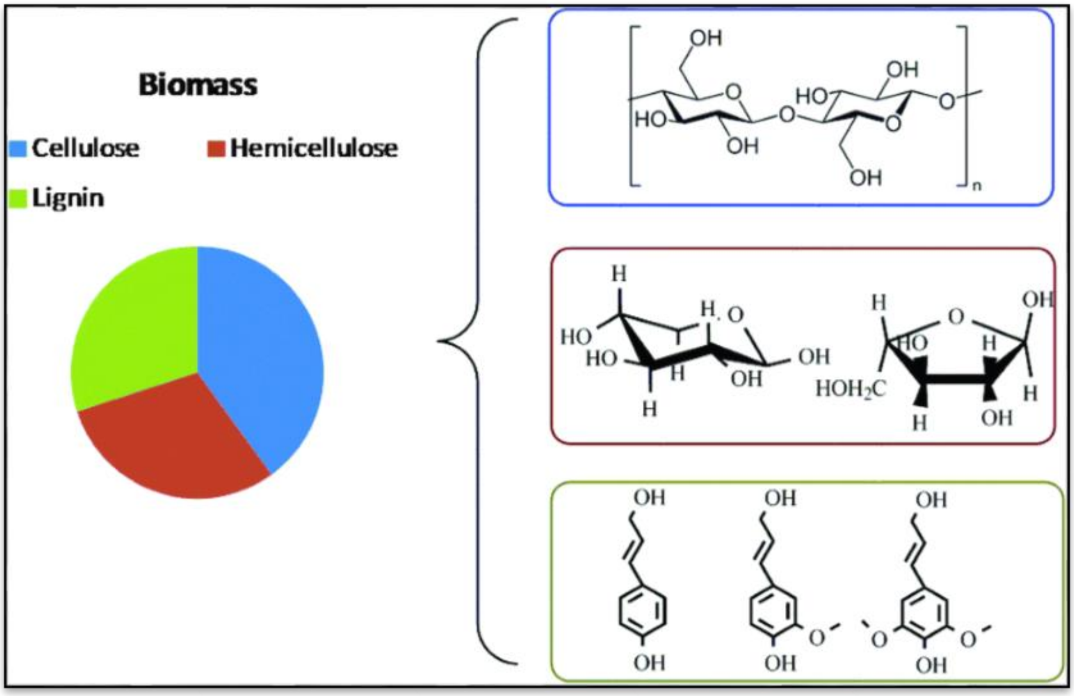

Figure 2.2. Composition of biomass and structure of cellulose, hemicellulose and lignin

Cellulose is a linear homo-polysaccharide of 1,4 beta-D linked anhydroglucose, a polymerization product of cellobiase linked with glucosidic bonds with an average molecular weight of approximately 100,000-200,000. The degree of polymerization of cellobiase in cellulose is about 10,000-15,000 [14]. Intermolecular and intramolecular hydrogen bonds between cellulose polymers oriented parallel to each other result in crystalline and amorphous segments. The hydrogen bonding in cellulose makes the linear structure resistant to hydrolysis and generally more stable when compared to hemicellulose [15]. Degradation of cellulose is an endothermic process that starts at approximately 300-315 ˚C and reaches a maximum weight loss at 350-360 ˚C [16, 17]. The reaction pathway for the degradation of cellulose has been interpreted to consist of three major pathways: 1) anhydrocellulose formation from the dehydration of cellulose between 200-280 ˚C; 2) formation of tar via a levoglucosan intermediate from the depolymerization of cellulose at 280 ˚C; 3) decomposition of anhydrocellulose and levoglucosan to form char and gaseous products [18]. Generally, cellulose pyrolysis follows this model, where an activated cellulose (AC) is formed in the first step, which is then followed by two competing reactions, one forming char and non-condensable gases while the other reaction yields volatiles such as levoglucosan.

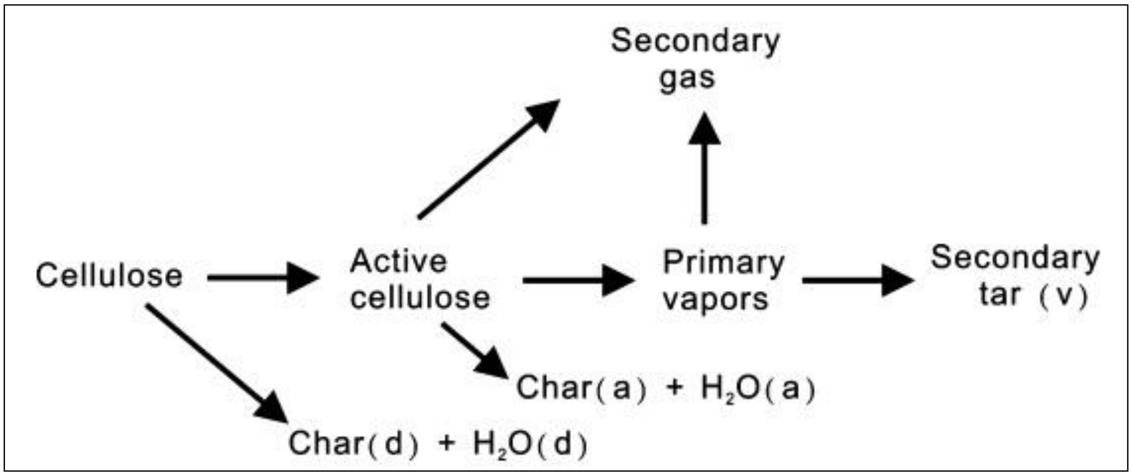

Figure 2.3. Mechanism of cellulose pyrolysis [16, 18, 19]

Hemicellulose is a polysaccharide made of five sugars: D-glucose, D-galactose, D-mannose, L-arabinose and D-xylose. Hemicellulose occurs as an amorphous mass around the cellulose strands. It has non-covalent bonding and is a branched polysaccharide which has a non-crystalline nature. This property is due to the steric hinderence caused by the side branches and the axial hydroxyl groups of hemicellulose. Due to these properties, hemicellulose is susceptible to thermal degradation at a much lower temperature than the range in which cellulose decomposition occurs [19]. It has a lower degree of polymerization (50-300) and its sugar composition varies from softwoods to hardwoods.

Lignin is the third constituent, which occurs between the cells and cell walls. In general, it can be defined as an amorphous aromatic polymer of phenyl propane units which has small amounts of extractives and inorganic materials. When compared to cellulose and hemicellulose, it has a larger percentage of carbon (about 60%) and a smaller percentage of oxygen (about 30%), which could vary from softwoods to hardwoods. It is a complex and high molecular weight polymer formed by the dehydrogenation of hydroxyl cinnamyl alcohols such as coniferyl and sinapyl alcohols. It is generally very stable in nature and is hard to isolate, offering strength and support to the cells. In biomass pyrolysis, lignin decomposition results in the formation of guaiacol, vanillin, syringol, anisole and phenolic compounds [20]. When a catalyst is used in the process, these compounds from lignin are mainly responsible for catalyst deactivation by coking of the active sites due to the formation of polyaromatic compounds (PAH's) [21].

The conversion of biomass to energy depends upon different factors which include the biomass type, quantity, required form of energy and required product quality. Conversion technologies can be broadly classified into two pathways – biochemical and thermochemical. The biochemical pathways involve the pretreatment of biomass, which is then followed by enzymes and microbes acting to convert the pretreated biomass into fuels [22]. Initial treatment is done using an acid or other chemicals. For example, H_2SO_4 is used to break down the hemicellulose in order to make the cellulose more easily accessible for the conversion process [23]. The pretreatment is followed by saccharification, where enzymes act on the carbohydrate material to produce a variety of sugars which are further fermented to produce ethanol. The variability of biomass feedstock, longer time required to obtain desired product, the need for more effective chemical treatments to break down the lignocellulosic materials are some of the barriers to the biochemical pathway [24]. The thermochemical pathway is carried out with two main techniques – gasification and pyrolysis. Gasification is a partial oxidation process where biomass is broken down at high temperatures ranging from 800-1100˚C to produce syngas/producer gas containing carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2) and p hydrocarbon molecules such as methane (CH_4) [25]. Syngas composition will depend on the gasification parameters, such as temperature and also the oxidizer used [26]. It can be used to either generate electricity using internal combustion engines or further processed through Fischer-Tropsch synthesis to produce liquid fuels [27]. Pyrolysis can be considered as a precursor to gasification as it consists of thermal decomposition in the absence of oxygen, at temperatures considerably lower (300-500˚C) than that used for gasification [28]. Products of pyrolysis include gas, liquid and a solid char, whose proportions differ based on the parameters of the process [29]. A schematic of the different methods of converting lignocellulosic biomass to fuels is shown in Figure 2.4.

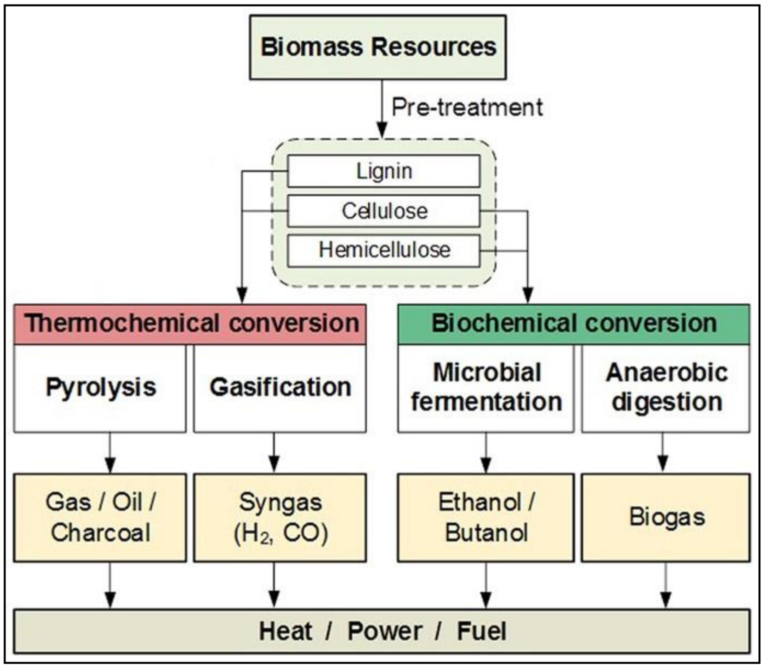

Figure 2.4. Technologies for the conversion of biomass to biofuels

Since pyrolysis is flexible to operate with different feedstock while also resulting in a high yield of valuable liquid fuel and syngas as product, it has garnered greater attention than other techniques [30, 31]. The research included in this thesis involves the use of pyrolysis technology for producing liquid fuels and thus, only the details pertaining to pyrolysis are given a greater emphasis here.

2.3. Pyrolysis

Pyrolysis is the process of thermal decomposition of biomass in the absence of air to produce gaseous (CO, CO_2, H_2, CH_4), solid (char) and liquid (bio-oil) products. The process can be understood by breaking it down into several steps [13, 30, 32, 33]:

1. Heat transfer to increase the temperature of the biomass.
2. Release of volatiles and formation of char as a result of primary pyrolysis reactions.
3. Internal heat transfer between the hot volatiles/biomass to the cooler solids.
4. Condensation of the volatiles to form bio-oil and initiation of secondary pyrolysis reactions.
5. Primary and secondary pyrolysis reactions take place simultaneously, along with a series of other reactions such as dehydration reaction, water-gas shift reaction, reforming, free radical reactions depending upon the process conditions employed [34].

Table 2.1. Operating parameters for pyrolysis

	Slow Pyrolysis	**Fast Pyrolysis**	**Flash Pyrolysis**
Pyrolysis Temp (˚C)	300-600	400-600	450-600
Heating Rate (˚C/s)	0.1-1	10-200	>1000
Particle Size (mm)	5-50	<1	<0.2
Solid Residence Time (sec)	450-550	0.5-2	<0.5

Pyrolysis processes could be further classified based on the operating parameters into slow, fast and flash pyrolysis (Table 2.1) [2, 29, 35]. Slow pyrolysis is traditionally used to produce charcoal since the long residence time gives the gas phase products enough time to react further to produce lesser liquid product and yield more char [36]. An increase in the pyrolysis temperature minimizes the solid yield, resulting in increases in liquid and gas yields [31, 37]. Flash pyrolysis employs very high heating rate and short residence time, resulting in a higher liquid yield [36]. However, it requires smaller particle size of biomass when compared to other processes due to heat transfer limitations as a result of the high heating rate and short residence time in the reactor [38]. In comparison, fast pyrolysis process produces liquid yields up to 75 wt. % dry feed, which could vary depending on the process parameters [39, 40]. A few important features of fast pyrolysis that help increase the liquid yield are: (1) high heating rate, (2) short residence time and (3) rapid quenching of product gas. At such high heating rates and short residence times, biomass is heated rapidly and the peak temperature is reached before it decomposes. It is considered to be better than slow and flash pyrolysis for producing bio-oil, since it produces a high liquid yield and does not require biomass particles to be as small as required for flash pyrolysis [41].

2.4. Factors Affecting Pyrolysis

2.4.1. Effect of Biomass Properties

The fraction of hemicellulose, cellulose and lignin varies from one biomass type to another [42]. Since these components have different pyrolysis behavior and make varying contributions to the gas, liquid and char yield, it has a significant effect on the pyrolysis yield with respect to the product composition. Physical properties of the biomass such as particle size, shape also have an influence due to their effect on heating rate [43]. Smaller particles of biomass offer lesser resistance to the condensable gases escaping the reactor, whereas bigger particles offer a greater resistance which causes more secondary reactions to take place. The size of biomass particles in pyrolysis also varies according to the type of reactor in use [44-46]. Auger reactors, circulating fluidized bed reactors and ablative pyrolyzer can handle larger size feedstock (upto 6 mm) whereas fluidized bed and entrained flow reactors require a smaller particle size (< 2 mm) [32].

2.4.2. Effect of Pyrolysis Temperature

The maximum temperature to which the feed particles are heated is referred to as the pyrolysis temperature and this temperature is held until the process is completed. It is very critical that this temperature be at an optimum in order to maximize the selectivity to obtain more of the desired product [47] [48]. The optimum temperature varies depending on the type of biomass being used for pyrolysis. For instance, the highest yield of liquid product from woody biomass was found to be between 450-500˚C [49]. It is also important that the reactor be adequately temperature controlled, as a non-uniform temperature profile could cause variability in the gas, char and liquid yields obtained. If such variations exist across the reactor, there will be local variations in the reaction rate and therefore in the composition of the products formed. At lower temperatures, formation of char is enhanced while at higher temperatures more gaseous products are evolved.

2.4.3. Effect of Heating Rate and Gas Residence Time

The rate of heating of the biomass particles and the gas residence time influence the yield and composition of fast pyrolysis products. Similar to the effect of temperature, a slower rate of heating yields more char while a rapid heating rate yields more volatiles [50]. It has been observed that increasing the heating rate from 5 to 250 ˚C/min to 400 to 500 ˚C/min resulted in an increase of the liquid yield from 45 to 68.5% [51]. Apart from heating rate, the gas residence time is also an important factor affecting the product composition. A longer gas residence time reduces the liquid yield as it allows more time for secondary reactions in the reactor between the char and the volatiles, causing secondary char formation and more gaseous product [52].

2.4.4. Effect of Reactor Configuration

The performance of a fast pyrolysis process depends mainly on the choice of reactor and its configuration. The process also includes several components such as biomass feed mechanism, particle separators and liquid collection systems which need to be designed carefully according to the objective of the experiment. Various reactors configurations have been used for fast pyrolysis, such as entrained flow reactor, auger reactor, bubbling fluidized bed reactor, circulating fluidized bed reactor, ablative pyrolyzer. However, fluidized bed reactors are mostly used for fast pyrolysis because of good solids mixing and approximately 90% of the heat is transferred to the biomass via solid-solid heat transfer with the bed material in the reactor [29].

The high heating rates, rapid de-volatilization, and good temperature control of fluidized beds makes it the reactor of choice for fast pyrolysis in this research. Fluidized beds and circulating fluidized beds are also popular due to their ease of operation and their ideal features as an R&D tool, which have also been scaled up to pilot plant size operations [53]. A schematic of the major reactor configurations used for biomass pyrolysis is shown in Figure 2.5 [54].

