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Destructive distillation of biomass

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Abstract

Energy is considered as a basis for the progress and prosperity of nation's economy. The limited supply of fossil fuels and greenhouse gas emissions affects the environment which reinforced the importance of biomass as an energy source in developed and developing countries. People have led to increase interest in the conversion of biomass into usable products such as fuels. Of the various technologies, thermochemical processing particularly pyrolysis have been identified as process having significant potential for converting biomass into fuels. The features of pyrolysis processes, products and advanced technologies are overviewed in this paper for focusing on the prospects, constraints and necessities for successful implementation in future.

Keywords: Biomass, pyrolysis, pyrolysis reactors.

1. Introduction

Biomass, as the important renewable energy source has attracted an extensive attention in developed and developing countries after the fossil fuel crises from last many years. These energy resources were mainly responsible for country's altitude of development. The conversion of biomass to energy encompasses a wide range of different types and sources of biomass, conversion options and end-user applications. Biomass is a term used for all organic material includes and water-based vegetation, along with all organic wastes and produced through photosynthesis. It also includes animal fats, greases, vegetable oils and packaging wastes (Klass, 1998; Rathore *et al.*, 2009) ^[22, 33]. Food processing wastes, sewage sludge, and the organic components of municipal solid waste (MSW) and pulping by-products (e.g., black liquor) can also be considered biomass (Anonymous, 2006; Anonymous, 2007; Demirbas, 2003) ^[1, 2]. Agricultural residues along with agro-industrial wastes can provide an economical source of renewable energy because of low sulphur fuel.

Biomass has been a chief energy source and at present estimated to contribute 10– 14% of the world's energy supply (McKendry, 2002) ^[27]. It is only one form of renewable energy that can be utilised to reduce the impact on the global environment. There are some limitations on the use and applicability of biomass and it must compete not only with fossil fuels but also with other renewable energy sources such as wind, solar and wave power.

Now a days, the interest should be persistent on new and emerging technologies for efficient conversion rather than the depletion of forests and agricultural resources for energy use. There are a number of sources of energy for both rural and urban residues. There is a need to diversify the traditional resources of energy to meet the demands. By planting high energy value crops and getting energy from municipal sewage and solid wastes we can produce energy efficiently.

Earlier, pyrolysis has been used for the production of charcoal but the fast pyrolysis at moderate temperatures of around 500 °C at residence time of up to 2 s has become of considerable interest. This is because the process directly gives high yields of liquids of up to 75 % by weight, which can be used directly in a variety of applications (Czerniket *et al.*, 2004) or used as an efficient energy carrier. In this paper, an overview on the pyrolysis processes is outlined, with importance on producing fuel for potential use. The energy produced from the biomass can be termed as a renewable energy source.

Pyrolysis

Pyrolysis or destructive distillation is the irreversible chemical change, converts the biomass into a liquid fraction (bio-oil), a solid fraction (charcoal) and a gaseous fraction in the absence of air. Pyrolysis is considered to be a technologically realized process for biomass conversion

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(Anonymous, 2006; Maschio *et al.*, 1992; Marsh *et al.*, 2007; Demirbas, 2001) [1, 26, 25, 17]. The important components of pyrolysis gas are hydrogen, carbon monoxide, carbon dioxide, methane and lesser amount of hydrocarbons. Capturing and combusting the methane and carbon monoxide in syngas makes use of the energy in the gas and produces carbon dioxide which is a less potent greenhouse gas than methane and offsets fossil fuel energy production (Bridgwater, 1996) [12]. Pyrolysis can be used to produce bio-oil if flash pyrolysis is used, the conversion efficiency of biomass to bio-crude up to 80% (Aston University and Teknik, 1993; EU, 1999; Aston University, 1996) [4, 19]. The bio-oil can be used in engines and turbines. Depending on the reaction temperature, heating rate and residence time, pyrolysis can be classified into slow pyrolysis, fast pyrolysis and flash pyrolysis (Table 1).

Slow pyrolysis: Slow pyrolysis, biomass was heated about 500 °C at slow heating rates (up to 10-20 °C/min) in which residence time varies from 5 min to 30 min (Mohan *et al.*, 2006) [30]. Thus, the components in the vapour phase continue to react with each other, as solid char and liquid are being formed. The heating rate in conventional pyrolysis is much slower than fast pyrolysis. The end products formed are charcoal, which have a wide range of application, domestic cooking and heating, activated carbon, fireworks, absorbents, soil conditioners and pharmaceuticals (Karaosmanoglu and Tetik, 1999) [21]. Mok *et al.* (1992) [31] investigated that a higher yield of charcoal can be obtained from biomass feedstock's having higher lignin contents and lower hemicellulose contents. In contrast to fast pyrolysis, slow pyrolysis does not necessarily require fine feedstock particle size (smaller than 1 mm). Torrefaction is also known as roasting, slow and mild pyrolysis (Medic *et al.*, 2011) [28] of biomass at a temperature range 200-300 °C near atmospheric pressure in the absence of oxygen. The biomass partly decomposes during the process giving off volatiles, results in a loss of mass and chemical energy to the gas phase. Biomass consists of three main *polymeric* structures i.e. cellulose, hemicellulose and lignin. Hemicellulose is most reactive and is subjected to limited devolatilisation and carbonisation below 250 °C. Above 250 °C it is subjected to extensive devolatilisation and carbonisation. Cellulose is most thermostable and is subjected to limited devolatilisation and carbonisation only. Lignin its reactive is in between both others.

