Fast Pyrolysis of Agricultural Wastes for Bio-fuel and Bio-char

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Abstract Fast pyrolysis is a thermo-chemical conversion method to produce liquid fuel from biomass. This process involves the rapid thermal decomposition of organic compounds in the absence of oxygen. The vapors formed are rapidly condensed to yield a liquid product called bio-oil. Since the major product is liquid, it is easy to store, and handle. Moreover, bio-oil can be readily transported to facilities where it can be most effectively used. Unlike other conversion methods for bio-fuel production, fast pyrolysis utilizes different types of feedstocks, therefore this process can be considered as a tool for solid waste management. Different types of feedstocks ranging from agriculture and forest residues to MSW, plastic wastes and animal manures have been utilized for pyrolysis studies around the world. Liquid fuel production using fast pyrolysis has received much attention in recent years. Bio-oil, the liquid product of fast pyrolysis, can be considered as an intermediate for fuel and chemical production. Bio-char, the solid product of pyrolysis, has multiple applications like bio-char from other methods. The chapter reviews different types of reactors used for fast pyrolysis, bio-oil properties, challenges and opportunities, and the current status of fast pyrolysis applications. In addition, the chapter discusses applications of bio-char and energy and economics of fast pyrolysis.

Keywords Biomass · Bio-char · Bio-oil · Fast pyrolysis · Reactors · Solid wastes

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1 Introduction

Energy is a vital ingredient for socio-economic development. Fossil fuel resources are finite, alternative sources are needed as supplements due to the fast past modernization. Long-term sustainability can be guaranteed if sources are renewable. Wind, solar, geothermal, and hydro have direct potential for renewable energy, however, biomass shows the highest capacity to supplement fossil fuels for both carbon-based fuels and chemicals.

Food production and consumption will inevitably produce organic residues/waste. These organic residues/wastes were formerly deposited in wastelands, where decomposition produces greenhouse gases such as CO_2 or methane. The organic part of these residues, termed biomass here, can be effectively used for energy applications. Therefore biomass can be considered as a sustainable source of fixed carbon for chemicals and fuels. There are different processes for the production of energy from biomass, which can be broadly classified as biochemical, thermochemical, catalytic and synthetic biology routes. Among these options, thermochemical methods have an advantage as they are somewhat feedstock agnostic. Bio-ethanol and biodiesel productions are the two major bioenergy routes, which depend on cellulosic biomass and lipid-rich biomass, respectively. Thermo-chemical routes, such as combustion, gasification and pyrolysis utilize all types of residues/feedstocks. Therefore, a successful implementation of thermo-chemical routes followed by catalytic upgrading would be a sustainable supplement for the increasing demands of fossil fuels.

This chapter discusses recent developments in the field of fast pyrolysis, one of the thermo-chemical biomass conversion methodologies. Bio-oil, the main product of fast pyrolysis of biomass, can be considered a substitute/additive for crude oil for fuels and chemicals, but there are challenges in achieving these aims. Since fast pyrolysis is feedstock agnostic and requires low capital investment, research into the chemical makeup arising from different feedstocks, bio-oil properties and potential applications are summarized along with upgrading of the bio-oils for the production of fuel and chemical feedstocks. Furthermore, major reactor configurations are discussed, as is progress in upscaling the technology from laboratory-scale to industrial-scales.
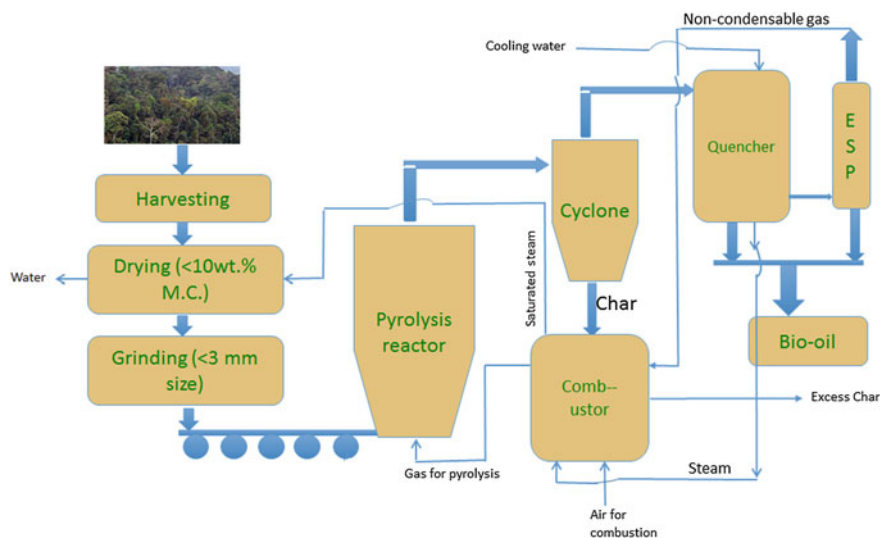
2 Fast Pyrolysis

Pyrolysis, thermal degradation of organic matter at high temperature in the absence of oxygen, involves changes in chemical composition and the physical phase. Pyrolysis has been practiced for centuries for the production of charcoal. Since the oil crisis in the mid-1970s, considerable effort has been directed towards the development of liquid fuels from ligno-cellulosic biomass (Czernik and Bridgwater 2004). Pyrolysis can also be utilized for the production of liquid fuels by changing

process parameters like temperature, heating rate and residence time of vapors: called fast pyrolysis. In fast pyrolysis, the biomass is decomposed thermally at a medium temperature (about 500 °C) in the absence of oxygen. Fast pyrolysis allows high heat transfer rate to the biomass feedstock and a short residence time (about 2 s) in the reaction zone. The major products of fast pyrolysis are vapors, aerosols, char and gases. Vapors and aerosols are condensed quickly to form a liquid, which is known as bio-oil. The yields and properties of bio-oil depend on the feedstock used, process conditions, and the product collection efficiency. There are some essential criteria for producing liquid fuels from fast pyrolysis such as (i) high heat transfer rate for biomass particle reaction with relatively fine biomass feedstock of less than 3 mm, (ii) short residence time of about 2 s to avoid secondary reactions, (iii) control of reaction temperature at around 500 °C, (iv) avoiding cracking of vapors by char and ash removal, and (v) rapid cooling of vapors to increase bio-oil yields (Meier et al. 2013; Bridgwater et al. 1999; Bridgwater 1999; Bridgwater and Peacocke 2000).

Fast pyrolysis is the most effective liquefaction method as it can yield around 80 wt% of dry biomass as bio-oil. Pyrolysis is a feedstock agnostic process where any type of organic wastes can be converted into liquid fuel. Most of the thermo-chemical biomass conversion technologies have challenges with high ash content organic biomass such as animal manure, sludge, municipal solid wastes. High temperature processes such as gasification and combustion (which work above the ash fusion temperature) have major issues with slag formation due to ash content. In contrast, in slow pyrolysis and hydrothermal carbonization, most of the ash content of the biomass will remain with the major product bio-char. Therefore, energy application of bio-char (gasification, combustion) would produce the same issue as slag formation. Fast pyrolysis is a medium temperature process and a minor portion of ash will be captured in the major product: bio-oil. Though fouling (due to ash content) can be an issue during bio-oil processing, the frequency of occurrence of this issue will be low.

The fast pyrolysis process can be divided into four sections: biomass pre-treatment, pyrolysis, char recovery and liquid collection (Bridgwater and Peacocke 2000). The process flow diagram for fast pyrolysis is given in Fig. 1. Harvesting of biomass is normally not considered as a part of fast pyrolysis systems since it is common for all biomass-using processes. However, one of the advantages for fast pyrolysis is the utilization of mobile units/pilot plants. Mobile units can be utilized for seasonal feedstocks and pilot plants can be utilized for decentralized feedstocks. Since the major product is liquid, subsequent transport to existing refining facilities is easy. Therefore harvesting and handling cost of feedstock can be reduced (Badger and Fransham 2006). However, an economic study on mobile plants in 2011 showed a low probability for a positive Net Present Value (NPV) compared to stationary plants. The economics of mobile plants could be improved, if feedstock costs were reduced and crude oil price increased (Palma et al. 2011).

