Bio-oil production through biomass pyrolysis and upgrading research

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■ **ABSTRACT :** Biomass can be utilized to produce bio-oil, a promising alternative energy source for the limited crude oil. Biomass can be converted to bio-fuel via different thermal, biological and physical processes. Among the biomass to energy conversion processes, pyrolysis has attracted more interest in producing liquid fuel. Pyrolysis processes may be conventional or fast pyrolysis, depending on the operating conditions that are used. The heart of a fast pyrolysis process is the reactor and considerable research development has focused on reactor types. Different types of reactor are used for bio oil production such as fluidized-bed reactor Ablative type, vacuum pyrolysis reactor, rotating cone reactor, auger pyrolysis reactor, pyros pyrolysis reactor, plasma reactor, microwave reactor and solar reactor. To improve the bio-oil production from biomass. Scientific and technical developments towards improving bio-oil yield and quality to date are reviewed, with an emphasis on bio-oil upgrading research.

■ **KEY WORDS :** Bio-oil, Biomass, Fast pyrolysis, Pyrolysis reactor, Bio-oil upgrading

The need for energy is increasing sharply due to the rapid increase in the world's population and developing technologies, while the current energy resources with limited reserves are decreasing. Biomass (plant materials) has been recognized as a major world renewable energy source to supplement declining fossil fuel resources. It is composed mainly of carbohydrate compounds which are determined as the elements of carbon, hydrogen and oxygen and posses a high energy content (Kim *et al.,* 2010). Biomass energy is destined to play an important role in the future energy systems of the world.

Biomass can be converted to bio-fuel via different thermal, biological and physical processes. Among the biomass to energy conversion processes, pyrolysis has attracted more interest in producing liquid fuel product because of its advantages in storage, transport and versatility in application such as combustion engines, boilers, turbines, etc. In addition, solid biomass and waste are very difficult and costly to manage which also gives impetus to pyrolysis research. However, it is still at an early stage in development and needs to overcome a number of technical and economic barriers to compete with traditional fossil fuel based techniques (Bridgwater, 2004 and Downie, 2007). The production of bio-liquids and other products (char and gas) by pyrolysis of different biomass species has been extensively investigated in the past. Some of these biomass species include beech wood, bagasse, woody biomass, straws, seedcakes and municipal solid waste (MSW).

What is Bio-oil?

Bio-oil is a kind of liquid fuel made from biomass by-products via thermo-chemical processes (Demirbas, 2005). As one kind of new inexpensive, clean and green bio-energies, bio-oil is considered as an attractive option instead of conventional fuel in the aspect of reducing environmental pollution.

Bio-oil is a free flowing brown colored thick complex mixture of oxygenated compounds produced in the fast pyrolysis process. It has almost 25 per cent water and has a HHV of about 17 MJ/kg. It is immiscible with other conventional petroleum fuels. It provides an opportunity and a challenge for its application as energy source. Bio-oil acts as an excellent energy carrier because of its higher energy intensity. Because of the low bulk density the transportation and storage of biomass is very expensive. Whereas, if the biomass is converted at the site of production in to bio-oil, the density increases to 1250 kg/m^3 which makes it much easier to transport and store and thus, serves as good energy carrier.

Bio-oil is a combustible product but not inflammable. It requires significant energy for initiation of ignition, but once ignited, it burns with self sustaining flame. Due to its burning capabilities it can be used for various thermal and mechanical applications. Upgrading of bio-oil is necessary to make it usable as fuel or feedstock for chemicals. The important properties of bio-oil that adversely affect its application as fuel are high moisture content, high viscosity, high solid content and chemical instability.

Pyrolysis is the thermal degradation of organic matter (biomass) in the absence of oxygen from air. It produces biochar, ash, permanent gases, and volatiles. Cooling and condensation of the volatiles produces bio-oil. The oxy- gen-free medium, usually nitrogen, is important to avoid burning the volatiles and permanent gases, consuming the products. This is the difference between pyrolysis and combustion. When oxygen is present, the volatiles and gases ignite.

Types of pyrolysis :

Pyrolysis processes may be conventional or fast pyrolysis, depending on the operating conditions that are used. Conventional pyrolysis may also be termed slow pyrolysis. The terms "slow pyrolysis" and "fast pyrolysis" are somewhat arbitrary and have no precise definition of the times or heating rates involved in each (Maschio

et al., 1992).