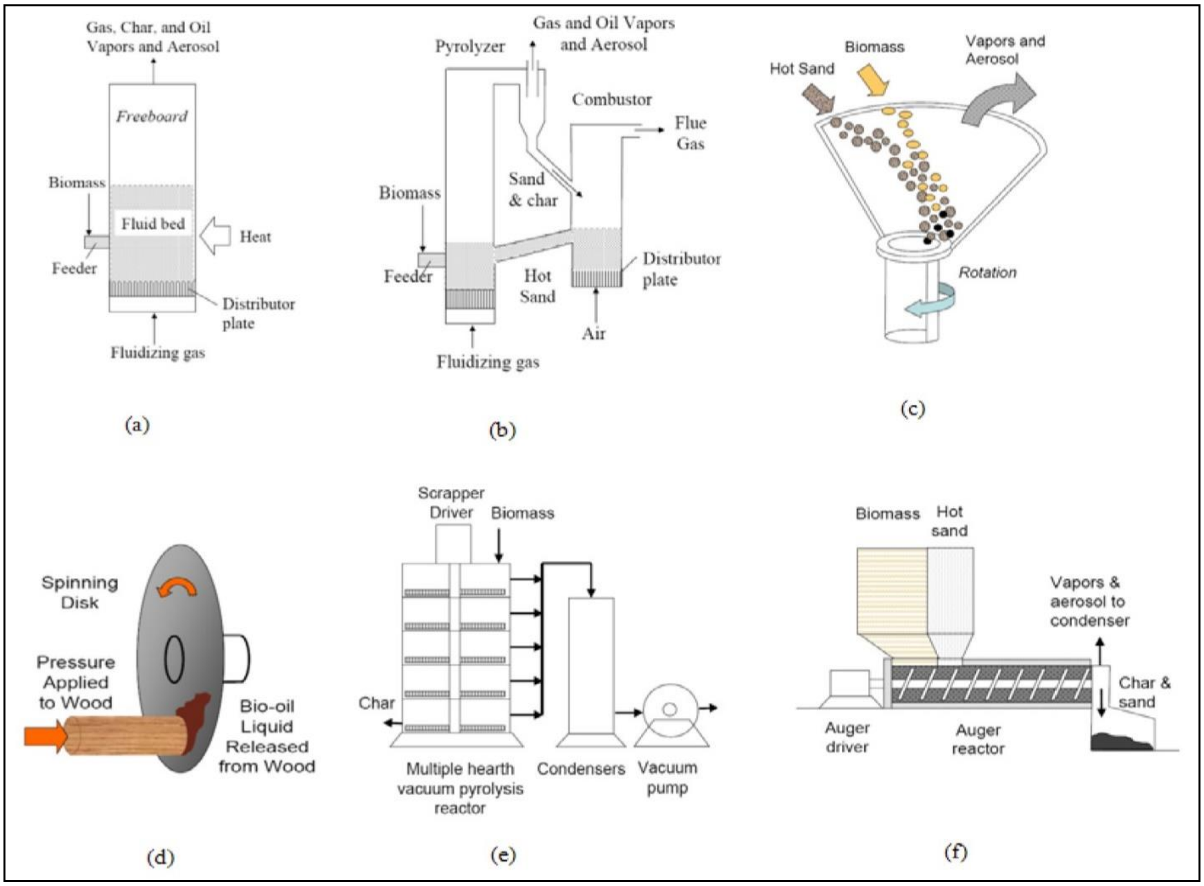

Figure 2.5. Major reactor configurations used for biomass pyrolysis (a) bubbling fluidized bed (b) circulating fluidized bed (c) rotating cone (d) ablative pyrolysis (e) vacuum pyrolysis (f) auger reactor [54]

The pyrolysis system also comprises of particle separation systems such as cyclone separators and filters, which are used to remove the char from the exit stream of the reactor. Char contains ash, unconverted carbon and metals present in the biomass and it also acts as a catalyst for undesirable polymerization reactions [39]. *In-situ* filters used inside the reactors are also being developed to separate the char in addition to having cyclones/filters to increase the efficiency of separation [55]. The vapors exiting the pyrolysis reactor would still be reacting as long as they are at a high temperature and they need to be condensed rapidly to prevent cracking and loss in the liquid yield. The allowable vapor residence time before condensation also depends on the end use of the liquid product. If it is to be used to produce chemicals or as a fuel, the vapors have to be condensed with a maximum residence time of a few milliseconds and two seconds, respectively [30, 56].

2.5. Bio-oil

The rapid heating and fragmentation of the biomass components results in the formation of pyrolysis vapors, which upon rapid cooling results in a viscous, dark brown liquid mixture of phenolics, carboxylic acids, esters, water and other compounds, commonly referred to as bio-oil. Being an intermediate product of the degradation of cellulose, hemicellulose and lignin, the properties of bio-oil are significantly different from conventional fuels, as listed in Table 2.2 [57]. It also has many active species among the hundreds of known compounds, which tend to react further during storage in order to reach thermodynamic equilibrium [58]. Operating parameters such as temperature, heating rate, residence time, reactor configuration as well as the composition of biomass can influence the properties of bio-oil obtained. For commercial utilization of bio-oil, it has to satisfy the required physical properties standards set by ASTM standard (ASTM D 7544-09), as listed in Table 2.2 [59]. A discussion of the important properties of bio-oil is given in the following section.

Table 2.2 Comparison of the properties of bio-oil with conventional fuels

Properties	Unit	Bio-oil	Diesel	Heavy fuel oil
Density	kg/m^3 at 15˚C	1220	854	963
Typical composition	% C	48.5	86.3	86.1
	% H	6.4	12.8	11.8
	% O	42.5	-	-
	% S	-	0.9	2.1
Viscosity	cSt at 50˚C	13	2.5	351
Flash point	˚C	66	70	100
Pour point	˚C	27	20	21
Ash	% wt	0.13	0.01	0.03
Sulfur	% wt	0	0.15	2.5
Water	% wt	20.5	0.1	0.1
LHV	MJ/kg	17.5	42.9	40.7
Acidity	pH	3	-	-

2.6. Properties of Bio-oil

2.6.1. Water Content

Bio-oil usually has a high water content of 15-30 wt% which is mainly due to the moisture content in the feedstock and due to the dehydration reactions taking place during pyrolysis and during storage [58]. The presence of water in bio-oil can be considered as an advantage as well as a drawback. While it lowers the energy density of the fuel and flame temperature, it also helps in reducing the viscosity and contributes to enhanced fluidity which is desirable for the combustion of bio-oil in an engine [60, 61].

2.6.2. Heating Value

Heating value or energy density of bio-oil is the energy released in the form of heat during complete combustion in the presence of oxygen. Typically, bio-oil has a higher heating value of 16-19 MJ/kg, which is about half of the heating value of petroleum based fuels. The lower heating value is directly related to the water content of the bio-oil. Bio-oil obtained from condensers usually have a water content of 15-30 wt%, which gives it a lower heating value whereas bio-oil obtained from electrostatic precipitators have very low water content (<5 wt.%) and correspondingly a much higher heating value 28-33 MJ/kg [62].

2.6.3. Oxygen Content and Acidity

Bio-oil contains about 35-45% of oxygen [63, 64], which is distributed among 300 compounds depending on the type of biomass and the operating conditions during pyrolysis. The major differences between petroleum based fuels and bio-oil can be attributed to the presence of oxygen and water content. The high percentage of oxygen contributes to the low energy density of bio-oil and also renders it immiscible with hydrocarbon fuels. The oxygen content and the presence of carboxylic acids such as acetic and formic acid contributes to the acidity of bio-oil. Generally, bio-oil has a pH of 2-3, which could provide challenges during handling, storage and in systems that use it as a fuel [65]. It would also require that storage and transportation equipment to be manufactured with expensive acid proof materials.

2.6.4. Viscosity

The chemical compounds in bio-oil are not at thermodynamic equilibrium and hence they react to make stable heavier compounds to form a thermodynamically stable mixture. This results in a greater viscosity of the aged bio-oil, which is generally unsuitable for use as a fuel due to its poor flow characteristics. Viscosity of bio-oil also varies widely depending upon the type of biomass and the water content. Bio-oil produced from rice straw had a kinetic viscosity of 5-10 mPa due to its high water content, whereas the viscosities of bio-oils from other feedstock such as pine were about 350 mPa s [66]. It has also been observed that bio-oil with lesser water insoluble components and higher water content had a lower viscosity [67]. Addition of a small amount of chemicals such as methanol to the bio-oil has also been found to significantly reduce the rate of viscosity increase during storage [68]. Although this addition causes a lowered flash point in the blend, it offers a greater advantage due to the reduced density and viscosity, while increasing the stability of the bio-oil over time.

2.7. Bio-oil Upgrading

The high carbon content and the presence of a wide range of chemical compounds make bio-oil a promising fossil fuel substituent and a source for value added chemicals [69]. While the possibility of producing value added chemicals has been investigated extensively [70, 71], application as a fuel is limited because of the highly oxygenated, viscous, corrosive and unstable nature of bio-oil [72]. These adverse properties are mainly due to the presence of many oxygenated groups in bio-oil such as carboxylic acids, water, carbonyl compounds, etc. This brings about the need to substantially deoxygenate bio-oil (upgrade) into a product with greater heating value and better stability. Bio-oil can be upgraded through catalytic and non-catalytic pathways. The non-catalytic pathway includes techniques to improve the stability of bio-oil, such as emulsification [73], solvent addition [74, 75], and super-critical treatment of bio-oil [76-78]. However, these methods are either not economically feasible or do not substantially improve the properties of bio-oil. Although the addition of solvents like methanol increases the storage stability by diluting the highly reactive groups [75], it is not a process that deoxygenates the bio-oil. On the other hand, catalytic processes like hydrodeoxygenation [79-82], aqueous phase reforming [83-86] and catalytic cracking [87] are upgrading techniques employed to convert bio-oil to different end products, including value added chemicals such as alkanes, olefins, hydrogen, gasoline range aliphatic and aromatic hydrocarbons [88].

Aqueous phase reforming is mostly used to transform the acids and sugars of the aqueous phase of bio-oil to hydrogen and other compounds of value [89]. The two most widely used methods of deoxygenating bio-oil are hydrodeoxygenation (HDO) and catalytic cracking. Hydrodeoxygenation utilizes hydrogen to remove oxygen in bio-oil in the form of water [90]. The need for hydrogen, which could be used as a fuel by itself [91] and the high pressure systems required for the process makes hydrotreating expensive and economically not feasible when compared to the cheaper catalytic cracking process to upgrade bio-oil. Comprehensive reviews on aqueous phase reforming, hydrotreating and catalytic cracking are available in literature [3, 80, 83, 85, 92].

In comparison to all the techniques mentioned previously, the low operational costs and the availability of a wide range of inexpensive catalysts makes catalytic upgrading more attractive for producing high quality fuel products from pyrolysis. Catalysts could be implemented in pyrolysis in two distinct pathways – *in-situ* or *ex-situ.* *Ex-situ* upgrading involves the use of the catalyst in a secondary reactor or unit, apart from the primary reactor used to pyrolyze biomass into vapors. *In-situ* upgrading involves the use of catalysts in the same reactor where the pyrolysis conversion takes place, with the catalyst actin on the pyrolysis vapors produced in the reactor. The main disadvantage of *Ex-situ* upgrading is the need to reheat the vapors/bio-oil to the catalytic upgrading temperature in the secondary reactor. This requirement also causes subsequent loss in liquid yield because of undesirable coke formation reactions. In comparison, *in-situ* upgrading eliminates this drawback since the vapor phase upgrading takes place in the same reactor where the biomass conversion takes place, eliminating the need for an additional reactor as well as removing the need to reheating the vapors, thereby minimizing the overall cost of the process [93].

Research on *in-situ* catalytic pyrolysis has been mostly focused on zeolites M41S type mesoporous materials, transition metal-modified zeolites and other solid acid catalysts [94-98]. However, many of the catalysts suffer either from thermal stability, deactivation due to coke formation or produce very low organic yields although they might be effective in deoxygenating the pyrolysis vapors. Zeolites, which are materials composed of Si/Al with a three dimensional structure have been the most promising and widely used catalyst for catalytic upgrading. The Bronsted acidity of zeolites can be controlled by modifying the Si/Al ratio to achieve the desired selectivity during conversion. While non-catalytic pyrolysis produces bio-oil containing high oxygen content with very low aromatic content, catalytic pyrolysis has been shown to significantly increase the aromatics in bio-oil. It also results in deoxygenation through decarboxylation, decarbonylation and dehydration reactions yielding more gaseous product and water. However, the organic yield is dramatically reduced as a result of catalytic activity [92]. Carlson et al. reported the selective production of high yield of aromatic hydrocarbons including benzene, toluene and xylene as well as naphthalene from *in-situ* catalytic pyrolysis using HZSM-

5 as the catalyst [99]. Enhanced product yields using zeolites have been reported by imparting the transition metal ions such as Ga, Mo, Co, Ni, Fe, etc, which has been found to decrease the number of Brönsted acid site, limiting the undesirable secondary reactions taking place in the vapor phase. Addition of these transition metals has also been reported to increase the selectivity towards hydrocarbons. These metal ions impart a bi-functional behavior to the catalyst, where the transition metal ions on the catalyst promote the cyclization, isomerization and dehydrogenation reactions. An extensive review of catalytic cracking using zeolites and metal modified zeolites is available in literature [92]. In comparison, very few studies have been conducted on the suitability of relatively inexpensive basic metal oxides such as MgO, CaO and ZnO as *in-situ* catalysts. Nokkosmaki et al. [100] studied the catalytic effect of ZnO on pyrolysis vapor and observed that the ZnO-treated bio-oil had much better stability than raw bio-oil when it is aged thermally. Veses et al. [101] evaluated the effect of using CaO and CaO.MgO (dolomite) in an auger reactor and observed positive effects on the acidity and oxygen content of the bio-oil produced. Kunwar et al. [102] observed that a reduction in the carboxylic acid compounds in bio-oil caused a marked improvement in the physical properties such as viscosity. Wang et al. [103] performed a TGA-FTIR analysis of CaO catalysts for the catalytic pyrolysis of corncob and found that CaO was effective in decreasing the molality of acids while increasing the hydrocarbons produced. Ding et al. [104] reported that CaO could increase the catalytic decarboxylation by converting the organic acids to hydrocarbons. These mild catalysts have been observed to improve certain specific properties of the bio-oil produced such as acidity and viscosity of the bio-oil, although the production of aromatic hydrocarbons are not significantly improved by using these catalysts.

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3. Fast Pyrolysis of Biomass: Influence of Operating Conditions and Pyrolysis of Biomass Blends

Abstract

Fast pyrolysis of biomass is a promising technique to produce a high yield of a valuable liquid product (bio-oil). However, its practical application is still hindered by a few negative properties, which affect the quality of the liquid product. These properties depend on process parameters chosen during conversion of biomass to bio-oil. This study was performed to understand the influence of important pyrolysis operating parameters (e.g., residence time, process temperature) on the product distribution, physical and chemical properties of the bio-oil obtained from a fluidized bed reactor. Experiments were then performed with southern pine, switchgrass and their blends to investigate the influence of feedstock composition on the product distribution as well as the properties of the bio-oil. It was observed that maximum bio-oil yield was obtained at a superficial residence time and process temperature of 1.54 s and 450 ˚C, respectively. Although the elemental composition of the bio-oils produced at various process conditions were not significantly different, the properties of pH and density were observed to improve with increase in process temperature and decrease in residence time. It was also observed that blending switchgrass with southern pine results in an improvement in the pH (2.39 to 3.16) and viscosity (12.12 to 6.96 cSt) of bio-oil. However, when the blend contained 50 % or more of switchgrass, the bio-oil obtained was observed to be phase separated due to the high water content of the liquid phase.

