Chapter 3
Biomass Conversion Technologies: Fast Pyrolysis Liquids from Biomass: Quality and Upgrading

A.V. Bridgwater

Abstract A thorough assessment has been made of the characteristics of bio-oil from fast pyrolysis of biomass. Fast pyrolysis uniquely gives high yields of a homogenous mobile liquid for direct use for heat and power and indirect use for biofuels and green chemicals. An improved understanding of the significance of the different aspects of quality of bio-oil helps to establish standards and key quality requirements which help to define limitations for use. An appreciation of the potential for bio-oil to meet a broad spectrum of applications in renewable energy has led to a significantly increased R&D activity in studying the science and technology of fast pyrolysis with increased emphasis on quality improvement. This increased activity is evident in North America, Europe and Asia with many new entrants as well as expansion of existing activities. The only disappointment is the continued limited industrial development and deployment of fast pyrolysis that are necessary to provide the basic bio-oil raw material for the development and exploitation of applications.

3.1 Introduction to Fast Pyrolysis and Bio-oil

3.1.1 Introduction

Pyrolysis is thermal decomposition occurring in the absence of oxygen. Lower process temperatures and longer vapour residence times favour the production of charcoal; high temperatures and longer residence times increase biomass conversion to gas; and moderate temperatures and short vapour residence time are optimum for producing liquids which is referred to a bio-oil. Three products are always produced, as summarised in Table 3.1, but the proportions can be varied over a

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Table 3.1 Typical product weight yields (dry wood basis) obtained by different modes of pyrolysis of wood

Mode	Conditions	Liquid	Solid	Gas (%)
Fast	~500 °C, short hot vapour residence time ~1 s	75% (bio-oil)	12% char	13
Intermediate	~500 °C, hot vapour residence time ~10–30 s	40% in 2 phases	40% char	20
Slow (carbonisation)	~400 °C, long vapour residence hours → days	30%	35% char	35
Gasification	~700–900 °C	1–5% (tar)	10% char	85
Torrefaction (slow low temperature pyrolysis)	~290 °C, solids residence time ~10–60 min	0% unless condensed, then up to 15%	80% solid	20

wide range by adjustment of the process parameters. Fast pyrolysis for liquids production is of particular interest as high yields of a liquid are obtained which can be stored and transported, and used for energy, chemicals or as an energy carrier (Bridgwater 2011, 2012; Czernik et al. 2004). Fast pyrolysis is the focus of this chapter.

Bio-oil, the main product from fast pyrolysis at temperatures of around 500 °C, is obtained in yields of up to 75 wt% on a dry-feed basis. The by-product char is normally combusted within the process to reheat the fluidising medium, usually sand, so char is not usually a by-product. The gas can also be utilised with in the process, so there are no waste streams other than hot flue gas and ash. Liquid yield and quality depend on many factors, which are described below.

3.2 Fast Pyrolysis Technology

3.2.1 Principles

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, which has a heating value about half that of conventional fuel oil. A high yield of liquid is obtained with most biomass feeds low in ash. The essential features of a fast pyrolysis process for producing liquids are:

- Very high heating rates and very high heat transfer rates at the biomass particle reaction interface. This usually requires 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 yield for most biomass types,

- Short hot vapour residence times of typically less than 2 s to minimise secondary reactions,
- Rapid removal of product char to minimise cracking of vapours,
- Rapid cooling of the pyrolysis vapours to give the bio-oil product.

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 critical issue is to bring the reacting biomass particles to the optimum process temperature and minimise their exposure to the lower temperatures that favour formation of charcoal. One way this objective can be achieved is by using small particles, for example in the fluidised bed processes that are described later. Another possibility is to transfer heat very fast only to the particle surface that contacts the heat source which is used in ablative processes that are also described later.

The main product, bio-oil, is obtained in yields of up to 75 wt% on a dry-feed basis, together with by-product char and gas which can be used within the process to provide the process heat requirements so there are no waste streams other than flue gas and ash. 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.

A fast pyrolysis process includes drying the feed to typically less than 10% water in order to minimise the water in the product liquid oil, grinding the feed to give sufficiently small particles to ensure rapid reaction, fast pyrolysis, rapid and efficient separation of solids (char), and rapid quenching and collection of the liquid product (often referred to as bio-oil).

Virtually any form of biomass or biogenic materials can be considered for fast pyrolysis. While most work has been carried out on wood because of its consistency and comparability between tests, well over 100 different biomass types have been tested by many laboratories, ranging from agricultural wastes, such as straw, olive pits and nut shells to energy crops such as miscanthus and sorghum, forestry wastes such as bark and solid wastes such as sewage sludge and leather wastes.

In all cases, a commercial process comprises three main stages from feed reception to delivery of one or more useful products:

- Feed reception, storage, handling, preparation and pretreatment such as comminution and drying;
- Fast pyrolysis of the prepared biomass to a more usable form of energy in liquid form known as bio-oil;
- Conversion of this primary liquid product by processing, refining or upgrading into a marketable end-product for production of electricity, heat, biofuels and/or chemicals.

3.2.2 Fast Pyrolysis Reactors

At the heart of a fast pyrolysis process is the reactor. Although it probably represents only about 10–15% of the total capital cost of an integrated system, most research and development has focused on developing and testing different reactor configurations on a variety of feedstocks, although increasing attention is now being paid to control and improvement of liquid quality and improvement of liquid collection systems. Several comprehensive reviews of fast pyrolysis processes for liquids production are available such as (Mohan et al. 2006; Kersten et al. 2005; Bridgwater 2003, 2009; Bridgwater et al. 2002a):

3.2.2.1 Bubbling Fluid Beds

All the early work on fluid beds was carried out at the University of Waterloo in Canada, which pioneering the science of fast pyrolysis and established a clear lead in this area for many years (Scott et al. 1985; Scott and Piskorz 1982; Scott 1997). Bubbling fluid beds were selected for further development by several companies, including Dynamotive, who have built a 100 t/d and a 200 t/d plant in Canada; Wellman, who built a 250 kg/h unit (McLellan 2000) in the UK which has not operated; and Fortum who built and extensively tested a 500 kg/h plant in Finland which has now been dismantled (Gust 2002). More recent activities include Ikerlan who are developing a spouted fluid bed in Spain (Fernandez 2010), Metso who are working with UPM and VTT in Finland who have constructed and are operating a 4 MWth unit in Tampere Finland (Lehto et al. 2010) and Anhui University of Science and Technology in China who have overseen the construction of a 10,000 t/y demonstration plants in China (Zhu 2009; Ming-qiang 2006). Many research units have also been built at universities and research institutions around the world, as fluid beds are relatively easy to construct and operate and give good results.