Fig. 1 Schematic of the fast pyrolysis process

In order to achieve heat and mass transfer restrictions of fast pyrolysis, biomass has to be dried to reduce the moisture content to below 10 wt% and ground to a particle size of less than 3 mm. In a self-sustained design of a fast pyrolysis plant, drying can be achieved by utilizing the heat from the bio-char recovery and bio-oil collection sections. The steam produced during the condensation of pyrolytic vapors could be passed through the combustion chamber (where char will be burned to recover heat) and the heat of this saturated steam could be used for drying. The heart of the fast pyrolysis process is the pyrolysis reactor. Reactors of different designs have been tested for fast pyrolysis in order to achieve high heating rate and heat transfer rate for biomass particles. A detailed description of reactor configurations is presented in Sect. 4. A char recovery system is installed downstream of the pyrolysis reactor. The char recovery system normally consists of a cyclone separator to remove the char and ash from the pyrolytic vapors. The recovered char will be sent to a combustion chamber. In the combustion chamber, the heat produced by burning of char will be transferred to the biomass pre-treatment section via saturated steam, while pyrolytic vapors from the cyclone will be sent to a quencher/condenser followed by an ESP (electrostatic precipitator) to recover all condensable compounds in liquid form which is called bio-oil. Bio-oil can be stored in a corrosive resistant vessel and transferred for further processing. The non-condensable gas from condenser and ESP will be recycled as pyrolyzing gas. One part of heat produced from char combustion can be transferred to the pyrolysis reactor through non-condensable gas. The steam produced from condenser could be used as saturated steam for drying by passing through the combustion chamber.

3 Biomass

According to ANSI/ASABE, any organic waste produced from living/dead matter other than fossil fuel can be considered as biomass (ANSI/ASABES593 2006). In this regard, there are many organic residues potentially available for bioenergy applications which can be categorized as forestland residues, farmland residues, and city residues (Loque et al. 2011). Forestland residues include tree residues and wood residues. Tree residues are solid wastes generated during the growth of forest such as leaves, needles, and branches while wood residues are generated during the wood harvest and processing such as branches, bark and saw dust (Loque et al. 2011). Farm land wastes are of two types such as straw residues and manures. Straw residues include all agriculture residues formed during the processing of seed, sugar or other food products. Manures, another type of farmland residues, are generated in large amounts from livestock production. In addition, the organic parts of urban land residue or municipal solid wastes (MSW) such as paper, cardboards, landscaping materials can be utilized as biomass (Loque et al. 2011).

According to International Energy Outlook 2013, the world energy consumption will increase from 524 quadrillion Btu in 2010 to 630 quadrillion Btu in 2020 and is estimated to further increase to about 820 quadrillion Btu in 2040, representing a 30-year increase of 56 % (EIA 2013). Crude oil is the major worldwide energy supply with 32 %, followed by coal 29 %, natural gas 21 %, nuclear 5 %, and renewable resources 13 %. Biomass contributed with 10 % to the total energy supply in 2011 (WBA 2014). Asia and Africa major consumers of bioenergy, however, most of the biomass consumption in these countries is as a heat source. Utilization of biomass for heating contributes significantly to air pollution in these countries. The utilization of biomass for biofuel production has increased in recent years, most of which occurs in developed countries. Brazil, however, ranks number one in the production of biofuel. A study on global potential of biomass for energy projected surplus agricultural land as major biomass source which would provide 76.7 % of total biomass energy (1300EJ) in 2050 (Ladanai and Vinterbäck 2009). According to the World Bioenergy Association (WBA), major biomass from forests are: fuel wood, charcoal, forest residues, black liquor, wood industry residues, and recovered wood; from agriculture: animal by-products, agricultural by-products, and energy crops; and from wastes such as MSW and landfill. The WBA has published the yield of major agricultural crops from different continents, as shown in Table 1.

Since fast pyrolysis is feedstock agnostic, different types of biomass have been utilized for fast pyrolysis. For example, animal manures when utilized as fertilizer results in nutrient leaching and water pollution. Another way of handling these wastes is anaerobic fermentation, which produces greenhouse gas emissions, if not handled efficiently. In this regard, fast pyrolysis is a potential candidate to utilize the organic portion of manure. Handling high ash-content biomass is a challenge for other thermo-chemical conversions, whereas in fast pyrolysis, most of the ash will remain in the byproduct: bio-char. However, most of the work done so far in fast

Table 1 Average yields of crops for year 2011 (tons/ha)

	World	Africa	Americas	Asia	Europe	Oceania
Cassava	12.7	10.7	13	19.7	–	10.9
Maize	5.16	1.92	6.84	4.81	6.66	6.81
Rapeseed	1.86	1.64	1.88	1.54	2.53	1.14
Sorghum	1.38	0.95	3.38	1.16	3.63	3.06
Soybeans	2.53	1.25	2.85	1.48	1.95	1.71
Sugar beet	54.9	52.8	55.1	49.2	56.2	–
Sugar cane	71.1	64.2	75.1	66.9	85.5	76.2

Source World Bioenergy Association (WBA 2014) (Reprinted with the permission from Dr. Bharadwaj V Kummamuru, World Bioenergy Association, Sweden (lead author))

pyrolysis was carried out on wood and agriculture wastes because of feedstock consistency and comparability between tests. More than one hundred different types of biomass have been tested ranging from agricultural wastes, energy crops, and forestry wastes and solid wastes, some examples are given in Table 5. The selection of biomass depends on their abundance in particular locations.

4   Reactor Configurations

A fast pyrolysis process normally starts with the preparation of feed, which is typically dried to have less than 10 % water content in order to minimize water content in the liquid oil product. The feed is then ground into small particles to reduce mass transfer resistance, then fast pyrolysis takes place, followed by the rapid and efficient separation of solid char from vapors and finally rapid quenching and collection of bio-oil (Fig. 1) (Bridgwater 2012a, b).

The fast pyrolysis process involves heat and mass transfer, phase transition, and chemical reactions in a few seconds or less. In this process, biomass will be suddenly exposed to optimum temperature with a reduced exposure to lower temperatures that favor char formation. In other words, the reactor configuration for fast pyrolysis process should be able to provide a high heating rate and heat transfer rates for biomass. Considerable research has focused on developing new reactor designs for a variety of feedstocks to control and improve the final liquids' quality and the collection systems (Bridgwater 2011, 2012a, b). Some reactor configurations can achieve liquid yields of 70–80 % based on dry biomass weight (Mohan et al. 2006). The choice of reactor mainly depends on the flexibility/ease in operation, feed size and the desired purity of the bio-oil.

Major reactor configurations are: bubbling fluidized bed, circulating fluidized bed, rotating cone, augur, and ablative reactors (Fig. 2). In addition to these reactors, other configurations were also investigated for biomass fast pyrolysis, which includes vacuum pyrolysis, fixed bed, entrained flow reactors, microwave
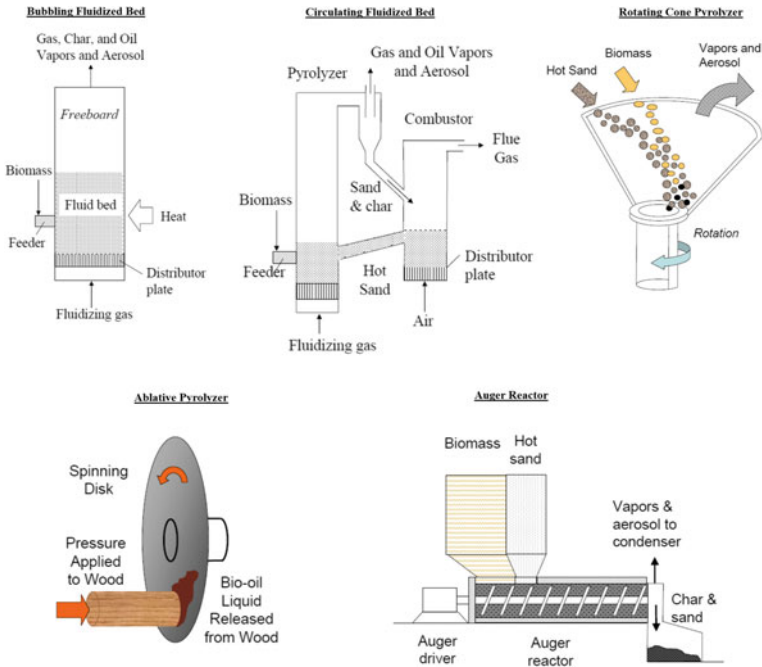
Fig. 2 Major reactor configurations for fast pyrolysis (reproduced with the permission from Prof. Robert C. Brown, Iowa State University)

pyrolyzer, plasma, and solar reactors. All of these reactors have advantages and drawbacks, depending on the types of raw biomass material and commercial scale of fast pyrolysis.

