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Master's Thesis of Science in Agriculture

**Comparative Study on Pyrolysis Features of
Woody Biomass and Waste Plastics by mean of
Various Pyrolytic Systems**

목질계 바이오매스 및 폐플라스틱의 열분해 특성의 비교 연구

August 2020

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**Comparative Study on Pyrolysis Features of
Woody Biomass and Waste Plastics by mean of Various
Pyrolytic Systems**

A thesis
submitted in partial fulfillment of the requirements to the faculty
of Graduate School of International Agricultural Technology
for the Degree of Master of Science in Agriculture

By
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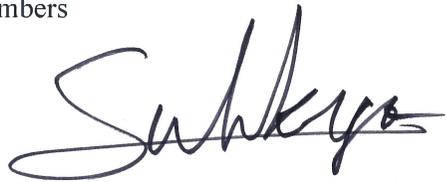
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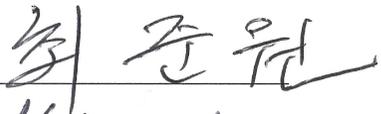
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Abstract

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In this study, in Part I, fast pyrolysis of pine wood sawdust was performed using 'screw type' and 'fluidized bed' pyrolyzer to investigate the effects of particle sizes on the mass balance and physicochemical properties of bio-oil. The particle size of pine wood sawdust was ranged from 1mm to 14mm, and the pyrolysis temperature was fixed at 500°C, the optimum temperature for bio-oil production. The results revealed that the type of pyrolyzer influenced the distribution of thermal degradation products (bio-oil, bio-char, and gas) from the woody biomass. The 'screw type' pyrolyzer was able to accept the feedstock of particle size ranged from 1mm to 14mm, while the 'fluidized bed' pyrolyzer could only accept the feedstock of particle size of 1mm and 2mm, but not 6mm and 14mm. The influence of feedstock particle size on the distribution of pyrolysis products in the 'screw type' pyrolyzer was not significant (bio-oil: 43.2% ~ 46.3%; biochar: 20.3% ~ 22.3%). However, the difference of pyrolysis product yields between two pyrolysis systems was significant. Within the same particle size, 'screw type' pyrolyzer produced less bio-oil and more gas compared with 'fluidized bed' pyrolyzer. Using GC/MS analysis, 25 chemical compounds were identified from the bio-oil.

Part II, pine wood sawdust were catalytically pyrolyzed with polyethylene (PE) using analytical pyrolysis-GC/MS system to investigate the effect of plastic on improving the quality of pyrolysis products. The analytical pyrolysis was performed at 600°C, loading 3.0 mg of samples, and the pyrolytic vapor was directly injected into GC/MS to determine the chemical compounds of pyrolytic products. 35~50 chemical compounds were identified and classified into six groups: Monomeric Aromatic Hydrocarbon (MAH), Polycyclic Aromatic Hydrocarbon (PAH), Phenols, Furfurals, Alkenes, and Alkanes. The results showed that the co-pyrolysis of pine with PE significantly decreased the oxygen content in the pyrolytic products from 23.4% (pine only) to 0.3% (pine+PE/ZSM-5), which increased the HHV of pyrolytic products from 25.9 MJ/kg to 34.4 MJ/kg. It also revealed that the ratio of pine and PE did not heavily influence the concentration of petrochemicals (aromatic hydrocarbons + alkenes ($C \leq 15$) + alkanes ($C \leq 13$)). However, a higher plastic ratio led to a higher wax production, which would be a critical reason for poor condensation performance of bio-oil capture in condenser. Pine wood sawdust to PE ratio of 3:1 showed the best result of higher petrochemicals, and low wax formation.

Key words: fast pyrolysis, screw type pyrolyzer, bio-oil, biomass, plastic, catalytic co-pyrolysis

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1. Introduction

1.1. Renewable energy and bioenergy

Since energy is the material basis of human social activities, and it requires high-quality energy supply and advanced energy production technology. However, the world faces severe problems such as global warming and depletion of fossil fuels caused by the indiscriminate use of fossil resources (Meinshausen et al., 2009). The balanced development of environment and energy is a common concern of humankind around the world. According to the International Energy Agency (IEA) on primary energy supply in the world from 2000 to 2011, the rate of increase in total energy usage was 2.96%. Bioenergy accounts for 10% of the world's primary energy consumption and is the fourth most used energy source (Shi, 2016). Many studies concerning carbon dioxide-neutral renewable energy have therefore been actively carried out across the world. The production of carbon-neutral and low-emission fuels from renewable resources, such as biomass, is of growing importance in the gradual substitution of conventional fossils.

Biomass is biological material from living, or recently living organisms produced directly or indirectly by photosynthesis (consist of cellulose, hemicellulose, and lignin, Figure 1), most often plants or plant-derived materials (Long et al., 2013; Brown, 2003). Biomass is a promising renewable energy resource due to its absorption of CO₂ extracted from the atmosphere during growing (Mohan et al., 2006). Biomass resources are widely available in nature, and a wide range of biomass has the potential to serve as a renewable energy resource due to low sulfur, nitrogen, and ash content, which do not constitute an environmental burden. It was estimated

that the global biomass production is approximately 100 billion tons per year. The only renewable carbonaceous resource, biomass, can produce heat, electricity, fuel, chemicals, and other products (Sheldon, 2014; Zhou et al., 2011).

Biomass can be converted into fuels and chemicals through biochemical or thermochemical processes. Digestion (anaerobic and aerobic) and fermentation are typical biochemical processes used to produce methane and alcohol (Kwietniewska & Tys, 2014; Limayem & Ricke, 2012). The main thermochemical processes include pyrolysis, gasification, combustion, hydrothermal liquefaction, and hydrothermal carbonization (Goyal et al., 2008; Stevens, 2011). Well-known liquid transportation fuels are bio-diesel and bio-ethanol from vegetable oils and cellulosic crops (Gray et al., 2006). Since these kinds of biomass are also edible, they can lead to an increase in food prices. Second-generation biomass, so-called lignocellulosic biomass, and energy crop are becoming prominent alternative sources of bioenergy (Wildschut et al., 2010b).

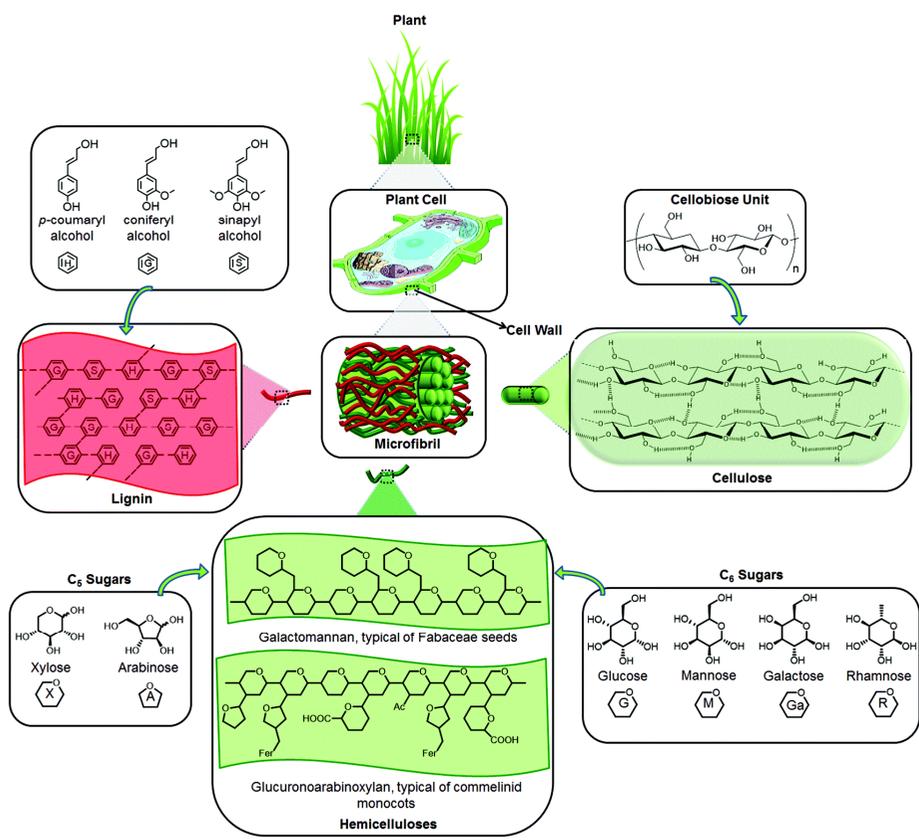


Figure 1. Major compounds of plant cell wall and their primary structures (Isikgor & Becer, 2015).

1.2 Thermochemical conversion of lignocellulosic biomass

Lignocellulosic biomass requires an efficient conversion process to replace conventional fossil fuels, due to its structural complexity and inherently high water content. The thermochemical conversion processes involve heating of biomass at high temperatures. There are three basic approaches in thermochemical conversion technology (Figure 2). The first is gasification of biomass and its conversion to hydrocarbons. The second approach is to produce char. The last one, pyrolysis, is to liquefy biomass directly by high-temperature.

Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at a very high temperature in the range of 800 to 1000°C. The resulting gas, known as syngas, is a mixture of carbon monoxide, hydrogen, methane, and carbon dioxide, and nitrogen. The syngas can be burnt directly or can be used as fuel for gas engines and gas turbines. The production of synthesis gas from biomass allows the production of methanol and hydrogen, each of which may have a future as fuels for transportation (Demirbas, 2006).

Combustion is the burning of biomass in air. It converts the chemical energy stored in biomass into heat, mechanical power, or electricity using different process equipment, such as stoves, furnaces, boilers, steam turbines. Combustion produces hot gases at a temperature of around 800 to 1000°C, an older method of utilizing biomass for obtaining energy (Baxter, 2005).

Fast pyrolysis, characterized by a simple process and short reaction time, has a capability of transforming the bulky and inhomogeneous lignocellulosics to a liquid form of fuel (which is called bio-oil) (Westerhof et al., 2007), this process is recently considered as one of the most promising thermal technologies in the world. Besides the broad applicability of liquid bio-oil

not only as alternative energy (Scott et al., 1999) but also green chemical resources. It can also be an excellent advantage for a fast pyrolysis process compared to other biofuel production processes that all kinds of biomass can be considered as the material for fast pyrolysis (Bridgwater, 2003). A wide variety of biomass has been studied for pyrolysis from agricultural residues to lignocellulosic biomass (Garcia-Perez et al., 2008; Mullen et al., 2009; Park et al., 2009). Bio-oil produced from fast pyrolysis of biomass is mainly used for electricity production in Europe (Bridgwater et al., 2009).

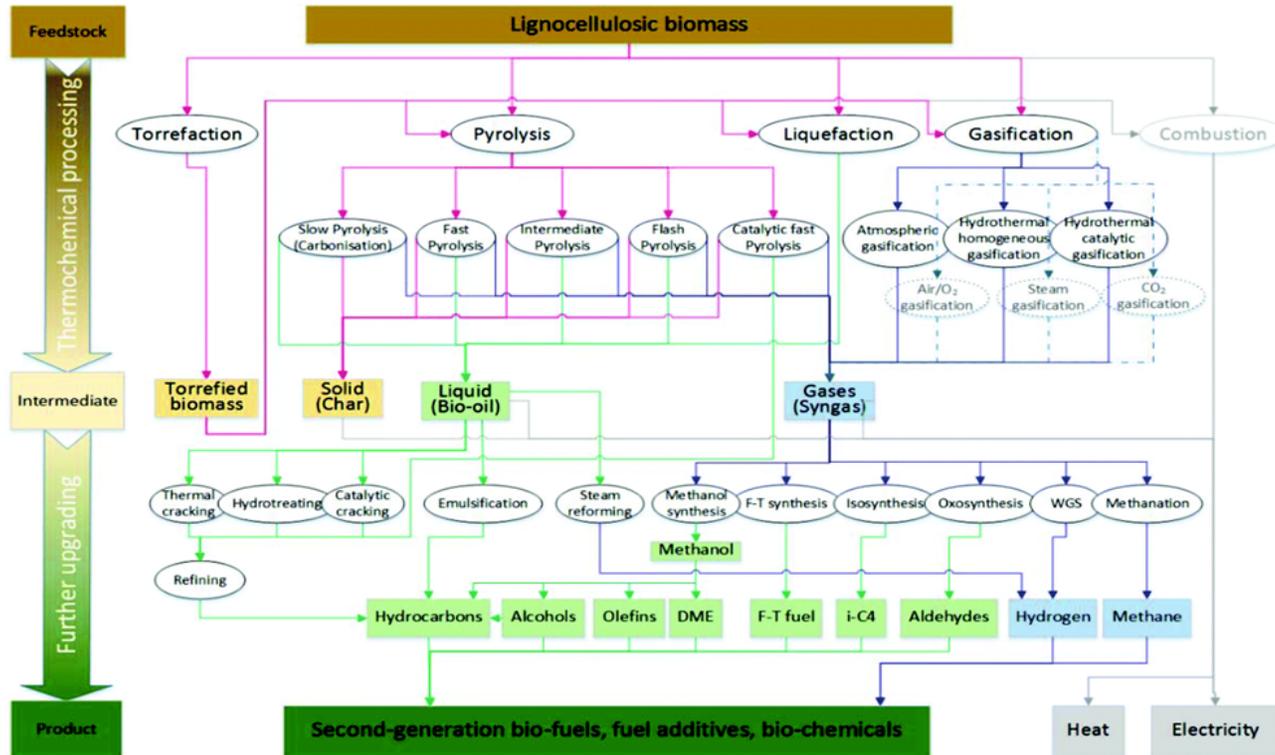


Figure 2. Thermochemical conversion methods of biomass (Zhang, 2016).