Keywords: Fast pyrolysis, Biomass blending, Bio-oil, Physical and chemical characterization, southern pine, switchgrass

3.1. Introduction

Growing environmental concerns and a reduced supply of fossil fuels has driven the interest in biomass for the production of liquid fuels and energy. According to the Billion-Ton study, approximately 1.3 billion tons of biomass is available annually in the U.S., which could help reduce the stress on fossil fuels by about 60 billion gallons [1]. Although different techniques have been investigated to convert biomass, fast pyrolysis is considered the most promising due to its high liquid yield and the useful applications for its by-products - char and syngas [2, 3]. The liquid product referred to as bio-oil can be used as a fuel for applications such as in boilers, furnaces and diesel engines [4]. Being a mixture of a wide range of compounds such as aldehydes, acids, ketones, hydrocarbons, phenols, furans and esters, it could also be used to produce many value-added chemicals [5]. However, the potential application of bio-oil as a transportation fuel is still hindered by a few negative attributes such as high oxygen content, high viscosity, low heating value and high acidity [6, 7]. These negative properties could be addressed by either simple physical treatments or by chemical treatments through various upgrading techniques that are described in published literature [8-11].

However, before such physical and chemical treatments which add to the overall unit cost of the process are considered, it seems reasonable to identify optimum process conditions to obtain maximum bio-oil yield. Factors that influence the yield of bio-oil such as temperature, residence time, particle size and feedstock composition have been studied extensively [12-16]. A wide range of biomass types have also been studied to investigate their potential as a feedstock for pyrolysis and their influence on the physical and chemical properties of bio-oil has been investigated [6, 16-20]. However, these studies mostly investigate different biomass types at different experimental designs and process conditions, which makes it essential that important process parameters such as temperature and residence time are identified for pyrolysis in the experimental setup used for this study. Furthermore, very few studies have investigated the effect of blending two biomass types as a feedstock for pyrolysis and its synergistic impact on the physical and chemical properties of the bio-oil produced. Blending two feedstocks with large availability could also offer an operational advantage of flexibility, reducing the dependence of the process on just on a particular feedstock.

Southern pine and switchgrass were chosen as the biomass types for this study, for the reasons outlined below. Southern pine was selected primarily due to its abundance in the southern part of United States, which makes it attractive as a renewable biomass feedstock. Switchgrass was chosen since it is gaining attention as a potential fast-growing energy crop producing high yields of upto 15 tons per acre. Switchgrass is also adaptable to harsh weather conditions and is a perennial crop which has been identified by the DOE for thermochemical conversion into useful forms of energy. In addition, these two feedstock are distinctly different in the amount of the inorganic constituents (ash), with switchgrass having a higher ash content since herbaceous grasses contain bark and leaves compared to clean woods such as southern pine [21, 22]. During pyrolysis, these inorganic elements such as Ca, Cu, K, Fe, Mg, and Na are concentrated in the bio-char produced. Therefore, the objective of this study was to identify the optimal conditions for obtaining maximum liquid yield, to study the pyrolysis behavior of southern pine and switchgrass blends to understand its influence on the properties of bio-oil produced. The effect of biomass blends were compared to the results obtained by pyrolyzing each feedstock separately. Product distribution from pyrolysis and properties of bio-oil such as heating value, pH, water content, viscosity, density and elemental composition were used as the basis for comparison.

3.2. Experimental Section

3.2.1. Pyrolysis Reactor Setup

Although many different reactor configurations have been developed for fast pyrolysis, a fluidized bed reactor was used in this study because of the several advantages it offers such as good heat transfer, continuous operation, ease of scale-up and is generally well understood [23]. Figure 3.13 shows the pyrolysis reactor setup consisting a biomass screw feeder system, fluidized bed reactor, char filter and a liquid collection system. A speed-controllable DC motor was used to drive the screw feeder, which was also cooled externally to avoid pre-treatment of biomass before reaching the fluidized bed reactor. The reactor was heated by a tubular furnace (Thermo Scientific model TF55035A-1) and the temperature inside the reactor was measured using a K-type thermocouple (Omega, Stamford, CT) connected to a data logger. The fluidized bed reactor was a 1” OD stainless steel tube with a height of 18” and ID 0.92’’. A distribution plate (Ace glass, porosity B) was placed at the bottom of the reactor through which fluidization gas (nitrogen) was distributed into the reactor. Quartz sand (ρ_p – 2.65 kg/l, ρ_b – 1.57 kg/l) with a particle size of 150-300 µm was used as the bed material. The liquid collection system consisted of a set of three condensers in an ice bath and an electrostatic precipitator (ESP). The exit stream from the ESP was passed through a flask filled with water to monitor whether the liquid collection system was working effectively. The non-condensable gas was vented out of the system.

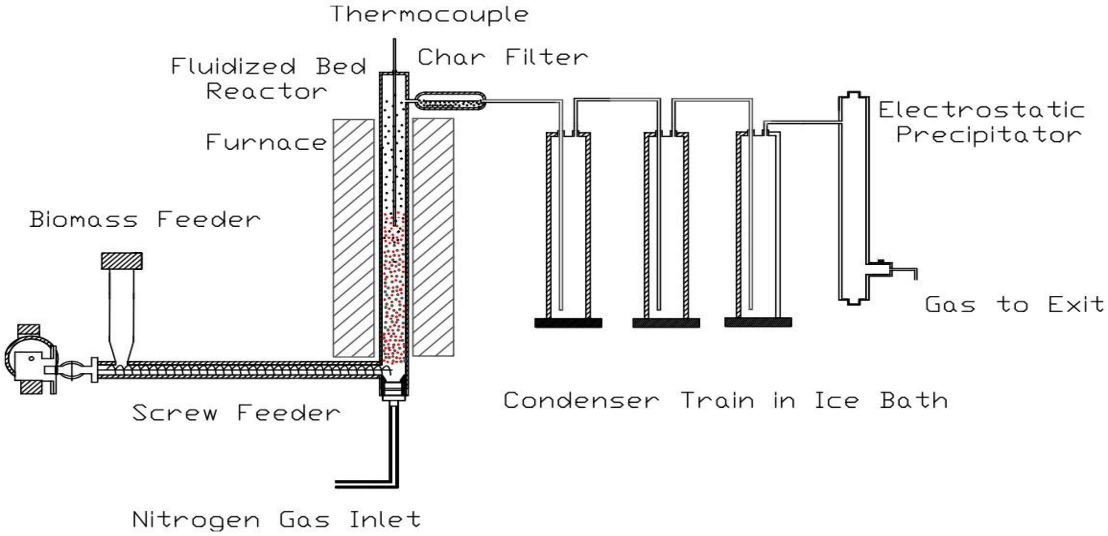

Figure 3.1. Schematic of the fluidized bed reactor system for catalytic pyrolysis

3.2.2. Materials

3.2.2.1. Biomass preparation and characterization

The biomass used in the optimization experiments was southern pine. In the blending experiments, southern pine and switchgrass were used. The woodchips and switchgrass were air dried for 72 h and ground in a hammer mill (New Holland Grinder Model 358) fitted with a 1.58 mm (1/16 in.) sized screen. The sawdust was then fractionated with a sieve shaker and the sample retained between 300 µm -500 µm (ASTM E-11 mesh no. 50 - 35) was used for bio-oil production. Proximate analysis was performed for moisture, volatile matter and ash, according to ASTM standards E871, E872 and E1755, respectively [24]. Higher heating value (HHV) of biomass was measured using a bomb calorimeter (IKA, model C2000). Ultimate analysis to determine the elemental composition was performed using a CHNS/O analyser (Perkin-Elmer, model CHNS/O 2400).

3.2.3. Experimental Procedure

The feed hopper was initially loaded with 60g of biomass sample and 60 g of the bed material was added to the reactor prior to heating the system for each experiment. For the blending experiments at different ratios of biomass, pinewood and switchgrass samples were weighed and mixed before being loaded into the feed hopper. A rotameter was used to control the gas flow rate, which was set according to the required experimental flow rate. Biomass was not fed into the reactor until the bed material was heated up to the preset experimental temperature. The average biomass feed rate was 67.2 g/hr or 1.12 g/min and the static bed height of the bed material was measured to be 7.5 cm with quartz sand. Once the set process temperature was achieved, biomass was fed to the reactor through the screw feeder where the biomass mixed with the bed material and was vaporized rapidly. The vapor escaped the fluidized bed reactor along with entrained char particles, which were trapped in the char filter. The vapor was then passed through a liquid collection system including a set of condensers in an ice bath and electrostatic precipitator, where the bio-oil was collected. The liquid yield from each experiment was determined gravimetrically by measuring the mass of the condenser train and ESP before and after each experiment. The char yield was determined by calculating the mass of solids left in the reactor and the char filter, subtracted by the known mass of bed material (60 g) in the system. The gas yield was calculated by difference (100 minus the mass of bio-oil and char). The experiments were performed in triplicates and statistical analysis of the data (ANOVA, Tukey's HSD) was performed to test the significance of the experimental factors. All the statistical analysis was performed at 95% confidence interval and the standard deviations for all the experimental results are presented in figures and tables.

3.2.4. Bio-oil Analysis

The bio-oil samples were homogenized by shaking before further analysis was performed. The bio-oil properties measured were pH, viscosity, water content and heating value. A digital pH meter (Oakton, Model PC 510) was used to measure the pH of the bio-oil. Water content of the bio-oil was determined using a volumetric Karl-Fischer titrator (Mettler Toledo, Model V20) using a hydranal-composite 5 solution (Sigma Aldrich). Kinematic viscosity measurements were performed in a standard Ubbelohde viscometer, according to ASTM D 445-12 standard [25]. Total acid number was determined with a Mettler Toledo T50 equipment by performing a potentiometric titration. Higher heating value (HHV) of bio-oil and ultimate analysis were performed as discussed in Section 3.2.2.1.

Chemical composition of bio-oil was analyzed with an Agilent 7890 GC/5975MS equipped with a DB-1701 column (30 m; 0.25 mm i.d.; 0.25 mm film thickness). Approximately 150 mg of bio-oil was mixed with 3 mL of methanol followed by dilution to 10 mL with dichloromethane. The diluted sample was injected into the column twice. The initial temperature of the column (40 ˚C) was maintained for 2 min, and the temperature was subsequently increased to 250 ˚C at 5 ˚C/min. The final temperature of 250 ˚C was held for 8 min. Ultra-high pure helium (99.999%) from Airgas Inc. (Charlotte, NC) was used as the carrier gas set at a flow rate of 1.25 mL/min. Bio-oil compounds were identified by comparing the mass spectra with the NIST (National Institute of Standards and Technology) mass spectral library.

3.3. Results and Discussion

3.3.1. Biomass Characterization

Elemental composition, ash, moisture and higher heating value (HHV) of the biomass used in this study are summarized in Table 3.1 1. Southern pine had a significantly lesser amount of ash content (0.44 wt. %) compared to switchgrass (4.83 wt. %). The switchgrass sample however had a lower carbon content and volatile matter, which translates to a lower heating value (17.25 MJ/kg) when compared to southern pine (18.76 MJ/kg).

Table 3.1 . Proximate and Ultimate analysis of biomass used in this study (Same letter in each group (or row) indicates that it is statistically not different)

Proximate Analysis (a.r)	**Analytical standard**	**Southern Pine**	**Switchgrass**
Ash content, wt. %	ASTM E1755	0.44 ± 0.05 ^{A}	4.83 ± 0.09 ^{B}
Volatile Matter, wt. %	ASTM E872	79.2 ± 0.47 ^{A}	71.55 ± 0.68 ^{B}
Moisture content, wt. %	ASTM E871	7.06 ± 0.61 ^{A}	11.73 ± 0.97 ^{A}
Fixed carbon, wt. %	By balance	13.3 ± 0.38 ^{A}	11.89 ± 0.61 ^{B}
Heating value, MJ/kg	ASTM E870	18.76 ± 0.29 ^{A}	17.25 ± 0.39 ^{B}
Ultimate analysis (a.r)	**Analytical instrument**	**Southern Pine**	**Switchgrass**
C, wt. %	Perkin-Elmer, model CHNS/O 2400	49.13 ± 0.27 ^{A}	47.16 ± 0.46 ^{A}
H, wt. %		6.52 ± 0.09 ^{A}	6.50 ± 0.29 ^{A}
N, wt. %		0.28 ± 0.06 ^{A}	0.68 ± 0.03 ^{B}
S, wt. %		0.12 ± 0.01 ^{A}	0.15 ± 0.0 ^{A}
O, wt. %	By difference	43.51 ± 0.26 ^{A}	40.68 ± 0.73 ^{B}

a.r. - as received; wt – weight

3.3.2. Identification of Optimum Experimental Conditions

Several experiments were performed initially using southern pine to quantify the effects of gas residence time and process temperature on liquid yield. The experiments on biomass blends were performed at the optimum conditions that were determined for this setup.

3.3.3. Effect of Residence Time

Fast pyrolysis is characterized by very short residence time (< 2s), while slow/intermediate pyrolysis and torrefaction techniques use a longer residence time resulting in a lower liquid yield [26]. In a fluidized bed reactor, the residence time (RT) can be controlled by the fluidization gas flow rate (in this case, nitrogen gas). A superficial residence time of 1.98 s was calculated to be equivalent to 7 LPM (Liters Per Minute) of the fluidization gas, which is the minimum condition to remain in the fast pyrolysis regime since reducing the gas flow rate below this would result in a longer residence time (> 2 s). However, the maximum fluidization gas flow rate that could be tested in this setup was 10 LPM, which corresponds to a residence time of 1.39 s. Therefore, experiments were performed at 7 LPM (RT - 1.98 s), 8 LPM (RT – 1.75 s), 9 LPM (RT – 1.54 s) and 10 LPM (RT – 1.39 s) of the fluidization gas flow rate to identify the residence time at which maximum bio-oil yield was obtained. The product distribution from these experiments at different flow rates is presented in Figure 3.2. From the statistical analysis of the results, it can be observed that at longer residence times (1.75 s, 1.98 s), the liquid yield is significantly lower when compared to the shorter residence time (1.39 s, 1.54 s). The highest liquid yield (50.98 wt.%) was obtained at a residence time of 1.54 s, while the lowest liquid yield (39.64 wt.%) was obtained at a residence time of 1.98 s. This result agrees well with the basic principle behind fast pyrolysis, yielding more liquid product at shorter residence time in the reactor. It is also comparable with the trend observed in the liquid yield obtained from fast pyrolysis in a fluidized bed reactor by previous studies [27, 28]. However, the elemental composition of the liquid product from Figure 3.3.3 shows that the elemental composition of the liquid phase was not significantly altered by change in the residence time in this study. It should also be noted that the yield of char and gas is highest at residence time of 1.98 s, while it shows a decreasing trend as the flow rate is increased. The decrease in char and gas yield could be a direct result of limiting the secondary cracking reactions at shorter residence times in the reactor, which was also observed by previous studies which reported a decrease in the char yield and gas yield at shorter residence times [27, 28].

