

Challenges and Opportunities in Fast Pyrolysis of Biomass: Part I

Introduction to the technology, feedstocks and science behind a promising source of fuels and chemicals

By Tony Bridgwater

Bioenergy Research Group, European
Bioenergy Research Institute, Aston University,
Birmingham B4 7ET, UK

Email: a.v.bridgwater@aston.ac.uk

Fast pyrolysis for liquids has been developed in recent decades as a fast and flexible method to provide high yields of liquid products. An overview of this promising field is given, with a comprehensive introduction as well as a practical guide to those thinking of applying fast pyrolysis liquids (bio-oil) in various applications. It updates the literature with recent developments that have occurred since the reviews cited herein. Part I contains an introduction to the background, science, feedstocks, technology and products available for fast pyrolysis. Part II will detail some of the promising applications as well as pre-treatment and bio-oil upgrading options. The applications include use of bio-oil as an energy carrier, precursor to second generation biofuels, as part of a biorefinery concept and upgrading to fuels and chemicals.

1. Introduction

1.1 Background

Pyrolysis has become of major interest due to the flexibility in operation, versatility of the technology

and adaptability to a wide variety of feedstocks and products. Pyrolysis operates in anaerobic conditions where the constituents of biomass are thermally cracked to gases and vapours which usually undergo secondary reactions thereby giving a broad spectrum of products. There are a number of conditions and circumstances that have a major impact on the products and the process performance. These include feedstock, technology, reaction temperature, additives, catalysts, hot vapour residence time, solids residence time, and pressure.

Pyrolysis has been applied for thousands of years for charcoal and chemicals production but it is only in the last 40 years that fast pyrolysis for liquids has been developed. This operates at moderate temperatures of around 500°C and very short hot vapour residence times of less than 2 seconds. Fast pyrolysis is of considerable interest because this directly gives high yields of liquids of up to 75 wt% which can be used directly in a variety of applications (1) or used as an efficient energy carrier. Intermediate and slow pyrolysis focus on production of solid char as the main product with the liquids and gases usually as byproducts, although increasing attention is being paid to maximising the value of these byproducts. Pyrolysis has also been used for many years to reduce quantities of waste that require disposal as well as making the residues less harmful to the environment. These processes have traditionally employed slow pyrolysis as the core technology.

1.2 Science of Pyrolysis

Pyrolysis is thermal decomposition occurring in the absence of oxygen. Lower process temperatures and longer hot vapour residence times favour the production of charcoal. Higher temperatures and longer hot vapour residence times increase biomass conversion to gas, and moderate temperatures and short hot vapour residence time are optimal for producing liquids. Three products are always produced, but the proportions can be varied over a wide range by adjustment of the process parameters. **Table I** indicates the product distribution obtained from different modes of pyrolysis, showing the considerable flexibility achievable by changing process conditions. Fast pyrolysis for liquids production is currently of particular interest commercially as the liquid can be stored and transported, and used for energy, transport fuels, chemicals or as an energy carrier.

2. Fast Pyrolysis

In fast pyrolysis, biomass decomposes very quickly to generate mostly vapours and aerosols and some charcoal and gas. After cooling and condensation, a dark brown homogenous mobile liquid is formed if wood or a low ash feed is used. The liquid has a heating value about 40% that of conventional fuel

oil on a weight basis or 60% that of fuel oil on a volume basis due to the high density. This liquid is referred to as bio-oil and is the basis of the recent ASTM standard (2). A high yield of liquid is obtained with most low ash biomass of up to 75 wt% on dry biomass feed. The essential features of a fast pyrolysis process for producing liquids are:

- Feed moisture content of less than 10 wt% since all the feed water reports to the liquid phase along with water from the pyrolysis reactions. High water contents in the liquid product can lead to phase separation.
- Very high heating rates and very high heat transfer rates at the biomass particle reaction interface usually require a finely ground biomass feed of typically less than 3 mm as biomass generally has a low thermal conductivity. As fast pyrolysis for liquids occurs in a few seconds or less, heat and mass transfer processes and phase transition phenomena, as well as chemical reaction kinetics, play important roles. The rate of particle heating is usually the rate-limiting step in most fast pyrolysis processes other than ablative pyrolysis where biomass directly contacts the hot reactor surface (3)
- Carefully controlled fast pyrolysis reaction temperature of around 500°C for most biomass maximises the liquid yield. Ash, particularly alkali metals, catalyses secondary reactions

Table I Typical Product Weight Yields from Wood (Dry Feed Basis) by Different Modes of Pyrolysis

Mode	Conditions	Liquid	Solid	Gas
Fast	~500°C Short hot vapour residence time <2 s Short solid residence time up to 10 s	75 wt% (bio-oil)	12 wt% char	13 wt%
Intermediate	~400°C Moderate hot vapour residence time 5–20 s Moderate solid residence time up to 20 minutes	40 wt% in two phases	40 wt% char	20 wt%
Slow pyrolysis (Carbonisation)	~400°C Long hot vapour residence time up to hours depending on technology Long solid residence time depending on technology	30 wt% in two phases	35 wt% char	35 wt%
Gasification (allothermal)	~750–900°C Short hot vapour residence time 5 s Short solid residence time	Minimal	Up to 2 wt% char	Up to 98 wt%
Torrefaction (slow)	~250–300°C Solids residence time up to 30 mins	0 wt% unless vapours are condensed, then up to 15 wt%	70–80 wt% solid	15 wt%

of the pyrolysis vapours to carbon dioxide and water resulting in lower liquid yields with a higher water content. In extreme cases (at ash levels typically above around 2.5 wt%) so much water is formed that phase separation of the liquid occurs. Therefore, short hot vapour residence times are required of typically less than 2 seconds to minimise secondary reactions

- Rapid removal of product char is necessary to minimise catalytic cracking of hot vapours since all the biomass ash is retained by the char. Failure to minimise contact with char results in cracking as above
- Rapid cooling of the pyrolysis vapours to minimise thermal cracking to give the bio-oil product, for similar reasons as for effective char removal. This is usually achieved in a quench system often employing a non-miscible liquid such as a hydrocarbon or cooled product bio-oil.