1.3. Catalytic co-pyrolysis of biomass and plastics

The high oxygen content of biomass leads to a low quality (high water content, low calorific value) of the inherently unstable bio-oil after pyrolysis (Karimi et al., 2014). Co-feeding biomass with hydrogen-rich plastics can improve the quality of bio-oil. Approximately 150 million tons of plastic waste is generated in the world annually (Rahimi and Garcia, 2017), but only less than 10% of the waste plastic is recycled (Zhang et al., 2016). Plastic waste originates from a variety of sources, including household use, commercial applications, packaging, and even agricultural activities, and recycling could be very costly because of impurities present in those feedstocks. Using plastics to provide hydrogen during the fast pyrolysis of biomass can also help mitigating plastic waste disposal problems (Dorado et al., 2013). Further, utilizing plastic via fast pyrolysis eliminates the need to separate impurities from plastics and edge over the conventional recycling processes (Scheirs and Kaminsky, 2006).

Catalytic pyrolysis is a thermochemical conversion process that enables the production of valuable aromatic hydrocarbons or other phenolics from lignin, which is one of the main components in biomass besides cellulose and hemicellulose. Zeolite is the most widely used solid acid catalyst for catalytic pyrolysis because it can efficiently remove oxygen derived from biomass, resulting in a final liquid product with low O/C and a high H/C ratio (Carlson et al., 2008). It has both Bronsted and Lewis acid sites, which possibly convert oxygenated compounds to aromatic hydrocarbons via cracking dehydration, decarbonylation, decarboxylation, aromatization, dealkylation, dehydrogenation, and oligomerization (Rezaei et al., 2014).

1.4. Objectives

Fast pyrolysis is one of the promising techniques for liquid fuel production from biomass. The liquid fuel has the potential to contribute to the global needs for transport fuels and chemical feedstock. However, most of the fast pyrolysis studies focus on fluidized bed reactors, not on the screw type reactor. The optimum condition of temperature, residence time, and feedstock particle size for a high capacity screw type reactor is still imperfectly understood.

On the other hand, screw type reactor has a better potential to handle the feedstocks which are not able or have a high risk of pyrolyzing in a fluidized bed reactor, such as big particle size ($> 5\text{mm}$) and plastics. However, few studies focus on the pyrolysis of plastics in a continuous screw type pyrolysis reactor.

For these reasons, this study will focus on the pyrolysis of various particle size woody biomass using a screw type reactor and the physicochemical properties of the pyrolytic product, the difference between the fluidized bed reactor and screw type reactor in yield and efficiency of various particle sizes of feedstocks. Furthermore, to prepare the catalytic co-pyrolysis of biomass and plastics in a screw type reactor, the optimum mixture ratio of biomass, plastic, and catalyst will be determined using a micro-reactor, which connected with GC/MS.

2. Literature review

2.1. Fast pyrolysis

2.1.1. Fast pyrolysis and bio-oil

Fast pyrolysis is a thermochemical conversion process commonly considered the best technology route for the production of liquid fuel, bio-oil (Lu et al., 2009). The yields of fast pyrolysis products are typically about 60~75 wt% for bio-oil, 15~25 wt% for bio-char, and 10~20 wt% for non-condensable gas. There have been numerous studies of optimizing experimental conditions for bio-oil production from fast pyrolysis and analyzing the physicochemical properties of pyrolytic products (Kim et al., 2011; Oasmaa & Peacocke, 2001; Pittman Jr et al., 2012; Bridgwater, 2012). In general, experimental conditions of temperature at 500°C, the residence time for less than 2s, and particle size of feedstock less than 3mm are proper for bio-oil production.

The bio-oil is dark brown, free-flowing liquid with an acidic or smoky odor. It is a complex mixture of compounds derived from the depolymerization of cellulose, hemicellulose, and lignin. Chemically, it contains quite a lot of water (15~30 wt%), more or less solid particles (~< 3wt%), and hundreds of organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds, and multifunctional compounds (Kim et al., 2011; Milne et al., 1997). In terms of fuel properties, viscosity and higher heating value of bio-oil are typically 30~200cP and 17.0 MJ/kg, respectively.

Bio-oil can be produced from a variety of forest and agricultural biomass wastes. The Bark-free Turkish red pine pyrolyzed in a laboratory-scale fixed-bed reactor was carried out at a temperature of 400~500°C with slow

heating rates of 7 and 40°C/min (Sensoz & Can, 2002). The bio-oil yield obtained was 21~30 wt%. It was reported that the highest bio-oil yield obtained at 500°C and a heating rate of 40°C/min. Fast pyrolysis of several wood feedstocks such as *Pterocarpus indicus*, *Cunninghamia lanceolata*, and *Fraxinus mandshurica* have been conducted in a fluidized-bed reactor (Luo et al., 2004). In this report, bio-oil production was most excellent at 500°C. Besides, various woody biomass as the raw material of fast pyrolysis for bio-oil production was carried out, for example, eucalyptus (Guerrero et al., 2005), spruce and pine (Paris et al., 2005), hybrid poplar (Diebold & Czernik, 1997).

Fast pyrolysis of agricultural residues, such as olive husks, corncobs, and tea wastes, has been studied. Rice straw pyrolysis was reported in a stainless steel fixed-bed Heinze reactor (Putun et al., 2004). The temperature, particle size, sweep gas flow rate and steam velocity were studied. The highest bio-oil yield of 27.3% was obtained at 550°C. The pyrolysis of olive bagasse in a fixed-bed reactor at 350~550°C with varying heating rates has been studied (Sensoz et al., 2006). According to this paper, the bio-oil yield was highest at 500°C, where a heating value of 31.8MJ/kg was observed. Furthermore, the fast pyrolysis of microalgae (Miao et al., 2004), switchgrass (Boateng et al., 2006), and sewage sludge (Sanchez et al., 2007) for renewable energy production have been carried out.

2.1.2. Properties and applications of bio-oil

The elemental composition of bio-oil resembles that of the original biomass. The oxygen content of bio-oil is usually 40wt%. This oxygen is present in most of the more than 300 compounds that have been identified in the bio-oil (Czernik & Bridgwater, 2004). The high oxygen content results in a low energy density of less than 50% of that for conventional fuels and immiscibility with hydrocarbon fuel.

Water in bio-oil was resulted from the original moisture in the feedstock and as a product of the dehydration reactions occurring during pyrolysis (Elliott, 1994). Therefore, the water content varies over a wide range (15~30%) depending on the feedstock and process conditions.

The viscosity of bio-oil can vary over a wide range (35~1000 cP at 40°C) depending on the feedstock and experimental conditions and especially on the efficiency of the collection of low boiling components (Czernik & Bridgwater, 2004). Also, bio-oil obtained from biomass is quite acidic (pH 2~3), and a typical heating value of bio-oil is ~17MJ/kg.

Chemically, bio-oil is a complex mixture of water, guaiacols, catechols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. It also contains other major groups of compounds, including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics (Piskorz et al., 1988). Oligomeric species in bio-oil are derived mainly from lignin but also cellulose. About 30% of the compounds are detectable by gas chromatography, 15% can be analyzed by high-performance liquid chromatography, 25% is high molecular weight pyrolytic lignin measured as water-insoluble, and 25% consists of water (Bridgwater et al., 1999).

Bio-oil can serve as a substitute for fuel oil or diesel in many static

applications, including boilers, furnaces, engines, and turbines for electricity generation (Bridgwater, 2003; Shihadeh & Hochgreb, 2000).

Flame combustion tests showed that bio-oil could replace heavy and light fuel oils in industrial boiler applications for heat production even though the heating value of bio-oil is lower than that for fossil fuels (Bridgwater, 2003). Emulsions were developed from biomass bio-oil with diesel fuel (Chiaramonti et al., 2003). These emulsions were characterized and tested in a diesel engine for electricity production.

A large fraction of the bio-oil is a phenolic fraction, consisting of relatively small amounts of phenols, eugenol, cresols, and many large quantities of alkylated phenols, so-called pyrolytic lignin. This fraction has exhibited excellent performance as an adhesive or adhesive extender for waterproof plywood (Chum et al., 1989).

Bio-oil from biomass could be a raw material for the future green chemical refinery. The bio-oil can be converted into useful chemicals. Nevertheless, because of bio-oil complexity, separation techniques have not been developed on an extensive scale (Czernik & Bridgwater, 2004). Among the various compounds, glycolaldehyde is the most abundant single component of bio-oil. It is also the most active meat-browning agent in "liquid smoke" and, therefore, it raised interest in the food flavoring industry. Levoglucosan (1,6-anhydro- β -D-glucopyranose) and levoglucosenone (6,8-dioxabicyclo[3.2.1]oct-2-en-4-one) are not typical components of bio-oil produced for fuel application but can be generated with high yields by a similar pyrolysis process from demineralized cellulose or biomass (Bennett et al., 2009; Loong et al., 1992).

2.1.3. Fast pyrolysis reactors

At the heart of a fast pyrolysis process is the reactor. Although it probably represents only about 10~15% of the total capital cost of an integrated system, most research and development have focused on developing and testing different reactor configurations on various feedstocks (Bridgwater, 2012; Wang et al., 2005).

The fluidized bed reactor (Figure 3a) has the advantage of a well-understood technology that is simple in construction and operation, reasonable temperature control, and very efficient heat transfer to biomass particles arising from the high solids' density. Small biomass particle sizes of less than 2~3mm are needed to achieve high biomass heating rates, and the rate of particle heating is usually the rate-limiting step. Vapor and solid residence time are controlled by the fluidizing gas flow rate and are higher for char than for vapors. As char acts as an active vapor cracking catalyst at fast pyrolysis reaction temperatures, rapid and effective char separation is necessary (Scott et al., 1997; Zhu, 2006).

There have been several developments that mechanically move biomass through a hot reactor rather than using fluids. Heating can be with recycled hot sand with heat carriers such as steel or ceramic balls, or external heating. The nature of mechanically driven reactors is that short residence times comparable to fluidized bed are difficult to achieve, and hot vapor residence time can range from 5 to 30 s depending on the design and size of the reactor (Ingram et al., 2008; Hornung et al., 2007). Screw reactors (Figure 3b) are particularly suitable for feed materials that are difficult to handle or feed, or are heterogeneous. The liquid product yield tends to be somewhat lower than fluidized beds and is often phase separated due to the longer residence times and contact with byproduct char. Also, the char yields are

higher. KIT has promoted and tested the concept of producing a slurry of the char with the liquid to maximize liquid yield in terms of energy efficiency, but this would require an alternative energy source to provide heat for the process (Ingram et al., 2008).

Rotating cone reactor (Figure 3c) is a relatively recent development and effectively operates as a transported bed reactor, but with transport effected by centrifugal forces in a rotating cone rather than gas. The centrifugation drives hot sand and biomass up a rotating heated cone, and the vapors are collected and processed conventionally, char and sand drop into a fluid bed surrounding the cone whence char is burnt to heat the sand.

Some basic research has been carried out on microwave driven pyrolysis (Figure 3d). Microwave heating is fundamentally different from all other pyrolysis techniques as the biomass particles are heated from within and not by external heat transfer from a high-temperature heat source. Microwave heating requires a material with a high dielectric constant or loss factor, of which water is a good example. So in microwave pyrolysis, water is rapidly driven off, then the particle heats up to start forming char. A further problem to be considered is that penetration of microwaves is limited to typically 1~2 cm, so the design of a microwave reactor presents exciting scale-up challenges.

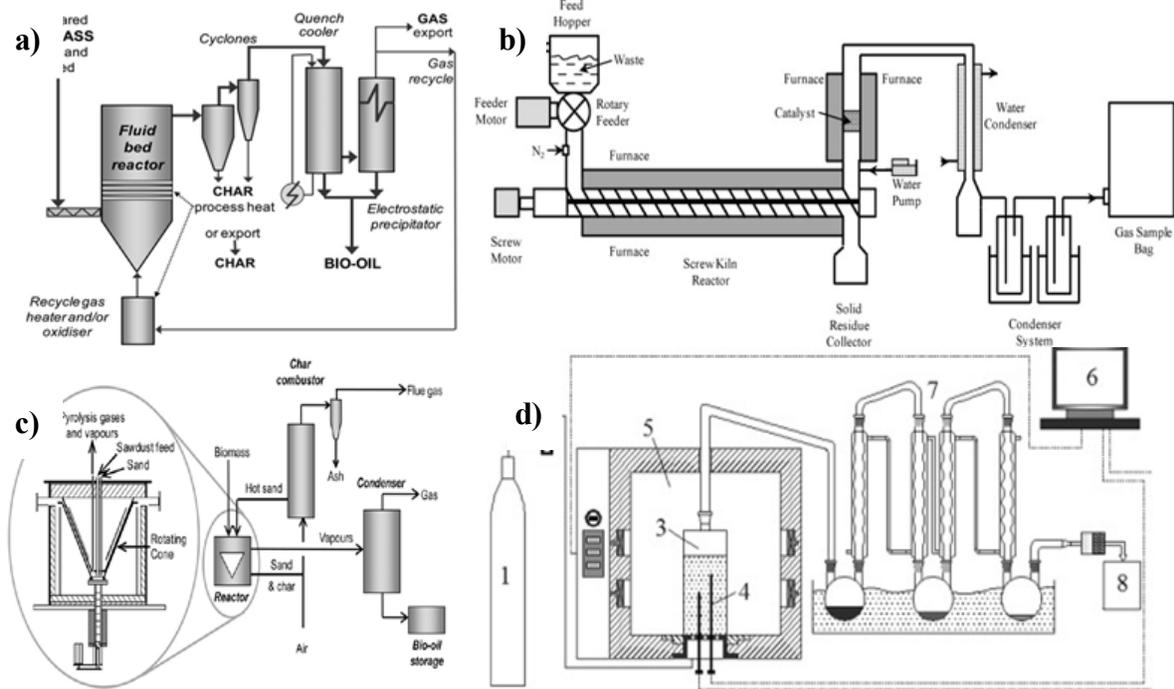


Figure 3. Schematic diagram of pyrolyzers (Bridgwater, 2012).