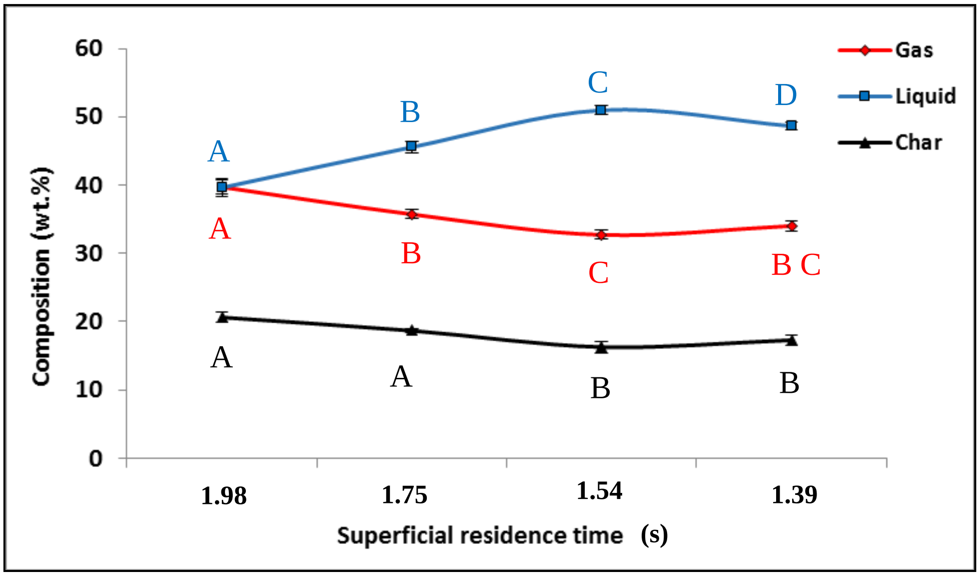

Figure 3.2. Effect of residence time at 500 ˚C on product distribution (Same letter in each group (liquid, char, gas) indicates that it is statistically not different)

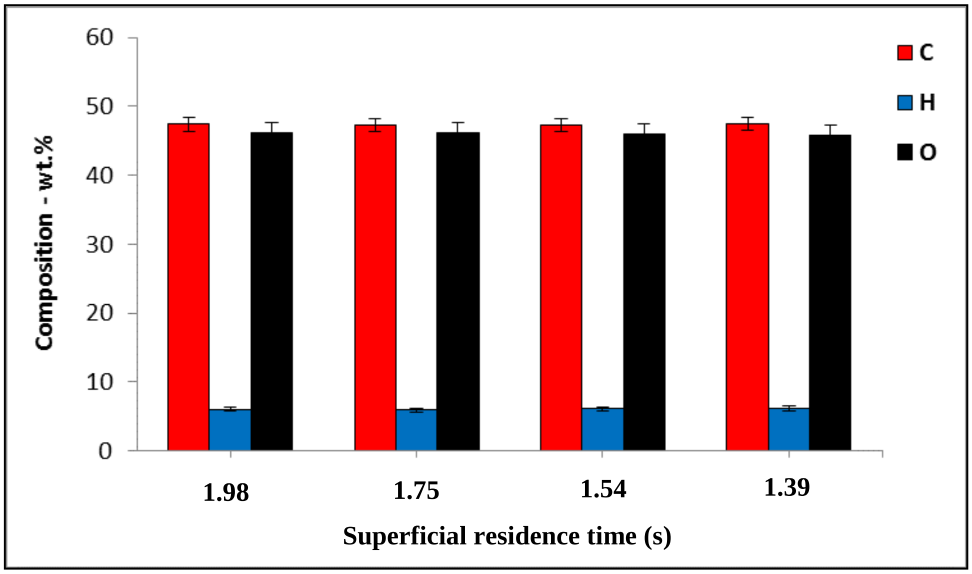

Figure 3.3.. Effect of residence time at 500 ˚C on elemental composition of bio-oil (The elemental compositions were not statistically different)

Table 3.2 shows the properties of bio-oil produced at different residence times. It can be observed that density, water content, viscosity and heating value of the bio-oil samples were not significantly affected by residence time. However, the pH of the bio-oil appears to be statistically significant between different levels, increasing from 2.29 at a residence time of 1.98 s to 2.57 at a residence time of 1.39 s (an increase of 12.2 %). Overall, since no significant changes were observed in the elemental composition as well as in most of the bio-oil properties which might influence the choice of the residence time, the condition at which maximum liquid yield was obtained (1.54 s) was chosen as the optimum condition for all the subsequent experiments in this study.

Table 3.2. Properties of bio-oil produced at 500 ˚C at different residence time (Same letter in each group (or row) indicates that it is statistically not different)

Superficial Residence Time (s)	**Density (kg/L)**	**pH**	**Water Content (wt.%)**	**HHV (MJ/kg)**	**Viscosity (cSt)**
1.98	1.09 ± 0.02 ^{A}	2.29 ± 0.07 ^{A}	21.5 ± 0.7 ^{A}	19.80 ± 0.11 ^{A}	12.28 ± 0.71 ^{A}
1.74	1.09 ± 0.03 ^{A}	2.38 ± 0.11 ^{A}	22.3 ± 1.4 ^{A}	19.73 ± 0.09 ^{A}	11.93 ± 0.53 ^{A}
1.54	1.11 ± 0.01 ^{A}	2.46 ± 0.10 $^{A\,B}$	22 ± 1.08 ^{A}	19.68 ± 0.15 ^{A}	12.13± 0.61 ^{A}
1.39	1.08 ± 0.02 ^{A}	2.57 ± 0.03 ^{B}	21.9 ± 0.84 ^{A}	19.91 ± 0.32 ^{A}	12.04 ± 0.94 ^{A}

3.3.4. Effect of Process Temperature

The process temperature (or pyrolysis temperature) is another critical parameter which has a major influence on the product distribution from pyrolysis [29]. In this study, pyrolysis of southern pine was performed at three different temperatures – 400, 450 and 500 ˚C. The product distribution from fast pyrolysis at these different temperatures is given in Figure 3.4. The highest bio-oil yield of 48.38 wt.% was obtained at 450 ˚C, while the yield was lower at both 400 ˚C (44.3 wt.%) and 500 ˚C (42.02 wt.%). Furthermore, Figure 3.5 shows that there is no significant effect of the different temperature levels on the elemental composition of the bio-oils produced. The yield of char was significantly different among each temperature level, decreasing from the highest yield at 400 ˚C (29.62 wt.%) to the lowest yield at 500 ˚C (17.64 wt.%). An opposite trend was observed with respect to the gas yield, which had an increasing behavior with increase in temperature. At 500 ˚C, the gas yield (40.34 wt.%) was almost equal to the liquid yield obtained in this system, which is not ideal for achieving the maximum liquid yield through fast pyrolysis. Similar trends showing reduced char yield and increased gas yield at higher temperatures in the product distribution was reported in literature for different types of feedstock [17, 18, 30, 31]. Thangalazhy Gopakumar et al. reported that this trend could perhaps be due to the fact that the reactive pyrolysis vapors produced are cracked more into lower molecular weight compounds and gases at higher temperatures.

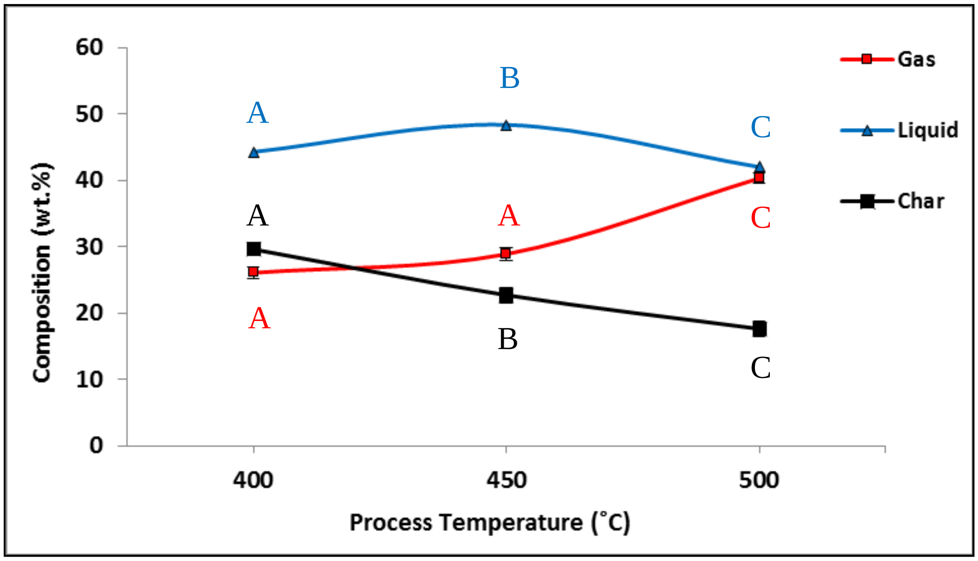

Figure 3.4. Effect of process temperature on product distribution (Same letter in each group (liquid, char, gas) indicates that it is statistically not different)

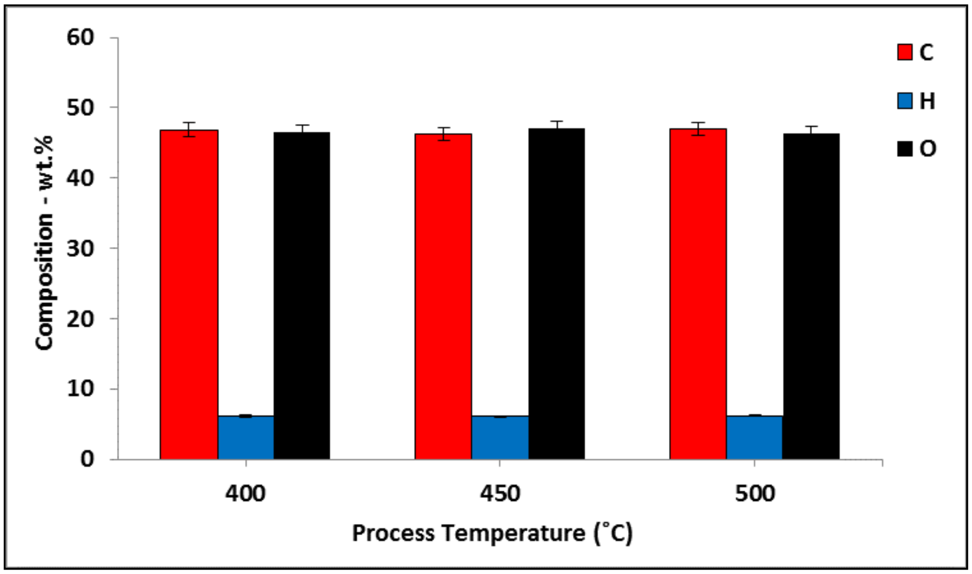

Figure 3.5. Effect of process temperature on elemental composition of bio-oil (The elemental compositions were not statistically different)

Table 3.3 .3 shows the properties of bio-oil produced at different process temperatures. The water content, viscosity and heating value of the bio-oil samples were not significantly affected by temperature. Although it would be reasonable to expect that at higher temperatures, many compounds formed during pyrolysis would be decomposed into smaller molecules leading to a less viscous liquid, it was surprising to observe that the viscosity of the bio-oil produced did not appear to be significantly change as temperature increased. However, the pH and density of the bio-oil appears to be statistically affected by temperature. The measured pH of the bio-oil was observed to increase from 2.21 at 400 ˚C to 2.50 at 500 ˚C (an increase of 13.1 %). He et al. [17] also reported an increase in the pH of bio-oil with increase in the temperature, which agrees well with the results obtained in this study. In the case of density, the bio-oil produced at higher temperatures (450 ˚C and 500 ˚C) showed a significantly lower density than the lowest temperature tested in this study (400 ˚C). Overall, since no significant changes were observed in the elemental composition as well as in most of the bio-oil properties which might influence the choice of the process temperature, the condition at which maximum liquid yield was obtained (450 ˚C) was chosen as the optimum condition for all the subsequent experiments in this study.

Table 3.3 Effect of process temperature on the physical and chemical properties of bio-oil (Same letter in each group indicates that it is statistically not different)

Temperature (˚C)	**Density (kg/L)**	**pH**	**Water Content (wt.%)**	**HHV (MJ/kg)**	**Viscosity (cSt)**
400	1.13 ± 0.04 ^{A}	2.21 ± 0.07 ^{A}	20.3 ± 0.09 ^{A}	19.35 ± 0.02 ^{A}	11.53 ± 0.71 ^{A}

450	1.08 ± 0.00 ^{B}	2.39 ± 0.11 ^{AB}	19.4 ± 0.22 ^{B}	19.07 ± 0.01 ^{B}	12.31 ± 0.53 ^{A}
500	1.05 ± 0.03 ^{B}	2.50 ± 0.10 ^{B}	19.8 ± 0.23 ^{B}	19.44 ± 0.17 ^{A}	11.92 ± 0.23 ^{A}

3.3.5. Effect of Biomass Blending

Southern pine (SP) and switchgrass (SG) were pyrolyzed individually as well as in various blending ratios (SP/SG - 75/25, 50/50 and 25/75). Figure.3.6 shows product distribution from pyrolyzing these biomass blends. Liquid yield obtained with 100 % southern pine (48.58 wt.%) is significantly higher than the yield obtained with using 100 % switchgrass (42.65 wt.%). The liquid yield obtained with the different ratios of biomass blends was observed to be decreasing as the amount of switchgrass blended is increased. This trend could be attributed to the lower volatile matter content of the switchgrass. A reverse trend was observed with respect to the char yield, which appears to increase as greater amount of switchgrass is used for pyrolysis, culminating in the greatest char yield of 28.3 wt.% when only switchgrass was used. These results agree well with results published on switchgrass pyrolysis by He et al., where a liquid yield of 43 wt.% and a char yield of 27 wt.% was obtained at the same temperature (450 ˚C) used in this study. Furthermore, it can be observed from Figure 3.7 that the elemental composition of the bio-oil produced differs significantly between several biomass blends. The carbon content (wt.%) which was the highest in the bio-oil produced from southern pine was observed to be decreasing with the addition of switchgrass to the pyrolysis feedstock, while the oxygen content of bio-oil increased with addition of greater amounts of switchgrass. Despite the increase in the oxygen content when adding more switchgrass in the feedstock, the increase is due to the higher water content which results in improving several properties of the bio-oil such as pH and viscosity, as seen in Figure.3.8 and Table 3.4 . Although the elemental composition of the pure southern pine and switchgrass matches well with other studies as reported earlier, there is a lack of information about the effect of blending these two biomass types on the bio-oil properties, which could be used to compare the results obtained in this study.

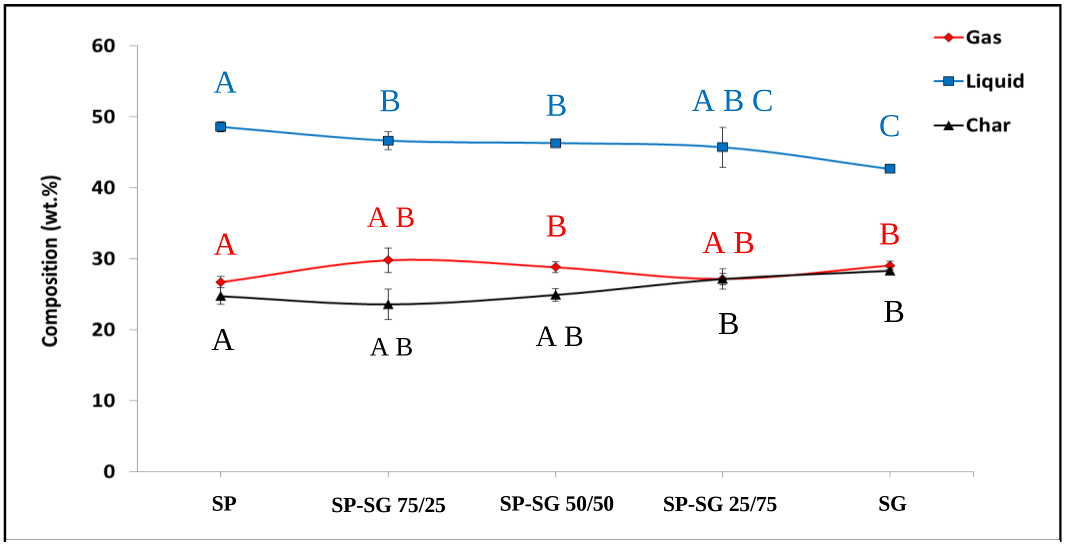

Figure.3.6. Effect of biomass blending on product distribution (Same letter in each group (liquid, char, gas) indicates that it is statistically not different)