Conventional/slow pyrolysis :

Conventional slow pyrolysis has been applied for thousands of years and has been mainly used for the production of charcoal. In slow wood pyrolysis, biomass is heated to 500°C. The vapor residence time varies from 5 min to 30 min. Vapors do not escape as rapidly as they do in fast pyrolysis. Thus, components in the vapor phase continue to react with each other, as the solid char and any liquid are being formed. The heating rate in conventional pyrolysis is typically much slower than that used in fast pyrolysis. A feedstock can be held at constant temperature or slowly heated. Vapors can be continuously removed as they are formed. Vacuum pyrolysis at slow or fast heating rates is another variant.

Fast pyrolysis :

Fast pyrolysis is a high-temperature process in which biomass is rapidly heated in the absence of oxygen (Bridgwater, 1994). Biomass decomposes to generate vapors, aerosols and some charcoal-like char. After cooling and condensation of the vapors and aerosols, a dark brown mobile liquid is formed that has a heating value that is about half that of conventional fuel oil (*http://www.pyne.co.uk*). Fast pyrolysis processes produce 60-75 wt per cent of liquid bio-oil, 15-25 wt per cent of solid char and 10-20 wt per cent of non-condensable gases, depending on the feedstock used. No waste is generated, because the bio-oil and solid char can each be used as a fuel and the gas can be recycled back into the process.

Fast pyrolysis uses much faster heating rates than traditional pyrolysis. Advanced processes are carefully controlled to give high liquid yields. There are four essential features of a fast pyrolysis process. First, very high heating and heat transfer rates are used, which usually requires a finely ground biomass feed. Second, a carefully controlled pyrolysis reaction temperature is used, often in the 425-500° C range.

Third, short vapor residence times are used (typically <2 s). Fourth, pyrolysis vapors and aerosols are rapidly cooled to give bio-oil. Heating rates of 1000°C/s, or even 10000 °C/s, at temperatures below 650°C have been claimed (Bridgwater, 2003). Rapid heating and rapid quenching produced the intermediate pyrolysis liquid products, which condense before further reactions break

down higher-molecular-weight species into gaseous products. High reaction rates minimize char formation. Under some conditions, no char is formed. (Demirbas, 2005). At higher fast pyrolysis temperatures, the major product is gas. Many researchers have attempted to exploit the complex degradation mechanisms by conducting pyrolysis in unusual environments.

Reactors for fast pyrolysis:

The heart of a fast pyrolysis process is the reactor and considerable research development has focused on reactor types. During the last two decades, several different reactor designs have been explored that meet the rapid heat-transfer requirements. These reactor configurations have been shown to achieve liquid-product yields as high as 70 per cent- 80 per cent, based on the starting dry biomass weight.

Fluidized-bed reactor:

The fluidized-bed reactor consists of a fluid-solid mixture that exhibits fluid like properties. This is generally achieved by the introduction of pressurized fluid through the solid particulate substance. Fluidized-bed reactors appear to be popular for fast pyrolysis as they provide rapid heat transfer, good control for pyrolysis reaction and vapour residence time, extensive high surface area contact between fluid and solid per unit bed volume, good thermal transport inside the system and high relative velocity between the fluid and solid phase (Lv *et al*., 2004). Different types of fluidized-bed reactors are described below.

Bubbling fluidised bed reactor:

Bubbling fluidized-beds are simple to construct and operate. They provide better temperature control, solids-to-gas contact, heat transfer and storage capacity because of the high solids density in the bed. Heated sand is used as the solid phase of the bed which rapidly heats the biomass in a non-oxygen environment, where it is decomposed into char, vapour, gas and aerosols. The fluidizing gas stream conveys the decomposed biomass constituents produced out of the reactor as shown in Fig.1 (Sadaka and Boateng, 2010). After the pyrolytic reaction, the charcoal is removed by a cyclone separator and stored. The remaining vapour is then rapidly cooled with a quenching system, condensed into bio-oil and stored. Bubbling fluidized-bed pyrolysis is very popular