Fast pyrolysis: Fast pyrolysis is a high-temperature process in which biomass is rapidly heated in the absence of oxygen (Boucher *et al.*, 2000; Bridgwater and Kuester, 1991; Bridgwater, 1996; Bridgwater, 2003) [6, 10, 8, 9]. Biomass decomposes very quickly to generate vapours, aerosol and char. After cooling and condensation of the vapours and aerosol, a dark brown homogeneous mobile liquid is formed which has a heating value about half that of the conventional fuel oil. A high yield of liquid is obtained with low in ash. Fast pyrolysis process produces 60-75% of liquid bio-oil, 15-25% of solid char and 10-20% of non condensable gas by weight, depending on the feedstock used. During this process no waste is generated because the bio-oil and solid char both are used as a fuel and the gas can be recycled back in the process. The essential features of fast pyrolysis process are:

- Very high heating rates and very high heat transfer rates, usually require a finely ground biomass feed of typically less than 3 mm as biomass generally has a low thermal conductivity,

- Carefully controlled pyrolysis reaction temperature of around 500 °C to maximise the liquid yields
- Rapid removal of product char to minimise cracking of vapours,
- Rapid cooling of the pyrolysis vapours to give the bio-oil product.

Rapid heating and rapid quenching produced the liquid products, which condense before further reactions break down of biomass into gaseous products. High reaction rates minimize char formation. Under some conditions, no char is formed (Demirbas, 2005) [16]. At higher fast pyrolysis temperatures, the major product is gas.

Table1: Operating parameters for pyrolysis parameters

Operating parameters	Slow pyrolysis	Fast pyrolysis	Flash pyrolysis
Pyrolysis temperature (°C)	300-700	600-1000	800-1000
Heating rate (°/sec)	0.1-1	10-200	> 1000
Particle size (mm)	5-50	< 1	< 0.2
Solid residence time (sec)	300-550	0.5-10	< 0.5

Flash pyrolysis: Flash pyrolysis is an improved version of fast pyrolysis (Demirbas and Arin, 2002) [18], which involves the rapid movement of substrate through a heated tube under gravity or in a gas flow. Higher temperatures and shorter residence times than fast pyrolysis are used; the main product distributions are similar to fast pyrolysis. Due to the rapid heating rates and short reaction times, for better yields, this process requires smaller particle size compared to the other processes. This process has some technological limitations, poor thermal stability and corrosiveness of the oil, solids in the oil, Increase of the viscosity over time by catalytic action of char, alkali concentrated in the char dissolves in the oil and production of pyrolytic water (Cornelissen *et al.*, 2008) [13].

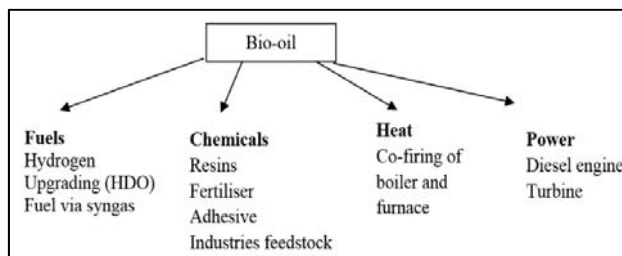
Pyrolysis Products

Char: Char is defined as the solid remains after pyrolysis. It is usually characterized for bulk density, proximate analysis which includes moisture, volatile, ash and fixed carbon contents. Char causes pollution with other components: mineral fractions and after incomplete pyrolysis, large fractions of hydrogen and oxygen, which is present in char. During pyrolysis char is converted into polycyclic aromatic hydrocarbon (PAHs), particularly at low temperature. Char is formed briquettes which can be used as a fuel. Char has a porous structure and a surface area that is appropriate to use as active carbon and used in purification processes (Islam *et al.*, 2005) [20]. The amount and type of pores determine the gas accessibility to the active surface sites. Properties of char are affected not only by properties of parent material but also by pyrolysis operating conditions, mainly the heating rate, the maximum temperature and the residence time.