- a) Fluidized bed pyrolyzer; b) Screw type pyrolyzer; c) Rotating cone pyrolyzer;
d) Microwave pyrolyzer.

2.2. Bio-oil upgrading technology

Bio-oil upgrading technologies can be roughly categorized into two kinds – physical and catalytic upgrading. Of the two, catalytic methods are known to be more effective (Bridgwater, 2012).

The representative physical upgrading method, emulsification, offers a simple way to use bio-oil as a transportation fuel, by combining it with diesel. Although bio-oil is not miscible with hydrocarbons, it can be emulsified with diesel fuel with the aid of surfactants (Czernik & Bridgwater, 2004). The emulsion is more stable and has a lower viscosity than bio-oil.

Catalytic cracking usually accomplishes deoxygenation through simultaneous dehydration, decarboxylation, and decarbonylation reactions occurring in the presence of zeolite catalysts. In the late 1970s, synthetic zeolites (e.g., ZSM-5) were successfully used to convert oxygenated organic compounds into hydrocarbons resulting in commercialization methanol-to-gasoline process. This discovery also stimulated research focused on the production of hydrocarbons from biomass-derived pyrolysis oil and pyrolysis vapors (Qin et al., 2013).

Esterification is a potential route to remove organic acids in bio-oil by reacting to the alcohol in bio-oil or with added alcohol, resulting in improved stability (Miao & Shanks, 2009).

HDO is one of the most effective hydrotreatment processes which uses hydrogen to reduce the high oxygen content in bio-oil in the presence of suitable catalysts, such as sulfided cobalt-molybdenum or nickel-molybdenum (Ohta et al., 2011). It is known to be an effective bio-oil reforming process, which not only removes the oxygen in bio-oil but also improves bio-oil stability by converting acids, aldehydes, alcohols, and unsaturated compounds into more stable forms (Bridgwater, 2012).

2.3. Catalytic co-pyrolysis of biomass and plastic

Plastics are regarded as an excellent additive for co-pyrolysis, as they can act as a hydrogen supplement. Önal et al. found that the co-pyrolysis of almond shells with high-density polyethylene (HDPE) promoted the quality and quantity of liquid yield (Önal et al., 2014). Further, low-density polyethylene (LDPE) has been found to inhibit the production of several aromatic compounds assigned to lignin pyrolysis (Jin et al., 2016). Chen et al. reported that HDPE's presence could promote the conversion of aldehydes and ketones from the waste newspaper into hydrocarbons and the formation of linear long-chain alcohols, and favor the generation of light hydrocarbons (Figure 4) (Chen et al., 2017). It was found that the effects of co-pyrolysis of cellulose with HDPE promoted the release of small-molecule volatile (Yuan et al., 2018)

On the other hand, polyethylene plastic wastes mainly could be converted into low-quality waxes by the thermal degradation, which could result in a breakdown of plant operations, ranging from pipeline blockages to shorter instrument life cycles (Lee, 2012). Thus, the co-pyrolysis of biomass and polyethylene plastic may promote the chain scission and breaking of the polymer.

The effects of catalyst properties on the reaction chemistry and product distribution during the catalytic co-pyrolysis of biomass with plastics, the characteristics of catalysts were studied by many researchers (Table 1, Figure 5). Zeolite Y achieved a more positive synergistic effect for the aromatic formation than ZSM-5 in the catalytic co-pyrolysis of biomass with plastics due to the effectiveness of the large pore size (Kim et al., 2016). This is possible because the diffusion of polymers into the small micropores of ZSM-5 was inhibited by biomass-derived coke. However, ZSM-5 displayed

better catalytic performance for aromatic production than Zeolite Y by increasing the loading of the catalyst or catalytic temperature due to its firm site acidity and proper pore structure for aromatization (Kim et al., 2016). Regarding the mechanism of LOSA-1, $\gamma\text{-Al}_2\text{O}_3$, and spent FCC in the catalytic co-pyrolysis, LOSA-1 is a microporous catalyst having a particular pore structure and acidity, which is favorable for monoaromatic hydrocarbons (MAH) production. In contrast, $\gamma\text{-Al}_2\text{O}_3$ as a mesoporous catalyst has little shape selectivity toward aromatics and alkenes (Zhang et al., 2014).

The mechanism of zeolite modified by other elements during the catalytic co-pyrolysis has also been investigated. The properties of typical catalysts are listed in Table 1 as well. To be more specific, when the parent ZSM-5 catalyst was impregnated with boron, the acidity and pore size of the modified Zeolite B/ZSM-5 decreased on increasing the boron loading. However, the Zeolite B/ZSM-5 preserved sufficient catalytic activities for the generation of valuable mono-aromatic hydrocarbons. In the catalytic co-pyrolysis, the pore narrowing of boron-modified ZSM-5 extensively promoted the yield of petrochemicals and improved p-xylene production over m-xylene and o-xylene. This result suggests that a slight decrease of ZSM-5 pore size by impregnating boron can enhance the selectivity toward valuable products.

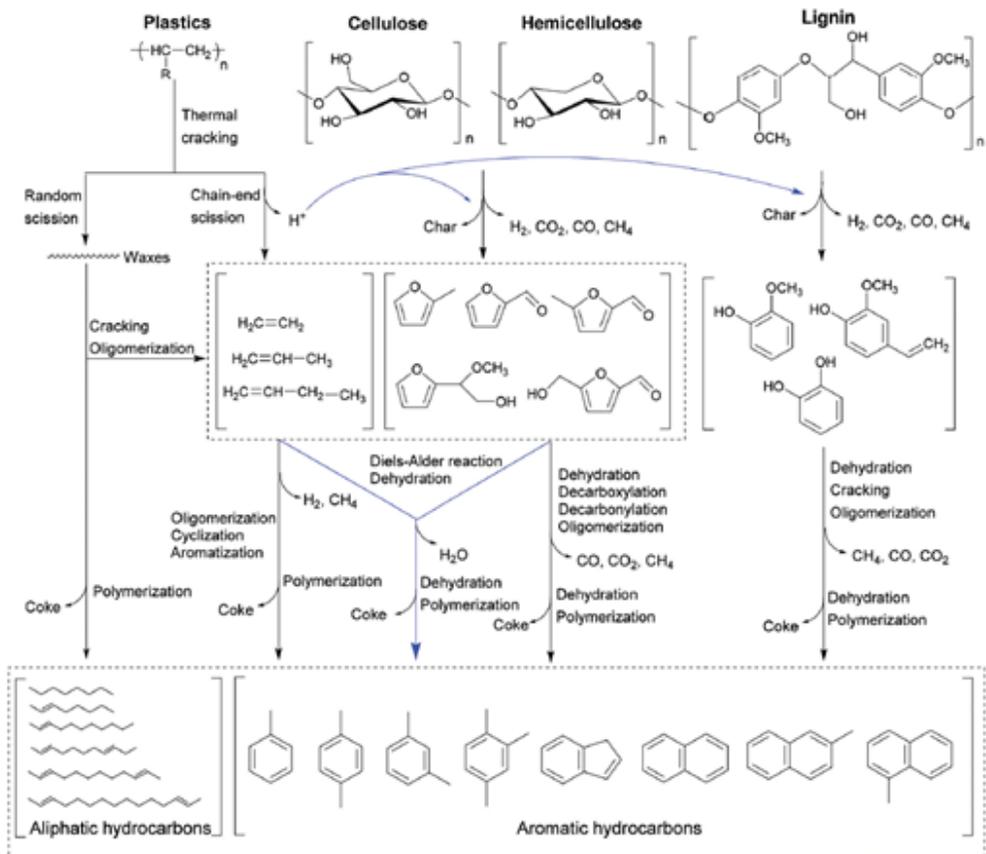


Figure 4. Proposed reaction pathways for the conversion of lignocellulosic biomass and plastics in co-feed catalytic pyrolysis (Zhang et al., 2016).

Table 1. Characterization of various zeolite-based catalysts* (Zhang et al., 2016).

Catalyst	S_{BET} (m ² /g)	V_{pore} (cm ³ /g)	S_{pore} (m ² /g)	d_{pore} (nm)	A_{Bronsted} (μmol/g)	A_{Lewis} (μmol/g)
ZSM-5	372.0	0.114	293.1	-	356.1	56.8
ZeoliteB/ZSM-5	229.6	0.077	194.6	-	242.1	56.7
ZeoliteY	780	-	-	11.24	-	-
P-ZSM-5	327.6	0.118	276.6	-	304.0	75.9
P/Ni-ZSM-5	322.3	0.113	270.7	-	264.9	197.7
LOSA-1	220.2	0.220	-	2.14	-	-
Spent FCC	242.7	0.210	-	4.85	-	-
γ-Al ₂ O ₃	134.7	0.220	-	6.41	-	-
Ga-ZSM-5	372.6	0.138	-	-	251.9	114.2
Ga-Si	355.6	0.132	-	-	132.4	118.8
Ga-Al-Si	330.5	0.124	-	-	157.4	126.9

* S_{BET} : BET surface area; V_{pore} : pore volume; S_{pore} : pore surface area; d_{pore} : average pore size; A_{Bronsted} : Brønsted site acidity; A_{Lewis} : Lewis site acidity.

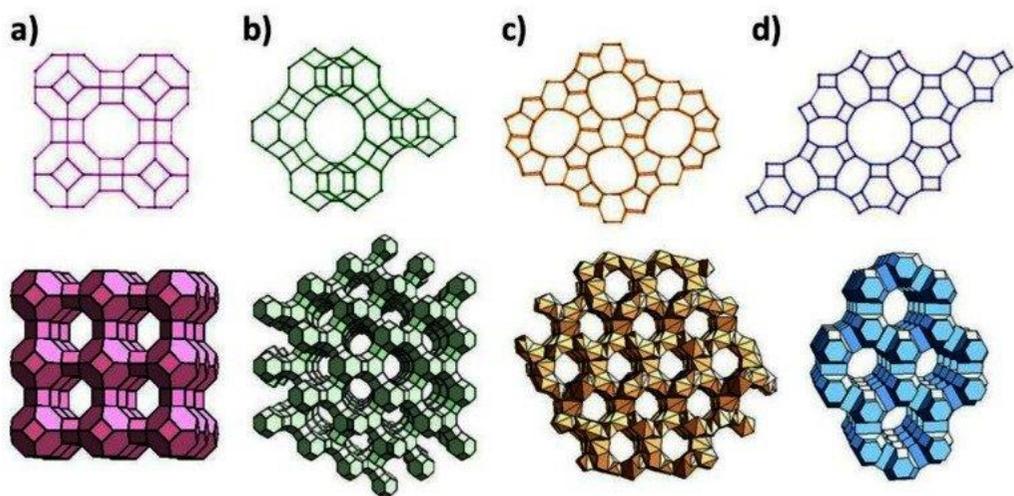


Figure 5. Representative zeolite frameworks with pore openings.

(a) zeolite A (3D, 4.2 Å); (b) zeolite Y (3D, 7.4 Å); (c) Zeolite L (1D, 7.1 Å); (d) ZSM-5 (silicalite) (2D, 5.3 × 5.6 Å, 5.1 × 5.5 Å) D—dimensions of channel system (Zheng et al., 2012).

3. Materials and methods

3.1. Fast Pyrolysis

3.1.1. Materials

The biomass sample for this study is pine wood sawdust. All samples were air-dried to under 10% of moisture content and milled into 1mm, 2mm, 6mm, and 14mm particle size (Figure 6) using 'pulverisette 19' (FRITSCH, Germany).

Holocellulose and lignin, the polymers constituting the biomass, were quantified by 'Wise Method' (1946) and '72 % H₂SO₄ Hydrolysis Method' (TAPPI method (T222 om-88)).

The element composition ratio was measured using the element analyzer (CHNS 932, LECO corp., USA). The contents of C, H, and N were measured, and O content was calculated by subtracting C, H, and N contents from 100%.

Thermogravimetric analysis (TGA) was performed to examine the pyrolytic behavior of raw materials according to the test temperature. 30mg of the sample was analyzed using 'TGA 8000' (PerkinElmer, USA) within the measurement range of 40~800°C under 10°C/min condition. Nitrogen gas was used as the carrier gas, with a flow rate of 25 ml/min.

Chemical composition of pine wood sawdust measured with methods above was displayed in Table 2.