Bubbling fluid beds have the advantages of a well-understood technology that is simple in construction and operation, provides good temperature control and very efficient heat transfer to biomass particles arising from the high solids density. This makes it ideal for laboratory scale research. Figure 3.1 shows a typical configuration with quench to cool and collect condensable vapours and an electrostatic precipitator to collect aerosols. 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. Fluid-bed pyrolysers give good and consistent performance with high liquid yields of typically 70–75 wt% from wood on a dry-feed basis. 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.

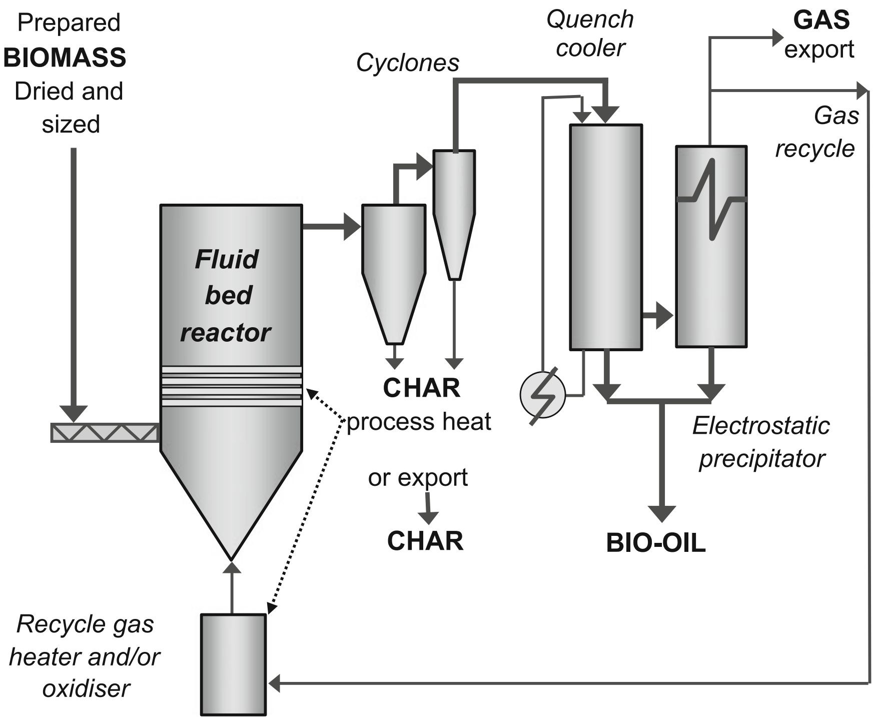

Fig. 3.1 Bubbling fluid bed reactor with electrostatic precipitator

Heating can be achieved in a variety of ways and scaling is well understood. However, heat transfer to fluid beds at large scales of operation has to be considered carefully because of the scale-up limitations of different methods of heat transfer. Dynamotive focused on indirectly heated fluid beds at all scales of processing using natural gas as fuel, although the byproduct char could in principle be used as fuel.

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 pressures 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.

The byproduct char is typically about 15 wt% of the products but about 25% of the energy of the biomass feed. It can be 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. Depending on the reactor configuration and gas velocities, a large part of the char will be of a comparable size and shape as the biomass fed. The 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.

3.2.2.2 Circulating Fluid Beds and Transported Beds

Circulating fluid bed (CFB) and transported bed reactor systems 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. A typical layout is shown in Fig. 3.2. 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.

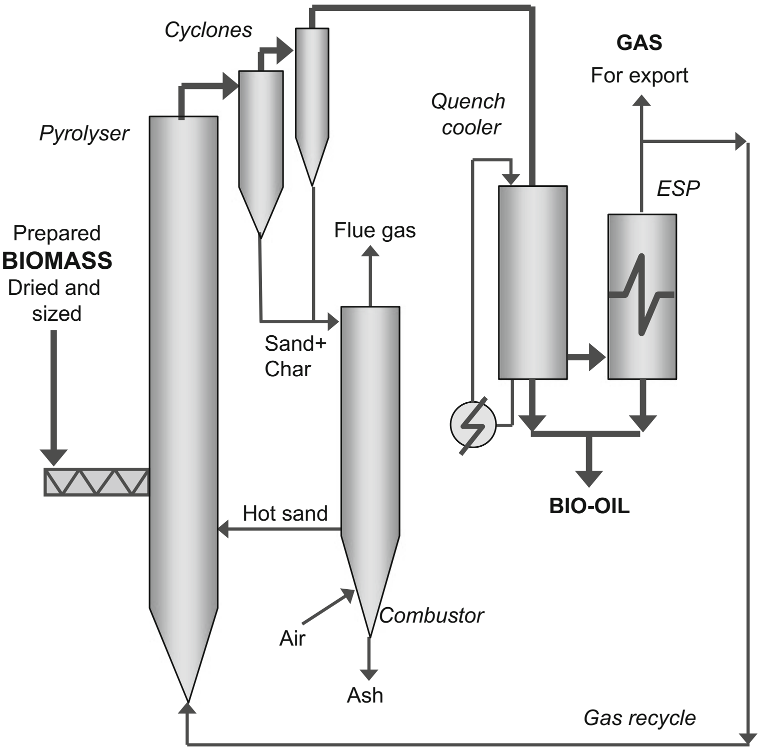

Fig. 3.2 Circulating fluid bed reactor

Heat supply is usually from recirculation of heated sand from a secondary char combustor, which can be either a bubbling or CFB. 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.

Ensyn in Canada has built several units, mostly for production of liquid smoke for the food industry. The company has a significant R&D operation including a 2 t/h unit which also currently produces bio-oil for utilisation in eastern Canada and the USA (Muller 2010). BTG has recently started up their 125 t/d rotating cone technology known as Empyro which is a version of a CFB. This is described below.

The rotating cone reactor, invented at the University of Twente (Prins and Wagenaar 1997) and developed by BTG (Wagenaar et al. 2001), is a relatively recent commercial development and effectively operates as a transported bed reactor, but with transport effected by centrifugal forces in a rotating cone rather than gas. A 250 kg/h unit is now operational, and a scaled up version of 50 t/d was commissioned in Malaysia in mid 2005. A 125 t/d plant was commissioned in 2015 (Muggen 2010). As with CFB and transported beds all the char is burned so is not a by-product.

3.2.2.3 Ablative Pyrolysis

Ablative pyrolysis is substantially different in concept compared with other methods of fast pyrolysis. 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 vapourises to a product very similar to that derived from fluid bed systems.

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.

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.