4.1 Bubbling Fluidized Bed Reactor

Fluidized bed is a well-developed technology, where the reactors are simple in construction and operation, which provide good and efficient temperature control, heating rate and heat transfer to biomass particles. Hence fluidized bed reactors are attractive and popular for biomass fast pyrolysis. Very small biomass particles of typically 2–3 mm is used in fluidized bed reactors to obtain good liquid yields. In this reactor configuration, the heat energy required is supplied by heating the walls of the reactor or by injecting hot inert gas. The distributor plate ensures that the fluidizing gas is well distributed. Normally, helium or nitrogen is used as the fluidizing gas and sand as the bed material. Shallow depth bed or a high rates of gas flow are usually both used to achieve short residence time for vapors (Scott et al. 1999). If the bio-char has a higher residence time, they act as a vapor cracking catalyst in the process and cause secondary cracking of vapors. Therefore char must

be rapidly and effectively separated. This is normally done by passing product vapors and gases to a separation system, which includes one or more cyclones (Mohan et al. 2006).

In catalytic pyrolysis, instead of sand, catalysts such as ZSM-5 or silica are used as bed material. The gas, vapors and aerosol formed are transferred to a series of condensers to obtain the bio-oil (Agblevor et al. 2010; Shi 2012). The fluidized bed reactor provides high yields and good quality bio-oil and does not allow char to accumulate as it is rapidly eluted. The liquid yield from fluid-bed pyrolyzers are typically 70–75 wt% from wood on a dry-feed basis. The yield of the by-product char is typically 15 wt% (Bridgwater 2012a, b).

4.2 Circulating Fluidized Bed Reactor (CFB)

The circulating fluidized bed reactor is quite similar in operation to that of fluidized bed reactors but the residence time for char in CFBs is almost same as that of vapors. A second vessel is employed as a char combustor to reheat the solids which are circulated back to the reactor by passing through a cyclone separator for separating the entrained particles (Lappas et al. 2002). In this reactor, the hot sand circulating between the combustor and the pyrolyzer provide heat. However, circulating fluidized bed reactors are as not efficient as bubbling fluidized bed reactors in terms of temperature control and heat transfer. CFB reactors are suitable for larger throughput (Bridgwater 2012a, b). The char is more attired, therefore higher char contents appear in the condensed bio-oil. There is no char available for export since all char is burned in the combustor and used as heat supply. CFBs also do not have high heat transfer rates because they are dependent on gas flow rates. The biomass ash builds up in the circulating solids, which can act as a cracking catalyst, causing the loss of volatiles and improving the properties of the bio-oil products (Mohan et al. 2006; Bridgwater 2012a, b). CFB technology is often developed in larger application with enhanced flexibility for igniting multi-fuels and it has efficiency up to 95 % (Bridgwater 2004).

4.3 Rotating Cone Pyrolyzer

University of Twente invented a new reactor design for fast pyrolysis, a rotating cone pyrolyzer developed by the Biomass Technology Group (Biomass Technology Group) in the Netherlands (Wagenaar et al. 1994, 2008). The rotating cone pyrolyzer is an innovative reactor configuration achieving high heating rates and a short vapor residence time (Wagenaar et al. 1993). The working principle of a rotating cone pyrolyzer is quite similar to circulating fluidized bed reactor in terms of the raw materials inlet direction and processing materials where centrifugal forces are used to transport sand and biomass. Biomass and sand are fed to the

bottom of a rotating cone and the biomass is pyrolyzed by hot sand while transported upward through a spiral motion along the hot sidewall of the cone. The pressure of the outgoing materials is slightly above atmospheric levels. The inner diameter of the cone has a maximum of 0.650 m. The rotational speed of the cone is 900 rpm. The reactor volume may range from 2 to 200 dm^3. The first industrial use of this reactor was for the pyrolysis of biomass (Wagenaar et al. 1994). Using sand in the process has the advantage of avoiding fouling of the cone wall and enhancing heat transfer. After leaving the impeller, the particles flow outwards from the cone and experience high heat transfer rate from the heated surface. This pyrolyzer is very compact in design, requires feeding with very small particles and can be used for high throughput (Bridgwater 2012a, b). The char produced is not a by-product since it is burned entirely for heat supply purpose. Liquid yields of 60–70 wt% on dry feed are typically obtained (Bridgwater 2012a, b).

4.4 Ablative Pyrolyzer

Ablative pyrolysis applies a mode of reaction similar to melting butter in a hot pan. The high heat from the wall causes wood to 'melt' on contact under high pressure. As the wood is pressed mechanically, the residual oil is evaporated to yield pyrolysis vapor, which can be collected by rapid cooling. The residual oil on the hot surface provides lubrication and helps to enhance evaporation rates of biomass. Liquid yields of 60–65 wt% on dry feed basis were typically obtained (Bridgwater 2011). Large particles including logs can be pyrolyzed without being ground. The char is deposited on the hot surface due to element cracking. A study comparing product yields for fluid bed- and ablative reactors (Peacocke et al. 1996) gave 59.4 wt% organics at 515 °C and 1.19 s residence time for a fluid bed reactor, and 62.1 wt% organics at 502 °C and 1.1 s residence time for the ablative reactor.

The main benefits of this reactor are that carrier gas is not required and larger biomass particles can be used (Scott et al. 1999). The rate of reaction in the reactor is strongly depended on the applied pressure, the reactor surface temperature, and the relative velocity between biomass and the hot surface. However, post-treatment of bio-oil is required for char removal.

4.5 Auger Reactor

The auger reactor is a compact design for continuous fast pyrolysis which does not require a carrier gas. Augers are moved with biomass feed through a heated cylindrical tube, which causes pyrolysis, producing bio-char, bio-oil and gas. Sand or steel shot are used as heat carriers. The mode of heat transfer in this reactor is mainly conduction. The rotating screw conveyors combine the biomass and the heat carrier effectively and pyrolysis reaction takes place. The design reduces energy

cost and the vapour residence time can be manipulated by the heated zone length (Mohan et al. 2006; Thangalazhy-Gopakumar et al. 2010; Bridgwater 2012a, b). Energy costs for the operation are very low compared to other reactor designs (Adjaye and Bakhshi 1995a, b, c). However, this it is only suitable for small scale production of bio-oil.

4.6 Vacuum Pyrolysis Reactor

Though vacuum pyrolysis provides low heat transfer rates, the vapor residence time is comparable with fast pyrolysis and therefore utilized for bio-oil production. Vacuum pyrolysis is the thermal decomposition of organics under reduced pressure. Vapors are rapidly removed from the reactor by vacuum, and recovered as bio-oils by condensation. Compared to other fast pyrolysis systems, lower liquid and increased char yields were typically obtained (Bouchera et al. 2000; Garcia-Perez et al. 2002). The advantages of the process are that larger particles can be used and less char contaminates the liquid product. However, the process is very complex, has less efficient heat and mass transfer rates and is costly as it requires large-scale equipment and higher capacity vacuum (Mohan et al. 2006; Bridgwater 2012a, b). The pressure in the vacuum reactor is maintained at 15 kPa by using a vacuum pump to remove the vapor formed due to the heating of biomass.

4.7 Fixed Bed

Fixed bed reactors are reactors in which the feedstock, carrier system, catalyst, filter media and other substances remain stationary. It has some advantages, such retention of high amount of carbon. The main advantage is the simplicity of equipment design and low fabrication cost for the equipment. Inert condition of the environment is maintained by the presence of pure nitrogen flow. A cold trap is used to collect condensable vapors to condense them into bio-oil. In a fixed bed reactor, the flow rate of nitrogen needs to be controlled in order to obtain optimum yields. This reactor configuration is widely used for laboratory studies.

4.8 Microwave Pyrolyzer

Some laboratory studies have been conducted with microwave reactors for fast pyrolysis. Conventional thermal heating, heat transfers from the surface to the center of the material by conduction, convection and radiation. Conventional heating is inefficient and slow, as it depends on the convection current and thermal conductivity of the feedstock. Conventional heating is characterized by high-energy

consumption therefore microwave reactors were developed to reduce the energy consumption of the process. Microwave heating is achieved by dielectric heating and transferring heat from electromagnetic energy to thermal energy which is a kind of energy conversion rather than conventional heating (Motasemi and Afzal 2013). However, microwaves consume high amount of electric power and the operating costs are very high.