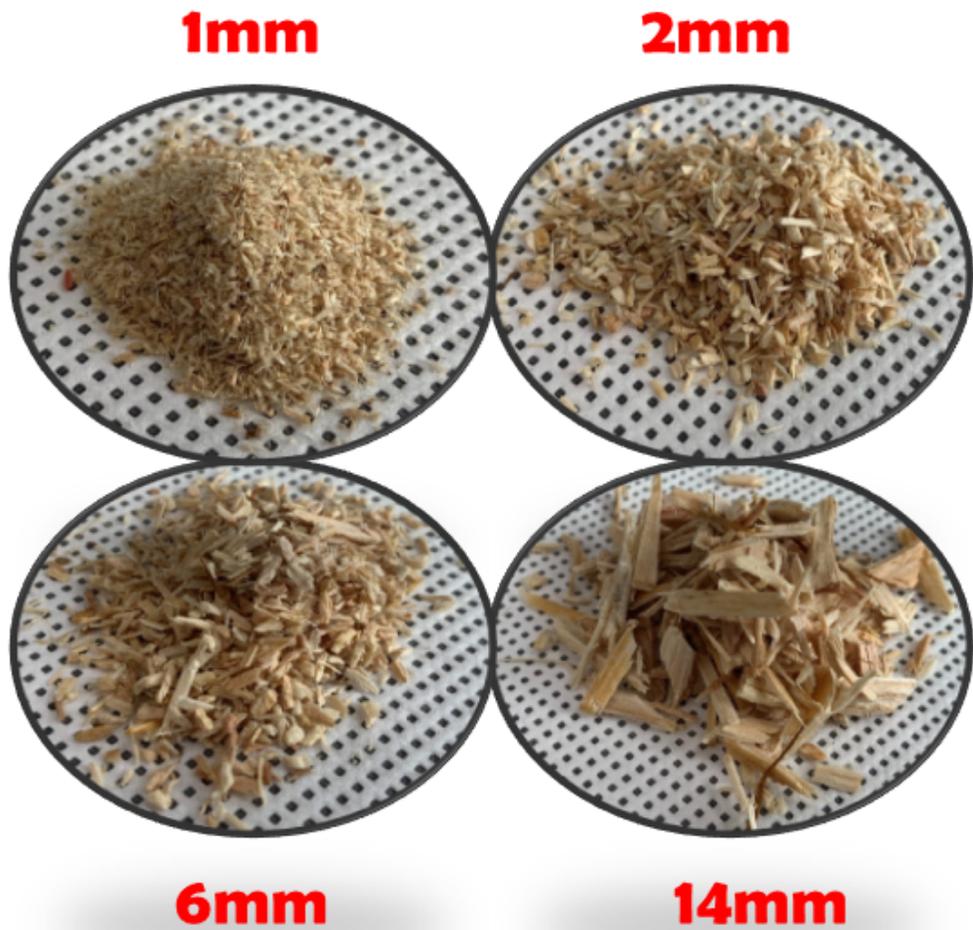


Figure 6. Different particle sizes of pine wood for pyrolysis.

Table 2. Chemical composition of pine wood sawdust.

Properties	Values
Moisture content (%)	7.40
Elemental analysis ^a (%)	
Carbon	49.7 ± 0.5
Hydrogen	5.3 ± 0.1
Nitrogen	0.2 ± 0.0
Oxygen ^b	44.8 ± 0.3
Components analysis ^a (%)	
Holocellulose	60.8 ± 3.5
Lignin	30.6 ± 1.3
Extractives	8.7 ± 2.0
Ash	0.4 ± 0.0
Higher heating value (MJ/kg)	18.9 ± 2.8

^a Dry basis

^b By difference

3.1.2. Fast pyrolysis process

Both 'Screw type reactor' and 'Fluidized bed reactor' were used to produce bio-oil from 4 particle size samples. Fast pyrolysis carried out at 500°C, the optimum temperature suggested by Bridgewater (Bridgewater, 2012).

1kg of the sample was transferred into the 'Screw type reactor' in 15 min, and the sample was pyrolyzed within 8s. The pyrolysis products generated during the pyrolysis process were separated into solid phase (carbon) and gas phase components through cyclones, and the condensable gaseous components were converted into liquid bio-oil through cooling condensers (approx. 0°C) and electrostatic precipitator (ESP), and collected into glass bottles.

For the 'fluidized bed reactor,' 150g of the sample was served into the reactor in 1h. The reactor was flowed by Nitrogen gas for maintaining a non-oxygen atmosphere, and also a fluidized state in the reactor. The pyrolysis products were collected in the same process as previous. After the experiment, the produced bio-oil in condensers and ESP were combined and keep in the refrigerator at 4°C for further analysis. The yield of pyrolytic products (gas, char, bio-oil) produced from the pyrolysis process was calculated with the following equations:

$$\text{Char yield (w/w\%)} = (\text{char weight} / \text{sample weight}) \times 100$$

$$\text{Bio-oil yield (w/w\%)} = (\text{bio-oil weight} / \text{sample weight}) \times 100$$

$$\text{Gas yield (w/w\%)} = 100 - (\text{char yield} + \text{bio-oil yield})$$

3.2. Characterization of pyrolytic products

3.2.1. Physicochemical properties of bio-oil

The water content of bio-oil was determined by the standard method of ASTM E203 using 870 KF Titrino plus (Radiometer, Switzerland) with Hydranal[®]-Composite 5 solution. The viscosity of bio-oil was measured using a capillary-type viscometer (Schott, Germany) at 40°C. The TAN (Total Acid Number) of bio-oil was analyzed by the method developed by Shao & Agblevor (Shao & Agblevor, 2015) using 848 Titrino plus (Radiometer, Switzerland). The higher heating value was measured by Parr 6400 (Parr Instrument Co., USA).

3.2.2. GC/MS analysis of bio-oil

Gas chromatography-mass spectrometry (GC/MS) analysis is performed to identify chemical compounds in bio-oil. The bio-oil samples (0.45 ml) were diluted in 0.5 ml of Acetone and 0.05ml of Fluoranthene was added as the internal standard. Quantitative determination was conducted using gas chromatography (Agilent 7890A, USA) equipped with a flame ionization detector (FID) and a DB-5 capillary column (30m' 0.25mm' 0.25µm). The oven was programmed to hold at 50°C for 5 min, ramp at 3°C/min to 280°C, and hold there for 10min. The injector and FID temperature were 250°C and 300°C, respectively, and the injector split ratio set at 1:20. Chemical compounds in bio-oil were qualified using a mass selective detector (Agilent 5975C, USA) with the NIST (National Institute of Standard and Technology) mass spectra library. For the quantification of compounds, the response factors (Rf) determined in a previous study (Eom et al., 2012b) were selectively used, and Rf values of the other compounds were semi-quantitatively

estimated based on their structural similarity.

3.2.3. Physicochemical properties of char

The element composition ratio was measured using the element analyzer (CHNS 932, LECO corp., USA). The contents of C, H, and N were measured, and O content was calculated by subtracting C, H, and N contents from 100%. The higher heating value was measured by Parr 6400 (Parr Instrument Co., USA).

3.3. Catalytic co-pyrolysis

3.3.1. Materials

Pine powder was used as the biomass material in the experiment. Biomass was air-dried to under 10% of moisture content and milled into < 0.5 mm particle size using 'pulverisette 19' (FRITSCH, Germany). Polyethylene (PE; $(C_2H_4)_n$) purchased from Sigma-Aldrich was used as the plastic material in the experiment. ZSM-5 (CBV 2314, Zeolyst International, Netherlands) purchased from Zeolyst International was used as a catalyst.

3.3.2. Catalytic co-pyrolysis

A coil-type CDS Pyroprobe 5000 (CDS Analytical Inc., USA) was used in this experiment. Before the catalytic co-pyrolysis, biomass, plastic, and catalyst were mixed. Then 3.0mg of each group of samples was introduced to a quartz tube block by quartz cotton on both sides. 2 μ L of internal standard (13mg of Fluoranthene / mL of methanol) was also introduced to the upper quartz cotton for quantification of pyrolysis products. The sample was pyrolyzed at 400°C, 500°C, 600°C with a heating rate of 10°C/ms and maintained for the 20s in an inert atmosphere. During pyrolysis, the pyrolyzer interface and transfer line maintained at 250°C.

3.3.3. GC/MS analysis of catalytic co-pyrolysis products

The released pyrolysis products were transferred online to a GC/MS (Agilent 7890A / Agilent 5975C, USA) equipped with a flame ionization detector (FID) and a DB-5 capillary column (30m' 0.25mm' 0.25 μ m). The oven was programmed to hold at 50°C for 5 min, ramp at 3°C/min to 280°C, and hold there for 10 min. The injector and FID temperature were 250°C, and 300°C, respectively, and the injector split ratio was set at 1:100. Chemical compounds in the pyrolysis products were qualified with the NIST (National Institute of Standard and Technology) mass spectra library. Elemental analysis of the chemical components observed in the GC/MS analysis was calculated summarizing C, H, and O portions by the concentration of all the identifiable compounds. The higher heating value was calculated by following Sheng and Azevedo's formula (Sheng & Azevedo, 2005), according to the elemental form of each set.

$$\text{HHV (MJ}\cdot\text{kg}^{-1}) = -1.3675 + (0.3137 \times C) + (0.7009 \times H) + (0.0318 \times O)$$

4. Results and discussion

4.1. Fast pyrolysis

4.1.1. Pyrolytic behavior of pine wood

Thermogravimetric analysis (TGA) is a common technique used to understand thermal degradation. Thus, the pyrolytic behavior of pine was investigated using TGA. TG and DTG (differential calculations of weight loss) curves for the pine are shown in Figure 7. Weight loss, up to 130°C, was linked to the release of water from the sample, and approximately 8% of the weight loss around this temperature indicated the moisture content of the sample. Thermal degradation of hemicellulose and cellulose takes place at 200~300°C, and 300~400°C, respectively. Generally, the temperature range of the hemicellulose degradation partially overlaps that of cellulose degradation, and its DTG curves appear as a shoulder rather than a well-defined peak (Gronil et al., 2002). The maximum weight loss of pine occurred at 348.5°C, which can be attributed to the thermal degradation of the cellulose. The decomposition of carbohydrates in biomass caused the formation of volatiles, which are the main components of bio-oil. Unlike the degradation of carbohydrates, it is difficult for lignin to decompose (Yang et al., 2007). Pyrolysis of lignin takes place from 200°C to 700°C. From the TG and DTG curves, the main components of the biomass appeared to decompose from 200°C to 600°C thermally.

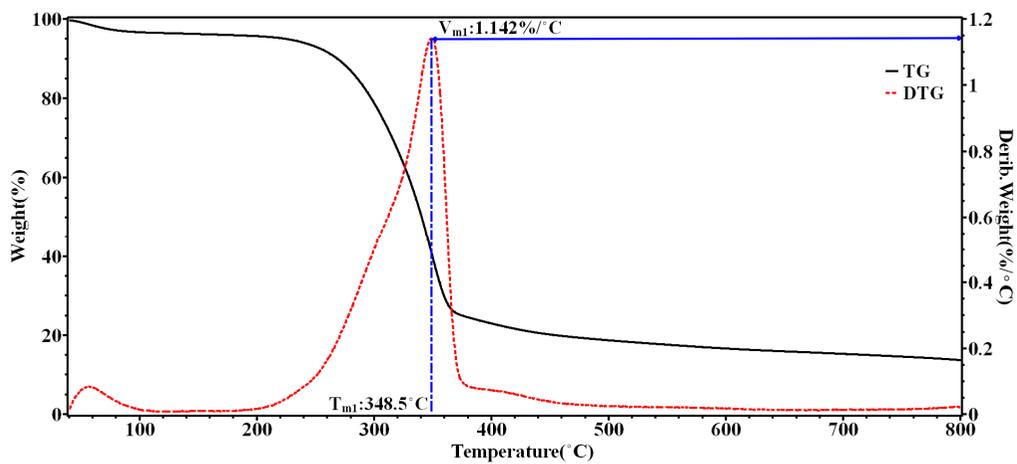


Figure 7. Thermogravimetric analysis of pine wood.

4.1.2. Effect of particle sizes of pine wood on the yield of pyrolytic products

Fast pyrolysis of pine (at 500°C) was performed using particle size of 1mm, 2mm, 6mm, 14mm in 'screw type' and 'fluidized bed' pyrolyzer, respectively, to investigate the effect of feedstock particle size on the pyrolysis of pine. At these conditions, three kinds of products (gas, char, and bio-oil) were obtained as pyrolysis products. The yield of each product was based on the weight of pine as a function of particle size, as presented in Figure 8 and Figure 9.

For 'screw type pyrolyzer,' the yield of bio-oil, which is the target product of the fast pyrolysis of woody biomass, was obtained 46.3%, 45.7%, 44.5%, 43.2%, respectively. At the same time, the yield of bio-char was 20.3%, 21.5%, 20.9%, and 23.3%, while the yield of gas was 33.4%, 32.8%, 34.6%, and 34.5%, respectively.

For 'fluidized bed pyrolyzer,' different with 'screw type' one, the big particle size material (6mm, 14mm) was not able to introduce into the reactor because of the limit of the original design of the pyrolysis system of 'fluidized bed pyrolyzer.' The yield of bio-oil, bio-char, and gas of 1mm particle size were 59.4%, 19.4%, and 21.2%; 54.5%, 23.5%, and 22.0% for 2mm particle size.

The yields of bio-oil produced from the 'screw type' pyrolyzer were slightly decreased when the particle size of feedstock increased from 1mm to 14mm. The maximum yield bio-oil yield, 46.3%, was obtained when the particle size was 1mm, and the minimum yield was 43.2% with the most significant particle size (14mm). However, the difference between the maximum and minimum bio-char yields was not significant, as well as the gas yields. It seems that the particle size of pine does not effectively influence the yields of each pyrolytic product when using the 'screw type' pyrolyzer. It is because of the longer residence time of solid in this pyrolyzer

leads to a sufficient primary and secondary degradation of feedstock (Ates et al., 2004).

In 'fluidized bed' pyrolyzer, as the biomass substrate particle size increased from 1mm to 2mm, the data in Table 3 indicate significant decreases in the yield of bio-oil and corresponding increases in the yield of gas and bio-char. The result is consistent with the result by Shen and coworkers (Shen et al., 2009)

The yields of bio-char in two pyrolyzers were similar. However, when comparing the yields of bio-oil from the same particle size of material in two pyrolyzers, it was significantly decreased from 59.4% to 46.3% (1mm), and 54.5% to 45.7% (2mm), respectively. It seems that the heat transfer property of 'screw type pyrolyzer' is weaker than 'fluidized bed' due to the absence of a heat carrier in the 'screw type' one. On the other hand, the longer residence time of material in 'screw type pyrolyzer' linked to the higher gas yields. This result could be explained by the residence time prolonging the primary degradation products to further exposure of secondary cracking reactions, thus converting the biomass to non-condensable gases but not bio-oil (Xu et al., 2009).