Much of the pioneering fundamental work on ablative pyrolysis reactors was performed by the CNRS laboratories in Nancy, France, where extensive basic research has been carried out onto the relationships between pressure, motion and temperature (Lédé et al. 1985). The National Renewable Energy Laboratory (NREL) in Boulder, Colorado developed the ablative vortex reactor, in which the biomass was accelerated to supersonic velocities to derive high tangential pressures inside a heated cylinder (Diebold and Power 1988). Unreacted particles were recycled and the vapours and char fines left the reactor axially for collection. Liquid yields of 60–65 wt% on dry-feed basis were typically obtained. Aston University has developed an ablative plate reactor (Peacocke and Bridgwater 1995) in which pressure and motion is derived mechanically, obviating the need for a carrier gas. Liquid yields of 70–75 wt% on dry-feed basis are typically obtained. A second-generation reactor has recently been built and commissioned and has been patented (Bridgwater et al.). Another configuration is the mechanically driven PyTec process in Germany (Meier 2005). The company has built and tested a laboratory unit based on hydraulically feeding wood rods onto a rotating electrically heated cone. The liquid collection system is analogous to other systems described above (Meier 2005). A 6 t/d unit has been built in north Germany in 2006 with the bio-oil fuelling an engine for power generation.

Ablative pyrolysis is an attractive concept that has too many challenging technical issues currently to be a serious commercial prospect.

3.2.2.4 Other Reaction Systems

Entrained flow fast pyrolysis is, in principle, a simple technology, but most developments have not been so successful because of the poor heat transfer between a hot gas and a solid particle. High gas flows are required to affect sufficient heat transfer, which requires large plant sizes and entails difficult liquid collection from the low vapour partial pressure. Liquid yields have usually been lower than fluid bed and CFB systems at 50–55 wt% as in Georgia Tech Research Institute (Kovac and O'Neil 1989) and Egemin (Maniatis et al. 1993) but neither is now operational. There is some basic research in this area in China.

Vacuum pyrolysis, as developed in Canada by the University of Laval and Pyrovac, is arguably not a true fast pyrolysis as the heat transfer rate to and through the solid biomass is much slower than in the previously described reactors although the vapour residence time is comparable. The basic technology was developed at the University of Laval using a multiple hearth furnace but was upscaled to a purpose-designed heated horizontal moving bed (Yang et al. 2001). The process operated at 450 °C and 100 kPa. Liquid yields of 35–50% on dry feed were typically obtained with higher char yields than fast pyrolysis systems. The process was complex and costly because the high vacuum necessitates the use of very large vessels and piping. The advantages of the process are that it can process larger particles than most fast pyrolysis reactors, there is less char in the liquid product because of the lower gas velocities, and no carrier gas is needed. The process has not operated for some years and no activities are currently known using vacuum pyrolysis.

There have been a number of developments that mechanically move biomass through a hot reactor rather than using fluids. These include screw and augur kilns. Heating can by external heating or with recycled hot sand as at the Bioliq plant at KIT (FZK until 2009) (Raffelt et al. 2006a), or with heat carriers such as steel or ceramic balls. The nature of mechanically driven reactors is that very short residence times comparable to fluid and CFBs are difficult to achieve, and hot vapour residence times can range from 5 to 30 s depending on the design and size of reactor. Examples include the Lurgi LR reactor at Karlsruhe Institute of Technology (KIT) (Ingram et al. 2008) and the Bio-oil International reactors which have been studied at Mississippi State University (Ingram et al. 2008). Screw and augur reactors have also been developed as intermediate pyrolysis systems such as Haloclean also at KIT (Hornung et al. 2007) and the twin screw Pyroformer technology at Aston (Yang et al. 2014). 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 often phase separated due to the longer residence times and contact with byproduct char. Also, the char yields are higher. KIT has promoted and tested the concept of producing a slurry of the char with the liquid to maximise liquid yield in terms of energy efficiency (Raffelt 2006a), but this would require an alternative energy source to provide heat for the process.

There have been claims of fast pyrolysis in fixed beds but it is difficult to envisage a fixed bed pyrolysis process that satisfies the basic requirements of fast pyrolysis which can be constructed at anything above laboratory or bench scale.

Some basic research has been carried out on microwave driven pyrolysis. Microwave heating is fundamentally difference from all other pyrolysis techniques as the biomass particles are heated from within and not by external heat transfer from a high temperature heat source. Microwave heating requires a material with a high dielectric constant or loss factor, of which water is a good example. So, in microwave pyrolysis, water is rapidly driven off then the particle heats up to start forming char. It is not clear that this can be considered fast pyrolysis. This is electrically conductive and eddy currents are created that provide very rapid heating. Therefore, control of a microwave system is quite challenging. A further problem to be considered is that penetration of microwaves is limited to typically 1–2 cm, so the design of a microwave reactor presents interesting scale up challenges.

One of the potentially valuable aspects of microwave pyrolysis is that due to the absence of thermal gradients, an environment is created for studying some of the fundamentals of fast pyrolysis. This offers possibilities to examine the effect of the thermal gradient in a pyrolysing particle and the secondary reactions that occur both within and without the biomass particle.

In an effort to reduce the oxygen content of the bio-oil product within a single step process, some attention has returned to the concept of integrating pyrolysis and hydrocracking in which hydrogen is added to the pyrolysis reactor. GTI is starting a new hydropyrolysis and hydroconversion programme to make gasoline and diesel in early 2010 (Marker et al. 2009) and a new patent has been applied for that includes hydrogen in the pyrolysis reactor with claims of producing hydrocarbons, alcohols and other oxygenates. The concept has some contradictory requirements—high pressure in pyrolysis increases char yields, e.g. Antal et al. (1996), and reduces liquid yields, while high pressures are required to provide effective hydrogenation.

3.3 Liquid Characteristics and Quality

3.3.1 Bio-oil General Characteristics

Crude fast pyrolysis liquid or bio-oil is dark brown and approximates to biomass in elemental composition. 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. Solid char may also be present as fine particles. The liquid is formed by rapid quenching of the vapours and aerosols which are thus prevented from secondary reactions. The product, therefore, is not as stable as many liquid fuels and has a tendency to slowly change some physical and chemical characteristics over time. This is referred to as ageing. Fast pyrolysis liquid has a higher heating value of about 17 MJ/kg as produced with about 25 wt% water that cannot readily be separated. There are some important characteristics of this liquid that are summarised in Table 3.2 and discussed below.