Several comprehensive reviews of fast pyrolysis for liquids production are available (4–10).

2.1 Feedstocks

Biomass is usually made up of three main components – cellulose, hemicellulose and lignin with water and ash. Cellulose is a polymer of glucose, a six-carbon molecule, which can be thermally and catalytically cracked to monomers and decomposition products. Hemicellulose is a polymer of five-carbon rings that can also be cracked to smaller organic molecules. Lignin is a complex polymer built up of phenolic units that can be cracked to a wide range of phenolic products. Other components of biomass include water at up to 60 wt% in freshly grown biomass; and ash, mostly alkali metals from nutrients, which is catalytically active and causes cracking of organic molecules. This is beneficial in gasification where they help to crack tars, but not beneficial in pyrolysis where they crack the organics in the vapour resulting in lower liquid yields with an adverse effect on liquid properties. The alkali metals that form ash which are essential for nutrient transfer and growth of the biomass are significant in fast pyrolysis. The most active is potassium followed by sodium and calcium. These act by causing secondary cracking of vapours and reducing liquid yield and liquid quality. The vast majority of these alkali metals report to the char which results in the char byproduct acting as a cracking catalyst thus requiring rapid and effective removal of char within the fast pyrolysis process.

Ash can be managed to some extent by selection of crops and harvesting time especially with rhizome crops like *Miscanthus* which senesces over winter with alkali metals returning to the rhizome, however it cannot be eliminated from growing biomass. Ash can be reduced by washing in water or dilute acid and the more extreme the conditions in temperature or concentration respectively, the more complete the ash removal. Recent work has shown that surfactants are the most effective (11). However as washing conditions become more extreme firstly hemicellulose and then cellulose is lost through hydrolysis. This reduces liquid yield and quality. In addition, washed biomass needs to have any acid removed as completely as possible and recovered or disposed of and the wet biomass has to be dried.

So washing is not often considered a viable possibility, unless there are some unusual circumstances such as removal of contaminants. Another consequence of high ash removal is the increased production of levoglucosan and levoglucosenone which can reach levels in bio-oil where recovery becomes an interesting proposition.

2.2 Technology

A conceptual fast pyrolysis process is depicted in **Figure 1** from biomass feed to collection of a liquid product. Each process step has several alternatives such as the reactor and liquid collection but the underlying principles are similar.

At the heart of a fast pyrolysis process is the reactor. Although it probably represents only about 10–15% of the total capital cost of an integrated system, most research and development has focused on developing and testing different reactor configurations on a variety of feedstocks, although increasing attention is now being paid to improvement of liquid collection systems and improvement of liquid quality. The rest of the fast pyrolysis process consists of biomass reception, storage and handling, biomass drying and grinding, product collection, storage and, when relevant, upgrading.

The byproduct char is typically about 15 wt% of the products but about 25% of the energy of the biomass feed. In commercial processes, it is used within the process to provide the process heat requirements by combustion or it can be separated and exported, in which case an alternative fuel is required to provide the heat for pyrolysis. Depending on the reactor configuration and gas velocities, a large part of the char will be of a

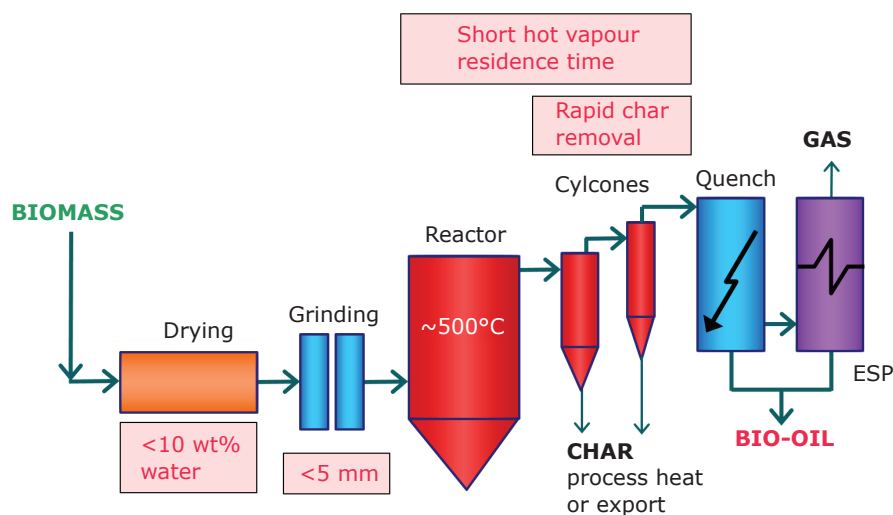


Fig. 1. Conceptual fast pyrolysis process

comparable size and shape as the biomass feed. Fresh char is pyrophoric i.e. it spontaneously combusts when exposed to air so careful handling and storage is required. This property deteriorates with time due to oxidation of active sites on the char surface.