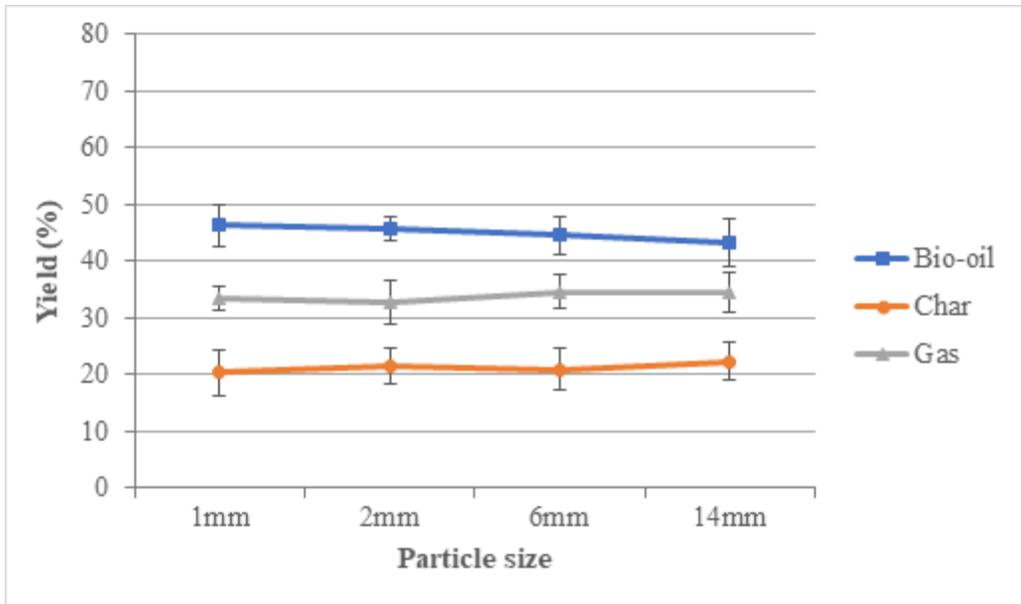


Figure 8. The distribution of products yields from screw type pyrolyzer (pyrolysis temperature: 500°C).

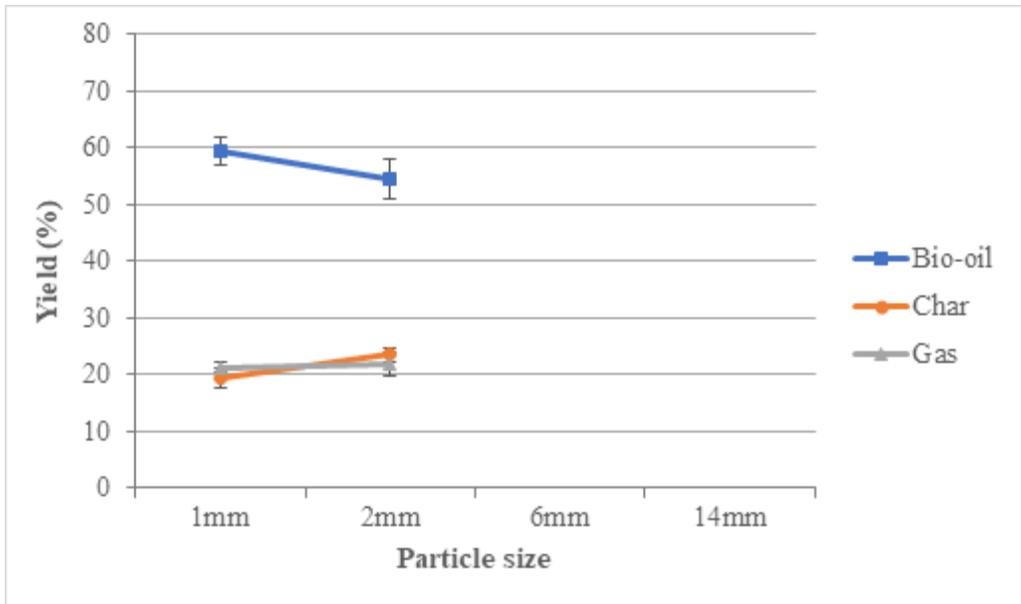


Figure 9. The distribution of products yields from fluidized bed pyrolyzer (pyrolysis temperature: 500°C).

4.1.3. Characterization of bio-oil

4.1.3.1. Physicochemical properties of bio-oil from two pyrolyzers

Water content, viscosity, TAN, and HHV of the bio-oils were determined and summarized in Table 3. It can be seen in Figure 10 that the bio-oil produced from the 'screw type' pyrolyzer is separated into two phases, light phase from condenser 1 and 2, and the heavy phase from ESP. The water contents, related to heating value and combustion properties, of light phase in the bio-oil produced from 'screw type' pyrolyzer, determined by Karl-Fischer titration, were 32.6 wt%, 33.4 wt%, 30.8wt%, and 38.6 wt%, respectively, while the feedstock particle size increases. The heavy phase of bio-oil from the same pyrolyzer recorded 19.5 wt%, 17.5 wt%, 19.5 wt%, and 20.9 wt%. Different from the bio-oil from 'screw type' pyrolyzer, bio-oil obtained from 'fluidized bed' pyrolyzer contained 15.8 wt% and 14.8 wt% of water, depending on the particle size of the material. The higher water content of bio-oil gained from the 'screw type' could be explained as the longer residence time, and weaker heating transfer property caused more dehydration reaction (Lu et al., 2009). Water in bio-oil has both positive and negative effects on the application of bio-oil. The presence of water reduces viscosity and helps to ensure a uniform temperature distribution in fuel chambers (Westerhof et al., 2007). However, the presence of water is one of the main reasons for the lower calorific values, ignition delay, and phase separation of bio-oil, which may lead to some problems for fuel utilization.

Previous studies reported that the viscosity of bio-oil produced from a 'fluidized bed' pyrolyzer ranged from 18.5~24.0 cSt (Oasmaa et al., 2004). In this study, the viscosity of bio-oil decreased from 16.4 to 15.1 sCt in the 'screw type' system, and 21.7~19.9 sCt in 'fluidized bed,' similar to previous studies. Several kinds of acids, such as acetic acid and benzoic acid are

formed from the wood components during fast pyrolysis, and TAN of the bio-oil was between 85.9 mg KOH/g and 96.2 mg KOH/g ('screw type'), 76.1 mg KOH/g and 81.3 mg KOH/g ('fluidized bed'). HHV, or calorific value, of bio-oil, was also determined. With the increase of particle size, HHV of bio-oil decreased from 17.5 MJ/kg to 15.9 MJ/kg ('screw type'), and 18.8 MJ/kg to 18.2 MJ/kg ('fluidized bed'). The relatively low HHV of the bio-oil was attributed to the high water content and oxygen-containing degradation products (Kim et al., 2012).



Biooil from screw reactor



Biooil from fluid bed reactor

Figure 10. Comparison of bio-oils obtained from 'screw type' and 'fluidized bed' pyrolyzer.

Table 3. Physicochemical properties of the bio-oil (wet basis).

Property	Screw*				Fluid	
	1mm	2mm	6mm	14mm	1mm	2mm
Water content (wt%)	32.6±3.1/ 19.5±2.1	33.4±2.7/ 17.5±3.5	30.8±2.1/ 19.5±3.8	38.6±6.3/ 20.9±4.1	15.8±3.7	14.8±2.9
Viscosity (cSt)	16.4±1.1	15.8±1.2	15.6±1.9	15.1±1.5	21.7±2.0	19.9±1.7
TAN (mg KOH/g)	92.3±5.7	85.9±6.8	96.2±6.1	92.8±5.5	81.3±5.0	76.1±6.7
HHV (MJ/kg)	15.5±2.0	16.8±1.3	16.2±1.1	15.9±1.2	16.8±0.9	18.2±1.4

*Light phase/heavy phase

4.1.3.2. Chemical properties of bio-oil from two pyrolyzers

During the fast pyrolysis, lignocellulosic biomass compounds (cellulose, hemicellulose, and lignin) suffer from various thermochemical degradation reactions (cracking, dehydration, decarbonylation, and ring-opening) (Furimsky, 2000; Sitthisa & Resasco, 2011). Therefore, bio-oil is considered a complicated mixture of various chemicals such as water, volatile low molecular weight compounds, polar high molecular weight compounds, and lignin fragments.

Table 4 shows 25 identified components by comparison with the NIST Spectral Mass Library, which was subjected to quantitative analysis by the addition of Fluoranthene as an internal standard. Due to the difficulty of finding some asthenic compounds, the response factor (Rf) of unknown compounds identified was equally assumed at 1.0.

Overall, 13 compounds were derived from carbohydrate (e.g., Acetic acid, Propanoic acid, 3-Furaldehyde, 1,2-Cyclopentanedione), 12 compounds were derived from lignin, including H unit derived components (e.g., Phenol, p-Cresol), and G unit derived components (e.g., p-Guaiacol, p-Creosol, 3-Methoxy-1,2-benzenediol, eugenol). Total carbohydrates derived compounds in bio-oil produced from 'screw type' pyrolyzer were decreased from 30.0 mg/g to 29.1 mg/g with the increase of feedstock particle size, while the ones in the 'fluidized bed' pyrolyzer produced bio-oil were 41.3 mg/g ~ 38.5 mg/g. The total of lignin-derived compounds in bio-oil from the 'screw type' pyrolyzer was 10.7 mg/g, 10.8 mg/g, 6.4 mg/g, and 6.3 mg/g, respectively, depending on the particle size of biomass. For the 'fluidized bed' pyrolyzer, the lignin-derived compounds were 21.3 mg/g (1mm) and 19.1 mg/g (2mm).

The difference of both carbohydrates and lignin-derived components between two pyrolyzers were significant, and especially the total lignin-derived components, which are a family of compounds possibly having

great impacts on bio-oil such as viscosity, in the bio-oil gained from 'screw type' were half to one-third of the ones from 'fluidized bed.' It could be caused by the absence of a heat carrier, which could transfer more heat to the biomass by contacting directly. The degradation of lignin oligomers needs more heating energy than carbohydrates because of the more complex 3-dimensional structure and stronger chemical bonds of lignin (Zhou et al., 2014). On the other hand, the particle size did not influence a lot to the carbohydrate derived components in bio-oils within the same pyrolyzer, but lignin-derived compounds were significantly decreased when the particle size of material increased from 1mm to 14mm. It is believed that the actual heating rates experienced by biomass, which decrease with increasing particle size, were a major factor contributing to the decreases in the yield of lignin-derived compounds (Shen et al., 2009).

Table 4. Quantitative analysis of low molecular weight compounds in the bio-oils.

Source	Compound	Concentration (mg / g dry biomass)						
		Screw type				Fluid bed		
		1mm	2mm	6mm	14mm	1mm	2mm	
Carbohydrates	1. Acetic acid	16.3	17.2	17.1	16.9	10.8	11.4	
	2. Propanoic acid	1.9	2.1	2.5	2.2	5.8	5.1	
	3. Propylaldehyde	0.8	1	1.9	1.7	5	4.4	
	4. 3-Furaldehyde	4.8	3.9	4.3	4.8	10.4	8.9	
	5. 2-Furaldehyde	1.2	1	0.7	0.8	3.4	3	
	6. 2-Butanone	0.8	0.7	0.4	0.3	2.5	2.4	
	7. 1-Acetyloxy-2-propanone	0.7	0.7	0.2	0.5	0.9	0.2	
	8. 4-Cyclopentene-1,3-dione	0.7	0.6	0.2	0.6	0.2	0.2	
	9. 2(5H)-Furanone	0.1	1.0	0.7	0.3	0.1	0.7	
	10. 3,4-Dihydro-2H-pyran-2-one	0.5	0.2	0.1	0.0	0.0	0.3	
	11. 1,2-Cyclopentanedione	0.8	0.6	0.9	0.5	1.0	0.6	
	12. 2-Hydroxy-3-methyl-2-cyclopentene-1-one	0.6	0.7	0.2	0.3	0.8	0.6	
	13. 3,5-Dihydroxy-2-methyl-4H-pyran-4-one	0.8	0.1	0.2	0.2	0.5	0.7	
Sum		30.0	29.8	29.5	29.1	41.3	38.5	
Lignin	H unit	14. Phenol	0.3	0.4	0.1	0.1	2.5	2.1
		15. 4-Methyl-phenol (p-Cresol)	0.6	0.7	0.2	0.3	4.6	3.9
	G unit	16. 4-Methoxyphenol (p-Guaiacol)	2.3	2.0	1.8	1.6	3.7	3.4
		17. 3,5-Dihydroxybenzaldehyde	0.7	0.8	0.3	0.4	2	2.2
		18. 2-Methoxy-4-methylphenol (p-Creosol)	0.9	1	0.2	0.2	1.4	1.1
		19. 3-Methoxy-1,2-benzenediol	2.5	2.1	1.5	1.4	4.2	3.8
		20. 2-Methoxy-4-(2-propenyl)-phenol (Eugenol)	0.7	0.7	0.2	0.5	0.9	0.2
		21. 4-Hydroxy-3-methoxybenzaldehyde (Vanillin)	0.7	0.6	0.2	0.6	0.2	0.2
		22. 4-Hydroxy-3-methoxybenzoic acid (Vanillic acid)	0.1	1.0	0.7	0.3	0.1	0.7
		23. 2-Methoxy-4-(1-propenyl)-phenol (Isoeugenol)	0.5	0.2	0.1	0.0	0.0	0.3
		24. 2-Methoxy-4-propyl phenol (4-Propyl-guaiacol)	0.8	0.6	0.9	0.5	1.0	0.6
		25. 4-Hydroxy-2-methoxycinnam aldehyde (Coniferaldehyde)	0.6	0.7	0.2	0.3	0.8	0.6
		Sum		10.7	10.8	6.4	6.2	21.3
Total		40.7	40.6	35.9	35.3	62.6	57.6	

4.1.4. Characterization of bio-char

The elemental composition and calorific value of the pyrolysis bio-char were analyzed and presented in Table 5. Carbon content in the bio-char produced from the 'screw type' pyrolyzer was determined as 84.3 wt%, 83.5 wt%, 82.8 wt%, and 82.0 wt% with the increase of particle size. Bio-char from 1mm and 2mm particle size of pine contained 82.7 wt% and 80.1 wt% of carbon when it was pyrolyzed in a 'fluidized bed' reactor. The biochar was composed of more than 80% of carbon in all experimental runs, having a calorific value of 25.0 MJ/kg ~ 26.7 MJ/kg, which is slightly lower than the heating value of coal (approximately 30 MJ/kg). Like the routine carbonization process, the formation of biochar with high carbon content and the calorific value was favored at longer residence time and smaller particle size of feedstock (Shen et al., 2009).