The liquid is formed by rapidly quenching, and thus ‘freezing’ of 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, which stabilises the discontinuous phase of pyrolytic lignin macromolecules through mechanisms such as hydrogen bonding. The dispersed phase is micelles of pyrolytic lignin of around 500 Å in diameter and the micro-emulsion is maintained by naturally derived surfactants. Ageing or instability is believed to result from a breakdown in this emulsion. In some ways, it is analogous to asphaltenes found in petroleum.

Table 3.2 Typical properties of wood-derived crude bio-oil

Physical property	Typical value
Moisture content (%)	25
pH	2.5
Specific gravity	1.2
Elemental analysis	
C (%)	56
H (%)	6
O (%)	38
N (%)	0–0.1
HHV[a] as produced (MJ/kg)	17
Miscibility with hydrocarbons	Very low
Viscosity (40 °C and 25% water) (cP)	40–100
Solids (char) (%)	0.05
Stability	Relatively poor
Vacuum distillation residue (%)	Up to 50

[a] *HHV* higher heating value

The typical product distribution all the products from fast pyrolysis of aspen wood is shown in Fig. 3.3. Bio-oil is a homogenous mixture of the organics, the reaction water as shown in the figure and the feed water.

Bio-oil is a homogenous mixture of organics + reaction water + feed water. The liquid has a distinctive odour, an acrid smoky smell due to the low molecular weight aldehydes and acids, which can irritate the eyes on prolonged exposure. The liquid contains several hundred different chemicals in widely varying proportions,

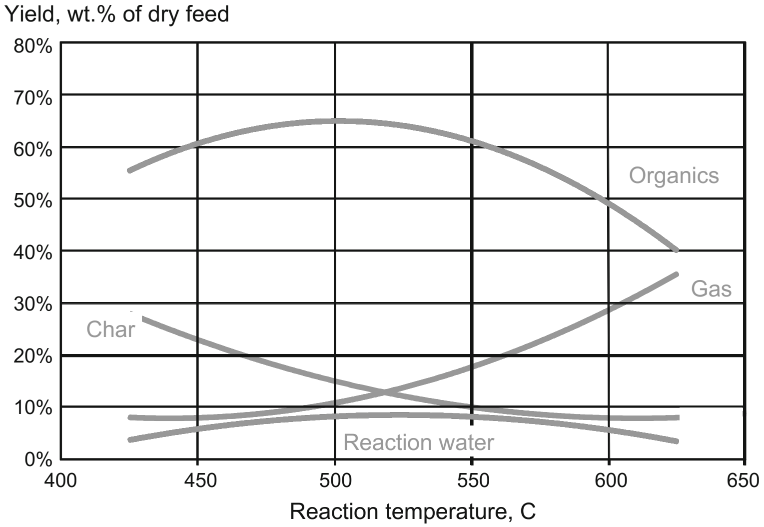

Fig. 3.3 Products from fast pyrolysis of Aspen

ranging from formaldehyde and acetic acid to complex high molecular weight phenols, anhydrosugars and other oligosaccharides.

The liquid contains varying quantities of water, which forms a stable single-phase mixture, ranging from about 15 wt% to an upper limit of about 35 wt % water, depending on the feed material and how it was produced and subsequently collected. 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.

The density of the liquid is very high at around 1.2 kg/L, compared with light fuel oil at around 0.85 kg/L. 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 (Diebold et al. 1997). The viscosity of the bio-oil as produced can vary from as low as 25 cSt (1 cSt = 1 mm^2/s) to as high as 1000 cSt (measured at 40 °C) or more depending on the feedstock, the water content of the 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 distill off lighter fractions, it rapidly reacts and eventually produces a solid residue of around 50 wt% of the original liquid and some distillate containing volatile organic compounds, including cracked compounds 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.

3.3.2 Upgrading Bio-oil

As the unusual nature of bio-oil has become more widely known, considerably greater effort has been undertaken to improve quality, or upgrade bio-oil, often with little appreciation of what properties are important. The objective or purpose of upgrading bio-oil is to improve its quality; that is, to reduce or remove one or more of its undesirable characteristics or properties. This requires a thorough appreciation of the characteristics or properties of bio-oil, which are listed in Table 3.3 with causes, effects and solutions. More important is the definition of the term “quality,” since different applications have different requirements in terms of characteristics, some of which have been reviewed (Czernik et al. 2004). Each of these characteristics is described in more detail later in this chapter, with an emphasis on those aspects that have attracted most interest and attention in recent years and which are of potentially

Table 3.3 Characteristics of bio-oil

Characteristic	Cause	Effect	Solution	Comments
Acidity or low pH	Organic acids from biopolymer degradation	Corrosion of vessels and pipework	Careful materials selection, such as polyolefins or stainless steel	Important in all applications
Ageing	Continuation of secondary reactions including polymerisation	Slow increase in viscosity from secondary reactions such as condensation Potential phase separation	Do not store for long periods Avoid exposure to air Add water Add co-solvents	Important
Alkali metals	Nearly all alkali metals report to char so 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	Pretreat feed to remove ash Hot-vapour filtration Process oil Modify application	Almost all alkali metals report to char, so good char separation minimises alkali metals in oil
Char	Incomplete char separation in process	Ageing of oil Sedimentation Filter blockage Catalyst blockage Engine injector blockage Alkali metal poisoning	Improved cyclones Multiple cyclones Hot-vapour filtration	
Chlorine	Contaminants in biomass feed	Catalyst poisoning in upgrading	Include suitable cleaning processes either upstream or downstream	Important for biofuel production
Colour	Cracking of biopolymers and char	Discolouration of some products such as resins	Efficient char filtration Deoxygenation	Only important where visible, such as resins or blended products
Contamination of feed	Poor harvesting practice	Contaminants, notably soil act, as catalysts and can increase particulate carryover	Improve harvesting practice Wash biomass	

(continued)

Table 3.3 (continued)

Characteristic	Cause	Effect	Solution	Comments
Distillability is poor	Reactive mixture of degradation products	Bio-oil cannot be distilled—maximum 50% typically. Liquid begins to react at below 100 °C and substantially decomposes above 100 °C	None known	Important for biofuel production and refinery integration
High viscosity		Gives high pressure drop, increasing equipment cost High pumping cost Poor atomisation	Careful heating up to 50 °C; rapid in-line heating to 80 °C is also possible Add water Add co-solvents	Important in heart and power applications
In-homogeneity	See Phase separation			
Low H:C ratio	Biomass has low H:C ratio	Upgrading to hydrocarbons is more difficult	Add hydrogen and/or remove oxygen	See upgrading to biofuels section
Low pH	See acidity			
Materials incompatibility	Phenolics and aromatics	Destruction of seals and gaskets	Careful materials selection	
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	Upgrading by hydrotreating or cracking with zeolites	See upgrading to biofuels section
Nitrogen	Contaminants in biomass feed High-nitrogen feed, such as proteins in wastes	Unpleasant smell Catalyst poisoning in upgrading NOx in combustion	Careful feed selection Feed blending Include suitable cleaning processes Add NOx removal in combustion applications	Important for biofuel production
Odour	See smell			