2.2.1 Bubbling Fluid Bed Reactors

Bubbling fluid beds have the advantages of a well understood technology that is simple in construction and operation, has good temperature control and very efficient heat transfer to biomass particles arising from the high solids density. The usual fluidising medium is sand, but increasing attention is paid to catalysts acting as the fluidising medium, but care is needed to manage deactivation of the catalysts. Heating can be achieved in a variety of ways and scaling is well understood. However, heat transfer to the fluid bed at large scales of operation has to be considered carefully because of the scale-up limitations of different methods of heat transfer. Bubbling fluid-bed pyrolysers give good and consistent performance with high liquid yields of typically 70–75 wt% from wood on a dry-feed basis, and for this reason, are widely used for smaller scale or laboratory experiments, such as the pioneering work at the University of Waterloo (12). Small biomass particle sizes of less than 2–3 mm are needed to achieve high biomass heating rates, and the rate of particle heating is usually the rate-limiting step. This technology is ideal for laboratory units due to the ease of operation and control, when heating is usually

achieved by electrical heaters. At a commercial scale Dynamotive built two fluid bed systems in Canada, one of which ran for a few years and has now been dismantled, and the second larger unit is not believed to have been commissioned before dismantling. Heat transfer to the reactor is understood to have been a cause for concern.

Vapour and solid residence time is controlled by the fluidising gas flow rate and is higher for char than for vapours. As char acts as an effective vapour cracking catalyst at fast pyrolysis reaction temperatures, rapid and effective char separation is important. This is usually achieved by ejection and entrainment followed by separation in one or more cyclones so careful design of sand and biomass/char hydrodynamics is important. The high level of inert gases arising from the high permanent gas flows required for fluidisation result in very low partial pressure for the condensable vapours and thus care is needed to design and operate efficient heat exchange and liquid collection systems. In addition the large inert gas flowrates result in relatively large equipment thus increasing cost. Liquid collection is either by indirect heat exchange or quenching in recycled bio-oil or an immiscible hydrocarbon such as Isopar – a proprietary mix of isoparaffins with a high boiling point to minimise evaporation and produce a high flash point.

Aerosols are a significant part of the liquid yield and are collected either by electrostatic precipitation or coalescence on demisters. These are incompletely depolymerised lignin fragments which seem to exist as a liquid with a substantial molecular weight. Evidence of their liquid basis is found in the

accumulation of liquid in the ESP which runs down the plates to accumulate in the bio-oil product. Demisters for agglomeration or coalescence of the aerosols have been used but published experience suggest that this is less effective.

2.2.2 Circulating Fluid Beds and Transported Beds Reactors

Circulating fluid bed (CFB) such as Empyro and transported bed reactor systems such as Ensyn have many of the features of bubbling beds described above, except that the residence time of the char is almost the same as for vapours and gas, and the char is more attrited due to the higher gas velocities. This can lead to higher char contents in the collected bio-oil unless more extensive char removal is included. An added advantage is that CFBs are potentially suitable for larger throughputs even though the hydrodynamics are more complex, as this technology is widely used at very high throughputs in the petroleum and petrochemical industry.

Heat supply is usually from recirculation of heated sand from a secondary char combustor, which can be either a bubbling or circulating fluid bed. In this respect the process is similar to a twin fluid-bed gasifier except that the reactor (pyrolyser) temperature is much lower and the closely integrated char combustion in a second reactor requires careful control to ensure that the temperature, heat flux and solids flow match the process and feed requirements. Heat transfer is a mixture of conduction and convection in the riser. One of the unproven areas is scale up and heat transfer at high throughputs.

All the char is burned in the secondary reactor to re-heat the circulating sand, so there is no char available for export unless an alternative heating source is used. If separated the char would be a fine powder that would require careful handling due to its pyrophoric nature.

2.2.3 Ablative Pyrolysis

Ablative pyrolysis is substantially different in concept compared with other methods of fast pyrolysis (13). In all the other methods, the rate of reaction is limited by the rate of heat transfer through the biomass particles, which is why small particles are required. The mode of reaction in ablative pyrolysis is like melting butter in a frying pan: the rate of melting can be significantly enhanced by pressing the butter down and moving it over the heated pan

surface. In ablative pyrolysis, heat is transferred from the hot reactor wall to 'melt' wood that is in contact with it under pressure. As the wood is moved away, the molten layer then vaporises to a product very similar to that derived from fluid bed systems. Some of the extensive fundamental work was carried out in Nancy, France (14) and this concept was scaled to laboratory processing (15).

The pyrolysis front thus moves unidirectionally through the biomass particle. As the wood is mechanically moved away, the residual oil film both provides lubrication for successive biomass particles and also rapidly evaporates to give pyrolysis vapours for collection in the same way as other processes. There is an element of cracking on the hot surface from the char that is also deposited. The rate of reaction is strongly influenced by pressure of the wood onto the heated surface; the relative velocity of the wood and the heat exchange surface; and the reactor surface temperature. The key features of ablative pyrolysis are therefore as follows:

- High pressure of particle on hot reactor wall, achieved by centrifugal force or mechanically
- High relative motion between particle and reactor wall
- Reactor wall temperature less than 600°C.

As reaction rates are not limited by heat transfer through the biomass particles, larger particles can be used and in principle there is no upper limit to the size that can be processed. The process, in fact, is limited by the rate of heat supply to the reactor rather than the rate of heat absorption by the pyrolysing biomass, as in other reactors. There is no requirement for inert gas, so the processing equipment is smaller and the reaction system is thus more intensive. In addition the absence of fluidising gas substantially increases the partial pressure of the condensable vapours leading to more efficient collection and smaller equipment. However, the process is surface-area-controlled so scaling is less effective and the reactor is mechanically driven, and is thus more complex. The char is a fine powder which can be separated by cyclones and hot vapour filters as for fluid bed reaction systems.