Figure 11 shows the bio-char obtained from the 'screw type' pyrolyzer and 'fluidized bed' pyrolyzer with a different particle size of raw materials. The particle size of bio-char was decreased in all the experimental runs, and the gap between the biggest and smallest particle size (14mm and 1mm) of bio-char were narrowed compared with the raw material particle size (Figure 13) during the pyrolysis. The particle size decrease observed in the pyrolysis char is believed to be caused by rapid devolatilization, creating very porous (macroporous) and fragmented char (Scala et al., 2006).

The results revealed that the pyrolysis of pine in 'screw type' pyrolyzer produced more carbon-rich bio-char because of the longer solid residence time compare with the 'fluidized bed' pyrolyzer. Char formations were favored at longer residence time, which could be explained as secondary reactions such as repolymerization and recombination were possibly occurred at a longer residence time (Kim et al., 2011). On the other hand, the engineering

structure of the 'screw type' pyrolyzer also could lead to a fragmentation of feedstock during the screw turning and mixing in the reactor. Furthermore, it helped the sufficient pyrolyze of the bigger particle size of feedstock.

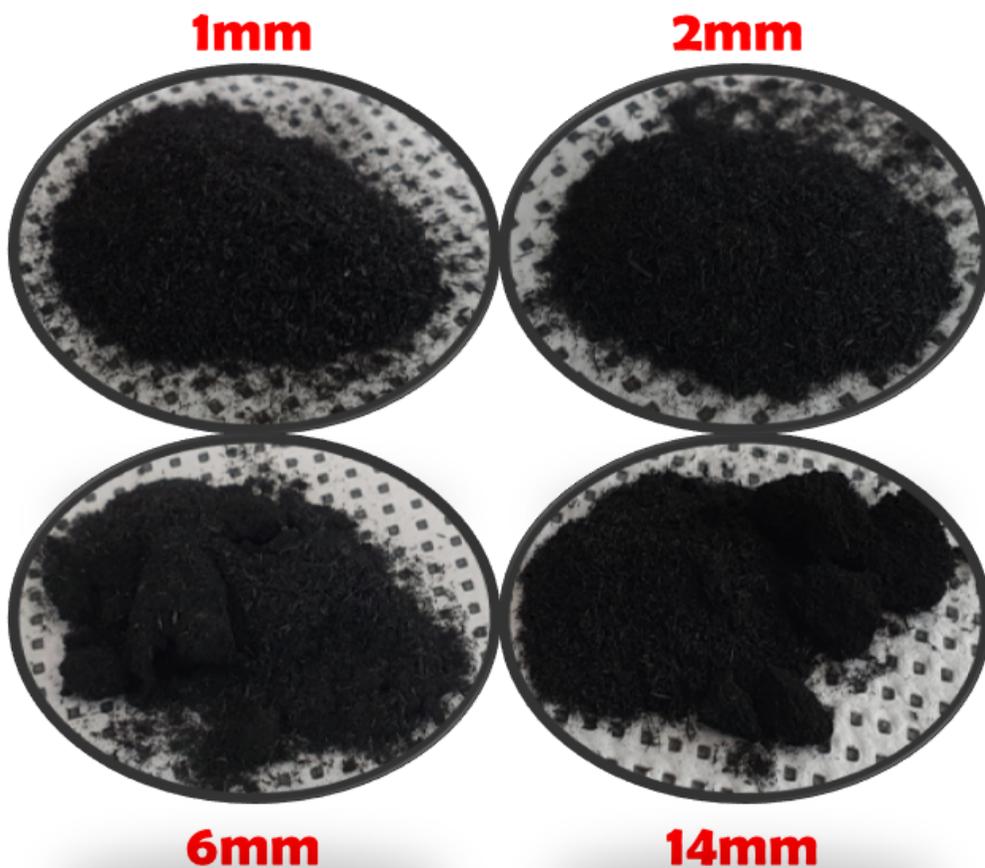


Figure 11. Comparison of bio-char obtained from 'screw type' pyrolyzer of each particle size.

Table 5. Elemental analysis and calorific value of bio-char obtained from fast pyrolysis of pine using two different pyrolyzers.

Properties	Values					
	Screw type				Fluid bed	
	1mm	2mm	6mm	14mm	1mm	2mm
Elemental analysis						
Carbon (wt%)	84.3	83.5	82.8	82.0	82.7	80.1
Hydrogen (wt%)	1.6	1.3	1.0	0.8	1.1	1.0
Nitrogen (wt%)		trace			trace	
Oxygen* (wt%)	14.1	15.2	16.2	17.2	16.2	18.9
HHV (MJ/kg)	26.7	26.2	25.8	25.5	25.9	25.0

*By difference

4.2. Catalytic co-pyrolysis of biomass and plastics

4.2.1. Chemical properties of pyrolytic products

Pine, PE, pine & PE with and without ZSM-5 as a catalyst, and various biomass to plastic ratio (1:1, 3:1, 1:3) were analytically pyrolyzed to investigate the effect of co-pyrolysis of biomass and plastic, catalyst, and blending ratio on the chemical properties of pyrolytic products. Kim et al. reported typical pyrolytic products of biomass model compounds (e.g., levoglucosan, 5-hydroxymethyl-furfural, furans, acetic acid, guaiacol, eugenol) and PE depolymerized compounds were reported by Predel & Kaminsky as alkanes and alkenes (together defined as aliphatics) with various chain lengths (Kim et al., 2012; Predel & Kaminsky, 2000).

The pyrolytic products produced from co-pyrolysis were separated by gas chromatograph and over 90 peaks found in the chromatogram. Among those peaks, around 65 were identifiable by comparison with the NIST Spectral Mass Library, which was subjected to quantitative analysis by the addition of Fluoranthene as an internal standard.

All the compounds were ruled in 6 groups according to the chemical structure of the organics – Aromatic Hydrocarbon (MAH: Monomeric Aromatic Hydrocarbon; PAH: Polycyclic Aromatic Hydrocarbon), phenols, furans, alkenes, and alkanes. Major compounds of each group are shown in Figure 12. MAH, PAH, and liquid phase chain hydrocarbons (at 0°C), which is called petrochemicals, are the target compounds with high HHV and great properties as fuel.

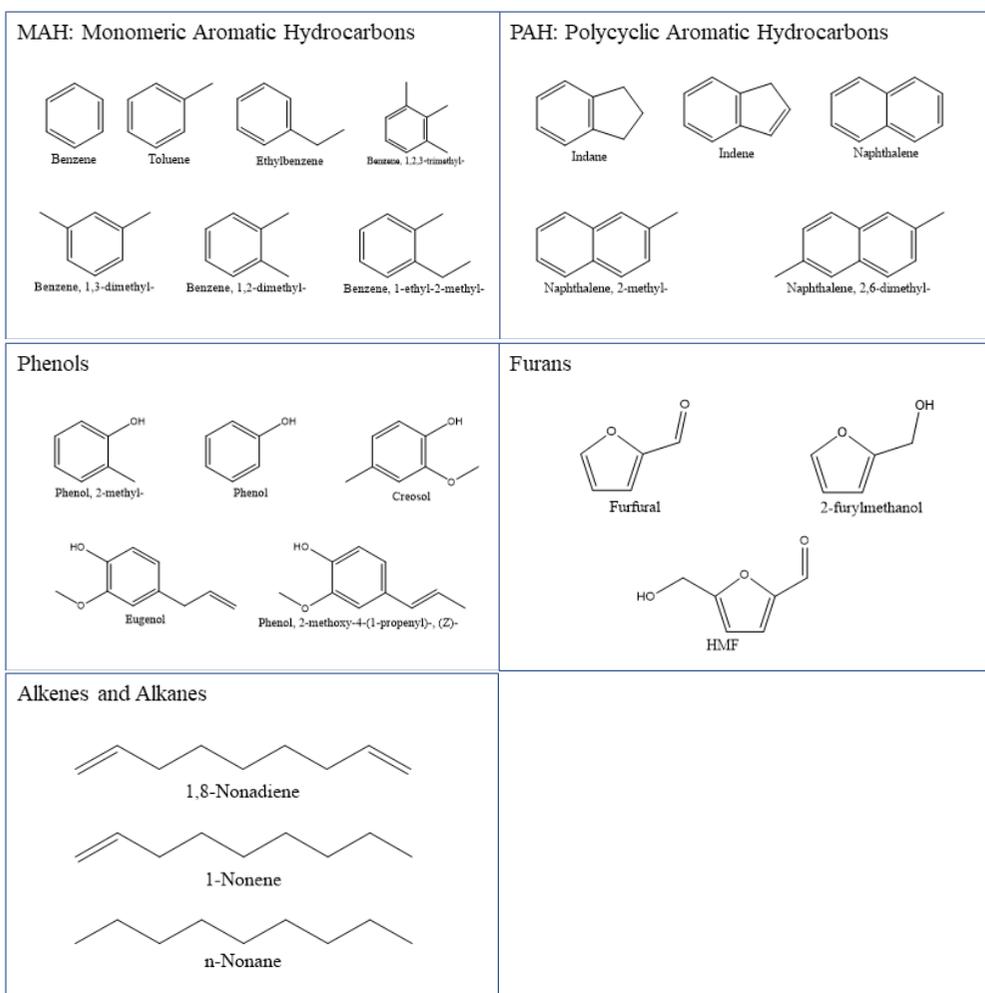


Figure 12. Typical compounds in each group of pyrolytic products.

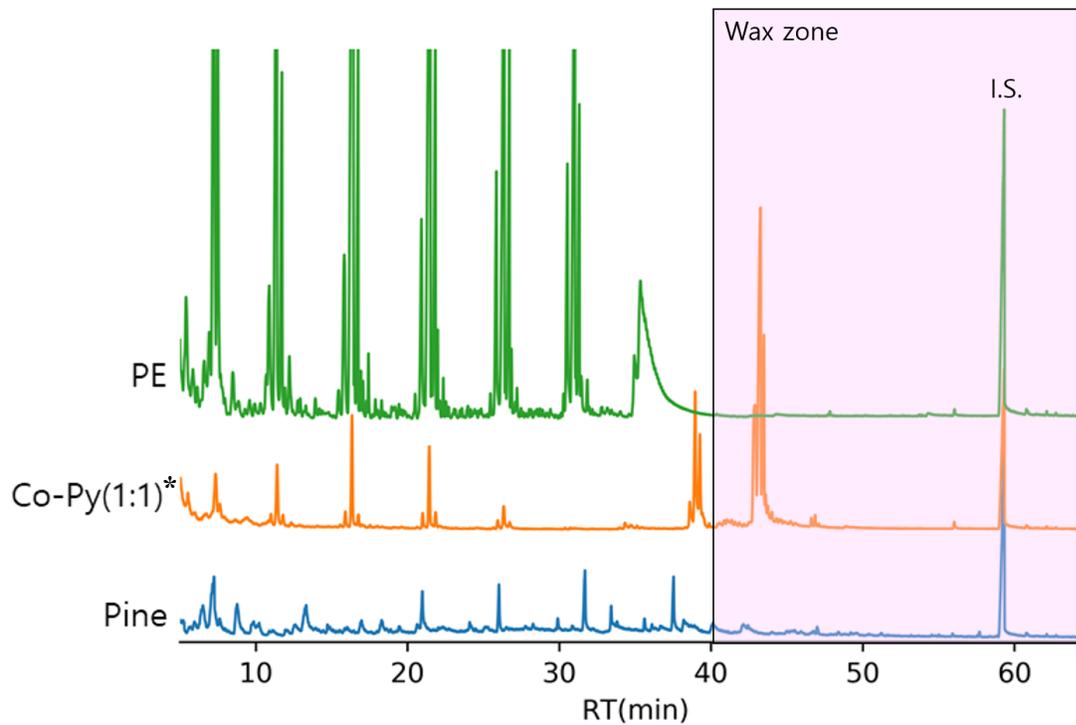
4.2.1.1. Influence of co-pyrolysis on the chemical properties of pyrolytic products

Chromatogram of pyrolytic products from the analytic pyrolysis of pine, PE, and co-pyrolysis (1:1) of pine and PE without a catalyst is shown in Figure 15. The concentration of each compound are listed in Table 6 and then classified into six groups. The percentage contribution of each group of chemicals is displayed in Table 7.

The biomass and plastic produced significantly different products when they were fast pyrolyzed in the absence of the catalyst. In general, the biomass samples produced predominantly oxygenated products, whereas the plastics produce hydrocarbons. The major products identified in this study for biomass and plastic samples were essentially the same as those reported in the literature (Bhattacharya et al., 2009; Miskolczi et al., 2006). Pyrolysis of 'pine only' derived a large amount (56.3%) of phenols (such as Guaiacol, Creosol, Vinyl guaiacol, trans-Isoeugenol), 34.1% of Furfural, and the only MAH was Toluene (9.6%). As seen in Figure 13, the pyrolytic products of PE without catalyst showed a repeating pattern of 3 peaks in a group. They are the typical products of PE: a triplet of diolefin, olefin, and alkane with the same carbon number which are formed from random scission of the original polymer chains of PE during thermal decomposition (Cit et al., 2010), such as 1,8-Nonadiene (C9 diolefin, C₉H₁₆), 1-Nonene (C9 olefin, C₉H₁₈), and n-Nonane (C9 alkane, C₉H₂₀) in a group. The PE was depolymerized into such kind of triplets from C9 to C13, and the highest yield compound was C13 olefin (17.5%).