because it produces high quality bio-oil and liquid yield is about 70 per cent–75 per cent weight of the biomass on a dry basis. Char does not accumulate in the fluidized bed, but it is rapidly separated. The residence time of solids and vapour is controlled by the fluidising flow rate. One important feature of bubbling fluidizing bed reactors is that they need small biomass particle sizes (less than 2–3 mm) to achieve high biomass heating rates.
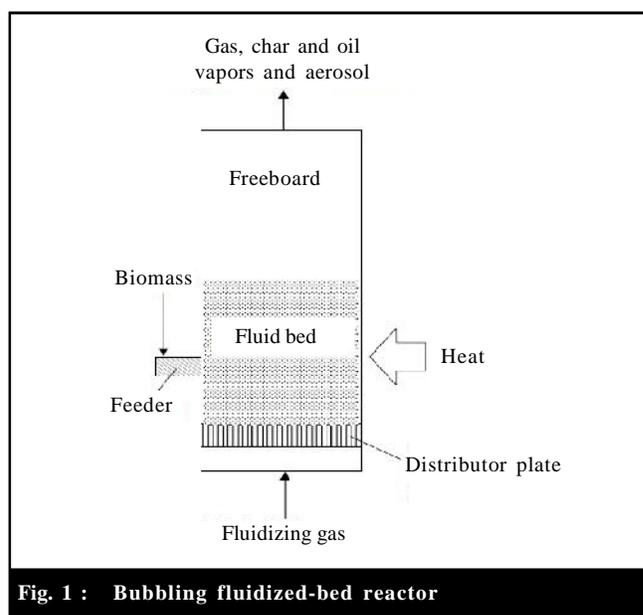
Fig. 1 :   Bubbling fluidized-bed reactor

Circulating fluidized beds and transported bed reactors:

Circulating fluidized bed (CFB) and transported bed reactor systems (Fig. 2) have many of the features of bubbling beds (described above), except that the residence time for the char is almost the same as that for the vapors (*http://www-.pyne.co.uk*). Furthermore, the char is more attrited, because of higher gas velocities. This can lead to higher char contents appearing in the condensed bio-oil.

Although many studies have been reported, only a few (Ambler *et al.*, 1990) are relevant in regard to investigating CFB reactor performance under suitable pyrolysis conditions. Most circulating beds are dilute phase units. Their heat transfer rates are not particularly high, because they are dependent primarily on gas-solid convective transfer. Moreover, if the CFB common twin-bed reactor type is used, with the second vessel employed as a char combustor to reheat the circulating solids, ash
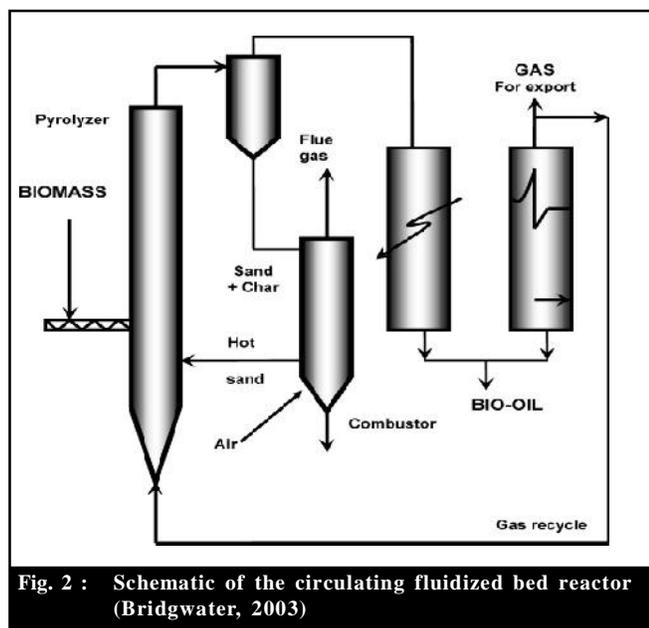
Fig. 2 :   Schematic of the circulating fluidized bed reactor (Bridgwater, 2003)

carryover to the pyrolyzer is possible. This leads to ash buildup in the circulating solids. Biomass ash is known to be a cracking catalyst for the organic molecules in the volatile pyrolysis products. This causes a loss of volatiles from the bio-oil yield. An advantage of CFBs is that they are suitable for very large throughputs, even though the hydrodynamics are more complex. This technology is widely used at very high throughputs in the petroleum and petrochemical industry.