2.2.4 Screw and Augur Kiln Reactors

There have been a number of developments that mechanically move biomass through a hot reactor rather than using fluids, including screw and augur reactors. Heating can be with recycled hot sand as at the Bioliq plant at Karlsruhe Institute of

Technology (KIT), Germany, (Forschungszentrum Karlsruhe (FZK) until 2009) (16), or with heat carriers such as steel or ceramic balls as in Haloclean, also at KIT (17), or external heating. The nature of mechanically driven reactors is that very short residence times comparable to fluid and circulating fluid beds are difficult to achieve, and hot vapour residence times can range from 5 to 30 seconds depending on the design and size of reactor. Examples include screw reactors and more recently the Lurgi LR reactor at KIT (10, 11) and the Bio-oil International reactors which have been studied at Mississippi State University, USA (18).

Screw reactors are particularly suitable for feed materials that are difficult to handle or feed, or are heterogeneous. The liquid product yield is lower than fluid beds and is usually phase separated due to the longer residence times and contact with byproduct char. Also the char yields are higher. KIT has promoted and tested the concept of producing a slurry of the char with the liquid to maximise liquid yield in terms of energy efficiency (19), but this would require an alternative energy source to provide heat for the process.

2.2.5 Microwave Pyrolysis

There is growing interest in microwave pyrolysis as a more direct way of heating biomass quickly (20, 21). This offers the advantage of avoiding or reducing the low thermal conductivity of biomass encountered in conventional thermal pyrolysis, but requires premium energy to drive the process and needs careful design to overcome the potentially poor penetration of microwaves through organic material. The uniform heating resulting from use of microwaves is likely to reduce secondary reactions as reaction products are less likely to interact with pyrolysed biomass. There are some interesting challenges in scale up and comparisons of products between microwave and conventional fast pyrolysis will be interesting.

2.2.6 Heat Transfer in Fast Pyrolysis

There are a number of technical challenges facing the development of fast pyrolysis, of which the most significant is heat transfer to the reactor. Pyrolysis is an endothermic process, requiring a substantial heat input to raise the biomass to reaction temperature, although the heat of reaction is insignificant. Heat transfer in commercial reactors is a significant design feature and the energy in the byproduct charcoal would typically be used in a commercial

process by combustion of the char in air. Typically the char contains about 25% of the energy of the feedstock, and about 75% of this energy is required to drive the process. The byproduct gas only contains about 5% of the energy in the feed and this is not sufficient for pyrolysis. The main methods of providing the necessary heat are listed below:

- Through heat transfer surfaces located in and/or on suitable positions in the reactor such as in-bed heating tubes and/or concentric annular heater around the bed
- By heating the fluidisation gas in the case of a fluid bed or circulating fluid bed reactor, although excessive gas temperatures may be needed to input the necessary heat that could result in local overheating and reduced liquid yield, or alternatively very high gas flows may be needed resulting in unstable fluid dynamics. Partial heating is usually satisfactory and desirable to optimise energy efficiency
- By removing and re-heating the bed material in a separate reactor as used in most CFB and transported bed reactors
- By the addition of some air, although this can create localised hot spots and increase cracking of the liquids to tars
- By use of microwaves (see Section 2.2.5).

There are a variety of ways of providing the process heat from byproduct char or gas or from fresh biomass. This facet of pyrolysis reactor design and optimisation is most important for commercial units and will attract increasing attention as plants become bigger. Examples of options include:

- Combustion of byproduct char, all or part
- Combustion of byproduct gas which normally requires supplementation for example with natural gas
- Combustion of fresh biomass instead of char, particularly where there is a lucrative market for the char
- Gasification of the byproduct char and combustion of the resultant producer gas to provide greater temperature control and avoid alkali metal problems such as slagging in the char combustor
- Use of byproduct gas with similar advantages as above, although there is unlikely to be sufficient energy available in this gas without some supplementation
- Use of bio-oil product
- Use of fossil fuels where these are available at low cost, do not affect any interventions allowable on the process or product, and the byproducts have a sufficiently high value.

2.3 Products

The liquid bio-oil is formed by rapidly quenching and thus 'freezing' the intermediate products of flash degradation of hemicellulose, cellulose and lignin. The liquid thus contains many reactive species, which contribute to its unusual attributes. Bio-oil can be considered a micro-emulsion in which the continuous phase is an aqueous solution of holocellulose decomposition products, that stabilises the discontinuous phase of pyrolytic lignin macro-molecules through mechanisms such as hydrogen bonding. One theory is that a surfactant is formed in fast pyrolysis that creates a stable micro-emulsion with the pyrolytic lignin. Aging or instability is believed to result from a breakdown in this emulsion.

Bio-oil typically is a dark brown, free-flowing liquid and approximates to biomass in elemental composition. Depending on the initial feedstock and the mode of fast pyrolysis, the colour can be almost black through dark red-brown to dark green, being influenced by the presence of micro-carbon in the liquid and chemical composition. Hot vapour filtration gives a more translucent red-brown appearance owing to the absence of char. High nitrogen content can impart a dark green tinge to the liquid.