Similar to what has been observed in non-catalytic fast pyrolysis of cellulose and LDPE mixture (Li et al., 2013), minimal interactions between biomass and plastic were observed when they were co-pyrolyzed in the absence of ZSM-5 catalyst. Non-catalytic fast pyrolysis of the mixture of pine

and PE just produced a "combined" chromatogram that resembles the superposition of the two individual components. All identified major products in the non-catalytic fast pyrolysis of two individual components. Similarly, Bhattacharya et al. (2009) found that negligible cross-over products of biomass and plastics were formed in the co-pyrolysis of pinewood with PE, PP, and PE. The pyrolytic products of pine and PE without ZSM-5 contained significant fractions of waxes, which may cause damage to the condenser in lab-scale or plant-scale fast pyrolysis systems.



(*Co-Py: Co-pyrolysis, pine+PE)

Figure 13. Gas chromatographic separation of low molecular weight compounds from co-pyrolysis without catalyst.

Table 6. Chemical compounds in pyrolytic products from various feedstock (600°C).

No.	Compound	Concentration		
		(% , based on total of each)		
		Pine	PE	Pine&PE
1	Toluene	9.6	0	0
2	Furfural	34.1	0	5.3
3	C9 Diolefin	0	1.1	0.9
4	C9 Olefin	0	9.3	4.6
5	C9 Alkane	0	3.7	0.8
6	C10 Diolefin	0	1.7	0.9
7	C10 Olefin	0	11.3	6.6
8	C10 Alkane	0	4.0	0.6
9	Guaiacol	10.9	0	0
10	C11 Diolefin	0	2.2	0.9
11	C11 Olefin	0	14.3	4.9
12	C11 Alkane	0	4.5	0.9
13	Creosol	11.0	0	0
14	C12 Diolefin	0	2.1	0.6
15	C12 Olefin	0	15.9	1.6
16	C12 Alkane	0	5.0	0
17	C13 Diolefin	0	2.4	0
18	C13 Olefin	0	17.5	0
19	C13 Alkane	0	5.1	0
20	Vinylguaiacol	20.2	0	0
21	Eugenol	4.5	0	0
22	trans-Isoeugenol	9.8	0	0
23	C15 Diolefin	0	0	1.2
24	C15 Olefin	0	0	8.6
25	C15 Alkane	0	0	4.5
26	C16 Diolefin	0	0	14.5
27	C16 Olefin	0	0	31.0
28	C16 Alkane	0	0	11.7
Total		100.0	100.0	100.0

Table 7. Classification of pyrolytic products of different feedstock from co-pyrolysis without catalyst (600°C).

Feedstock	Aromatic Hydrocarbons ^a		Phenols	Furans	Alkenes	Alkanes	Petrochemicals ^b	Waxes ^c
	MAH	PAH						
Pine	9.6	0	56.3	34.1	0	0	9.6	0
Pine & PE	0	0	0	5.3	76.2	18.5	38.8	55.9
PE	0	0	0	0	77.7	22.3	94.9	5.1

^aMAH: Monomeric Aromatic Hydrocarbons; PAH: Polycyclic Aromatic Hydrocarbons.

^bPetrochemicals = Aromatics + Alkenes (C_≤15) + Alkanes (C_≤13).

^cWaxes = Alkenes (C_>15) + Alkanes (C_>13).

4.2.1.2. Influence of catalyst on the chemical properties of pyrolytic products

Chromatogram of pyrolytic products from analytic pyrolysis of pine, PE, and co-pyrolysis (1:1) of pine and PE with ZSM-5 catalyst is shown as Figure 14. The concentration of each compound are listed in Table 8 and then classified into six groups. The percentage contribution of each group of chemicals is displayed in Table 9.

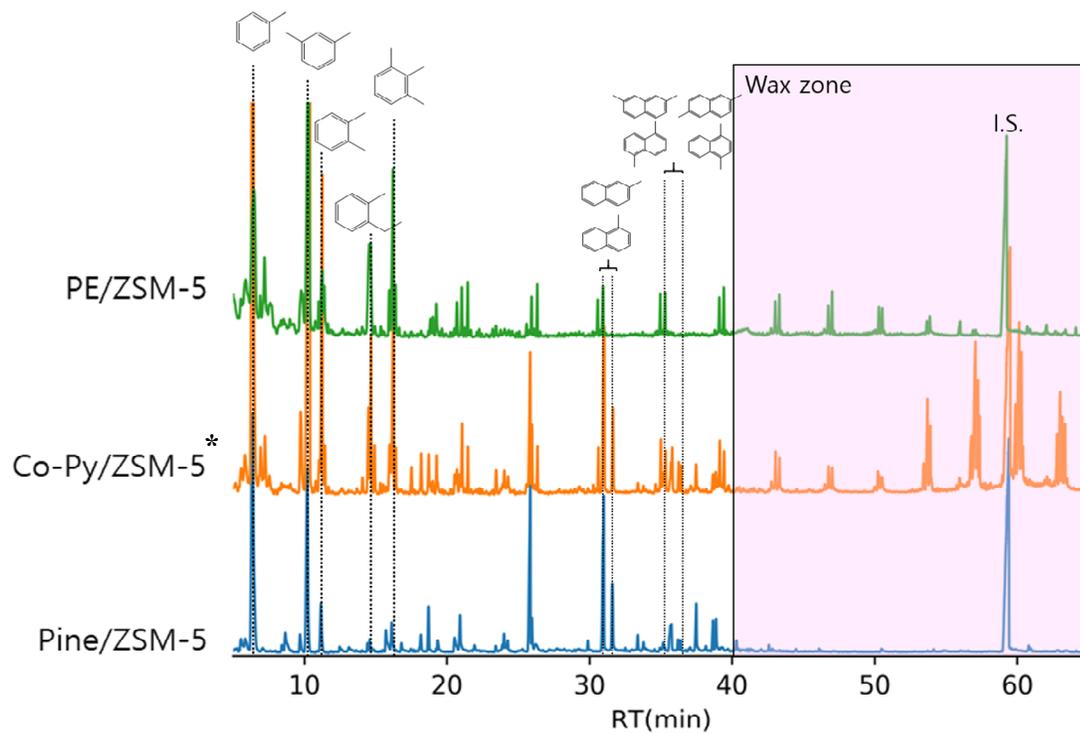
Although the biomass and plastic produced significantly different products in non-catalytic fast pyrolysis, they produced similar final products when catalytically pyrolyzed with ZSM-5 zeolites. Furthermore, co-feeding of the pine with PE in catalytic fast pyrolysis also produced similar products.

When pine was pyrolyzed with catalysts, some phenols and furans were converted into aromatic hydrocarbons, such as Toluene, Xylene, and Naphthalene, because of the ring modification reaction were activated by ZSM-5. When PE was co-pyrolyzed with pine, it was observed that a huge quantity of chain hydrocarbons was produced because of the chain structure of PE. However, if ZSM-5 was introduced together, chain hydrocarbons could be converted into aromatic hydrocarbons. Long-chain hydrocarbon (alkene, $C > 15$; Alkane, $C > 13$) could be condensed as solid when the temperature is lower than 0°C , which is the normal condensing temperature in the fast pyrolysis process. The solid is called wax, and it is harmful to the fast pyrolysis industry because it could be stuck on the condenser and reduce the efficiency of collecting bio-oil.

The concentration of petrochemicals, which exclude wax hydrocarbons, in the pyrolytic products from the catalytic co-pyrolysis was 76.58%, lower than the catalytic pyrolysis of pine, could be the presence of long-chain hydrocarbons. However, the content of phenols and furans were significantly decreased compare as well as the oxygen ratio.

Many researchers have investigated the reaction pathways in catalytic

conversion of biomass (e.g., cellulose, lignin, hemicellulose, and their model compounds) and plastics (e.g., PE, PP, and PS) over ZSM-5 zeolites (Calson et al., 2008; Gayubo et al., 2004; Serrano et al., 2005). The results suggest that although the starting feedstocks may have very different molecular structures and chemical compositions, they may undergo several common reaction steps to form similar products (e.g., aromatics and olefins) during ZSM-5 catalyzed conversion processes: (1) cracking (and deoxygenation) of polymer structures to small alkenes (C2~C5); (2) oligomerization of the small alkenes to C6~C10 alkenes, which then transform to C6~C10 diolefins via hydride transfer reactions; and (3) cyclization and aromatization of the diolefins to form aromatics. As a result, catalytic co-pyrolysis of biomass and plastic with ZSM-5 zeolites produced similar final products.



(*Co-Py: Co-pyrolysis, pine+PE)

Figure 14. Gas chromatographic separation of low molecular weight compounds from co-pyrolysis with catalyst.

Table 8. Chemical compounds in pyrolytic products from various feedstock in the presence of ZSM-5 (600°C).

No.	Compound	Concentration		
		(% , based on total of each)		
		Pine&PE/ ZSM-5	Pine/ ZSM-5	PE/ ZSM-5
1	Benzene	0	17.7	0
2	Toluene	20.2	22.5	16.9
3	Furfural	0	4.1	0
4	Ethylbenzene	2.2	1.1	5.4
5	p-Xylene	22.6	0	14.3
6	m-Xylene	5.5	13.2	13.0
7	o-Xylene	0	3.3	4.9
8	C9 Alkane	0.6	0	2.2
9	Benzene, 1-ethyl-2-methyl-	1.4	0.4	6.2
10	Benzene, 1-ethyl-4-methyl-	2.2	0	4.5
11	Benzene, 1,2,4-trimethyl-	0.7	0	0
12	Phenol	0	0.9	0
13	C10 Olefin	1.1	0	0
14	Benzene, 1,2,3-trimethyl-	4.5	1.0	8.5
15	C10 Alkane	0.5	0	1.8
16	Benzene, 1,3,5-trimethyl-	0.4	0	0
17	Indane	0.6	0.9	0
18	Indene	0.7	1.9	0
19	Benzene, diethyl-	0.7	0	1.6
20	Phenol, 2-methyl-	0	0.4	0
21	Phenol, 3-methyl-	0	0.7	0
22	p-Isopropyltoluene	0	0	1.5
23	Phenol, 2-methoxy-	0	2.6	0
24	Cyclopropane, 1-methyl-2-pentyl-	0.9	0	0
25	C11 Alkane	0.5	0	1.7
26	Naphthalene	2.1	8.1	0
27	Creosol	1.1	1.8	0
28	C12 Olefin	0	0	1.4
29	C12 Alkane	0.5	0	1.5
30	Guaiacol, 4-ethyl-	0	0.4	0
31	C13 Olefin	0.5	0	1.2
32	C13 Alkane	0	0	1.8

(Continue)

No.	Compound	Concentration		
		(% , based on total of each)		
		Pine&PE/ ZSM-5	Pine/ ZSM-5	PE/ ZSM-5
33	Naphthalene, 2-methyl-	3.7	8.4	0
34	Naphthalene, 1-methyl-	1.3	3.4	0
35	Eugenol	0	1.3	0
36	C14 Olefin	0.7	0	1.3
37	C14 Alkane	0.5	0	1.2
38	Naphthalene, 2,7-dimethyl-	0	1.4	0
39	Naphthalene, 1,5-dimethyl-	1.0	0.9	0
40	Naphthalene, 1,4-dimethyl-	0	0.6	0
41	Naphthalene, 1,7-dimethyl-	0.4	0	0
42	Naphthalene, 2,6-dimethyl-	0.3	0.4	0
43	trans-Isoeugenol	0.4	2.2	0
44	C15 Olefin	0.8	0	1.1
45	C15 Alkane	0.5	0	1.4
46	(E)-Calamene	0	0.6	0
47	C16 Olefin	0.5	0	1.0
48	C16 Alkane	0.5	0	1.3
49	C17 Olefin	0.3	0	1.0
50	C17 Alkane	0.3	0	1.4
51	C18 Olefin	0.2	0	0.9
52	C18 Alkane	0.1	0	0.9
53	C19 Diolefin	0.4	0	0
54	C19 Olefin	1.5	0	0
55	C19 Alkane	1.0	0	0
56	C20 Diolefin	1.1	0	0
57	C20 Olefin	3.2	0	0
58	C20 Alkane	2.0	0	0
59	C21 Diolefin	1.4	0	0
60	C21 Olefin	3.3	0	0
61	C21 Alkane	2.2	0	0
62	C22 Diolefin	0.7	0	0
63	C22 Olefin	1.4	0	0
64	C22 Alkane	0.8	0	0
Total		100.0	100.0	100.0

Table 9. Classification of pyrolytic products of different feedstocks from co-pyrolysis with catalyst (600°C).

Feedstock	Aromatic Hydrocarbons ^a		Phenols	Furans	Alkenes	Alkanes	Petrochemicals ^b	Waxes ^c
	MAH	PAH						
Pine/ZSM-5	59.0	26.7	10.2	4.1	0	0	85.7	0
Pine&PE/ZSM-5	61.2	10.2	1.5	0	17.0	10.1	76.6	21.9
PE/ZSM-5	76.9	0	0	0	8.0	15.1	91.0	9.0

^aMAH: Monomeric Aromatic Hydrocarbons; PAH: Polycyclic Aromatic Hydrocarbons.

^bPetrochemicals = Aromatics + Alkenes (C_≤15) + Alkanes (C_≤13).

^cWaxes = Alkenes (C_>15) + Alkanes (C_>13).