According to the IEA (International Energy Agency) Bioenergy Task 34 for Pyrolysis (http://www.pyne.co.uk/), bubbling fluidized bed reactors are the most favorable configuration in terms of technical strength and market attractiveness, followed by circulating fluidized bed and auger reactors respectively. Rotating cone and ablative pyrolyzers are very difficult to scale up and therefore less attractive than other three reactors. In terms of bio-oil yield, both fluidized bed and ablative reactors perform better than rotating cone and auger reactors.

5 Bio-oil

Fast pyrolysis liquid, which is known as bio-oil, has a higher heating value (HHV) of about 17 MJ/kg when produced with about 25 wt% water that cannot readily be separated. Though known as bio-oil, this liquid will not mix with hydrocarbon liquids. Bio-oil is a multi-component dark brown organic liquid. The liquid is formed from rapid and simultaneous thermal depolymerization, fragmentation and quenching of cellulose, hemicellulose and lignin of biomass (Czernik and Bridgwater 2004; Mohan et al. 2006). Though bio-oil is homogeneous in appearance, it contains compounds of different sizes and structures, difference in their functional groups, polarity and density. Therefore, bio-oil should be mixed thoroughly before analysis.

5.1 Analysis

The composition or properties of bio-oil depends on the composition of the biomass (percentage of cellulose, hemicellulose, and lignin). In addition, the presence of alkali metals (in the form of ash) and other extractives in biomass. Due to the complexity, chemical characterization of bio-oil cannot be done with one or two simple analyses (Kanaujia et al. 2014; Staš et al. 2014).

For detailed characterization, bio-oil should be fractionated as water-soluble and -insoluble or pentane-soluble and -insoluble, and further fractionated to methanol-, ether- or toluene-soluble and so on (Sipila et al. 1998; Oasmaa et al. 2003; Garcia-Perez et al. 2007; Salehi et al. 2011). Each of these fractions will be analyzed for the compounds/functional groups present. Gas Chromatography (GC) equipped with Mass Spectroscopy (GC-MS) or Flame Ionization Detector (GC-FID) are the most common analytical instruments used for most of the

chemical composition studies of bio-oil (Branca et al. 2003; Bhattacharya et al. 2009; Thangalazhy-Gopakumar et al. 2010; Kantarelis et al. 2013). However, GC can detect only volatile compounds. Some of the non-volatile compounds (especially anhydro-sugar compounds) can be detected by utilizing polar columns such as 1701. Most GC analyses quantify compounds such as phenol derivatives i.e. alkyl phenols, guaiacols, syngols, benzenediols, oxygenated aromatics, furans, pyrrols, higher aldehydes and ketones, and some anhydro-sugar compounds, all these compounds accounting for a maximum 40 wt% of the bio-oil (Staš et al. 2014). Another 25–30 wt% is the water content of the bio-oil. Water content in bio-oil is normally analyzed using the Carl-Fischer titration method. Remaining fraction of bio-oil remains unknown in most of the studies. High Performance Liquid Chromatography (HPLC) has been utilized to analyze organic acids, aldehydes, and sugars in bio-oil (Salehi et al. 2011; Choi et al. 2014). Another chromatographic techniques such as gel permeation-, ion-, and column chromatography are also utilized for bio-oil analysis. Fourier Transform Infrared Spectroscopy (FTIR) is another technology widely used for characterization of different functional groups present in bio-oil. Some of the common absorption bands identified in bio-oil are C=O stretching (aldehydes, ketones, acids), C=C stretching (aromatics), C–O stretching (alcohols, ethers) O–H stretching (phenols) (Pütün 2002; Onay and Kockar 2006; Sensoz et al. 2006). ^{1}H NMR (Nuclear Magnetic Resonance) studies have also conducted to identify the different H atoms present in bio-oils (Pütün 2002; Onay and Kockar 2006; Sensoz et al. 2006). Chemical formulae for bio-oil are developed by analyzing the elemental composition (Choi et al. 2014). FTIR spectra for bio-oils from wheat straw or HWSP (*Triticum aestivum*), timothy grass or HTGP (*Phleum pratense*) and pinewood or HPWP (*Pinus banksiana*) are given in Fig. 3.

In addition to the above analytical techniques, some methods used in the food industry such as total water, soluble sugars, and total phenol contents have been evaluated for bio-oil analysis. Water soluble total carbohydrates in bio-oil was evaluated using the phenol–sulfuric acid assay developed by the Association of Analytical Communities, Inc. (AOAC), Method 988.12 (44.1.30) (Albalasmeh et al. 2013; Rover et al. 2013). In this method, bio-oil is treated with phenol and concentrated sulfuric acid, and the treated sample taken for UV analysis (∼490 nm). The results were comparable with sugar analysis of the bio-oil by HPLC. However, presence of water-soluble furan compounds influence the results. Similarly, the total phenol content in bio-oil was evaluated by the Folin–Ciocalteu (FC) colorimetry method (Rover and Brown 2013). In this method, gallic acid is used as standard and the results are reported as gallic acid equivalent. The FC reagent will react with phenols to form chromogens that can be detected spectrophotometrically (Ikawa et al. 2003). However, this method is non-specific and can be affected by the presence of other compounds.

Bio-oil properties depend on its chemical composition. Therefore, there are several properties that need to be considered for bio-oil.
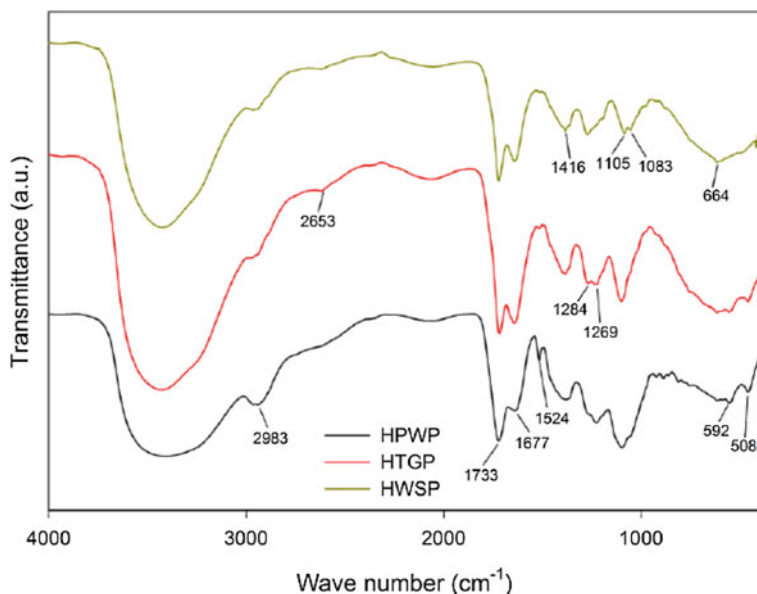
Fig. 3 FTIR spectra for bio-oil (Nanda et al. 2014) (Reprinted with the permission from Prof. Ajay K. Dalai, University of Saskatchewan, Canada)

5.2 Properties

Density: The density of the liquid is very high at around 1.2 g/mL as compared to light fuel oil at around 0.85 g/mL. This is due to the presence of some high molecular weight compounds such as syringols and sugar compounds. The feedstock used and the residence time of vapors also influence the density of bio-oil.

pH: The pH of the lignocellulosic bio-oil normally is about 2–3 which is due to the presence of the organic acid, such as acetic and formic acids. Therefore, the material of storage vessels must be made of acid-proof material such as stainless steel. The pH of bio-oil from sludge and animal manures are basic due to the presence of nitrogen compounds.

Higher Heating Value (HHV): The HHV of bio-oil is normally in the range of 16–19 MJ/kg, which is less than half of the values of conventional fuel. However, the energy density of bio-oil is 10 times higher than biomass. Therefore, it is easily transported. Bio-oil has about 42 % of the energy content of fuel oil on a weight basis, but 61 % on a volumetric basis (Abdullah et al. 2007; Bridgwater 2012a, b).

Solid Content: Some char, which is relatively fine, might be suspended in the liquid product, acting as a vapor cracking catalyst. Therefore char separation is needed to prevent vapor cracking which affect the yield of the liquid product. It is, however, difficult to achieve complete removal. Currently, two types of filtration methods are used cyclone separator and hot vapor filtration, to collect char from vapors before condensation as bio-oil.