It is composed of a very complex mixture of oxygenated hydrocarbons with an appreciable proportion of water from both the original moisture and reaction product. Some solid char may also be present. Typical organics yields from different feedstocks and their variation with temperature are shown in **Figure 2** and **Figure 3** shows the temperature dependence of the four main products from a representative feedstock (22). Similar

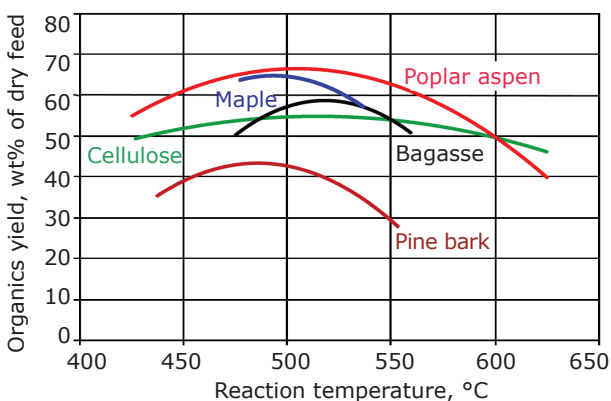


Fig. 2. Variation of organics yield with different feedstocks (3)

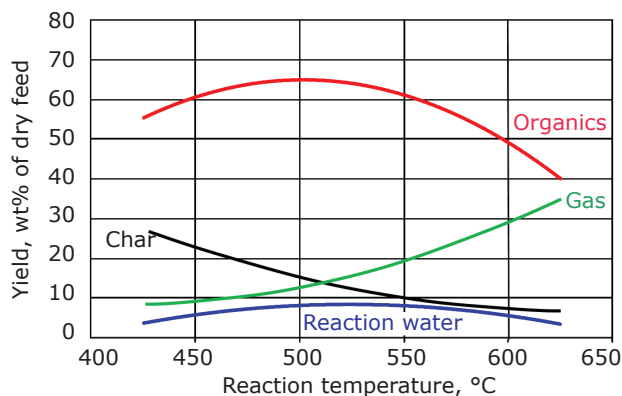


Fig. 3. Typical yields of the major products from fast pyrolysis of biomass (3)

results are obtained for most biomass feedstocks, although the maximum yield can occur between 480°C and 525°C depending on feedstock. Grasses, for example, tend to give maximum liquid yields of around 55–60 wt% on a dry feed basis at the lower end of this temperature range, depending on the ash content of the grass. Liquid yield depends on biomass type, temperature, hot vapour residence time, char separation and biomass ash content, the last two having a catalytic effect on vapour cracking. It is important to note that maximum yield is not the same as maximum quality, and quality needs careful definition if it is to be optimised. Bio-oil quality and quality management and improvement have also been reviewed (23).

The liquid typically contains about 25 wt% water which forms a stable single-phase mixture, but it can range from about 15 wt% to an upper limit of about 30–50 wt% water, depending on the feed material, how it was produced and subsequently collected. Above 50 wt% water (and sometimes lower) the liquid phase separates. A typical feed material specification is a maximum of 10% moisture in the dried feed material, as both this feed moisture and the water of reaction from pyrolysis, typically about 12% based on dry feed, both report to the liquid product. Pyrolysis liquids can tolerate the addition of some water, but there is a limit to the amount of water which can be added to the liquid before phase separation occurs, in other words the liquid cannot be dissolved in water. Water addition reduces viscosity, which is useful; reduces heating value which means that more liquid is required to meet a given duty; and can improve stability. The effect of water is therefore complex and important. Bio-oil is miscible with polar solvents such as methanol, acetone, but

totally immiscible with petroleum-derived fuels. This is due to the high oxygen content of around 35–40 wt%, which is similar to that of biomass, and provides the chemical explanation of many of the characteristics reported. Removal of this oxygen by upgrading requires complex catalytic processes which are described in Part II.

The density of the liquid is very high at around 1200 kg t⁻¹, compared with light fuel oil at around 0.85 kg l⁻¹. This means that the liquid has about 42% of the energy content of fuel oil on a weight basis, but 61% on a volumetric basis. This has implications for the design and specification of equipment such as pumps and atomisers in boilers and engines.

Viscosity is important in many fuel applications (24). The viscosity of the bio-oil as produced can vary from as low as 25 m² s⁻¹ to as high as 1000 m² s⁻¹ (measured at 40°C) or more depending on the feedstock, the water content of the bio-oil, the amount of light ends collected and the extent to which the oil has aged.

Pyrolysis liquids cannot be completely vaporised once they have been recovered from the vapour phase. If the liquid is heated to 100°C or more to try to remove water or distil off lighter fractions, it rapidly reacts and eventually produces a solid residue of around 50 wt% of the original liquid, some distillate containing volatile organic compounds that have been cracked and water. While bio-oil has been successfully stored for several years in normal storage conditions in steel and plastic

drums without any deterioration that would prevent its use in any of the applications tested to date, it does change slowly with time, most noticeably there is a gradual increase in viscosity. More recent samples that have been distributed for testing have shown substantial improvements in consistency and stability, demonstrating the improvement in process design and control as the technology develops.

Ageing is a well known phenomenon caused by continued slow secondary reactions in the liquid which manifests as an increase in viscosity with time. It can be reduced or controlled by the addition of alcohols such as ethanol or methanol. In extreme cases phase separation can occur. It is exacerbated or accelerated by the presence of fine char. This has been reviewed by Diebold (25, 26).