Ablative reactor:

Ablative pyrolysis is fundamentally different from fluid bed processes with the mode of heat transfer being through a molten layer at the hot reactor surface and the absence of a fluidizing gas. Mechanical pressure is used to press biomass against a heated reactor wall. Material in contact with the wall essentially "melts" and, as it is moved away, the residual oil evaporates as pyrolysis vapours (Jones *et al.*, 2009). Advantages of ablative reactors are that feed material does not require excessive grinding and the process allows much larger biomass particle size than other types of pyrolysis reactors. These types of reactor can use particle sizes upto 20 mm in contrast to the 2 mm particle size required for fluidized bed designs.

On the other hand, this configuration is slightly more complex due to mechanical nature of the process. Scaling is a linear function of the heat transfer as this system is

surface area controlled. Therefore, ablative reactors do not benefit from the same economies of scale as the other reactor types (Bridgwater, 2007). The commonly used ablative reactor types are ablative vortex and ablative rotating disk, which are described in the following paragraphs.

Vacuum pyrolysis reactor :

Vacuum reactors perform a slow pyrolysis process with lower heat transfer rates which results in lower bio-oil yields of 35 per cent – 50 per cent compared to the 75 wt per cent reported with the fluidized bed technologies. The pyrolysis process in vacuum reactor is very complicated mechanically and requires high investment and maintenance costs. A moving metal belt conveys biomass into the high temperature vacuum chamber.

On the belt, biomasses are periodically stirred by a mechanical agitator. A burner and an induction heater are used with molten salts as a heat carrier to heat the biomass (Roy *et al.,*1997) Because of operating in a vacuum, these types of pyrolysis reactors require special solids feeding and discharging devices to maintain a good seal at all times. The main benefit of vacuum reactors is that they can process larger sized biomass particles (upto 2–5 cm) than fluidized bed reactors.

Rotating cone reactor:

Intense mixing of biomass and hot inert particles is the most effective way to transfer heat to biomass in the pyrolysis process. However, fluidised bed mixing requires too much ineffective inert gas. In the rotating cone reactor the pyrolysis reaction takes place upon mechanical mixing of biomass and hot sand, instead of using inert gas.

The biomass feedstock and sand are introduced at the base of the cone while spinning causes centrifugal force to move the solids upward to the lip of the cone. As the solids spill over the lip of the cone, pyrolysis vapours are directed to a condenser. The char and sand are sent to a combustor where the sand gets re-heated before again being introduced at the base of the cone with the fresh biomass feedstock. Although the design of the rotating cone reactor is complex, it demonstrates high bio-oil yield (Bramer and Holthuis, 2005). Two million tons per day plant operating on palm oil empty fruit bunches was commissioned in Malaysia in 2006 (Jones

et al., 2009).

Auger reactor:

In this type of reactor, augers are used to move biomass feedstock through an oxygen free cylindrical heated tube. A passage through the tube raises the feedstock to the desired pyrolysis temperature ranging from 400°C to 800°C which causes it to devolatilize and gasify. Char is produced and gases are condensed as bio-oil, with non-condensable vapour collected as bio-gas. In this design the vapour residence time can be modified by changing the heated zone through which vapour passes prior to entering the condenser train (Mohan *et al., 2006*).

PyRos reactor:

PyRos pyrolysis is implemented in a cyclonic reactor with an integrated hot gas filter (the rotational particle separator) in one unit to produce particle free bio-oil. The biomass and the inert heat carrier are introduced as particles into the cyclone and the solids are transported by recycled vapours from the process.

By centrifugal force the particles are moved downwards to the periphery of the cyclone. During the transport downwards in the reactor, the biomass particles are dried, heated up and devolatilized. The average process temperature is 450 °C–550 °C. The typical gas residence time in the reactor is 0.5 to 1 s, so secondary cracking reactions of tars in the reactor can be reduced. Evolved vapours are transported rapidly to the centre of the cyclone and leave the cyclone via the rotating filter. The remaining gases and char can be used to heat up the heat carrier and transportation gas. This reactor is comparatively compact and low cost, with 70 per cent–75 per cent bio-oil yield capability (Bramer and Halthuis, 2005).