Oxygen content: More than three hundred compounds are present in bio-oil; most of them are oxygenated. Therefore oxygen content of bio-oil is usually in the range of 35–40 %, and this is the primary reason for the vast differences between bio-oils and petroleum fuels. These oxygenated compounds make bio-oil polar, and thus non-miscible with non-polar petroleum fuels. High oxygen content results in low heating values and also makes the bio-oil unstable. The oxygen content can be reduced by increasing the process severity leading to cracking of vapors and removal of oxygen due to deoxygenation and dehydration reactions. However, this will also lead to the reduction of organic liquid yield.

Water content: Water content in bio-oil is the result from original moisture content of biomass (normally at a maximum of 10 %) and from the dehydration reactions occurring during pyrolysis (typically about 12 % based on dry feed) (Asadullah et al. 2007). The presence of water in bio-oil has advantages and disadvantages. Water content (15–30 wt%) gives homogeneity to bio-oil. The solubilizing effect of water for other polar hydrophilic compounds usually helps to ensure miscibility with the oligometric lignin-derived components (Bridgwater et al. 2002). However, increasing the water content leads to separation of the bio-oil into two distinct phases: aqueous phase (with polar compounds) and organic phase (non-polar compounds (Bridgwater 2012a, b). The disadvantages are lowering heating values, increasing ignition delay and decreasing the rate of combustion. Water content on the other hand is advantageous since it improves bio-oil flow characteristics and also leads to a more uniform temperature profile in a cylinder of a diesel engine (Czernik and Bridgwater 2004).

Volatility distribution: Bio-oil cannot be completely vaporized once it is condensed as a liquid and during vaporization, compounds in bio-oil will rapidly react and produce char/solid. Bio-oil contains substantial amounts of oxygenated compounds such as sugar and oligomeric phenolics, therefore, slow heating of oil during distillation results in polymerization of some reactive components. Consequently the oil starts boiling below 100 °C and stops at 250–280 °C (Czernik and Bridgwater 2004).

Viscosity and Aging: Viscosity of bio-oil varies over a wide range (35–1000cP at 40 °C), depending on feedstock, the process conditions and aging. An increase in temperature causes a decrease in viscosity thus the bio-oil can be pumped easily by heating the pipeline. The viscosity can also be reduced by the addition of polar solvents such as methanol or acetone (Diebold and Czernik 1997; Bridgwater 2012a, b). If the bio-oil is subjected to high temperature for a long period of time, viscosity will increase. This is a result of a chemical reaction between the various compounds that will result in the formation of larger molecules (Diebold 2000).

Corrosiveness: Corrosiveness of bio-oil is caused by the presence of organic acids, which result from the pH of bio-oil (2–3).. Corrosiveness is elevated at high temperature and also with the increase in water content of bio-oil. Storage tanks for bio-oil can be made up of polyolefins as they are more resistant to corrosion than steel (Czernik and Bridgwater 2004).

Combustion behavior: Bio-oil is combustible but not flammable. Due to the abundance of non-volatile components, bio-oil requires significant energy for

ignition. But once ignited, it burns with a stable self-sustaining flame (Czernik and Bridgwater 2004). Cetane number is a parameter that determine the ignition quality. A high cetane number reduces ignition delay before combustion. However, the cetane number of bio-oil is difficult to measure which is very low (close to 5) due to the absence of straight hydrocarbons (Ikura et al. 2003).

Flash Point and Pour Point: The flash point is the lowest temperature where enough fluid can evaporate to form a combustible gas. Fuels with higher flash point are less flammable or hazardous. However, this property does not contribute to the performance of oil in engines. The pour point of a fuel is an indication of the lowest temperature, at which fuel starts flowing. The pour point of bio-oil is varies from −12 to −36 °C which depends on the biomass feedstock (Oasmaa and Peacocke 2001). Therefore, the low pour point indicates the low viscosity bio-oil is obtained.

5.3 Standards and Norms

ASTM D7544 -12 is the standard specification covers grades of pyrolysis liquid biofuel produced from biomass. These grades can divide into Grade G and Grade D. Grade G is for the use in industrial burners and Grade D is for use in commercial or industrial burners requiring lower solids and ash content. Table 2 summarizes requirements for pyrolysis liquid biofuels. However, these grades are not intended for use in residential heaters, small commercial boilers, engines or marine applications (Oasmaa et al. 2015).

Recently, CAS number 1207435-39-9 has been issued for fast pyrolysis bio-oil. In order to transport bio-oil, it is classified as Class-8 (corrosive) substances, however no UN number has been assigned for transportation (Oasmaa et al. 2015).

Table 2 ASTM standard for bio-oil (ASTMD7544 2012)

Property	Test Method	Grade G	Grade D
Gross heat of combustion, MJ/kg, min	D240	15	15
Water content, % mass, max	E203	30	30
Pyrolysis solids content, % mass, max	D7579	2.5	2.5
Kinematic viscosity at 40 °C mm^2/s, max	D455[A]	125	125
Density at 20 °C kg/dm^3	D4052	1.1–1.3	1.1–1.3
Sulphur content, % mass, max	D4294	0.05	0.05
Ash content, % mass, max	D482	0.25	0.15
pH	E70	Report	Report
Flash point, °C min	D93, Procedure B	45	45
Pour point, °C max	D97	-9	-9

A—without filtering

5.4 Applications

Bio-oil has several advantages and disadvantages in terms of applications. Bio-oil is a renewable carbon-based liquid that is derived from agricultural wastes, animal manure, forest residue, sludge, or any type of volatile feedstocks. Bio-oil can be readily stored, transported and used for production of value-added bio-products, such as chemicals. The significant disadvantage of bio-oil as a fuel is the acidity, high viscosity and high oxygen content. High acidity tends to corrode most steel and aluminium storage tanks, fuel lines and engine parts. Due to the high viscosity and high flash (40–100 °C), the heavy pyrolysis oil is not auto-igniting. Though bio-oil heating value is low as compared to conventional liquid fuels, it has higher energy density for higher efficiency energy production. Besides, bio-oil will be possessed with alkali metals (ash content), which cause the incomplete solid separation. These metals might cause the catalyst poisoning, slag formation, deposition of solids in combustion, erosion and corrosion (Bridgwater 2012a, b). The potential applications for bio-oil are as follows:

Furnaces and Boilers: Bio-oil has been tested in furnaces and boilers, for heat and power generation although at a presently unacceptable energetic and financial cost. Bio-oil has similar characteristics to light fuel, although significant differences in energy content, viscosity, pH, emission levels and ignition are observed. One of the difficulties with bio-oil is that different bio-oils show different combustion characteristic. The Red Arrow Products pyrolysis plant in Wisconsin uses bio-oil to generate heat (Freel et al. 1996).

Diesel Engines: The main concerns for operating diesel engines on bio-oils are the difficult in ignition due to high water content and low heating value, corrosiveness and thermally unstable compounds which cause coking. The most identified problems are fuel pumping, high CO emissions, wear and corrosion of lining, wax formation, poor atomization, and injector coking (Chiaramonti et al. 2007). Bio-oil could be efficiently used in pilot-ignited medium-speed diesel engines. Bio-oil emulsified with diesel showed that a stainless steel or similar corrosive resistant material should be used as the material of construction for injector and fuel pump (Chiaramonti et al. 2003a, b). The test at VTT Energy (84 kWe engine) showed that the bio-oil could be efficiently used in pilot-ignited medium-speed diesel engines (Solantausta et al. 1994).

Gasifiers: Gasification of bio-oil can be done to obtain maximum amount of the high-value components such as synthesis gas (syngas). In the Fischer-Tropsch process, the further processing of syngas produced by gasification of bio-oil with pure oxygen may become economically and technically feasible. The production of syngas from the pyrolysis of bio-oil was studied (Panigrahi et al. 2003; Wang et al. 2007). The bio-oil conversion to gas was 83 wt% at 800 °C. The compositions of product gases as the following ranges: syngas:16–36 mol%; CH_4:19–27 mol%; and C_2H_4:21–31 mol%. The heating values of the gas product were 1300–1700 Btu/SCF (standard cubic foot) (Panigrahi et al. 2003).