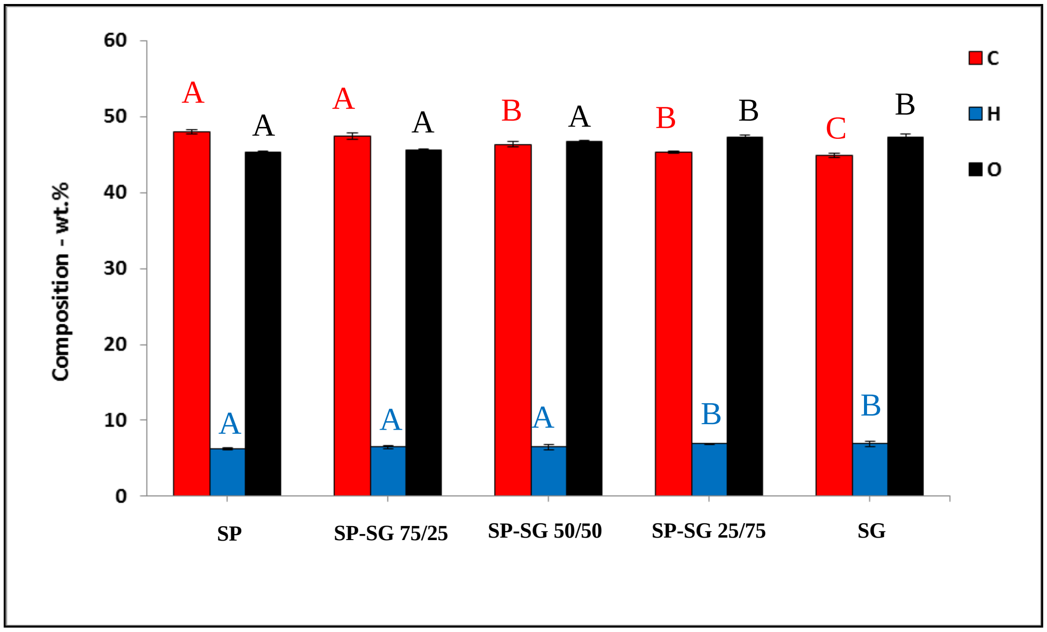

Figure 3.7. Elemental composition of bio-oil produced using different biomass blends (Same letter in each group indicates that it is statistically not different)

Table 3.4 shows the properties of bio-oil produced using different biomass blends. It can be observed that the effect of blending biomass has significantly influenced all the properties of the bio-oil produced. For the intended use as a fuel, neutrality of pH is highly desirable. Figure.3.8 shows the effect of biomass blends on the pH and water content of the bio-oil produced. Although the bio-oil produced through blending switchgrass with southern pine is still acidic in nature, a significant improvement of pH from 2.39 for southern pine to 3.16 for switchgrass was observed. Therefore, increasing the amount of switchgrass in the biomass blend appears to positively influence the pH value of the bio-oil. In terms of the water content of bio-oil, higher feedstock moisture content generally results in higher water content in the bio-oil. In this study, it was observed that the water content increased dramatically as more switchgrass is added to the biomass blend. One particular negative aspect of such an increase in water content is that in the experiment where more than 50 % switchgrass was used, the bio-oil obtained was phase separated. The viscosity of bio-oil showed the expected decrease as the water content increased. Although the viscosity obtained through blending switchgrass with southern pine is still well short of the expected values for a transportation fuel (Gasoline – 0.12 cSt, Diesel – 2.1 cSt), it shows a significant improvement when compared to the viscosity obtained by using only southern pine.

Table 3.4 . Effect of biomass blending on the properties of bio-oil (Same letter in each group indicates that it is statistically not different)

Biomass Blend	**pH**	**Water Content (wt.%)**	**HHV (MJ/kg)**	**Viscosity (cSt)**
SP	2.39 ± 0.06 A	19.4 ± 0.86 A	19.79 ± 0.02 A	12.12 ± 0.63 A
SP-SG 75/25	2.45 ± 0.09 A	21.4 ± 0.51 B	19.36 ± 0.04 B	11.29 ± 0.53 A
SP-SG 50/50	2.87 ± 0.04 B	23.3 ± 0.96 C	18.82 ± 0.01 C	10.32 ± 0.29 B
SP-SG 25/75	2.99 ± 0.08 B C	25.9 ± 0.32 D	18.47 ± 0.07 D	9.62 ± 0.94 B
SG	3.16 ± 0.11 C	28.5 ± 0.91 E	18.07 ± 0.03 E	6.96 ± 0.41 C

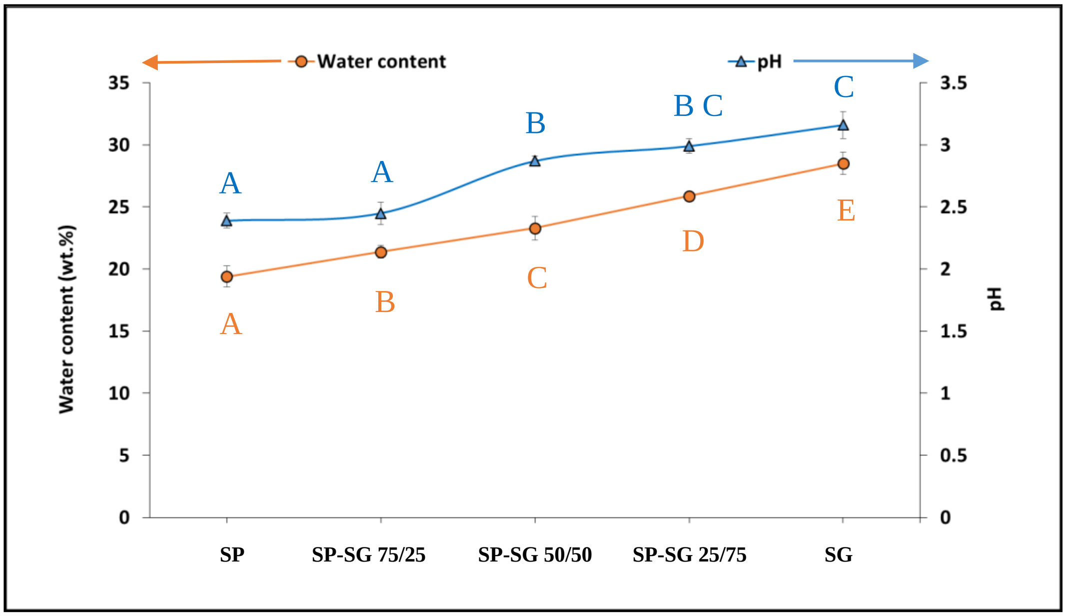

Figure.3.8. Effect of biomass blending on the water content and pH of bio-oil (Same letter in each group indicates that it is statistically not different)

3.4. Conclusion

The influence of pyrolysis operating conditions (residence time and process temperature) on the product distribution, physical and chemical properties of the bio-oil was examined in a fluidized bed reactor. The optimum conditions using southern pine were identified for the fast pyrolysis of biomass and it was observed that maximum bio-oil yield was obtained at a residence time of 1.54 s and at a process temperature of 450 ˚C. pH of bio-oil produced was observed to improve with decreasing vapor residence time and increased with increase in process temperature. However, the process conditions did not appear to significantly alter the elemental composition of the bio-oil produced. At the optimum conditions, biomass blends of southern pine and switchgrass were pyrolyzed to understand its influence on the physical and chemical properties of bio-oil. From the results obtained, it was observed that blending switchgrass with southern pine results in an improvement in the pH and viscosity of the bio-oil produced. pH was observed to increase (2.39 to 3.16) as the amount of switchgrass in the blend is increased, with the highest pH obtained using 100 % switchgrass as the feed. Viscosity of the bio-oil also increased (12.12 to 6.96 cSt) as more switchgrass was blended in the feed. While the improvement in these properties appear to be positive, it was also observed that having more than 50 % of switchgrass in the biomass blend resulted in higher water content in the bio-oil, yielding a phase separated bio-oil.

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4. Physical and chemical properties and accelerated aging test of bio-oil produced from *in-situ* catalytic pyrolysis in a bench-scale fluidized bed reactor

Abstract

In-situ catalytic upgrading is a promising technique to improve the properties of bio-oil because the bio-oil produced from conventional method has several negative attributes such as low heating value, highly acidic nature and is also unstable during storage. In this study, the catalytic effect of CaO, MgO and ZSM-5 as *in-situ* upgrading catalysts during biomass pyrolysis was studied in a fluidized bed reactor. Loblolly pine sawdust were subjected to pyrolysis with inert bed material (quartz sand) and subsequently with the catalysts. The quality of bio-oil obtained was compared to the baseline values (i.e., with the use of sand as bed material without any catalyst) in terms of its chemical composition, heating value, viscosity, pH, total acid number (TAN), oxygen and water contents. The use of CaO resulted in an improvement in pH (2.39 to 3.98) and TAN (88.9 to 46.6) of the bio-oil when compared to the results when using only sand. In comparison, MgO was a mild catalyst as it altered the bio-oil quality slightly while ZSM-5 had no effect on the acid content in bio-oil although it produced bio-oil with the least oxygen content at a significantly lower yield and higher water content (38.5%). In terms of chemical composition, the catalysts exhibited different behaviors to various groups of compounds. Anhydrosugars were reduced by all the catalysts tested to different extents, but CaO significantly altered the quality of bio-oil by reducing organic acids, while CaO and ZSM-5 reduced the abundance of phenolic compounds with higher oxygen content. Accelerated aging test was performed to compare the efficacy of these *in-situ* catalysts on improving the stability of bio-oil, and it was observed that the bio-oil produced using CaO was the most stable when compared to the baseline and other catalytic bio-oils tested in this study.

Keywords: Catalytic Pyrolysis, *In-Situ* Upgrading, CaO, MgO, ZSM-5, Stability

4.1. Introduction

The conversion of biomass to pyrolysis oil (a.k.a. bio-oil or biocrude) and its subsequent upgrading to gasoline and diesel range compounds is a promising technology which could minimize our dependence on imported petroleum products [1, 2]. Over the past few decades, the focus of researchers has largely been on increasing the bio-oil yield, reaction kinetics, process design and development [3]. However, the primary oil obtained from pyrolysis of biomass is still acidic in nature, has a high oxygen content (typically 45% oxygen), low heating value and also polymerizes over time, resulting in an increase in viscosity (*i.e.*, ageing) [4-8]. Storage, transportation and utilization of bio-oil becomes complicated and renders the technology commercially not competitive as a result of these drawbacks. Although multiple upgrading steps could be designed for the refining of bio-oil, it requires greater energy expenditure resulting in an increased cost of production [9].

Various techniques to upgrade bio-oil such as hydrotreatment [10-13], catalytic cracking [14] emulsification and solvent addition [15] have been investigated extensively. Hydrotreatment is limited by the need for hydrogen, which could be used as a fuel by itself and by the cost of high pressure systems required for the process which makes it economically not feasible when compared to the cheaper catalytic cracking process [11, 16, 17]. Recently, *in-situ* or integrated catalytic pyrolysis has been touted as a promising technique by which bio-oil could be upgraded at a significantly lower cost when compared to upgrading steps involving multiple reactors using bio-oil produced from conventional method. It combines direct conversion of biomass to pyrolysis oil and vapor phase catalytic upgrading in the same reactor, with the catalyst also serving as a heat carrier or bed material. It could be the simplest solution to reduce the oxygen content during pyrolysis and improve the quality of raw bio-oil, which would contribute to a reduced cost during subsequent processing steps. Various cracking catalysts (zeolites, metal-modified zeolites, alumina, MCM-41 materials) have been studied extensively and have been proved to be effective for cracking, deoxygenation and for producing aromatic hydrocarbons [6, 18-20]. However, one of the disadvantages of using these catalysts is the significant reduction in the bio-oil yield due to the increased cracking resulting in more gaseous product and water. Rapid deactivation of catalysts due to coke deposition has also been a cause for concern [20].

In comparison, very few studies have explored the possibility of using inexpensive base materials such as CaO, MgO and ZnO as *in-situ* catalysts in a fluidized bed reactor. Nokkosmaki et al. [19] studied the catalytic effect of ZnO on pyrolysis vapor and observed that the ZnO-treated bio-oil had much better stability than raw bio-oil when it is aged thermally. Veses et al. [21] evaluated the effect of using CaO and CaO.MgO (dolomite) in an auger reactor and observed positive effects on the acidity and oxygen content of the bio-oil produced. Kunwar et al. [22] observed that a reduction in the carboxylic acid compounds in bio-oil caused a marked improvement in the physical properties such as viscosity. Wang et al. [23] performed a TGA-FTIR analysis of CaO catalysts for the catalytic pyrolysis of corncob and found that CaO was effective in decreasing the molality of acids while increasing the hydrocarbons produced. Ding et al. [24] reported that CaO could increase the catalytic decarboxylation by converting the organic acids to hydrocarbons. Therefore, the objective of this paper was to study the effect of metal oxide catalysts – CaO and MgO, which seem to be promising catalysts for biomass pyrolysis and compare it with the performance of ZSM-5 in the same system. The catalysts were evaluated primarily based on the quality in terms of its chemical composition, heating value, viscosity, pH, TAN, oxygen and water content and stability of the bio-oil produced using accelerated aging test. Also, evaluating the performance of a generally well understood catalyst such as ZSM-5 in the same system offers a strong basis for comparison with the metal oxide catalysts.

4.2. Experimental Section

The pyrolysis reactor setup, biomass and bio-oil characterization methods followed were previously described in Section 3.2.

4.2.1. Experimental Procedure

The feed hopper was initially loaded with the known amount of biomass sample and 60 g of the bed material (quartz sand in non-catalytic experiments (also referred to as baseline/control) and MgO, CaO and ZSM-5 in the catalytic experiments) was added to the reactor. Fluidization gas flow rate was set at 8 L/min, which resulted in good fluidization of the bed material. Biomass was not fed into the reactor until a stable operating temperature is achieved, and the bed material was heated up to the preset temperature of 450˚C, which was deemed ideal for maximum liquid yield for fast pyrolysis of pinewood in this experimental setup. Several experiments were performed to verify the repeatability of the experimental setup and procedure at different operating conditions of temperature and fluidization gas flow rate. Once the set process temperature was achieved, biomass was fed to the reactor through the screw feeder where the biomass mixed with the bed material and was vaporized rapidly. The vapor escaped the fluidized bed reactor along with entrained char particles, which were trapped in the char filter. The vapor was then passed through a liquid collection system including a set of condensers in an ice bath and electrostatic precipitator, where the bio-oil was collected. The liquid yield from each experiment was determined gravimetrically by measuring the weight of the condenser train and ESP before and after each experiment. The char yield was determined by calculating the weight of solids left in the reactor and the char filter, subtracted by the known weight of bed material (60 g) in the system. The gas yield was calculated by difference (100 minus the weight of bio-oil and char). The non-catalytic and catalytic experiments with MgO, CaO and ZSM-5 were performed in triplicates and statistical analysis of the data (ANOVA, Tukey's HSD) was performed to understand whether or not the obtained results were statistically different. All the statistical analysis was performed at 95% confidence interval.

4.2.2. Catalyst

The ZSM-5 catalyst used in this study (SiO_2/Al_2O_3 Molar Ratio – 38, Specific Surface Area ≥ 250 m^2/g) was purchased in the form of pellets from ACS Material (Medford, MA). To get the desired particle size (150-300 µm) for the zeolite catalysts, the pellets were crushed and then sieved (ASTM E-11 mesh no. 100 - 50). The catalyst was then calcined at 550˚C for 2 h prior to use in the experiment. Basic oxides CaO and MgO used in this work was of analytical grade (>99% purity) purchased from Alfa Aesar (Ward Hill, MA) and sieved to get particle size between 150-300 µm (ASTM E-11 mesh no. 100 - 50) screens. The metal oxide catalysts were dried at 120˚C for 2 h to remove the absorbed water prior to its use in the experiments.

4.2.3. Bio-oil Analysis

Bio-oil was obtained as phase separated liquid when ZSM-5 was used as a catalyst, existing in two distinct phases – an aqueous top phase and a thick, darker bottom phase (Figure 4.1).