Plasma reactor:

The plasma pyrolysis reactors are usually made with a cylindrical quartz tube surrounded by two copper electrodes. Biomass particles are fed at the middle of the tube using a variable-speed screw feeder located on the top of the tube. Electrodes are coupled with electrical power sources to produce thermal energy to gas flows through the tube. Oxygen is removed by an inert gas incorporated in the reactor. This inert gas also serves as working gas to produce plasma. The pyrolysis product vapours are evacuated from the reactor by means of a variable speed vacuum pump (Tang and Huang, 2005) Although consuming high electrical power and having high operating costs, plasma reactors offer some unique advantages in biomass pyrolysis compared with conventional reactors. The high energy density and temperature produced in plasma pyrolysis corresponds with a fast reaction which provides a potential solution for the problems that occur in slow pyrolysis such as the generation of heavy tarry compounds and low productivity of syngas (Yaman, 2004 and Chen *et al.*, 2003). In this type of reactor, tar formation is eliminated due to the cracking effects of the highly active plasma environment with a variety electron, ion, atom and activated molecule species (Tang and Huang, 2005). However, a significant proportion of heat from the thermal plasma is released to the surrounding environment by means of radiation and conduction.

Upgrading and separation:

As a renewable energy source, biomass can be convent to bio-oil and has some advantages compared with conventional fossil fuel. Unfortunately, the application range for such oils is limited because of the high acidity (pH~2.5), high viscosity, low volatility, corrosiveness, immiscibility with fossil fuels, thermal instability, tendency to polymerise under exposure to air and the presence of oxygen in a variety of chemical functionalities (Gandarias *et al.*, 2008; Wildschut *et al.*, 2009 and Zhang *et al.*, 2007). Hence, upgrading and separation of the oils is required for most applications. The recent upgrading techniques are described as follows.

Catalytic hydrogenation:

The catalytic hydrogenation is performed in hydrogen providing solvents activated by the catalysts of Co-Mo, Ni-Mo and their oxides or loaded on Al_2O_3 under pressurized conditions of hydrogen and/or CO. For catalytic hydrogenation, it's important to select a catalyst with higher activity. There's actually been studies show that the Ni-Mo catalyst presented a higher activity than the Ni-W catalyst for the phenol HDO reactions in all the temperature (Gandarias *et al.*, 2008). Moreover, Senol et al. investigated the elimination of oxygen from carboxylic groups with model compounds in order to understand the reaction mechanism of oxygen-containing

functional groups, and obtained three primary paths of producing hydrocarbons through aliphatic methyl esters (Senol *et al.*, 2005).

In order to improve the properties of pyrolysis liquids and achieve higher liquid yield, A two-stage hydrotreatment process was proposed (Elliott, 2007 and Furimsky, 2000). The first stage is to remove the oxygen containing compounds which readily undergo polymerization at high temperature condition. In the second stage, the primary reactants will further convert to other products.

Hydrotreatment is an effective way to convert unsaturated compounds into some more stable ones, but it requires more severe conditions such as higher temperature and hydrogen pressure. Although hydrogenation of bio-oil has made huge progresses, more stable catalysts maybe the largest challenge to make production of the commercial fuels from the bio-oil more attractive.

Catalytic cracking :

Catalytic cracking is that oxygen containing bio-oils are catalytically decomposed to hydrocarbons with the removal of oxygen as H_2O, CO_2 or CO. Guo *et al.* (2003) investigated the catalytic cracking of bio-oil in a tubular fixed-bed reactor with HZSM-5 as catalyst. The results show that the yield of organic distillate is about 45 per cent and that the amount of oxygenated compounds in the bio-oil reduce greatly (Guo *et al.*, 2003). Moreover, seven mesoporous catalysts were compared in converting the pyrolysis vapours of spruce wood for improving bio-oil properties (Adam *et al.*, 2006). The experiment results confirmed the advantageous of catalyst usage, and the Al-SBA-15 catalyst performs more balanced among all the catalysts tested. Catalytic cracking can converting macromolecule oxygenated substances to lighter fractions (Adjaye and Bakhshi, 1995 and Zhang *et al.*, 2005). Furthermore, it is considered as a promising method and has drawn wide attention due to the price advantage.

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