(continued)

Table 3.3 (continued)

Characteristic	Cause	Effect	Solution	Comments
Oxygen content is very high	Biomass composition	Poor stability Nonmiscibility with hydrocarbons	Reduce oxygen thermally and/or catalytically	Important for biofuel production
Phase separation or inhomogeneity	High feed water High ash in feed Poor char separation	Phase separation Partial phase separation Layering Poor mixing Inconsistency in handling, storage and processing	Modify or change process Modify or change feedstock Add co-solvents Control water content	May be important for biofuel production
Smell	Aldehydes and other volatile organics, many from hemicellulose	While not toxic, the smell is often objectionable	Better process design and management Reduction in hemicelluloses content of feed Containment and/or venting to flare	
Solids	See also char Particulates from reactor such as sand Particulates from feed contamination	Sedimentation Erosion and corrosion Blockage	Filtration of vapour or liquid	
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	None known	See ageing
Sulfur	Contaminants in biomass feed	Catalyst poisoning in upgrading	Include suitable cleaning processes	Important for biofuel production

(continued)

Table 3.3 (continued)

Characteristic	Cause	Effect	Solution	Comments
Temperature sensitivity	Incomplete reactions	Irreversible decomposition of liquid into two phases >100 °C Potential phase separation >60 °C	Store liquids at room temperature, preferably in absence of air	Important for all applications
Toxicity	Biopolymer degradation products	Human toxicity is positive but small Eco-toxicity is negligible	Health and safety precautions	
Viscosity	Nature of bio-oil	Fairly high and variable with time Greater temperature influence than hydrocarbons	Water and/or solvent addition reduces viscosity	Important for heat and power
Water content	Pyrolysis reactions Feed water	Complex effect on viscosity and stability: increased water lowers heating value, density, stability, and increase pH Affects catalysts	Control water in feed Optimise at 25% for consistency and miscibility Optimise for application	Important in biofuel production

greater significance. This includes biofuels by hydro-treatment, biofuels by zeolite cracking, biofuels by gasification and synthesis, hydrogen production by steam reforming, chemicals recovery and stability improvement.

3.4 Significant Factors Affecting Bio-oil Characteristics and Quality

3.4.1 Feed Material

The composition of the biomass feed has a significant effect on both the yield and quality of the resulting bio-oil. The main parameters are ash, water content biomass, composition of biomass and contamination of biomass. Each of these is discussed below.

3.4.1.1 Ash Content and Composition

Biomass contains a variety of metals that are necessary for the movement of nutrients within the plant, of which the most significant are potassium and sodium. Both are catalytically active in fast pyrolysis through cracking to water and CO_2 in the vapour phase, and ash contents above around 2.5 wt% often lead to a phase-separated product in significantly lower yields (Chiaramonti et al. 2007). Ash and inorganics can also arise from contamination during harvesting, as discussed below.

3.4.1.2 Water Content of Prepared Biomass

As bio-oil is oleophobic, all feed water reports to the bio-oil. Water is also formed from fast pyrolysis reactions; so, to maintain a reasonable water level in bio-oil, feed water is usually limited to 10 wt%. This typically gives water content of 25 wt% in the bio-oil. This level minimises the potential for phase separation and gives a manageable viscosity.

3.4.1.3 Composition of Biomass

In addition to hemicellulose, cellulose, and lignin, biomass can contain other components, including ash and water (as discussed above), contaminants (discussed below), and minor organic components (such as extractives, oils and proteins). The extractives and oils can lead to a separate phase separating at the top of the bio-oil. Proteins have high nitrogen content and lead to a distinctive and unpleasant odour.

3.4.1.4 Contamination of Biomass

Biomass can be contaminated in many ways, such as: chlorine from seaside locations and biocide applications; sulphur from fertiliser applications; metals and inorganic compounds from soil during harvesting, such as mud splashing during rain and accumulation from dragging over soil. All contaminants will have an influence on the yield and quality of the bio-oil produced, as discussed below.

3.4.2 Reactors

At the heart of a fast pyrolysis process is the reactor. Although it represents only one stage in the overall fast pyrolysis system, most research and development has focused on the reactor, although increasing attention is now being paid to control and improve liquid quality and improvement of collection systems. The rest of the process consists of biomass reception, storage and handling, biomass drying and grinding, product collection, storage, and, when relevant, upgrading. Several comprehensive reviews of fast pyrolysis processes for liquids production are available, for example, see Refs Czernik et al. (2004), Mohan et al. (2006), Bridgwater et al. (2002b).

Both the time-temperature profile of the gases and vapours, and the char and the liquid collection system influence the quality of bio-oil. Temperatures below 400 °C in the vapour handling section can result in fractional condensation of high molecular weight oligomers derived from lignin. While the removal of these oligomers reduces the viscosity and stability of the remaining bio-oil, control of this fractionation is difficult and usually results in blockage. Temperatures above around 550 °C promote secondary cracking reactions, resulting in lower liquid yields and higher water and gas yields, especially CO_2. This increases the propensity of the oil to age and phase separate. Systems with sand recycle thus need to balance the flow rate of hot sand with sand temperature to minimise these effects. Entrained-flow reactors require such a high temperature gradient between gas and pyrolysis to affect the necessary heating rates and reaction temperature that the liquid yield and quality usually suffer.

3.5 Norms and Standards

For bio-oil to successfully become a traded commodity, norms and standards are required. The first attempts at defining quality was carried out in 1995 by an international group from North America and Europe (Diebold et al. 1997). This was developed subsequently with exploration and development of standard tests for bio-oil (Oasmaa et al. 1997; Oasmaa and Czernik 1999; Oasmaa and Peacocke 2001; Gust et al. 2003) up to certification by CEN in Europe and ASTM in North America (ASTM D7544—09 2009; Oasmaa et al. 2009). The evaluation and development of test methods is very important in defining quality and setting standards for definition and marketing.

3.6 Bio-oil Upgrading

Bio-oil can be upgraded in a number of ways: physically, chemically and catalytically. This has been extensively reviewed (Diebold 2002; Czernik and Bridgwater 2004; Bridgwater 1966, 1994; Chheda et al. 2007). Some aspects are particularly significant and have attracted more extensive attention, including stability improvement, which is reviewed in Section Ageing.