Fast pyrolysis liquid has a higher heating value (HHV) of about 17 MJ kg⁻¹ as produced with about 25 wt% water that cannot readily be separated. While the liquid is widely referred to as 'bio-oil', it will not mix with any hydrocarbon liquids. It is composed of a complex mixture of oxygenated compounds that provide both the potential and challenge for utilisation. There are some important properties of this liquid that are summarised in **Table II** and **Table III**. There are many particular characteristics of bio-oil that require consideration for any application (6). Oasmaa and Peacocke have reviewed physical property characterisation and methods (27, 28).

Table II Typical Properties of Wood-Derived Crude Bio-Oil

Physical property	Typical value
Moisture content	25%
pH	2.5
Specific gravity	1.20
Elemental analysis C	56%
H	6%
O	38%
N	0–0.1%
HHV as produced	17 MJ kg ⁻¹
Viscosity (40°C and 25% water)	40–100 mPa s
Solids (char) which also includes ash	0.1%
Vacuum distillation residue	up to 50%

Table III Characteristics of Bio-Oil		
Characteristic	Cause	Effects
Acidity or low pH	Organic acids from biopolymer degradation	Corrosion of vessels and pipework
Ageing	Continuation of secondary reactions including polymerisation	Slow increase in viscosity from secondary reactions such as condensation Potential phase separation
Alkali metals (ash)	Virtually all alkali metals report to char so this not a big problem High ash feed Incomplete solids separation	Catalyst poisoning Deposition of solids in combustion Erosion and corrosion Slag formation Damage to turbines
Char	Incomplete char separation in process	Ageing of oil Sedimentation Filter blockage Catalyst blockage Engine injector blockage Alkali metal poisoning
Chlorine	Contaminants in biomass feed	Catalyst poisoning in upgrading
Colour	Cracking of biopolymers and char	Discolouration of some products such as resins
Contamination of feed	Poor harvesting practice	Contaminants notably soil act as catalysts and can increase particulate carry over
Distillability is poor	Reactive mixture of degradation products of biomass	Bio-oil cannot be distilled – maximum 50% typically Liquid begins to react at below 100°C and substantially decomposes above 100°C
High viscosity		Gives high pressure drop increasing equipment cost High pumping cost Poor atomisation
Low H:C ratio	Biomass has low H:C ratio and thermal degradation products replicate this ratio	Upgrading to hydrocarbons is more difficult
Materials incompatibility	Phenolics and aromatics	Destruction of seals and gaskets
Miscibility with hydrocarbons is very low	Highly oxygenated nature of bio-oil	Will not mix with any hydrocarbons so integration into a refinery is more difficult
Nitrogen	Contaminants in biomass feed High nitrogen feed such as proteins in wastes	Unpleasant smell Catalyst poisoning in upgrading NOx in combustion
Oxygen content is very high	Biomass composition has high oxygen so thermal degradation products have high oxygen	Poor stability Non-miscibility with hydrocarbons
Phase separation or inhomogeneity	High feed water High ash in feed Poor char separation in process	Phase separation Partial phase separation Layering Poor mixing Inconsistency in handling, storage and processing
Smell or odour	Aldehydes and other volatile organics, many from hemicellulose	While not toxic, the smell is often objectionable

(Continued)

Characteristic	Cause	Effects
Solids	Particulates from reactor such as sand Particulates from feed contamination Small particles of char	Sedimentation Erosion and corrosion Blockage
Structure	The unique structure is caused by the rapid de-polymerisation and rapid quenching of the vapours and aerosols	Susceptibility to ageing such as viscosity increase and phase separation
Sulfur	Contaminants in biomass feed	Catalyst poisoning in upgrading
Temperature sensitivity	Incomplete or 'frozen' degradation reactions	Irreversible decomposition of liquid into two phases above 100°C Irreversible viscosity increase above around 60°C Potential phase separation above around 60°C
Toxicity	Biopolymer degradation products	Human toxicity is positive but small Ecotoxicity is negligible
Viscosity	Chemical composition of bio-oil gives high viscosity, which tends to increase with time due to ageing	Fairly high and tends to increase with time Greater temperature effect on viscosity change than for hydrocarbons Increasing temperature to lower viscosity requires care due to thermal sensitivity
Water content	Pyrolysis reactions Feed water	Complex effect on viscosity and stability: increased water lowers heating value, density and stability; and raises pH Affects catalysts for example through hydrolysis

2.4 Liquids Collection

The gaseous products from fast pyrolysis consist of aerosols, true vapours and non-condensable gases. These require rapid cooling to minimise secondary reactions and condense the true vapours, while the aerosols require additional coalescence or agglomeration. Simple indirect heat exchange can cause preferential deposition of lignin-derived components leading to liquid fractionation and eventually blockage in pipelines and heat exchangers. Quenching in product bio-oil or in an immiscible hydrocarbon solvent is widely practised.

Orthodox aerosol capture devices such as demisters and other commonly used impingement devices are not reported to be as effective as electrostatic precipitation, which is currently the preferred method at both laboratory and commercial scale units. The vapour product from fluid bed and transported bed reactors has a low

partial pressure of condensable products due to the large volumes of fluidising gas, and this is an important design consideration in liquid collection. This disadvantage is reduced in the rotating cone and ablative reaction systems, both of which exclude inert gas which leads to more compact equipment and lower costs (29).