However, it was a homogenous liquid in all other experiments where two phases were not clearly observed (Figure 4.2). The recovered sample was homogenized by shaking before the liquid analysis was performed. Physical analysis, including pH, viscosity, total acid number (TAN), water content and heating value measurements were performed. A digital pH meter (Oakton, Model PC 510) was used to measure the pH of the bio-oil. Water content of the bio-oil was determined using a volumetric Karl-Fischer titrator (Mettler Toledo, Model V20) using a hydranal-composite 5 solution (Sigma Aldrich). Kinematic viscosity measurements were performed in a standard Ubbelohde viscometer, according to ASTM D 445-12 standard. Total acid number was determined with a Mettler Toledo T50 equipment by performing a potentiometric titration. Higher heating value (HHV) of bio-oil and ultimate analysis were performed as discussed in Section 3.2.4. Chemical composition of bio-oil was analyzed with an Agilent 7890 GC/5975MS equipped with a DB-1701 column (30 m; 0.25 mm i.d.; 0.25 mm film thickness). Approximately 150 mg of bio-oil was mixed with 3 mL of methanol and it was diluted to 10 mL with dichloromethane. The diluted sample was injected into the column and each sample was injected twice. The initial temperature of the column, 40 ˚C, was maintained for 2 min, and the temperature was subsequently increased to 250 ˚C at 5 ˚C/min, and the final temperature was held for 8 min. Ultra-high pure helium (99.999%) from Airgas Inc. (Charlotte, NC) was used as the carrier gas set at a flow rate of 1.25 mL/min. Bio-oil compounds were identified by comparing the mass spectra with the NIST (National Institute of Standards and Technology) mass spectral library. For the accelerated aging tests, the liquids produced from three consecutive runs using each catalyst were combined, sealed in glass tubes kept at 80˚ C for 24 h [25]. The analytical methods for bio-oil mentioned previously were repeated again to follow the chemical and physical changes as a result of bio-oil aging.

Figure 4.1. Bio-oil produced using ZSM-5 as the catalyst

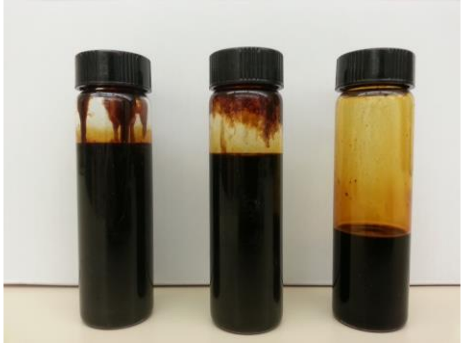

Figure 4.2. Bio-oil produced using (i) No catalyst (ii) MgO (iii) CaO (Left to Right)

4.3. Results and Discussion

4.3.1. Biomass Characterization

The elemental composition, ash, moisture and higher heating value (HHV) of the southern pine used are summarized in Table 4.. Ash content of the biomass tested in this study was low when compared to other materials like switchgrass, miscanthus, rice straw [26], whereas the volatile matter in the biomass was greater than the aforementioned species [27]. The lower ash content could help avoid operational difficulties due to inorganic metal deposits on the process equipment, while higher volatile matter makes it more attractive to be used as a source of fuel.

Table 4.1. Proximate and ultimate analyses of biomass used in this study

Proximate Analysis (a.r)	**Analytical standard**	**Result**
Ash content, wt. %	ASTM E1755	0.44 ± 0.05
Volatile Matter, wt. %	ASTM E872	79.2 ± 0.47
Moisture content, wt. %	ASTM E871	7.06 ± 0.61
Fixed carbon, wt. %	By balance	13.3 ± 0.38
Heating value, MJ/kg	ASTM E870	18.76 ± 0.29
Ultimate analysis (a.r)	**Analytical instrument**	**Result**
C, wt. %	Perkin-Elmer, model CHNS/O 2400	46.05 ± 0.15
H, wt. %		6.86 ± 0.07
N, wt. %		0.28 ± 0.06
S, wt. %		0.12 ± 0.01
O, wt. %	By difference	46.31 ± 0.14

a.r. - as received; wt – weight

4.3.2. Influence of Catalyst on Product Distribution

Presence of a catalyst during pyrolysis could influence the product distribution by either cracking the product vapor into lighter compounds or by increased coke formation as a result or polymerization reactions. The effect of each catalyst on the product distribution was analysed in terms of the gas, liquid and char yield (wt%, g of product/ g of biomass converted, as received) is shown in Figure 4.3. For comparison, the results obtained using sand as the bed material is also shown. It can be observed that each catalyst affected the product distribution to a different extent. The product distribution is altered significantly when CaO and ZSM-5 were used as the catalyst, while statistical analysis on the yield data revealed the product distribution with MgO was not significantly different to the baseline experiments, indicating that the catalytic effect of MgO was minimal. The liquid yield was reduced from 51.5 wt. % in the control to 40.3 wt. % in the case of CaO and 34.7 wt. % with ZSM-5. The amount of char produced was higher in experiments with MgO and CaO, while it did not significantly differ with ZSM-5. Veses et al. [21] reported a different behavior using CaO and CaO. MgO (dolomite – 58% CaO, 36 % MgO), observing no significant changes in the product distribution. However, it was performed in an auger reactor utilizing a greater gas residence time, which could be the reason for the variation in result. A better comparison could be made with the results reported by Lin et al. [28] using CaO in a fluidized bed reactor, where the liquid yield reduced from 39.4 wt.% without a catalyst to 34.1 wt. % with CaO, which is comparable to the liquid yield obtained in this study using the same catalyst. The liquid yield obtained with ZSM-5 (34.7 wt. %) was low when compared to published results by Zhang et al. [29] and Iliopoulou et al. [30], where 46.4 wt. % and 46.5 wt. % liquid yield was obtained.

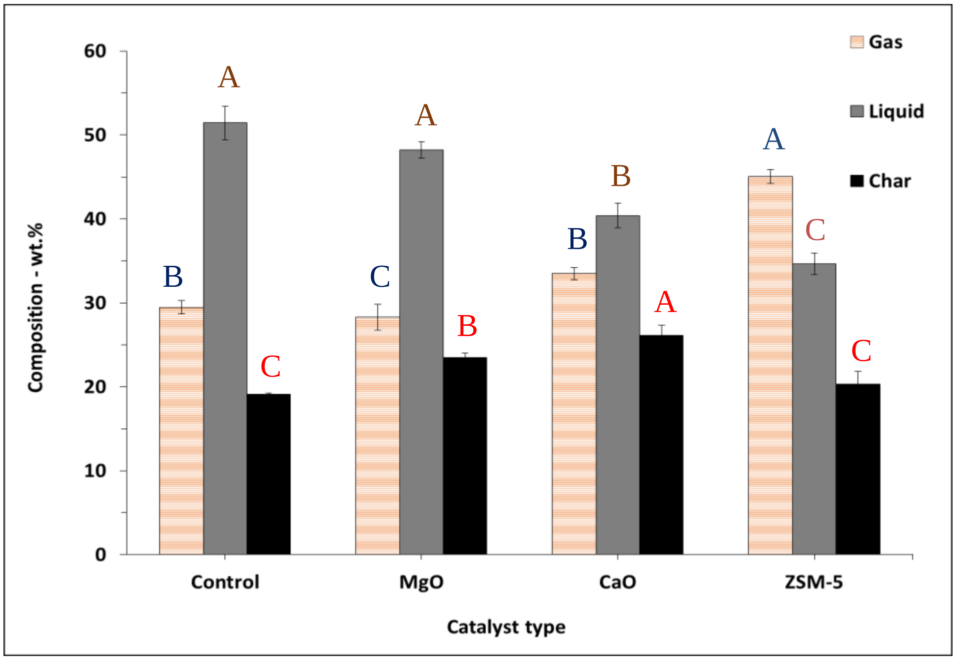

Figure 4.3. Effect of catalyst on product distribution (Same letter in each group (liquid,char, gas) indicates that it is statistically not different)

4.3.3. Influence of Catalyst on the Properties of Bio-oil

The C, H and O content and the corresponding O/C and H/C molar ratios of the bio-oil produced using different catalysts are shown in Figure 4.4 and Figure 4.5 respectively. The effectiveness of each catalyst in deoxygenating bio-oil was in the order: ZSM-5 > CaO > MgO. The extent of deoxygenation is characterized by a drop in the O/C ratio from 0.73 for the control experiment to 0.58 with CaO and 0.46 with ZSM-5. A relative reduction of oxygen content of 13 wt. % was achieved with CaO, while a relative reduction of 21.5 wt. % was achieved with ZSM-5 in this study. In comparison, at a higher CaO to biomass ratio of 5:1, a reduction of 21 wt.% was reported by Lin et al. [28], while Iliopoulou et al. [30] reported a 26.4 wt.% reduction of oxygen content with ZSM-5. It should also be noted that while the catalysts tested in this study produce an increase in the carbon content and a decrease in the oxygen content of the bio-oil; the hydrogen content remains relatively unchanged as shown by the H/C ratio in Figure 4.5.

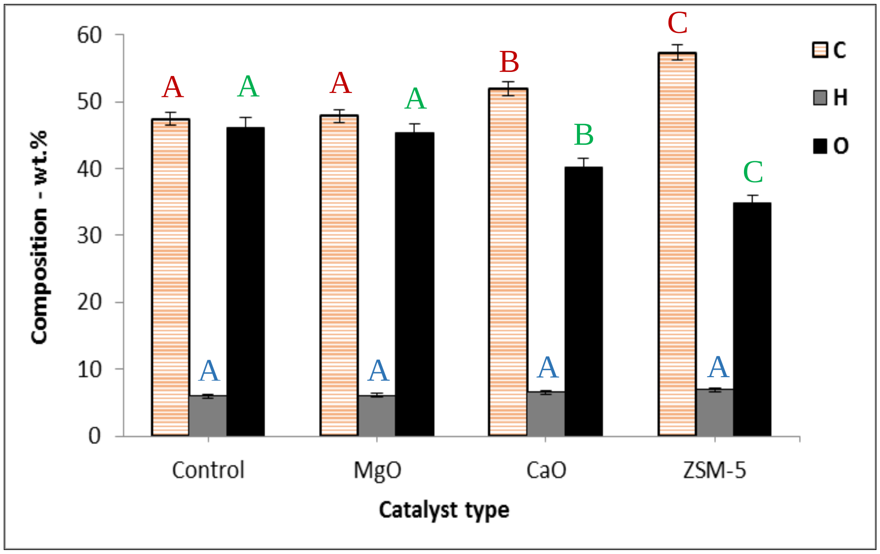

Figure 4.4. Elemental composition of the bio-oil produced using catalysts (Same letter for each group (C, H, O) indicates that it is statistically not different)

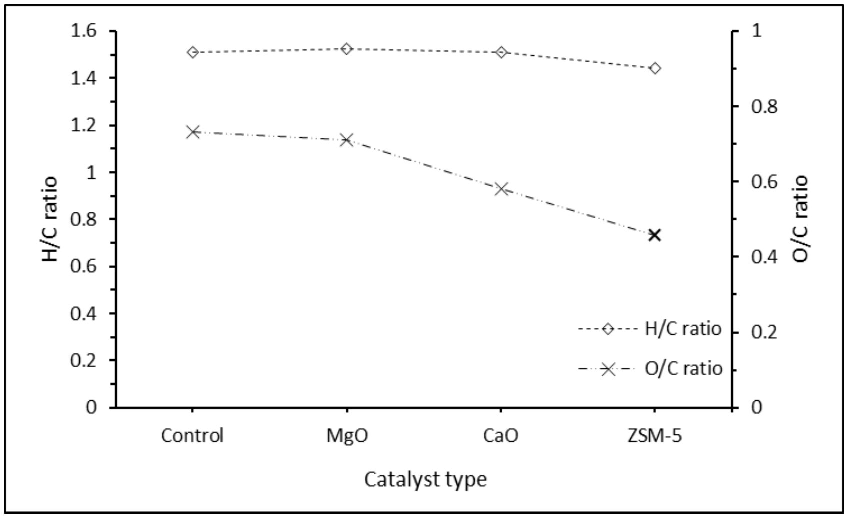

Figure 4.5. H/C and O/C atomic ratios of the bio-oil produced using catalysts

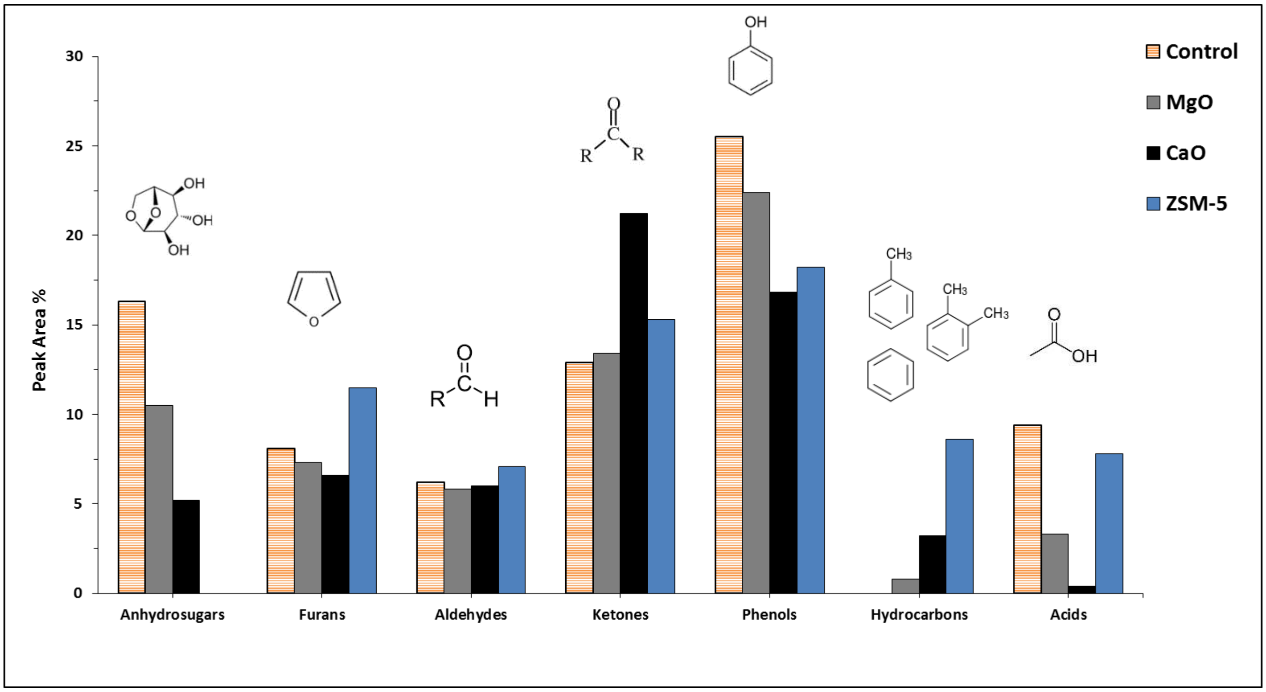

Figure 4.6. Chemical composition of bio-oil produced using different catalysts

Bio-oil is a complex mixture containing a wide range of chemical compounds and these compounds were analyzed by comparing their mass spectra with the NIST mass spectral library. The peak area percentage of these compounds are grouped in Figure 4.6 into the following classes: anhydrosugars, furans, aldehydes, ketones, phenols, hydrocarbons and acids (List of compounds in the Appendix A). Primary decomposition of cellulose and hemicellulose during fast pyrolysis through depolymerization and ring scission forms different anhydrosugars and ultimately other products such as furans [31]. From Figure 4.6, it can be observed that the anhydrosugars were reduced by all the catalysts, ZSM-5 being the most effective in converting them. Srinivasan et al. [32] described the reaction mechanism for the decomposition of cellulose, hemicellulose into furans and subsequent decarbonylation and oligomerization reactions to produce olefins and aromatic hydrocarbons in the presence of ZSM-5. A decrease in the anhydrosugars and the formation of aromatic hydrocarbons such as benzene, toluene and xylene in the presence of the catalyst supports this reaction pathway for conversion of anhydrosugars into furans and aromatic hydrocarbons. Furan, 2-methyl furan and furfural were all increased by both CaO and ZSM-5, indicating the ability of the catalyst to promote dehydration reactions.

Lignin derived phenolic compounds are one of the major components in bio-oil, which contribute to the high molecular weight and viscosity of bio-oil. Figure 4.6 shows that the overall phenolics yield was decreased by all the catalysts. However, when compared to the non-catalytic bio-oil, a different distribution of these compounds was observed in the presence of catalysts. In the presence of CaO and ZSM-5, the abundance of phenolic compounds with high oxygen content such as 2-methoxyphenol (guaiacol), 2-methoxy-4-methylphenol (creosol) decreased while the yield of light phenols with lower oxygen content, such as phenol, 2-methylphenol (cresol), 4-methylphenol, 2,4-dimethylphenol (xylenol) increased, which is shown in Figure 4.7. These light phenols are formed through cracking of the heavier, more oxygenated compounds derived from lignin, which contributes to the overall aim of the upgrading process to deoxygenate bio-oil and improve its stability. Although a similar decrease in the phenolics yield was observed with MgO, the composition was similar to the non-catalytic bio-oil. It is very unlikely that MgO significantly cracked the phenols to gases or deoxygenated them to form aromatic hydrocarbons. Therefore, it is probable that MgO catalysed the polymerization of phenols to form coke or char.