3.6.1 Acidity or Low pH

Bio-oil has a typical pH of around 2.5 from the organic acids formed by degradation or cracking of the biopolymers that make up biomass, particularly the cellulose and hemicellulose. Hemicellulose can be preferentially reduced by washing in hot water or dilute acid and by torrefaction (see Section Smell below for references to torrefaction). Neither method is very effective, since cellulose is also affected in both methods. There has been little work on corrosion of metals in bio-oil (Darmstadt et al. 2004). The general view is that polyolefins and stainless steel are acceptable materials of construction. High acidity can be managed in several ways, including esterification and addition of magnesium powder, an alloy or a magnesium compound (Nemoto et al. 2013).

3.6.2 Ageing

Ageing or instability is a known problem that affects most bio-oils. It is caused by continued reaction of the decomposition products from fast pyrolysis (Diebold 2002). Polar solvents have been used for many years to homogenise and reduce the viscosity of biomass oils. The addition of solvents, especially methanol, showed a significant effect on the oil stability. Diebold and Czernik (1997) found that the rate of viscosity increase ("ageing") for the oil with 10 wt% of methanol was almost 20 times less than for the oil without additives. A stability test based on changes in viscosity is described in Section Viscosity.

3.6.3 Alkali Metals

All biomass contains ash in which alkali metals, notably potassium and sodium, dominate. Potassium, in particular, and other alkali metals are catalytically active and enhance secondary cracking reactions. This results in loss of liquid yield, higher water (and carbon dioxide) production, and potential phase separation from higher water content and loss of naturally derived surfactants that maintain the micro-emulsion of bio-oil.

Woody feeds typically contain up to 1 wt% ash, while grasses can range up to 8 wt% ash. The amount of ash in perennial crops depends upon harvesting time, since a significant proportion of the nutrients in above-ground plant matter returns to the rhizome at the end of the growing season. In addition, ash will be leached from the standing crop during winter from rainfall to potentially give ash contents below 2.5 wt%. The limiting value of ash content to reduce or avoid this effect is believed to be around 2.5 wt%, although this depends on other process parameters and the composition of the ash.

Washing biomass with water or dilute acid is feasible to remove ash, but is costly in financial and energy terms both for washing and subsequent drying. However, a further advantage of acid washing is the potential removal of hemicelluloses, from which are derived aldehydes and related degradation products that contribute an unpleasant odour to bio-oil and are partially responsible for the ageing effect. So, as with many other characteristics of bio-oil, effects are complex and can be difficult to evaluate comprehensively.

3.6.4 Char

Char acts as a vapour cracking catalyst, so rapid and effective separation from the pyrolysis product vapours is essential. 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. A more effective, but more difficult, method is hot-vapour filtration, which is also described below.

3.6.4.1 Cyclones

It is important to separate char as quickly as possible to minimise vapour cracking reactions. This is conventionally carried out in two or more cyclones, with the first, higher capacity cyclone removing coarse particles and the second removing fines. However, cyclones are not efficient with very small char particles, so these are usually carried over to the liquid collection system.

3.6.4.2 Filtration

Hot-vapour filtration can reduce the ash content of the oil to less than 0.01% and the alkali content to less than 10 ppm, much lower than reported for biomass oils produced in systems using only cyclones. There is limited information available on the performance or operation of hot-vapour filters, but they can be specified and perform similar to hot-gas filters in gasification processes (Diebold et al. 1994a). An alternative approach is insertion of the filter medium in the fluid bed (Hoekstra et al. 2009). Hot-vapour filtration gives a higher quality product with lower char however, the liquid yield is reduced by about 10–20% due to the char accumulating on the filter surface that cracks the vapours which is countered to some extent by preferential cracking of pyrolytic lignin in aerosol form on the char cake. More recent work using state-of-the-art filter elements reported similar results, with lower viscosities and reduced yields (Sitzmann and Bridgwater 2007).

Diesel engine tests performed on crude and on hot-filtered oil showed a substantial increase in burning rate and a lower ignition delay for the latter, due to the lower average molecular weight for the filtered oil (Shihadeh 1998). Hot-gas filtration has not yet been demonstrated over a long-term process operation. Despite its promise, only a few institutions have investigated hot-vapour filtration, including NREL (Diebold et al. 1994a), VTT, University of Twente (Hoekstra et al. 2009) and Aston University (Baker and Elliott 1988a).

Pressure filtration of the liquid for substantial removal of particulates (down to <1 μm) is very 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. Filtration down to 10 μm is not so difficult, but it increases process complexity and cost, as well as potentially leading to lower liquids yields due to losses. 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, as described below.

3.6.4.3 Slurries

An alternative approach to separation of char is to deliberately leave all of it in the bio-oil to create a bio-oil—char slurry. KIT (which used to be known as FZK) in Karlsruhe, Germany has developed and promoted the production and processing of slurries made from bio-oil and char (Raffelt et al. 2006a, b; Henrich et al. 2007). The liquid from straw pyrolysis in a twin-screw reactor is phase separated, but a homogeneous slurry from this separated liquid and the char is claimed. The slurry has been gasified by what was Future Energy (now Siemens) in Freiberg, Germany in a pressurised oxygen-blown gasifier (Volkmann 2004). There are unresolved questions over the source of energy for the pyrolysis reaction if all the char is used in the slurry; over the separation of char and sand from the reactor; and over the long-term stability of the slurry and its suitability for oxygen pressure gasification. Dynamotive also produced a bio-oil-char slurry known as Intermediate Bio-oil (Dynamotive 2007) that has also been tested at the Future Energy gasifier unit in Germany (now Siemens) (Dynamotive 2009).

3.6.5 Chlorine

Use of chlorine biomass, such as straw, will result in a high chlorine bio-oil from the hydrochloric acid formed in pyrolysis which is dissolved in the bio-oil. There is little work reported on measurement and control, but the levels rarely affect the low pH of the bio-oil, which is mostly due to organic acids. Combustion of a higher chlorine bio-oil will result in hydrogen chloride formation, which can be removed in conventional emissions control. The absence of alkali metals in a relatively char-free bio-oil would not be expected to lead to ash deposition and chlorine mobility.

3.6.6 Colour

The dark brown colour of bio-oil is only noticeable and potentially problematic in applications where it is visible. For example, use of whole bio-oil or fractionated bio-oil as a substitute for phenol in wood panel resins gives a dark brown-coloured resin. In many applications this is not a real problem but may cause customer concern from an aesthetic viewpoint. A similar problem of adverse consumer or customer reaction could arise in any application, where the conventional “white” material is replaced by a dark brown material; for example, diesel-bio-oil emulsions for engine fuel. Even hydrotreated bio-oil with greater than 99% deoxygenation that is water white when produced has been observed to blacken and thicken with time.