Pyrolysis liquid: The liquid product obtained from pyrolysis is known as bio-oil. Bio-oil is produced with short residence times and rapid cooling or quenching from the pyrolysis temperature. This condensate is not at thermodynamic equilibrium at storage temperatures. The chemical composition of bio-oil tends to change toward thermodynamic equilibrium during storage. The oils have heating values of 40-50% of that of hydrocarbon fuels (Yaman, 2004) [38]. The problem arises in combustion systems when these liquids are burnt raw without upgrading. Due to very high water content

and this is main disadvantage for ignition. Bio-oil can be used as a substitute for fossil fuels to generate heat, power and chemicals (Fig. 1). These liquids contain many chemical compounds that can be used as feedstock for synthesis of fine chemicals, adhesives, fertilizers and other processes (Meir and Faix, 1999) [29].

Gas: The third main product from pyrolysis is gas. It is also known as syngas. The gas mainly consists of H₂, CO₂, CO and CH₄ depending on the composition of biomass (Oladeji, 2012). CO₂ and CO are produced at low temperature, while H₂ is produced at high temperature. This gas can be used as household cooking gas and as fuel for gas lamps (Bamigboye and Oniya, 2003; Cornelissen *et al.*, 2008) [5, 13].



Various applications of pyrolysis bio-oil

Pyrolysis Reactors

1. Bubbling Fluidized Bed Reactor: Bubbling fluidized beds (Sadaka and Boateng, 2010) [36], biomass particles are introduced into a bed of hot sand fluidized by a recirculated product gas. The high heat transfer rates from fluidized sand cause rapid heating of biomass particles and some ablation by rubbing with the sand particles occurs. In bubbling fluidized bed gasifier proper control of temperature and high reaction rates. They also have higher particulates and more moderate tar levels in product gas tar cracking catalysts can be added to the bed.

2. Circulating Fluidized Bed Reactor: For circulating fluidized bed reactors, biomass particles are introduced into a circulating fluidized bed of hot sand. The recirculated product

gas, sand, and biomass particles move simultaneously. The high heat transfer rates from sand ensure rapid heating of biomass particles and ablation is more popular than with regular fluidized beds. This type of reactor is suitable for large outputs (Li *et al.*, 2004) [24]. They are in-bed catalytic processing and circulation of hot solids can cause erosion problems inside the reactor vessel. The char is attrited more due to higher gas velocities, which result in high char contents. The produced char is typically separated by cyclone.

3. Vacuum Furnace Reactor: For this reactor, biomass is thermally decomposed under reduced pressure. The vapours produced are quickly removed from the vacuum and recovered as bio-oil as condensation. This reactor includes ability to produce larger particles than fast pyrolysis reactors (Roy *et al.*, 1997) [35] and there is less char in the liquid product due to lower gas velocities. There is also no requirement for carrier gas and the process is mechanically complicated. The liquid yields for dry biomass feed obtained in this process vary from 35 to 50%.

4. Ablative Reactor: In ablative reactor there is a high velocity impact of particle on a hot reactor wall which is achieved by centrifugal force. High relative motion is achieved between particles and the reactor wall which is typically less than 600 °C. The system is more intensive and the process is mechanically driven so the reactor is so complex. Ablative reactors do not benefit from the same economies of scale as the other reactor types (Bridgwater, 2007) [11].

5. Rotating Cone Reactor: The rotating cone reactor is a novel reactor type for flash pyrolysis of biomass with negligible char formation, in which rapid heating and a short residence time of the solids can be realized. Carrier gas requirements in the pyrolysis reactor are much less than for fluid bed and transported bed systems. The gas is needed for char burn off and for sand transport. Design of the rotating cone reactor is complex, but results in high bio-oil yield (Wagenaar *et al.*, 2001) [37]. Comparison of pyrolysis reactors are discussed in table 2.

Table 2: Advantages and disadvantages of different pyrolysis reactors (Ringer *et al.*, 2006; Lam *et al.*, 2010) [34, 23]

Reactor type	Advantages	Disadvantages
Bubbling fluidized bed	Simple design Easy operation Good temperature control	Small particle sizes are needed
Circulating fluidized bed	Well-understood technology Good thermal control Large particle sizes can be used	Not suitable for large scale Char is finer
Vacuum furnace	Can process larger particles of 3–5 cm No carrier gas required Lower temperature required Easier liquid product condensation	Slow process Solid residence time is too high Require large scale equipment Poor heat and mass transfer rate Generates more water
Ablative	Inert gas is not required Large particle sizes can be processed System is more intensive Moderate temperature required	Reactor is costly Low reaction rate
Rotating cone	Centrifugal force moves heated sand and biomass No carrier gas required	Complex process Small particle sizes needed

Conclusions

From this review study, it is concluded that the pyrolysis is a thermal decomposition of the organic matter in the absence of oxygen to obtain three major products, which are char, bio-oil and pyrolytic gas. The quantity of three major products of pyrolysis depends mainly on the pyrolysis temperature and heating rate. The pyrolysis at lower temperatures favours the production of char, water, CO₂ and CO whereas at higher

temperatures favours the production of tar. Flash pyrolysis at still high temperatures results in volatile products.

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