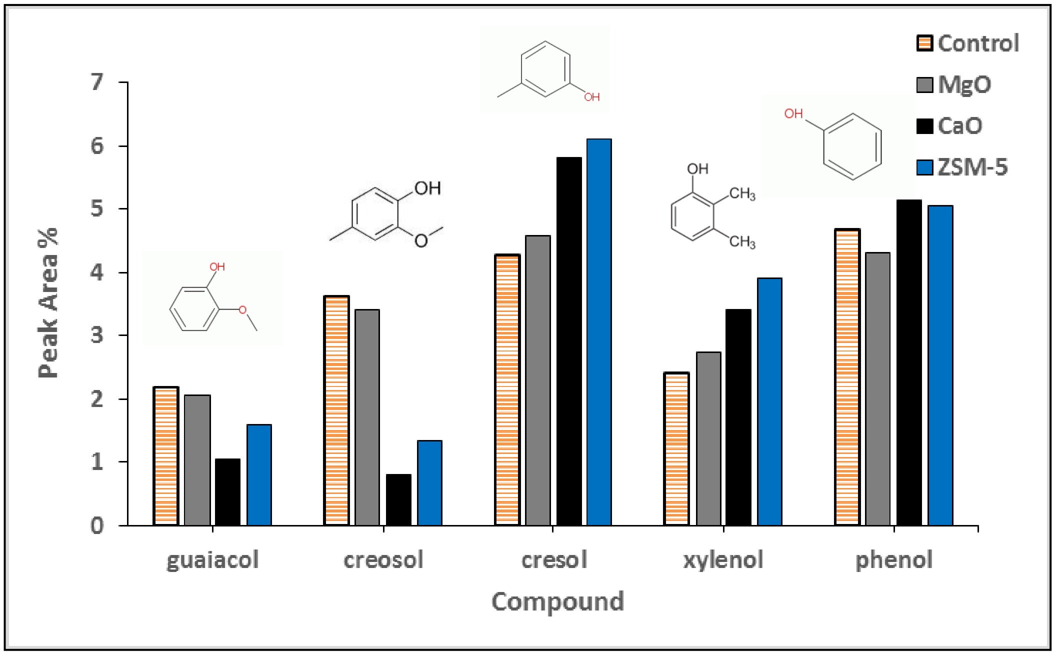

Figure 4.7. Effect of catalyst type on phenolic compounds

The predominant carboxylic acid in the bio-oil was acetic acid, which is well known for being a major cause of accelerating aging, by catalysing polymerization reactions that cause an increase in the viscosity and molecular weight of bio-oil [33]. Basic catalysts tend to favor ketonization reactions, resulting in the conversion of acids in the pyrolysis vapor to ketones.

$CaO + 2R\text{-}COOH \longrightarrow (RCOO)_2Ca + H_2O$ ………………………….………………… (Eq. 1)

$(RCOO)_2Ca \longrightarrow CaCO_3 + R\text{-}COR$ ……………………………..…………………...… (Eq. 2)

$R\text{-}COOH \xrightarrow{CaO} CO_2 + RH$ ……………………………………….………………..… (Eq. 3)

$CaO + R\text{-}COOH \longrightarrow CaCO_3 + RH$ …………………………………………………..... (Eq. 4)

While it is clear that ZSM-5 does not help reduce the undesirable organic acids, they are reduced remarkably when CaO is used as the catalyst. The removal of organics acids could be attributed to different reaction pathways: neutralization of acids by CaO to form calcium carboxylate and H_2O, followed by the decomposition of calcium carboxylate to form ketones and $CaCO_3$, which is favored at the operating temperature range of fast pyrolysis (Eq. 1&2) [23]; thermal cracking and direct fixation of acids to form hydrocarbons (Eq. 3&4) [24]. The increase in the abundance of ketones in the CaO catalysed bio-oil suggests that the ketonization pathway (Eq. 1&2) is more favored and dominates over the catalytic cracking to form aromatic hydrocarbons. The ketonization pathway was also reported by Peters et al. [34], Deng et al. [35] and Veses et al. [21] although the reactor configurations used were different in those studies. Lin et al. [28] reported that acid compounds and CO_2–like substances (active quasi-CO_2 intermediates) react with CaO during pyrolysis to cause a direct reduction in the relative abundance of organic acids in bio-oil. While this established mechanism could be assumed to be the main pathway, a definitive statement about the reaction mechanism can only be made by analysing the gas composition and hence, further investigation is required in order to confirm the ideas postulated based on the chemical composition of bio-oil.

Table 4.2 . Properties of upgraded bio-oils produced using different catalysts. Results after accelerated aging tests in parenthesis (Same letter in each group (or row) indicates that it is statistically not different)

Property	Control	MgO	CaO	ZSM-5
Water content (wt.%)	20.3 ± 0.40^{A} (22.8)	21.7 ± 0.61^{A} (23.9)	21.4 ± 0.58^{A} (22.1)	38.5 ± 1.66^{B} (40.2)
TAN (mg KOH/g)	88.9 ± 2.11^{A} (103.1)	78.5 ± 3.30^{B} (92.2)	46.6 ± 3.01^{C} (50.2)	93.9 ± 2.15^{A} (105.8)
pH	2.39 ± 0.05^{A}	2.76 ± 0.06^{B}	3.98 ± 0.05^{C}	$2.45\ ^{a} \pm 0.08^{A}$ $3.84\ ^{b} \pm 0.06^{C}$
Kinematic viscosity at 40° C (cSt)	20.2 ± 0.81^{A} (63.8)	19.1 ± 1.15 $(47.1)^{A}$	15.4 ± 1.13 $(23.9)^{B}$	$23.4^{a} \pm 0.78^{C}$ (75.7) $11.2^{b} \pm 1.61^{C}$

				(28.8)
HHV (MJ/kg) †	19.2 ± 0.16^{A}	19.6 ± 0.10^{A}	20.9 ± 0.29^{B}	23.4 ^{a} ± 0.26 ^{C} 18.6 ^{b} ± 0.29^{C}
HHV (MJ/kg) ¥	24.1	25.03	26.59	30.24 $^{\mathbf{b}}$
O/C *	0.73	0.71	0.58	0.45
H/C *	1.51	1.52	1.50	1.44

†- as received; * - mol/mol; ^{a} – Organic phase; ^{b} – Whole bio-oil; ¥- dry basis

The physical and chemical properties of the liquid phase were analyzed and are listed in Table 4.. While the baseline experiments performed without a catalyst produced the bio-oil with the least water content, the use of ZSM-5 resulted in a significant increase in the water content due to the dehydration reactions caused by the catalyst. It is well known that calcium based materials could also promote dehydration reactions of oxygenated compounds during catalytic pyrolysis and hence, it would be expected that the resulting bio-oil has a greater water content. However, it was surprising to note that the water content of the bio-oil produced using CaO was relatively close to the non-catalytic bio-oil. This could be a result of the catalytic effect of CaO on water-gas shift (WGS) reaction [36], due to the enhanced ability of CaO to react with CO_2 and active CO_2 precursors produced during pyrolysis. This effect was also reported by Lin et al.[28], where an increase in H_2 yield and a decreased CO_2 and CO yield was observed during catalytic pyrolysis with CaO. The absorption of CO_2 by CaO favored shifting the equilibrium of the reaction to the right side of Eq. 5, increasing the formation of the product H_2. This mechanism could also explain the reduced water content observed in the bio-oil obtained when using CaO as the catalyst. As shown later, characterization of the spent CaO revealed 8.5 wt.% absorbed CO_2, which supported the possibility of this mechanism. It should be noted that the relative inactivity of MgO as a catalyst in this study could be attributed to the fact the carbonate form decomposes at a relatively low temperature of 350˚ C and it exists as the stable metal oxide form in the process conditions.

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \text{. . . . . (Eq.5)}$$

Although the heating value of the bio-oil was not improved by the metal oxide catalysts, their effect was pronounced on improving other properties such as acidity and viscosity. The observed results for improvement in TAN using metal oxide catalysts agrees with the reported reduction of the molality of acid components as reported in the literature [21, 23, 28]. Although the lowest value of TAN obtained in this study using CaO (46.6) is still well short of the specification required for bio-oil to be used in a refinery (TAN<15, to give an acid number after blending < 2 [37]), it still represents a significant improvement on the TAN of the bio-oil when compared to both baseline and bio-oil produced using ZSM-5. Since the acidic components in bio-oil are known to catalyze polymerization reactions which increase the viscosity and decrease the storage stability of bio-oil, the ability of CaO to improve this specific property becomes particularly important. The measured viscosity of the bio-oil depends on the water content of the sample, as well as its chemical composition. Among the catalysts tested in this study, bio-oil produced using CaO as the catalyst had the lowest viscosity, with a 24% reduction when compared to the non-catalytic experiment. A direct comparison with the ZSM-5 bio-oil was not possible, since it was phase separated and had a much higher water content when compared to the other bio-oils produced. Energy return through catalytic pyrolysis in the form of the liquid product was calculated from Eq. 6, while carbon ratio was calculated according to Eq. 7. Figure 4.8 shows that the carbon ratio and energy return followed a similar trend with different catalysts. Catalysis by CaO and ZSM-5 resulted in a lesser overall energy return in the form of the liquid product, since the catalytic activity resulted in a lower yield of bio-oil.

$$Energy\ return = \frac{Energy\ content\ of\ bio-oil * liquid\ yield}{Energy\ content\ of\ biomass} \qquad \text{(Eq.6)}$$

$$Carbon\ ratio = \frac{Carbon\ content\ in\ bio-oil * liquid\ yield}{Carbon\ content\ in\ biomass} \qquad \text{(Eq.7)}$$

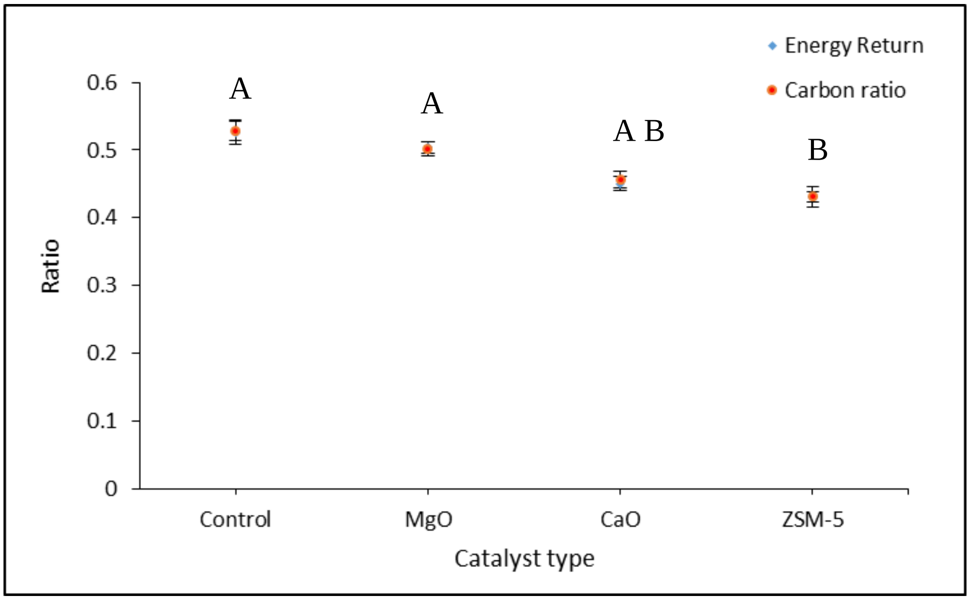

Figure 4.8. Energy return and carbon ratio of the bio-oil produced (Same letter indicates that it is statistically not different)

4.3.4. Bio-oil Stability Analysis

Diebold [38] reviewed various possible chemical mechanisms which could be the cause of storage instability of bio-oil, including the reactions of organic acids, aldehydes such as esterification, transesterification and acetalization. Most of the reactions continue primarily because of tendency of these active species to reach thermodynamic equilibrium. The organic acids in particular, are mainly responsible for catalysing undesirable polymerization reactions that cause an increase in molecular weight and the viscosity of bio-oil. The acetalization reaction can be considered as a prime example to illustrate this effect, where acid catalysts cause the reaction of aldehydes and sugars, starches and cellulose resulting in the formation of a cross-linked polymer of higher molecular weight. However, such reactions are minimized in the absence of organic acids in the bio-oil. Elliot et al. [39] stated viscosity as one of the major parameters to study the pyrolysis liquid stability since it correlates with the increase in molecular weight and is a measure of the extent of aging, which is reported in terms of the aging index (Eq.8).

$$\text{Aging Index} = \frac{(\text{Viscosity after aging} - \text{Initial viscosity})}{\text{Initial viscosity}} * 100 \qquad \text{(Eq. 8)}$$

Accelerated aging tests on the bio-oils produced in this study showed an increase in viscosity with all the samples, as shown in Figure 4.9. However, the relative increase of viscosity is extreme in the case of non-catalytic bio-oil, which showed an aging index of 216 %. ZSM-5 and MgO catalysed bio-oils also showed a significant viscosity increase, with the aging index being 157 % and 147 %, respectively. However, the bio-oil produced using CaO as the catalyst had an aging index of only 55 %. The order of stability of these bio-oils was CaO > MgO > ZSM-5 > Control, which matches with the composition of organic acids in bio-oil. The composition of bio-oil produced using CaO as the catalyst which had the lowest amount of acids in its composition was the most stable, while the non-catalytic bio-oil with the highest amount of acids had poor stability. While the stability tests showed the prospect of using a cheap basic metal oxide such as CaO to produce a stable bio-oil, it also further confirmed that the presence of organic acids in bio-oil accelerates the aging of bio-oil.