4.2.1.3. Influence of biomass to plastic ratio on the chemical properties of pyrolytic products

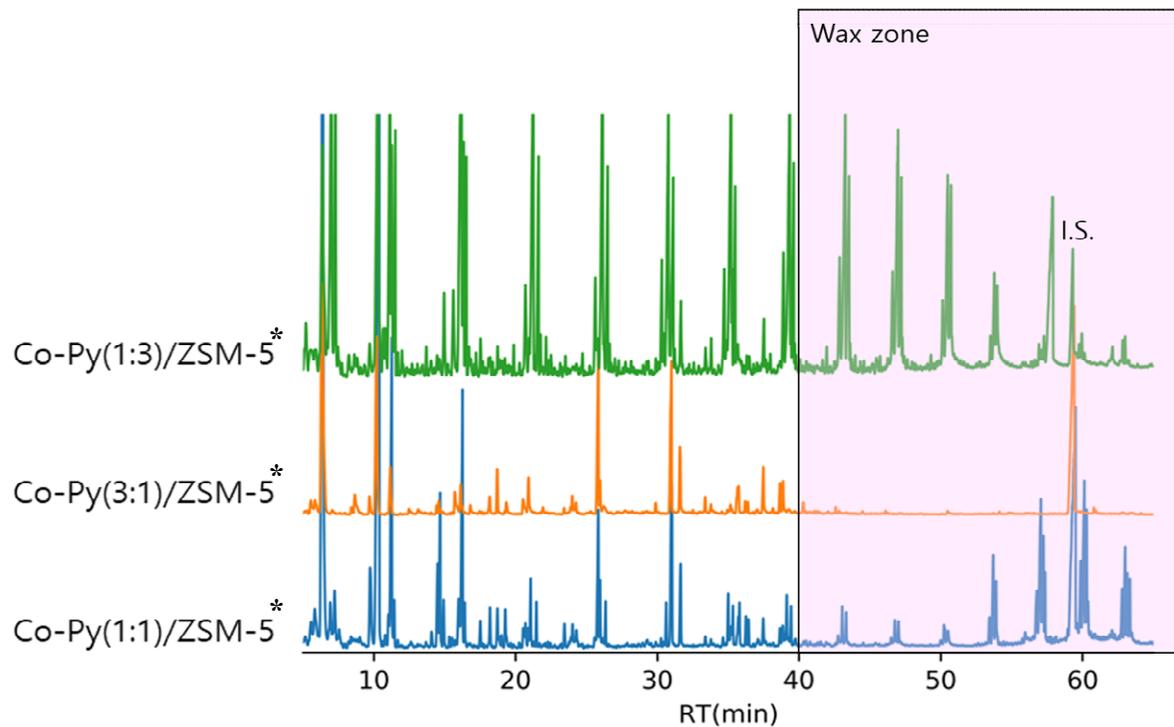
Chromatogram of pyrolytic products from analytic pyrolysis of three co-feeding ratios (3:1, 1:1, 1:3) of pine and PE with ZSM-5 catalyst is shown as Figure 15. The concentration of each compound are listed in Table 10 and then classified into six groups. The percentage contribution of each group of chemicals is displayed in Table 11.

The co-feed ratio of pine and PE influenced the distribution of aromatics and alkenes considerably. As the pine-to-PE ratio was decreased (more PE in the co-feed mixture), the selectivity for most MAH (toluene, xylenes, and others) increased considerably, while the selectivity for PAH declined steadily (Table 10). Previous studies have indicated that in catalytic fast pyrolysis of biomass, polyaromatics are formed mainly from the reactions of MAH with small oxygenates (Cheng & Huber, 2012). Co-feeding of pine with PE in catalytic co-pyrolysis can thus protect MAH from being converted to PAH because PE derived alkenes would compete with MAH for reacting with pine derived oxygenates. This result indicates that co-feeding of pine with PE in catalytic co-pyrolysis can improve the distribution of aromatic products because MAH (especially BTX: Benzene, Toluene, Xylenes) are more valuable products than PAH.

The concentration of petrochemicals in 3:1 (pine: PE) ratio was increased compared with 1:1 due to the increase of PE and decrease of phenols, but most importantly, because of the decrease of waxes. On the other hand, when the PE was served more, the alkenes were decreased, and MAH was increased, it seems that in the 1:1 ratio pine adsorbed energy and led to a lack of energy for long-chain plastic cracking.

The results presented above indicate that co-feeding of pine with PE can greatly enhance the production of valuable petrochemicals (especially

aromatics) and decrease the wax formation in catalytic fast pyrolysis. Besides, aromatic distribution was also improved by co-pyrolysis, which increased the selectivity for more valuable MAH. The petrochemical yield (aromatics plus aliphatics) was similar at the pine-to-PE ratio of 3:1 and 1:3 (81.0% and 83.7%); however, the wax yield of the two ratios were significantly different (8.4% for 3:1 and 15.6% for 1:3). Thus from the perspective of petrochemical production and wax reduction, only small quantities of PE are needed to co-pyrolysis with pine. Adding more PE will not increase petrochemical yield considerably and create waxes.



(*Co-Py: Co-pyrolysis, pine+PE)

Figure 15. Gas chromatographic separation of low molecular weight compounds from co-pyrolysis of different ratios of biomass and plastic with catalyst.

Table 10. Chemical compounds in pyrolytic products from co-pyrolysis of different ratios of pine wood sawdust and PE in the presence of ZSM-5 (600°C).

No.	Compound	Concentration		
		(% , based on total of each)		
		1:1	3:1	1:3
1	Benzene	0	17.7	0
2	Toluene	20.2	22.5	16.9
3	Furfural	0	4.1	0
4	Ethylbenzene	2.2	1.1	5.4
5	p-Xylene	22.6	0	14.3
6	m-Xylene	5.5	13.2	13.0
7	o-Xylene	0	3.3	4.9
8	C9 Alkane	0.6	0	2.2
9	Benzene, 1-ethyl-2-methyl-	1.4	0.4	6.2
10	Benzene, 1-ethyl-4-methyl-	2.2	0	4.5
11	Benzene, 1,2,4-trimethyl-	0.7	0	0
12	Phenol	0	0.9	0
13	C10 Olefin	1.1	0	0
14	Benzene, 1,2,3-trimethyl-	4.5	1.0	8.5
15	C10 Alkane	0.5	0	1.8
16	Benzene, 1,3,5-trimethyl-	0.4	0	0
17	Indane	0.6	0.9	0
18	Indene	0.7	1.9	0
19	Benzene, diethyl-	0.7	0	1.6
20	Phenol, 2-methyl-	0	0.4	0
21	Phenol, 3-methyl-	0	0.7	0
22	p-Isopropyltoluene	0	0	1.5
23	Phenol, 2-methoxy-	0	2.6	0
24	Cyclopropane, 1-methyl-2-pentyl-	0.9	0	0
25	C11 Alkane	0.5	0	1.7
26	Naphthalene	2.1	8.1	0
27	Creosol	1.1	1.8	0
28	C12 Olefin	0	0	1.4
29	C12 Alkane	0.5	0	1.5
30	Guaiacol, 4-ethyl-	0	0.4	0
31	C13 Olefin	0.5	0	1.2

(Continue)

No.	Compound	Concentration		
		(% , based on total of each)		
		1:1	3:1	1:3
32	C13 Alkane	0	0	1.8
33	Naphthalene, 2-methyl-	3.7	8.4	0
34	Naphthalene, 1-methyl-	1.3	3.4	0
35	Eugenol	0	1.3	0
36	C14 Olefin	0.7	0	1.3
37	C14 Alkane	0.5	0	1.2
38	Naphthalene, 2,7-dimethyl-	0	1.4	0
39	Naphthalene, 1,5-dimethyl-	1.0	0.9	0
40	Naphthalene, 1,4-dimethyl-	0	0.6	0
41	Naphthalene, 1,7-dimethyl-	0.4	0	0
42	Naphthalene, 2,6-dimethyl-	0.3	0.4	0
43	trans-Isoeugenol	0.4	2.2	0
44	C15 Olefin	0.8	0	1.1
45	C15 Alkane	0.5	0	1.4
46	(E)-Calamene	0	0.6	0
47	C16 Olefin	0.5	0	1.0
48	C16 Alkane	0.5	0	1.3
49	C17 Olefin	0.3	0	1.0
50	C17 Alkane	0.3	0	1.4
51	C18 Olefin	0.2	0	0.9
52	C18 Alkane	0.1	0	0.9
53	C19 Diolefin	0.4	0	0
54	C19 Olefin	1.5	0	0
55	C19 Alkane	1.0	0	0
56	C20 Diolefin	1.1	0	0
57	C20 Olefin	3.2	0	0
58	C20 Alkane	2.0	0	0
59	C21 Diolefin	1.4	0	0
60	C21 Olefin	3.3	0	0
61	C21 Alkane	2.2	0	0
62	C22 Diolefin	0.7	0	0
63	C22 Olefin	1.4	0	0
64	C22 Alkane	0.8	0	0
Total		100.0	100.0	100.0

Table 11. Classification of pyrolytic products of different biomass and plastic ratios from co-pyrolysis (600°C).

Biomass:Plastic	Aromatic		Phenols	Furans	Alkenes	Alkanes	Petro-chemicals ^b	Waxes ^c
	Hydrocarbons ^a							
	MAH	PAH						
3:1	57.5	16.8	7.9	2.7	10.3	4.9	81.0	8.4
1:1	61.2	10.2	1.5	0	17.0	10.1	76.6	21.9
1:3	70.4	1.8	0.7	0	12.9	14.2	83.7	15.6

^aMAH: Monomeric Aromatic Hydrocarbons; PAH: Polycyclic Aromatic Hydrocarbons.

^bPetrochemicals = Aromatics + Alkenes (C_≤15) + Alkanes (C_≤13).

^cWaxes = Alkenes (C_>15) + Alkanes (C_>13).

4.2.2. Elemental analysis and higher heating value of pyrolytic products

The pyrolytic products from pine wood sawdust only contained 70.3% of carbon, 3.6% of hydrogen, and 23.4% of oxygen, which is a quite high content of oxygen in pyrolytic products which linked to a low heat value at 25.9 MJ/kg. When the pine and PE were pyrolyzed without catalyst, the carbon and hydrogen contents were increased but still contained around 10% of oxygen.

Pyrolysis of pine with ZSM-5 as catalyst performed better than pine only in reducing oxygen content to 3.9%, and increased HHV up to 31.9 MJ/kg, because of the effect of zeolite. Catalytic co-pyrolysis of pine and PE obtained 88.2% of carbon, 11.5% of hydrogen, and only 0.3% of oxygen, which is similar to catalytic pyrolysis of PE only. HHV of 34.4 MJ/kg seems to be a good performance when compared with pine only. The high C/H ratio of PE led to decreasing the oxygen content when served together with biomass and catalyst.

To investigate the effect of the co-feeding ratio of biomass and plastic, three different ratios (3:1, 1:1, 1:3) of pine and PE were also pyrolyzed. The elemental analysis and HHV were calculated and summarized in Table 12. As we can see in the table, compared with a 1:1 ratio when biomass was served more led to higher oxygen content and lower HHV in pyrolytic products. However, when PE was served two times more than pine, the C/H ratio did not change significantly to the 1:1 ratio sample.

Table 12. Physicochemical properties of pyrolytic products of different feedstock from co-pyrolysis (600°C).

Feedstock	Elemental Analysis (wt%)			HHV ^a (MJ·kg ⁻¹)
	C	H	O	
Pine	70.3	6.3	23.4	25.9
PE	85.7	14.3	0	35.5
Pine&PE	80.9	9.5	9.6	31.0
Pine/ZSM-5	88.3	7.8	3.9	31.9
Pine&PE/ZSM-5 (1:1)	88.2	11.5	0.3	34.4
PE/ZSM-5	88.6	11.4	0	34.4
Pine&PE/ZSM-5 (3:1)	88.6	8.5	2.9	32.5
Pine&PE/ZSM-5 (1:3)	88.9	11.0	0.1	34.2

^aHigher heating value was calculated by following formula,
dry basis HHV (MJ·kg⁻¹) = -1.3675 + (0.3137 × C) + (0.7009 × H) + (0.0318 × O).

5. Conclusion

The pine wood sawdust was pyrolyzed to convert it into bio-oil and char with two different pyrolyzers, and their physicochemical properties were characterized. From the mass balance analysis of pyrolytic products, the distributions of products were significantly influenced by the type of reactor. The bio-oils produced from two pyrolyzers with pine were composed of approximately 30 low molecular weight compounds, mainly organic acids, aldehydes, ketones, alcohols, and phenols derived from cellulose, hemicellulose, and lignin. Among them, high amounts of oxygen-containing compounds and high water content indicated the main reasons for the low calorific values, as compared with conventional fossil fuels.

Fluidized bed pyrolyzer produced more amount (approximately 60%) and better quality of bio-oil, but the large particle size of materials could not be introduced into the reactor. On the other hand, the screw-type pyrolyzer produced around 45% of bio-oil, based on the biomass weight at 500°C, and lower HHV for the bio-oil, due to the weakness heat transfer property caused by the absence of heat carrier and longer residence time. However, it showed a better capacity for the large particle size of materials, which can be expected to perform in-situ catalytic co-pyrolysis of biomass and plastics using screw type pyrolyzer.

At the same time, analytical catalytic co-pyrolysis of pine and PE with ZSM-5 was carried out under different experimental conditions, and the elemental distribution and chemical components of pyrolytic products were studied. Catalytic co-pyrolysis significantly decreased the oxygen ratio in the products from 23.4% (pine only) to 0.3%, and increased the HHV from 25.9 MJ/kg to 34.4 MJ/kg. It also revealed that the content of hydrocarbons was increased as well as the phenols and furans decreased. As far as the ratio of pine and PE, the concentration of petrochemicals were not significantly

influenced. However, a higher plastic ratio led to a higher wax production, which would be a critical reason for poor condensation performance of bio-oil capture in condenser. Pine wood sawdust to PE ratio of 3:1 showed the best result of higher petrochemicals, and low wax formation.

6. References

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