3.6.7 Contamination of Feed

Biomass can be contaminated by soil, etc. from the harvesting process. Forest residues that are removed by dragging over ground and energy grasses that are cut and recovered later by ground collection will accrete soil. Soil often contains a variety of metals, such as iron that can be catalytically active in fast pyrolysis (Salter 1999). The solution is either improved harvesting techniques and/or washing to remove contamination. An example is hog fuel washing experiments in Canada (Smith 2005). However, there is an energy and financial cost of washing which is difficult to justify in most cases unless more valuable chemical products are produced.

3.6.8 Distillability

Pyrolysis liquids cannot be completely vapourised 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 and some distillate containing volatile organic compounds and water. The distillate contains those compounds that are volatile, together with thermally cracked products from higher temperatures.

3.6.9 High Viscosity

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 in round-robin exercises have shown substantial improvements in consistency and stability, demonstrating the improvement in process design and control as the technology develops. Bio-oil viscosity is important particularly for direct combustion applications, where it needs to be atomised, such as in burners, engines and turbines. There is quite extensive testing of bio-oil in engines reviewed in Czernik et al. (2004), Leech (1997), Ormrod and Webster (2000) and in burners in Czernik et al. (2004), Oasmaa and Czernik (1999), Oasmaa et al. (2001). For engines, the preferred maximum viscosity is 17 cSt, above which the pressure requirements become excessive. Conventional fuels can be preheated to reduce viscosity, but above around 55 °C there is an irreversible change in the bio-oil properties; thus, preheating can only be used on a once through, very short residence time basis, as used in combustion tests by Canmet and MIT (reviewed in Bridgwater 2012). Viscosity is most affected by water content and temperature and is thoroughly covered in Diebold's review (2002).

3.6.10 Inhomogeneity

See section *Phase separation or Inhomogeneity* below.

3.6.11 Low H:C Ratio

The poor C:H ratio for bio-oil conversion to hydrocarbons means that either hydrogen needs to be added and/or carbon lost. This is considered more fully in section *Acidity or low pH above*.

3.6.12 Low pH

See section *Acidity or low pH* above.

3.6.13 Materials Incompatibility

The complex nature of bio-oil and the many different oxygenated compounds present mean that materials selection needs to be carefully considered. Polyolefins and stainless steel are acceptable materials for vessels and pipelines. Seals and gaskets can be sensitive to some of the organics, such as phenolics, and careful compatibility testing is needed for many polymers used as seals and gaskets. For example, synthetic rubber has been known to swell to three times its thickness when in contact with bio-oil.

3.6.14 Miscibility with Hydrocarbons

Pyrolysis oils are not miscible with hydrocarbon fuels so co-utilisation applications that require mixing are unsuitable without further processing, such as upgrading, blending, and emulsification.

3.6.14.1 Blending

As bio-oil is not miscible in any proportions with hydrocarbons, blending is only possible with polar compounds or mixtures, such as alcohols. This has been used to improve viscosity and reduce ageing, as reviewed by Diebold (2002). Blends have successfully been produced with biodiesel and butanol as a co-solvent (Alcala and Bridgwater 2013) and more recently also with diesel. Some blending with slow pyrolysis oil, diesel, and alcohols has been reported (Weerachanchai et al. 2009), although the bio-oil used is quoted as having a heating value of nearly 40 MJ/kg, which suggests that it is quite dissimilar to usual fast pyrolysis bio-oil.

3.6.14.2 Emulsions

Bio-oil can be emulsified with diesel oil with the aid of surfactants. A process for producing stable micro-emulsions with 5–30% of bio-oil in diesel has been developed at CANMET (Ikura et al. 1998). The University of Florence, Italy, has been working on emulsions of 5–95% bio-oil in diesel (Baglioni et al. 2001, 2003) to make either a transport fuel or a fuel for power generation in engines that does not require engine modification to dual-fuel operation. There is limited experience of using such fuels in engines or burners, but significantly higher levels of corrosion/erosion were observed in engine applications compared to bio-oil or diesel alone. A further drawback of this approach is the cost of surfactants and the energy required for emulsification.

3.6.15 Nitrogen

Biomass contains relatively small quantities of nitrogen which report to bio-oil. In most applications this is not a problem. However, some wastes with a high protein content, such as vegetable oil cake (e.g. rape or colza-meal) can have nitrogen contents above 5 wt% from the proteins in the waste. Two problems result from use of such feedstocks. The first is the very noxious smell of high-nitrogen bio-oils from the extensive nitrogen-containing degradation products. This is substantially worse than wood- or grass-derived bio-oil. Second, much of the nitrogen reports to the liquid, meaning that most applications will need to consider nitrogen pretreatment for its removal (hydro-denitrogenation) or post-use emissions control if the bio-oil is combusted or gasified. An interesting solution is recovery of the high-value proteins prior to pyrolysis, which becomes an embryonic biorefinery.

3.6.16 Other Solid Particulates, Excluding Char

The inert solids in fluid beds and CFBs, usually sand, will suffer from slow attrition and the fines are likely to substantially bypass cyclones. While not significant in terms of concentration (Strenziok et al. 2001), the solids could accumulate over time and create handling, pumping, and erosion problems. Solids are likely to be easier to filter than char, which seems to create a complex with bio-oil, but char would usually be the dominant solid contaminant compared with sand.

A potentially more significant problem is catalyst fines from fluid-bed and circulating-fluid-bed catalytic reactors. There is insufficient evidence that attrition is a serious problem, but the mechanical properties of catalysts need to be considered carefully.

3.6.17 Oxygen Content

Bio-oil approximates biomass in elemental composition with typically 40–45 wt% oxygen from the diverse oxygenated organic compounds. This means that it is not miscible with hydrocarbons, but miscible with polar solvents like methanol, ethanol, acetone, and so on. Upgrading to hydrocarbons for transport fuels or biofuels is reviewed in section *Chemical and catalytic upgrading of bio-oil* below. Hydrocarbon biofuel production thus requires the reduction or removal of oxygen, and there are many methods reviewed below.

3.6.18 Phase Separation or Inhomogeneity

The microstructure of bio-oil is briefly discussed in Sect. 5.20 below. Diebold has provided a thorough review of storage instability and methods for upgrading bio-oil (Lehto et al. 2010).