2.5 Byproducts

Char and gas are byproducts, typically containing about 25% and 5% of the energy in the feed material respectively. The pyrolysis process itself requires about 15% of the energy in the feed, and of the byproducts, only the char has sufficient energy to provide this heat. The heat can be derived by burning char in orthodox reaction system design, which makes the process energy self-sufficient. More advanced configurations could gasify the char to a lower heating value (LHV) gas and then burn the resultant gas more effectively

to provide process heat with the advantage that the alkali metals in the char can be much better controlled. The waste heat from char combustion and any heat from surplus gas or byproduct gas can be used for feed drying and in large installations could be used for export or power generation. An important principle of fast pyrolysis is that a well-designed and well-run process should not produce any emissions other than clean flue gas i.e. CO₂ and water, although they will have to meet local emissions standards and requirements.

2.5.1 Char

Char acts as a vapour cracking catalyst, so rapid and effective separation from the pyrolysis product vapours is essential, although it is not clear to what extent cracking is caused by the alkali metals in the char. Cyclones are the usual method of char removal, however some fines always pass through the cyclones and collect in the liquid product where they accelerate ageing and exacerbate the instability problem which is described below. Some success has been achieved with hot vapour filtration which is analogous to hot gas cleaning in gasification systems (30–33). Problems arise with the sticky nature of fine char and disengagement of the filter cake from the filter.

Pressure filtration of the liquid for substantial removal of particulates (down to <5 µm) can be difficult because of the complex interaction of the char and pyrolytic lignin, which appears to form a gel-like phase that rapidly blocks the filter. Modification of the liquid microstructure by addition of solvents such as methanol or ethanol that solubilise the less soluble constituents can improve this problem and contribute to improvements in liquid stability. However the suitability of this approach depends on the application for the bio-oil.

2.5.2 Gas

The gas contains only a small proportion (around 5%) of the initial energy of the biomass feed and is insufficient to provide all the necessary process heat. The heating value depends on the process technology and the extent to which the off gas is diluted by inert and/or recycle gas.

2.6 Environment, Health and Safety

As bio-oil becomes more widely available, attention will be increasingly placed on environment, health

and safety aspects. A study was completed in 2005 to assess the ecotoxicity and toxicity of 21 bio-oils from most commercial producers of bio-oil around the world in a screening study, with a complete assessment of a representative bio-oil (34). The study includes a comprehensive evaluation of transportation requirements as an update of an earlier study (35) and an assessment of the biodegradability (36). The results are complex and require more comprehensive analysis but the overall conclusion was that bio-oil offers no significant health, environment or safety risks.

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References

1. S. Czernik and A. V. Bridgwater, *Energy Fuels*, 2004, **18**, (2), 590
2. 'Standard Specification for Pyrolysis Liquid Biofuel', ASTM D7544-12, ASTM International, West Conshohocken, Pennsylvania, USA, 2012
3. G. V. C. Peacocke, 'Ablative Pyrolysis of Biomass', PhD Thesis, Aston University, Birmingham, UK, October, 1994
4. A. V. Bridgwater, *Biomass Bioenergy*, 2012, **38**, 68
5. D. Mohan, C. U. Pittman Jr. and P. H. Steele, *Energy Fuels*, 2006, **20**, (3), 848
6. S. R. A. Kersten, X. Wang, W. Prins and W. P. M. van Swaaij, *Ind. Eng. Chem. Res.*, 2005, **44**, (23), 8773
7. A. V. Bridgwater, *Chem. Eng. J.*, 2003, **91**, (2–3), 87
8. A. V. Bridgwater, S. Czernik and J. Piskorz, 'The Status of Biomass Fast Pyrolysis', in "Fast Pyrolysis of Biomass: A Handbook", ed. A. V. Bridgwater, Vol. 2, CPL Press, Newbury, UK, 2002, pp. 1–22
9. A. V. Bridgwater, 'Fast Pyrolysis of Biomass', in "Thermal Biomass Conversion", ed. A. V. Bridgwater, H. Hofbauer and S. van Loo, CPL Press, Newbury, UK, 2009, pp. 37–78
10. R. H. Venderbosch and W. Prins, *Biofuels, Bioprod. Bioref.*, 2010, **4**, (2), 178
11. S. W. Banks and A. V. Bridgwater, 'Catalytic Fast Pyrolysis for Improved Liquid Quality', in "Handbook of Biofuels Production: Processes and Technologies", eds. R. Luque, C. S. K. Lin, K. Wilson and J. Clark, Elsevier Ltd, Duxford, UK, 2016, pp. 391–429