Chemicals: The chemicals commercially produced from bio-oil are food products such as food flavors and liquid smokes. Some of the fine chemicals extracted from bio-oil are acetic acid, levoglucosan, hydroxyaceladehyde, and levoglucosenone. In addition some other commercial chemicals have been produced from bio-oil such as phenol resins, wood adhesives, slow fertilizers, calcium or magnesium acetate (de-icers), BioLime (to remove sulfur dioxide from flue gas), MNRP (commercial resin), and plasticizers and emulsions (Bridgwater 2012a, b). The aqueous phase of bio-oil has been studied for the production of hydrogen through reforming. Though some aqueous phase reforming (under high pressure) has been conducted, most studies focus on steam reforming (Pan et al. 2012; Trane et al. 2012). Many catalysts have been tested in which Ni, Ru and Rh achieved high performance (Trane et al. 2012). However, carbon deposition on catalyst is still a challenge with bio-oil. Including water-gas shift reactions, bio-oil reforming yield an average of one mole of hydrogen from one mole of carbon in bio-oil.

In addition to the above applications, bio-oil has the potential for other end-use markets. The sticky, resin-like quality of bio-oil can substitute for some petroleum products in asphalt emulsions and so it can be utilized as an asphalt binder. Another potential application of bio-oil is in coal dust suppression. The environmental and physical requirements of bio-oil such as biodegradability, water immiscibility and the strength of its polymerization reactions have to be analyzed in order to coat the coal piles (Farag et al. 2002).

Transportation fuels: Bio-oil can be upgraded as transportation fuel, which is still in research.

5.5 Upgrading

In a nutshell, bio-oil has the potential to be available in large amounts, environmental friendly and competitively priced. Upgrading bio-oil in a cost-effective fashion is essential. In order to improve the fuel quality, bio-oil has to be completely deoxygenated. Hydro-treating and catalytic cracking are the two main processes used to upgrade bio-oil. Recent research and development of technologies that attempt to address this challenge will give bio-oil great promise as a domestically grown, green feedstock for production of fuels and chemicals using the current refining and transportation infrastructure. Bio-oil obtained through pyrolysis can be upgraded through hydrogenation, hydro-deoxygenation, catalytic cracking, molecular distillation, esterification, emulsification, catalytic pyrolysis and the co-pyrolysis of biomass with different material.

Hydro-deoxygenation (HDO) is a method for upgrading bio-oil by removing the oxygen under high pressure of hydrogen with a catalyst such Pt, NiMO or CoMO. Oxygen in the feed is converted into H_2O (Furimsky 2000). The H_2 consumption and severity of the operation required for achieving high HDO conversion depends on the content and type of the oxygen compounds in bio-oil. In order to convert bio-oil to commercial fuels, the first stage is performed under 573 K to remove oxygen

compounds by readily undergo polymerization, this stage is also known as stabilization stage. The phenols which are formed by methoxyphenols, biphenols and ethers in the first stage are removed at about 623 K (Furimsky 2000). The compounds, such as ketones and carboxylic acids have a low HDO reactivity. Therefore, a higher H_2 pressure and a higher temperature are necessary for their conversion to oxygen free products. Most of the HDO studies are done with model compounds. Reaction mechanism and kinetic models have been developed for HDO of many oxygenated compounds (Furimsky 2000; Elliott 2007; Mortensen et al. 2011; Graça et al. 2013). General reaction can be expresses as Eq. 1 (Adhikari et al., 2013).

$$C_xH_yO_z + \left(x + z - \frac{y}{2}\right)H_2 \rightarrow xCH_2 + zH_2O \qquad (1)$$
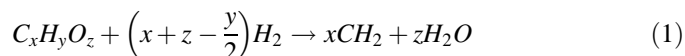
Wildschut et al. (2009) tested novel-metal catalysts (Ru/C, Ru/TiO$_2$, Ru/Al$_2$O$_3$, Pt/C, and Pd/C) and conventional bimetal catalysts (sulfided NiMo/Al$_2$O$_3$ and CoMo/Al$_2$O$_3$) for HDO of bio-oil. Their results showed an inverse relationship between increase in severity of HDO and oxygen content of bio-oil. Ru/C was identified as the most promising catalyst. Hydro-treatment of bio-oil with Ru/C as a catalyst at 350 °C and 200 bar, for 4 h upgraded the HHV of bio-oil from 20 MJ/kg to 43 MJ/kg, pH from 2.5 to 5.8. The upgraded bio-oil had two layers, where top oil had 11 wt% and bottom oil had 5 wt% oxygen content. The results of their study were very promising (Wildschut et al. 2009).

Catalytic cracking is the thermal conversion of bio-oil with the presence of cracking catalysts at a specific temperature higher than 350 °C and atmospheric pressure. Major products from this process are aromatic hydrocarbons. Main catalysts used for cracking are FFC catalysts (HY zeolite) and HZM-5. Catalyst coking is a major challenge in this process. The catalyst can be regenerated by combusting the coke at higher temperature (650–700 °C) (Graça et al. 2013). Comparisons of different acid catalysts such as HZM-5, HY, silicate-alumina have been undertaken (Sharma and Bakhshi 1993; Adjaye and Bakhshi 1995a, b, c; Williams and Horne 1995). Model compounds such as alcohols, acids, furans have been studied for reaction mechanism. Reactivities of each group of compounds towards cracking are different. Moreover, the synergistic effects will be different from individual reactivities (Adjaye and Bakhshi 1995a, b, c; Graça et al. 2013).

Molecular distillation was particularly suitable for bio-oil separation to fractionate as light, medium and heavy fractions. The light fraction mostly contains water and is strongly acidic, with poor stability but good fluidity. The middle fraction is more viscous than the light fraction due to lower water content. The heavy fraction, without volatile substances, was similar to a black solid in appearance and had a relatively higher heating value compared to the raw bio-oil (Wang et al. 2009). By using this method, acidity and water content are removed as light fraction from high heating value compounds. However, the yield is highest in the light fraction, which is the undesirable fraction as it has low or even zero heating value.

Catalytic esterification is considered as a promising method for increasing the pH of bio-oil. Esterification of bio-oil with methanol in the presence of

ion-exchange resins as catalyst has showed a significant decrease in acid number and an increase in heating value (Wang et al. 2010). Li et al. showed that the oxygen containing groups were stabilized due to catalytic esterification (Li et al. 2011). In addition to catalytic esterification, the esterification in presence of supercritical CO_2 gave promising results (Cui et al. 2010).

Emulsification: To promote bio-oil as a combustion fuel. Acidity and viscosity problems can be tolerated, if stable bio-oil in diesel emulsions could be produced (Ikura et al. 2003). Emulsification is suggested to be carried out just after the production of bio-oil through fast pyrolysis. As the diesel percentage increases, the stability of bio-oil increases (Chiaramonti et al. 2003a, b). Crossley et al. have developed a recoverable noble metal catalyst (Pd) on nanotubes which can be used to make stable emulsified bio-oil for downstream processes (Crossley et al. 2010).

Catalytic pyrolysis: Catalysts can be introduced during the pyrolysis so that the cracking occurs simultaneous with pyrolysis. Catalytic pyrolysis is conducted in two ways. One is called *in situ* catalytic pyrolysis in which pyrolytic vapors pass through a catalyst bed where cracking occurs before condensation. The other is in-bed catalytic pyrolysis where the biomass will be mixed with the catalyst resulting in more uniform cracking of pyrolytic vapors (Thangalazhy-Gopakumar et al. 2011; Tan et al. 2013). The Zeolite ZSM-5 catalyst has been widely studied for catalytic pyrolysis. Other molecular sieve catalysts such as Al-MCM-41, Al-MSU-F, β-zeolite, SBA-15, silica-alumina and alumina have also been utilized (Pattiya et al. 2008; Carlson et al. 2010; Zhao et al. 2010). 30–40 wt% carbon from biomass can be recovered as aromatic hydrocarbon from biomass through this process (Carlson et al. 2010; Zhao et al. 2010; Thangalazhy-Gopakumar et al. 2011).

Co-pyrolysis: Recently co-pyrolysis is getting more attention as a method for recycling plastics and as well as improving bio-oil properties (Abnisa and Wan Daud 2014). Different types of materials were used for co-pyrolysis with biomass, such as polystyrene, high density polyethylene, bisphemol A, waste tire, polypropylene and plastic film. When biomass and tires are co-pyrolyzed, the C, O and H can be balanced due to the high C content and low O content in tires. In addition, it is worth highlighting that some physico-chemical properties of the tire pyrolysis liquids are fairly comparable to those found in commercial automotive diesel fuels (Martínez et al. 2014). Through co-pyrolysis with plastic, the oxygen content of the bio-oil can be reduced, resulting in higher hydrogen and carbon content and with a higher heating value (Sajdak and Muzyka 2014). The co-pyrolysis with plastic will increase the yield of the liquid product, which is the most desirable product (Bhattacharya et al. 2009).