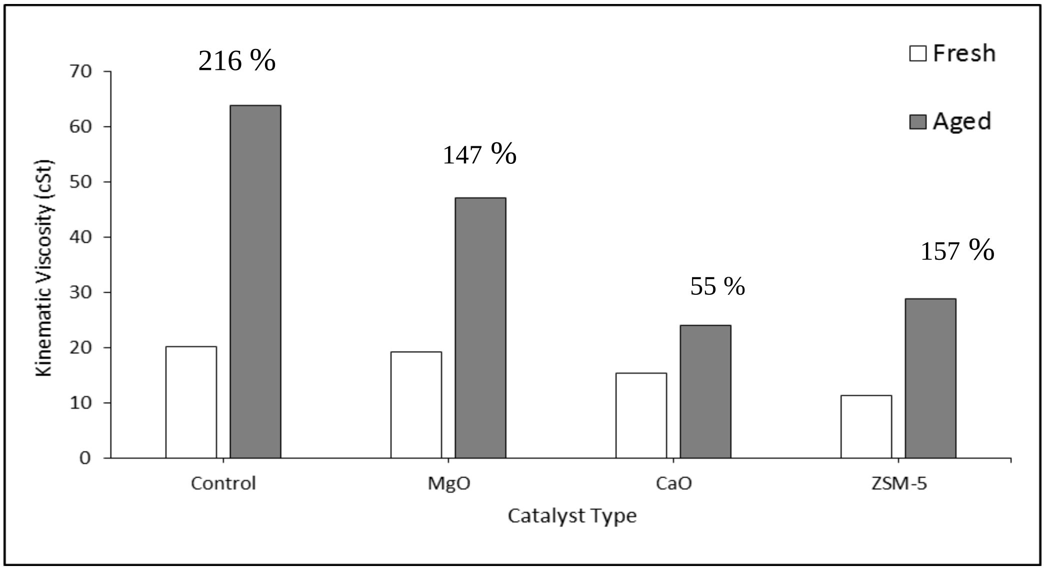

Figure 4.9. Viscosity of fresh and aged bio-oils tested in this study (Aging Index values represented on top of each column, calculated from Eq. 8)

4.3.5. Spent Catalyst Characterization

Spent catalysts and char collected from the filter/reactor were separated after each experiment by sieving. Thermogravimetric analysis was performed on the spent catalyst to quantitatively determine the amount of coke. About 5 g of the catalyst was heated at 30 ºC /min to 800 ºC while an air flow rate of 20 mL/min was maintained. The catalyst sample is assumed to be dry when the TGA temperature reached 150 ˚C and that all the coke was removed when the temperature was 800 ˚C. Eq. 9 was used to calculate the relative amount of coke on the catalyst. Figure 4.10 shows the TGA curve for spent ZSM-5 and the relative amount of coke deposited on each catalyst is given in Table 4..

$$\text{Relative amount of coke (\%)} = \frac{(M\ 100\ ^{\circ}C - M\ 800\ ^{\circ}C) * 100}{M\ 100\ ^{\circ}C} \qquad \text{(Eq. 9)}$$

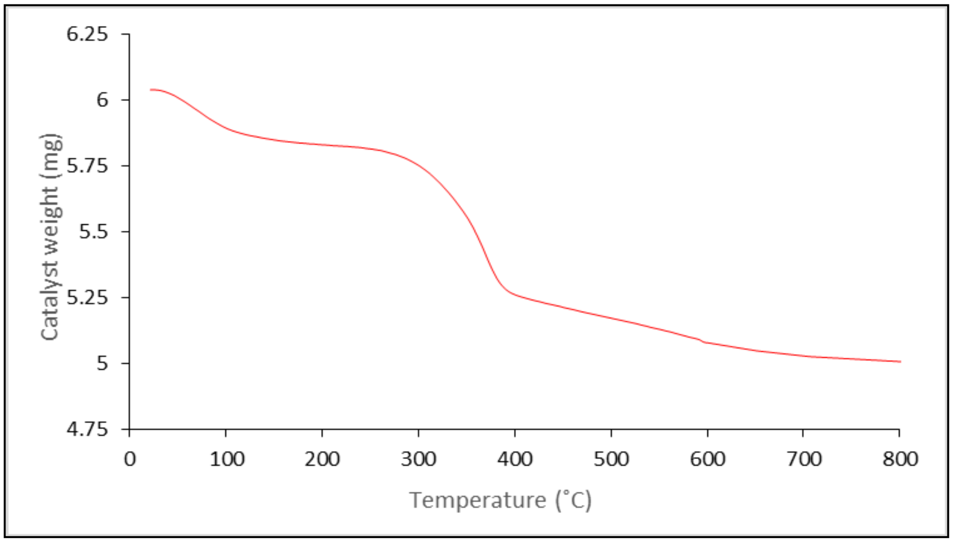

Figure 4.10. TGA of spent ZSM-5 catalyst

For the metal oxide catalysts, in addition to the coke deposited on the surface, some CO_2 is also absorbed by the catalyst. To measure the amount of CO_2 absorbed, the spent catalysts were calcined at 850 ˚C for 3h. The difference between the relative amount of coke (wt. %)calculated from TGA analysis and the weight loss (wt. %) after calcination at 850 ˚C for 3h revealed the percentage of CO_2 absorbed in MgO and CaO to be 1.5 wt. % and 8.9 wt. % respectively, which is in accordance with the greater CO_2 sorption capacity of CaO when compared to MgO.

Table 4.3. Spent catalyst characterization results

Catalyst	Relative amount of coke (wt. %)	Absorbed CO_2 (wt. %)
ZSM-5	15.04 ± 0.83	-
MgO	4.31 ± 0.21	1.52 ± 0.57
CaO	7.84 ± 0.43	8.91 ± 0.72

4.4. Conclusions

In-situ catalytic pyrolysis of biomass has been studied in a bench-scale fluidized bed reactor and the performance of three different catalysts were evaluated based on the properties of bio-oil produced. Among the catalysts tested, MgO was observed to be only a mild catalyst which did not have a discernible impact on the product quality and distribution, while CaO and ZSM-5 showed different behaviors in altering the quality and distribution of the pyrolytic products. Although ZSM-5 produced an organic phase with the highest heating value, it resulted in a phase separated product and the catalyst had no effect on reducing the undesirable acid components of bio-oil. Catalysis by CaO showed a contrasting result by producing qualitative improvements on the TAN and viscosity of the bio-oil, while not improving the heating value significantly. The CaO catalysed bio-oil with reduced acidic components also showed greater stability, having the lowest aging index when subjected to accelerated aging tests as compared to other bio-oils produced in this study.

4.5. References

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5. Summary and Future Directions

5.1. Summary

The main objective of this study was to investigate different techniques to improve the physical and chemical properties of bio-oil from fast pyrolysis of biomass in a fluidized bed reactor. This goal was successfully achieved through two specific objectives. In the first objective, optimum conditions of residence time and temperature for fast pyrolysis were identified, followed by investigation of the effect of blending biomass feedstocks (southern pine and switchgrass) to study their effect on the quality of bio-oil. The results from this study showed that the optimum conditions to achieve maximum bio-oil yield were a residence time of 1.54 s and a temperature of 450 ˚C. In addition to this, it was observed that the elemental composition of bio-oil did not differ significantly at the various operating conditions tested in this study. Finally, blending switchgrass with southern pine improved the properties of bio-oil, specifically pH (2.39 to 3.16) and viscosity 12.12 to 6.96 cSt). However, bio-oil produced with blends having greater amounts of switchgrass (> 50 wt.%) resulted in a phase separated bio-oil due to the higher water content. Blending different types of biomass could be very useful, especially because it'll ensure that the process will be flexible to operating with different feedstocks and won't rely solely on any particular type of biomass. It also creates the possibility of selectively blending chosen biomass types to achieve an improvement in the properties of the bio-oil produced.

In the second objective, *in-situ* catalytic upgrading was investigated in the fluidized bed reactor, to analyze and compare the effect of different catalysts (MgO, CaO and ZSM-5) on the properties of bio-oil produced, with non-catalytic experiments performed with inert bed material acting as a control. Properties of the bio-oil produced, such as TAN, viscosity, heating value, pH, water content, and elemental composition were measured for comparing the quality of bio-oil. It was observed that the use of CaO as the *in-situ* catalyst improved the pH (2.39 to 3.98) and TAN (88.9 to 46.6) of the bio-oil. MgO showed very less catalytic activity, since it did not significantly alter the product composition and quality of the bio-oil. ZSM-5 did not show any effect on improving the acidic nature of bio-oil, but produced the bio-oil with the least oxygen content. Chemical analysis of the bio-oils showed that CaO was very effective in removing the organic acids usually found in bio-oil, by converting them to ketones, while CaO and ZSM-5 proved to be effective in reducing the abundance of phenolic compounds with higher oxygen content. On evaluating the stability of bio-oils produced using each catalyst through accelerated aging test, it was observed that the bio-oil produced with CaO as the catalyst was the most stable when compared to the bio-oils produced in control, MgO and ZSM-5 experiments. From the results obtained in this study, a clear correlation was observed between stability and the amount of organic acids in bio-oil.

5.2. Future directions

This research has shown the possibility of improving the properties of bio-oil through different techniques - blending biomass feedstocks, *in-situ* catalysis. Although the results have been very promising, there is still room for future studies in this area.

1. Due to the availability of a large amount of southern pine in Alabama and the potential of switchgrass as an energy crop, only these two feedstocks were investigated in this study. However, there are a wide variety of biomasses which differ in their composition and properties. The results from this study for the two specific biomass types tested might not be applicable for all the other feedstocks. Hence, a more extensive study is required to investigate further to build on the results from this research.

2. In this study, we have investigated the effect of using basic oxides as *in-situ* catalysts for pyrolysis. Based on the chemical composition and properties of bio-oil produced, the possible chemical mechanism was proposed. However, a more detailed study using model compounds for biomass using metal oxide catalysts to investigate the fundamental chemical mechanism is required to extend the results from this study.

3. The non-condensable gases from pyrolysis include C2-C4 olefins, methane and hydrogen, which could be recycled back into the pyrolysis reactor to further promote deoxygenation in reactive gas environments. Metals such as Co, Mo, Fe, Ni and other transition metals could be impregnated on acidic and basic catalysts to identify the best catalyst for pyrolysis in such a reducing atmosphere. The easy availability of a large amount of natural gas as a result of the shale gas exploitation makes such a process more attractive and if an efficient catalyst is identified, it would also reduce the amount of hydrogen required for upgrading bio-oil.

Appendix A: Data for Graphs

Table A.1: Data for Figure 3.2

Product distribution	Superficial residence time (s)			
	1.98	1.75	1.54	1.39
Liquid (wt. %)	39.64 ± 1.32	45.57 ± 0.89	50.98 ± 0.59	48.66 ± 0.62
Char (wt. %)	20.64 ± 0.71	18.69 ± 0.23	16.3 ± 0.82	17.3 ± 0.70
Gas (wt. %)	39.72 ± 0.98	35.74 ± 0.63	32.72 ± 0.68	34.04 ± 0.78

Table A.2: Data for Figure 3.3

Elemental composition	Superficial residence time (s)			
	1.98	1.75	1.54	1.39
C (wt. %)	47.39 ± 0.84	47.23 ± 0.93	47.28 ± 0.79	47.45 ± 0.99
H (wt. %)	6.03 ± 0.12	5.97 ± 0.08	6.14 ± 0.19	6.18 ± 0.12
O (wt. %)	46.19 ± 0.92	46.26 ± 0.62	46.07 ± 0.75	45.85 ± 0.91

Table A.3: Data for Figure 3.4

Product distribution	Process Temperature (˚C)		
	400	450	500
Liquid (wt. %)	44.3 ± 0.93	48.38 ± 0.75	42.02 ± 0.12
Char (wt. %)	29.62 ± 0.61	22.72 ± 1.18	17.64 ± 1.24
Gas (wt. %)	26.08 ± 0.86	28.9 ± 0.98	40.34 ± 0.72

Table A.4: Data for Figure 3.5

Elemental composition	Process Temperature (˚C)		
	400	450	500
C (wt. %)	46.88 ± 0.83	46.32 ± 0.82	46.97 ± 0.90
H (wt. %)	6.12 ± 0.12	6.04 ± 0.07	6.19 ± 0.14
O (wt. %)	46.61 ± 0.92	47.1 ± 0.95	46.33 ± 0.79

Table A.5: Data for Figure 3.6

Product distribution	**Biomass blend (ratio)**				
	SP	**SP/SG:75/25**	**SP/SG:50/50**	**SP/SG:25/75**	**SG**
Liquid (wt. %)	48.58 ± 0.75	46.65 ± 1.24	46.3 ± 0.44	45.71 ± 2.82	42.65 ± 0.51
Char (wt. %)	24.72 ± 1.18	23.57 ± 2.12	24.9 ± 0.91	27.14 ± 1.41	28.3 ± 0.63
Gas (wt. %)	26.7 ± 0.78	29.78 ± 1.73	28.8 ± 0.74	27.15 ± 0.78	29.05 ± 0.57

Table A.6: Data for Figure 3.7

Elemental composition	**Biomass blend (ratio)**				
	SP	**SP/SG:75/25**	**SP/SG:50/50**	**SP/SG:25/75**	**SG**
C (wt. %)	47.97 ± 0.48	47.41 ± 0.63	46.34 ± 0.57	45.29 ± 0.23	44.86 ± 0.39
H (wt. %)	6.32 ± 0.15	6.48 ± 0.23	6.49 ± 0.34	6.91 ± 0.12	6.92 ± 0.31
O (wt. %)	45.32 ± 0.58	45.57 ± 0.62	46.66 ± 0.71	47.28 ± 0.81	47.3 ± 0.92

Table A.7: Data for Figure 4.3

Product distribution	**Bed material**			
	Control	**MgO**	**CaO**	**ZSM-5**
Liquid (wt. %)	51.43 ± 2.02	48.23 ± 0.99	40.4 ± 1.45	34.63 ± 1.30
Char (wt. %)	19.1 ± 0.20	23.46 ± 0.51	26.1 ± 1.21	20.3 ± 1.49
Gas (wt. %)	29.46 ± 0.81	28.3 ± 1.55	33.5 ± 0.72	45.06 ± 0.85

Table A.8: Data for Figure 4.4

Elemental composition	**Bed material**			
	Control	**MgO**	**CaO**	**ZSM-5**
C (wt. %)	47.42 ± 0.94	47.91 ± 0.85	51.97 ± 1.03	57.36 ± 1.14
H (wt. %)	5.97 ± 0.09	6.08 ± 0.12	6.53 ± 0.15	6.9 ± 0.11
O (wt. %)	46.2 ± 0.62	45.38 ± 0.91	40.24 ± 0.52	34.92 ± 0.69

Table A.9: Data for Figure 4.5

Ratio	**Bed material**			
	Control	**MgO**	**CaO**	**ZSM-5**
H/C	1.51	1.52	1.50	1.44
O/C	0.73	0.71	0.58	0.45

Table A.10: Data for Figure 4.6

Group (Area %)	**Bed material**			
	Control	**MgO**	**CaO**	**ZSM-5**
Anhydrosugars	16.3	10.5	5.2	0
Furans	8.1	7.3	6.6	11.5
Aldehydes	6.2	5.8	6	7.1
Ketones	12.9	13.4	21.2	15.3
Phenols	25.5	22.4	16.8	18.2
Hydrocarbons	0	0.8	3.2	8.6
Acids	9.4	3.3	0.4	7.8

Table A.11: Data for Figure 4.7

Compound (Area %)	**Bed material**			
	Control	**MgO**	**CaO**	**ZSM-5**
Guaiacol	2.19	2.05	1.04	1.58
Creosol	3.62	3.41	0.80	1.33
Cresol	4.28	4.57	5.82	6.10
Xylenol	2.40	2.73	3.40	3.90
Phenol	4.67	4.31	5.13	5.04

Table A.12: Classification of chemical compounds in chemical composition

Anhydrosugars	**Furans**	**Aldehydes**	**Ketones**	**Phenols**	**Hydrocarbons**	**Acids**
1,6-Anhydro-beta-D-glucopyranose (levoglucosan)	Furfural	Butanedial	2-Cyclopenten-1-one	Phenol	Benzene	Acetic acid
	2-Furancarboxaldehyde, 5-methyl	Pentanal	1H-Inden-1-one, 2,3-dihydro-	Phenol, 2-methyl	Toluene	Propanoic acid
	Furan-2-methyl	2,3-Dihydroxypropanal	2-Cyclopenten-1-one, 2-methyl-	Phenol, 3-methyl	o-Xylene, p-Xylene	Butanoic acid
	4-methyl furan	Hydroxy-acetaldehyde	Cyclopentanone	Phenol, 2,3 dimethyl-	Styrene	Acetic acid, 4-methylphenyl ester
	Benzofuran	Benzaldehyde, 2-hydroxy-	2-Cyclopentene-1,4-dione	Phenol, 2,4 dimethyl-	Benzene, 1-ethyl- 2-methyl-	Acetic acid, phenyl ester
	Benzofuran, 2-methyl-	2-Furancarboxaldehyde	2(5H)-Furanone	Phenol, 2-methoxy-4-methyl-	Benzene, 1,2,3-trimethyl-	Acetic acid, 4-methylphenyl ester
	Benzofuran, 2-ethenyl-	Furfural	3-Methyl-2-cyclopenten-1-one	1,2-Benzenediol	Indene	Acetic acid, m-tolyl ester
	Benzofuran, 2-ethenyl-	2-Furancarboxaldehyde, 5-methyl	2,3-Dimethyl-2-cyclopenten-1-one	Phenol, 4-methyl-	Benzene, 1-ethenyl-4-methyl-	
	Benzofuran, 7-methyl-		2-Cyclopenten-1-one, 2,3-dimethyl-	1,2-Benzenediol, 4-methyl-		
	2-Dibenzofuranol			Phenol, 4-ethyl-		
	Benzofuran, 2,3-dihydro-			Phenol, 3-ethyl-		
	Ethyl-2-benzofuran			Phenol, 3,5-dimethyl-		
				Phenol, 2-ethyl-		
				Phenol, 3-ethoxy-		
				Phenol, 2,4,6-trimethyl-		
				2-Methoxy-phenol		
				2-Methoxy-6-methylphenol		