12. J. Piskorz, D. S. Scott, D. Radlein and S. Czernik, 'New Applications of the Waterloo Fast Pyrolysis Process', in "Biomass Thermal Processing", Eds. E. Hogan, J. Robert, G. Grassi and A. V. Bridgwater, CPL Scientific Press, Thatcham, UK, 1992, pp. 64–73
13. J. Diebold and J. Scahill, 'Ablative Pyrolysis of Biomass in Solid-Convective Heat Transfer Environments', in "Fundamentals of Thermochemical Biomass Conversion", eds. R. P. Overend, T. A. Milne and L. K. Mudge, Elsevier Applied Science Publishers Ltd, Essex, UK, 1985, pp. 539–555
14. J. Lédé, *J. Anal. Appl. Pyrolysis*, 2003, **70**, (2), 601
15. G. V. C. Peacocke and A. V. Bridgwater, *Biomass Bioenergy*, 1994, **7**, (1–6), 147
16. C. Pfitzer, N. Dahmen, N. Tröger, F. Weirich, J. Sauer, A. Günther and M. Müller-Hagedorn, *Energy Fuels*, 2016, **30**, (10), 8047
17. A. Hornung, A. Apfelbacher, F. Richter and H. Seifert, 'Thermo-Chemical Conversion of Energy Crops: Haloclean: Intermediate Pyrolysis', 6th International Congress on Valorisation and Recycling of Industrial Waste (VARIREI, 2007), L'Aquila, Italy, 27–28 June, 2007
18. L. Ingram, D. Mohan, M. Bricka, P. Steele, D. Strobel, D. Crocker, B. Mitchell, J. Mohammad, K. Cantrell and C. U. Pittman Jr., *Energy Fuels*, 2008, **22**, (1), 614
19. E. Henrich, N. Dahmen and E. Dinjus, *Biofuels, Bioprod. Bioref.*, 2009, **3**, (1), 28
20. E. T. Kostas, D. Beneroso and J. P. Robinson, *Renew. Sustain. Energy Rev.*, 2017, **77**, 12
21. D. Beneroso, T. Monti, E. T. Kostas and J. Robinson, *Chem. Eng. J.*, 2017, **316**, 481
22. A. J. Toft, 'A Comparison of Integrated Biomass to Electricity Systems', PhD Thesis, Aston University, Birmingham, UK, 1996
23. A. V. Bridgwater, 'Upgrading Fast Pyrolysis Liquids', in "Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power", ed. R. C. Brown, John Wiley & Sons Ltd, Chichester, UK, 2011
24. J. P. Diebold, T. A. Milne, S. Czernik, A. Oasmaa, A. V. Bridgwater, A. Cuevas, S. Gust, D. Huffman and J. Piskorz, 'Proposed Specifications for Various Grades of Pyrolysis Oils', in "Developments in Thermochemical Biomass Conversion", eds. A. V. Bridgwater and D. G. B. Boocock, Vol. 1, Springer Science+Business Media, Dordrecht, The Netherlands, 1997, pp. 433–447
25. J. P. Diebold and S. Czernik, *Energy Fuels*, 1997, **11**, (5), 1081
26. J. P. Diebold, 'A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils', in "Fast Pyrolysis of Biomass: A Handbook", ed. A. V. Bridgwater, Vol. 2, CPL Press, Newbury, UK, 2002, pp. 243–292
27. A. Oasmaa and C. Peacocke, "A Guide to Physical Property Characterisation of Biomass-Derived Fast Pyrolysis Liquids", VTT Publications 450, Valtion teknillinen tutkimuskeskus (VTT), Espoo, Finland, 2001, 102 pp
28. A. Oasmaa and C. Peacocke, "Properties and Fuel Use of Biomass-Derived Fast Pyrolysis Liquids: A Guide", VTT Publications 731, VTT, Espoo, Finland, 2010, 134 pp
29. G. V. C. Peacocke, A. V. Bridgwater and J. G. Brammer, 'Techno-Economic Assessment of Power Production from the Wellman Process Engineering and BTG Fast Pyrolysis Processes', in "Science in Thermal and Chemical Conversion", eds. A. V. Bridgwater and D. G. B. Boocock, CPL Press, Newbury, UK, 2004, pp. 1785–1802
30. J. P. Diebold, J. W. Scahill, S. Czernik, S. D. Philips and C. J. Feik, 'Progress in the Production of Hot-Gas Filtered Biocrude Oil at NREL', in "Bio-Oil Production and Utilisation", eds. A. V. Bridgwater and E. N. Hogan, CPL Press, Newbury, UK, 1996, pp. 66–81
31. E. Hoekstra, K. J. A. Hogendoorn, X. Wang, R. J. M. Westerhof, S. R. A. Kersten, W. P. M. van Swaaij and M. J. Groenveld, *Ind. Eng. Chem. Res.*, 2009, **48**, (10), 4744
32. S. Vivarelli and G. Tondi, 'Pyrolysis Oil: An Innovative Liquid Biofuel for Heating the COMBIO Project', International Workshop: Bioenergy for a Sustainable Development, Casino Viña del Mar, Chile, 8th–9th November, 2004
33. J. Sitzmann and A. V. Bridgwater, 'Upgrading Fast Pyrolysis Oils by Hot Vapour Filtration', 15th European Energy from Biomass Conference, Berlin, Germany, 7th–11th May, 2007
34. 'Renewable Energy: Moving Towards A Low Carbon Economy', European Commission, Brussels, Belgium: http://ec.europa.eu/energy/renewables/bioenergy/doc/pyrolysis/biotox_publishable_report.pdf (Accessed on 16th February 2011)
35. G. V. C. Peacocke, 'Transport Handling and Storage of Fast Pyrolysis Liquids', in "Fast Pyrolysis of Biomass: A Handbook", ed. A. V. Bridgwater, Vol. 2, CPL Press, Newbury, UK, 2002, pp. 293–338
36. J. Blin, G. Volle, P. Girard, T. Bridgwater and D. Meier, *Fuel*, 2007, **86**, (17–18), 2679
37. A. V. Bridgwater, 'Pyrolysis of Biomass', in "Transformations to Effective Use: Biomass Power for the World" eds. W. van Swaaij, S. Kersten and W. Palz, Vol. 6, Taylor & Francis Group LLC, Boca Raton, USA, 2015, pp. 473–514

The Author



Tony Bridgwater is a professor of chemical engineering at Aston University, Birmingham, UK. He has worked at Aston University for most of his professional career and is currently director of the European Bioenergy Research Institute (EBRI). He has a world-wide research portfolio focusing on fast pyrolysis as a key technology in thermal biomass conversion for power, heat, biofuels and biorefineries. He is a fellow of the Institution of Chemical Engineers and a fellow of the Institute of Energy.