6 Bio-char

Bio-char is the carbon-rich solid product from pyrolysis of biomass, which comprises mainly stable aromatic forms of organic carbon (Kim et al. 2012). Bio-char is mostly derived from the lignin part in the case of lingo-cellulosic biomass.

The balance between char, gas and oil products in pyrolysis depends largely upon the rate of heating where slow pyrolysis produces the most amount of char. The characteristics of the char depend on the extent of the pyrolysis (peak temperature), particle size of the feed as well as residence time in the reactor. The vapor residence time for volatiles and gases is also an important factor as longer residence time result in secondary reactions, most notably the reaction of tar on char surfaces and also the charring of tar (Mohan et al. 2006).

Bio-char is widely applied for many environmental applications in addition to energy applications. The high HHV of bio-char makes it a good source to generate energy (Thangalazhy-Gopakumar et al. 2010). Bio-char can be used as a carbon sink, storing large amounts of CO_2 in a stable and fixed form for centuries thus reducing greenhouse gases in the atmosphere.

Bio-char can improve water quality, reduce soil emissions of greenhouse gasses, reduce nutrient leaching, reduce soil acidity as well as reduce irrigation and fertilizer requirements. The complex structure of bio-char helps to attract more bacteria and fungi which are needed by plants to absorb more nutrients from the soil (Ahmad et al. 2014). In addition, bio-char has the ability to attract and retain water, due to the porous structure and high surface area, retaining also nutrients, phosphorus and agro-chemicals. Biochar therefore reduces leaching of fertilizers into surface or groundwater. An approximate 18 % increase in the water holding capacity of soil containing bio-char has been reported (Glaser et al. 2002). Another application of bio-char is as an adsorbent to remove heavy metals from water (Fonts et al. 2012). Recently some studies of fast pyrolysis char have reported the adsorption of metals and tetracycline from aqueous solutions (Liu et al. 2012; Cho et al. 2013). Table 3 provides some examples of metal removal studies of fast pyrolysis bio-char.

7 Current Status

Major industrial examples of conversion of biomass to bio-oil are DynaMotive Energy Systems Corp, Ensyn Technology and BTG Biomass Technology Group BV (BTG), KiOR (Table 4).

Ensyn Techonlogy produce bio-oil in a fast pyrolysis plant from wood biomass. The core technology is Rapid Thermal Processing (RTP), a fast pyrolysis technology for conversion of cellulosic wood feedstock. RTP is analogous to fluid catalytic cracking (FCC), which is a key process in gasoline production. Ensyn is producing RTP liquids with around 75 % yield. Ensyn has been operating for 25 years. Ensyn has a strategic relationship with UOP, a Honeywell company, to develop biorefineries. Current production capacity at the Ontario plant is being increased to 3 million gallon/year. Envergent Technologies LLC (www.envergenttech.com) utilize Honeywell's hydro-processing technology to upgrade RTP bio-oil to high-quality drop-in fuels.

Table 3 Fast pyrolysis bio-char as adsorbent for heavy metals

Feedstock	Adsorbate	Adsorption capacity (mg/g)	Reference
Pinewood	Pb (II)	4.13	Mohan et al. (2007)
	Cd (II)	n/a	
	As (III)	1.2	
Oak wood	Pb (II)	2.62	
	Cd (II)	0.37	
	As (III)	5.85	
Pine bark	Pb (II)	3	
	Cd (II)	0.34	
	As (III)	12.15	
Oak bark	Pb (II)	13.1	
	Cd (II)	5.4	
	As (III)	7.4	
P. terebinthus L.	Cr (VI)	3.97	Deveci and Kar (2013)
Almond shell	Ni (II)	22.22	Kılıç et al. (2013)
	Co (II)	26.95	
Municipal sewage sludge	Cd (II)	42.8	Chen et al. (2015)

Table 4 Bio-oil industries and their projected applications

Company's name	Bio-oil applications (current/R&D)	References
Ensyn technologies	– Food chemicals – Resins	Ensyn corporation. Retrieved from: http://www.ensyn.com/
BTG-BTL	– Heat and power (boilers, gas turbines, diesel engines) – Biobased chemicals	BTG Retrieved from: http://www.btg-btl.com/en
Anellotech	– Bio-aromatics/bio-BTX	Anellotech Inc Retrieved from: http://anellotech.com/

BTG-BTL (a daughter company of BTG) has specialized in the process of conversion of biomass into useful fuels and energy. The reactor used by BTG for fast pyrolysis is a modified Rotating Cyclone Reactor. Char and sand are separated from vapors through cyclones, passed a fluidized bed combustor. Hot sand is recycled back to the reactor. Empyro (a joint project of BTG with Tree Power) announced that the construction of its pyrolysis oil production plant has started at the AkzoNobel site in Hengelo (The Netherlands). The production capacity will then be gradually increased to its maximum of over 20 million liters of pyrolysis oil per year.

DynaMotive Energy Systems Corporation is a Canadian-based renewable energy company, which specializes in fast pyrolysis. Dynamotives' patented fast pyrolysis process involves rapid heating of a biomass feedstock in the absence of oxygen. The yield of the Dynamotive`s pyrolysis is typically 60–75 wt% for bio-oil and 15–20 wt% for bio-char. In order to produce high quality bio-oil, Dynamotive has a pyrolysis upgrading process, which is a two stages process, involving hydro-reforming and hydro-treating. In the hydro-reforming stage, hydrogen is added to the pyrolysis oil in a reactor in the presence of an industrial catalyst. Water, methanol and acetic acid are removed from the pyrolysis oil in this stage. The second stage is hydro-treating, where more hydrogen is added additionally removing remaining oxygen. Current status of Dynamotive is not available.

KiOR Inc. utilize a circulating fluid bed reactor for catalytic pyrolysis of biomass. The condensed bio-oil undergoes hydrotreating. The product can be used as a gasoline/diesel blend. Their technology Biomass Fluid Catalyst Cracking (BFCC) was planned for a commercial scale up to 40 million gallons/year. However, currently KiOR is out of business.

KIT Bioliq, Germany (http://www.bioliq.de/) in cooperation with Lurgi GmbH utilize the Lurgi/Auger reactor for fast pyrolysis. Their product called bioliqSyncrude is atomized in a gasifier for syngas production. PYTEC GmbH Thermochemische Anlagen (http://www.pytecsite.de/) is another company in Germany. PYTEC utilizes an ablative reactor for fast pyrolysis. Their pilot plant (design capacity 6 Mg/d dry mass) include a diesel-based CHP plant for power production (approximately 300 kW/h output) (Meier et al. 2007). Renewable Oil International is another well-known company producing bio-oil using a vacuum pyrolysis reactor (http://www.renewableoil.com). Anellotech Inc is another booming industry; their core process known as Thermo Catalytic Biomass Conversion (Bio-TCAT™) is used to produce chemicals from biomass (http://anellotech.com/). Pyrovc, utilizing vacuum pyrolysis for bio-oil production, has now developed a new vacuum reactors, which encounters heat transfer limitations.

Since the major industries currently practicing fast pyrolysis are located in North America and Europe, global bio-oil production is currently based on wood. In Malaysia and Indonesia, fast pyrolysis studies are based on solid wastes from the palm industry. Currently, Ensyn is constructing their plants in Malaysia for bio-oil production from empty fruit bunch palm biomass, whereas, BTG-BTL has already constructed a plant in Johor Bahru, Malaysia, which is dormant now. Other location for potential industrial applications for fast pyrolysis are Brazil, Cuba and Argentina in South America.

In addition to these major industries many research institutions and universities have built pilot plants, which have feedstock capacities from 10–1000 kg/h. Major institutions/universities in this list are Aston University, UK; University of Western Ontario, Canada; Virginia Tech, USA; University of Science and Technology of China, China; Mississippi State University, USA; USDA-ARS-ERRC USA; RTI international, USA; VTT Ltd., Finland; Iowa State University, USA; NREL USA; CANMET, Canada (Wagenaar et al. 1994). Some examples of different types of feedstock used in laboratory studies of fast pyrolysis around the world are given in Table 5.

Table 5 Laboratory studies of fast pyrolysis around the world

Feedstock	Reactor	Country	Bio-oil yield (wt%)	Bio-char yield (wt%)	Bio-oil HHV (MJ/kg)	Reference
Agriculture waste						
Rice straw	Fluidized bed	Thailand	54.1	~27	28.4	Pattiya and Suttibak (2012)
Rice husk			57.1	~31	25.4	
Sugarcane	Fixed bed	Bangladesh	56.0	33.0	23.5	Islam et al. (2010)
Empty fruit bunch	Fluidized bed	Malaysia	55.1	23.9	36.06	Abdullah et al. (2010)
Cassava rhizome	Fluidized bed	Thailand	64.93	19.97	15.8	Pattiya (2011)
Cassava stalk			61.71	20.91	12.7	
Palm kernel shell	Fluidized bed	Republic of Korea	48.7	~25	17.9	Kim et al. (2010)
Black cumin seed cake	Fixed bed	Turkey	48.21	~26	38.48	Sen et al. (2011)
Corncob	Fluidized bed	China	56.8	23.2	18.8	Zhang et al. (2009)
Jatorpha curcas de-oiled seed cake	Fluidized bed	India	48	35.1	n/a	Biradar et al. (2014)
Forest residue						
Pine wood	Auger reactor	USA	50	26	19.10	Thangalazhy-Gopakumar et al. (2010)
Eucalyptus wood	Fluidized bed	China	~58	~18	16.62	Chang et al. (2013)
Pinewood waste (*Pinus insignis*)	Spouted bed reactor	Spain	75	~17	14.6 (LHV)	Amutio et al. (2012)
Hybrid Poplar Wood	Fluidized bed	USA	63.3	12.7	24.48	Agblevor et al. (2010)
Solid wastes						
Furniture Saw dust	Fluidized bed	Republic of Korea	58.1	~30	n/a	Heo et al. (2010a, b)

(continued)

Table 5 (continued)

Feedstock	Reactor	Country	Bio-oil yield (wt%)	Bio-char yield (wt%)	Bio-oil HHV (MJ/kg)	Reference
Chicken litter	Fluidized bed	USA	23.39	33.85	27.98	Kim et al. (2009)
Turkey litter			26.32	24.49	26.24	
Rubber from tires	Fluidized bed	Germany	27.8	36.7	n/a	Kaminsky et al. (2009)
Rubber from hand gloves			72.2	1.1	n/a	
Algae						
C. vulgaris	Fluidized bed	USA	53	31	24.57	Wang et al. (2013)
C. vulgaris	Fixed bed	USA	52.7	25.7	18.6	Thangalazhy-Gopakumar et al. (2012)
Energy plants						
Switchgrass	Fluidized bed	USA	~43.0	~26	19.6	He et al. (2009)
Switchgrass	Fluidized bed	USA	60		18.445	Mullen et al. (2008)
Alfalfa bud and flower			45		25.852	
Alfalfa stem			53		26.542	
Miscanthus	Fluidized bed	Republic of Korea	69.2	~25	22.5	Heo et al. (2010a, b)
Catalytic pyrolysis						
Wheat spent grains	Fluidized bed (alumina catalyst)	UK	~53.0	~17	22.8	Sanna et al. (2011)
Brewers spent grains			~48.0	~15	24.07	
Corncob	Fluidized bed (HZM-5)	China	39.3	20.1	34.6	Zhang et al. (2009)
Hybrid poplar wood	Fluidized bed (HZM-5)	USA	33	12.6	30.5	Agblevor et al. (2010)

(continued)

Table 5 (continued)

Feedstock	Reactor	Country	Bio-oil yield (wt%)	Bio-char yield (wt%)	Bio-oil HHV (MJ/kg)	Reference
Co-pyrolysis						
50:50::pine wood/polystyrene	Auger	USA	64.9	12.1	28.42	Bhattacharya et al. (2009)
50:50::pine wood/HDPE			338.9	25.9	27.68	
50:50::pine wood/polypropylene			46	32.2	36.94	
50:50::pine cone: PE	Fixed bed	Romania	63.9	19.6	46.33	Brebu et al. (2010)
50:50::pine cone: PP			64.1	19.1	45.58	
50:50::pine cone: PS			69.7	21.5	46.43	
30:40:20:10::pine cone: PE: PP:PS			76	12.7	41.33	
66.6: 33.3::Swine Solid: plastic mulch film	Fixed Bed	USA	45.3	15.7	59	Ro et al. (2014)
80:20::walnut shell: tar sands	Fixed Bed	Turkey	31.84	30.3	27.45	Kar (2011)

8 Energy and Economics

Energy requirement for pyrolysis is mainly for drying, grinding, pyrolysis and condensation. Energy will be recovered in terms of the heating content of products, mainly bio-oil and bio-char. Therefore energy efficiency can be written as Eq. 2

$$\eta_{energy} = \frac{E_{Bio-oil} + E_{Bio-char}}{E_{Biomass} + E_{process}} \qquad (2)$$

where $E_{Bio-oil}$, $E_{Bio-char}$, and $E_{Biomass}$ are the energy contents of bio-oil, bio-char and biomass respectively and $E_{Process}$ is the external energy required for the complete pyrolysis process from biomass pre-treatments to product collection (Jahirul et al. 2012). Energy recovery studies on three hardwoods by Stals et al. showed that 34–39 % energy can be recovered through a fast pyrolysis process (Stals et al. 2010). Daugaard and Brown found that the average enthalpy for fast pyrolysis for biomass having 8–10 wt% moisture content is about 1.5 MJ/kg (Daugaard and Brown 2003). Life cycle analysis by Steele et al. proved near carbon neutrality for bio-oil production. According to their study, for the production of bio-oil, based on 2000 dry tons/day input feed, 0.52 MJ/MJ energy was required for the complete process (from cradle to grave) whereas residual fuel oil required 1.2 MJ/MJ. The overall energy use for bio-oil was negative. A 70 % reduction in potential global warming emission was calculated for bio-oil as compared to residual fuel oil and it was 0.0323 kg CO_2 eq per MJ bio-oil production (Steele et al. 2012).

Reinger et al. conducted a detailed economic analysis to evaluate the capital and operating costs of a biomass fast pyrolysis plant with a capacity of 550 dry tonnes/day of wood chips (Ringer et al. 2006). In the design basis, there are five major processing areas; feed handling and drying, pyrolysis, char combustion, product recovery, and steam generation. The total capital investment of the project was estimated to be $48.29 million and a total operating cost of around $9.6 million. Feedstock accounted for the largest variable in operating cost. About 61 % of total capital investment ($29.7 million) was equipment and installation costs. The selling value for bio-oil/t was projected to be $7.62/GJ, LHV (Ringer et al. 2006).

The capital cost for a 2000 dry metric tons/day of a hybrid poplar wood chips in another design was $303 million accounting for upgrading of bio-oil to gasoline and diesel fuels (Jones et al. 2009). Similar work was done for 2000 dry tonne per day corn stover fast pyrolysis. Two scenario were considered for upgrading bio-oil to gasoline and diesel range fuels: hydrogen production from bio-oil for upgrading and hydrogen purchase for upgrading. The capital cost for the hydrogen production scenario was $287 million and $200 million for the hydrogen purchase scenario. Therefore the first scenario had higher fuel prices than second scenario (Wright et al. 2010).

9 Conclusions

Fast pyrolysis for the production of liquid fuels is a relatively new biomass conversion method which is emerging commercially. Major attributes of fast pyrolysis are high heat and mass transfer rates and low residence time in the vapor state. A wide range of organic wastes have been investigated as feedstock for fast pyrolysis. The basic principle behind fast pyrolysis feedstock selection is decentralized densification and centralized upgrading. Therefore research on different types of other feedstocks still continue around the world. The selection of this feedstock basically depends on regional abundance.

Many reactor configurations have been tested and developed in order to achieve fast pyrolysis quality attributes during the process. Though each configuration has its own benefits and challenges, none of the reactors is superior to another one. Norms and standards for bio-oil have been established recently. However, bio-oil cannot be used as it is. Even the utilization as a feedstock for energy or chemicals is still underway. Based on the proposed applications of bio-oil, many upgrading techniques are being researched. In addition to upgrading studies, some demonstration of raw bio-oil for CHP application with modified engines are being developed around the world. In a concluding remark, though fast pyrolysis bio-oil has a bright future, it has a long path to general implementation.

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