3.6.19 Smell

The liquid has a distinctive odour, an acrid smoky smell due to the low molecular weight aldehydes and acids, which can irritate the eyes on prolonged exposure. This characteristic smoky smell is exploited in the production of liquid smoke by several companies around the world. Pretreatment of biomass to reduce hemicelluloses, the source of the noxious components, will reduce the problem, but at the expense of lower yields, a more viscous product, and a significant energetic and/or financial cost. Pretreatment includes acid washing to preferentially hydrolyse hemicelluloses (Oasmaa et al. 2009) and torrefaction (Boerrigter et al. 2006; Zanzi et al. 2005; Prins et al. 2006) to pyrolyse the hemicelluloses preferentially. Neither is very efficient, as some cellulose is also converted by both methods, resulting in loss of yield and significant emissions control problems.

3.6.20 Structure of Bio-oil

Bio-oil is a complex mixture of water-soluble derivatives of cellulose and hemicellulose degradation and water-insoluble pyrolytic lignin. It is believed to be a micro-emulsion of pyrolytic lignin micelles around 500 Å in diameter maintained as an emulsion by a surfactant derived from the cracking reactions that create the liquid. This is a poorly researched area with few publications (Fratini et al. 2006). Dilution of the aqueous phase by adding water reduces the surfactant concentration to a level when it is no longer effective, resulting in phase separation. The complex aqueous-oil-surfactant relationship can be destroyed by a number of other circumstances, including cooling, heating, addition of emulsion-breaking additives, shear, etc. Phase separation is one of the consequences of ageing (see sections *Ageing* and *Water content*).

3.6.21 Sulphur

Biomass usually contains little sulphur. Wood is typically 0.05–0.1% S and some crops and wastes or residues can be higher. Sulfur levels in bio-oil have invariably been quoted in trace quantities (for example 0.03 mg/kg (ASTM D7544—09 2009) and have attracted little attention in utilisation activities. Sulfur in biomass feed would mostly report to the gas product. For synfuel applications, parts per million or even parts per billion levels would typically be required, which would normally be met by guard beds, such as zinc oxide.

3.6.22 Temperature Sensitivity

Bio-oil is formed by rapid freezing of a complex degradation process and the resultant liquid is therefore inherently unstable and wanting to continue reacting. This is the cause of the instability discussed previously. Raising the temperature, therefore, will increase the tendency for chemical reactions to continue. Up to around 55 °C the changes are reversible, so preheating to 50 °C or less will have no adverse effects on oil quality or behaviour. Above around 55 °C the changes are increasingly less reversible, and prolonged exposure to higher temperatures causes increased viscosity and an increased propensity for phase separation. Around 100 °C, bio-oil separates into a light bitumen-type phase mostly from the pyrolytic lignin and a low-viscosity aqueous fraction, but both are different to phase separated bio-oil at ambient conditions. The heavier material will hinder heat transfer and as temperatures increase will eventually carbonise to form a coke layer. This is what happens in attempts at distillation.

Temperature is widely used to control viscosity in combustion applications, but for bio-oil this needs to be carefully considered. In-line preheating immediately prior to combustion works well, but recirculation of a heated bio-oil, as for example, in some engine designs, needs to be managed carefully due to the temperature sensitivity of bio-oil.

3.6.23 Toxicity

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. The study included a comprehensive evaluation of transportation requirements as an update of an earlier study (Peacocke 2002) and an assessment of the biodegradability (Blin et al. 2007). The results are complex and require more comprehensive analysis, but the overall conclusion is that bio-oil offers no significant health, environment or safety risks.

3.6.24 Viscosity

Viscosity is important in many fuel applications (Antal et al. 1996). The viscosity of the bio-oil as produced can vary from as low as 25 cSt to as high as 1000 cSt (measured at 40 °C) or more, depending on the feedstock, the water content of the oil, the amount of light ends collected, and the extent to which the oil has aged.

An accelerated ageing or stability test was introduced to provide an index of stability that represents the effect of long-term storage at ambient conditions. This is known as a stability or ageing index (Oasmaa et al. 1997) and is measured by heating the sample to 80 °C for 24 h and comparing the increase in viscosity with the original viscosity. This is believed to approximate to 12 months’ storage and is an indication of the propensity for viscosity increase and possible phase separation. A similar test can be carried out on water content which increases with ageing but this appears to be a less reliable method and does not correlate well with the viscosity method.

3.6.25 Water Content

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; it reduces heating value, which means that more liquid is required to meet a given duty; and it can improve stability. The effect of water, therefore is complex and important. Bio-oil is miscible with polar solvents, such as methanol, ethanol, acetone, etc., but totally immiscible with petroleum-derived fuels.

3.7 Chemical and Catalytic Upgrading of Bio-oil

Bio-oil can be upgraded in a number of ways: physically, chemically and catalytically. These have been extensively reviewed (Czernik et al. 2004; Maggi and Elliott 1997; Zhang et al. 2007) and only the more significant features are reported here. A summary of the main methods for upgrading fast pyrolysis products and the products is shown in Fig. 3.4.

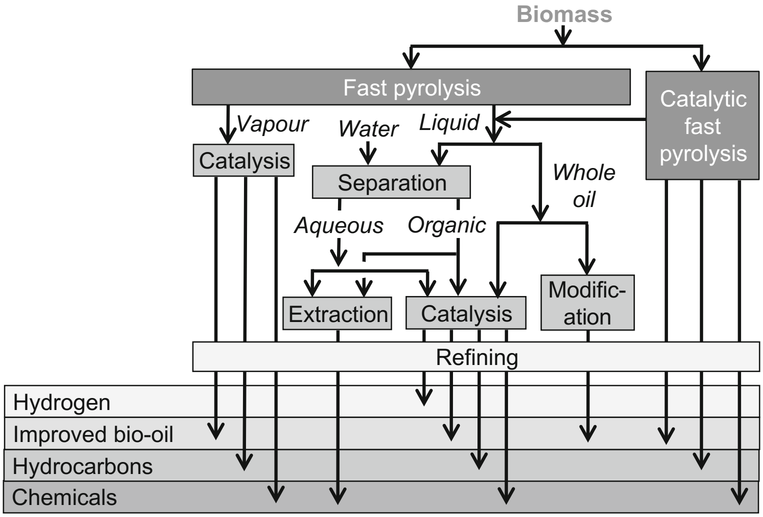

Fig. 3.4 Overview of fast pyrolysis upgrading methods

3.7.1 Physical Upgrading of Bio-oil

The most important properties that may adversely affect bio-oil fuel quality are incompatibility with conventional fuels from the high oxygen content of the bio-oil, high solids content, high viscosity and chemical instability.

3.7.1.1 Filtration

Hot-vapour filtration can reduce the ash content of the oil to less than 0.01% and the alkali content to less than 10 ppm, much lower than reported for biomass oils produced in systems using only cyclones. This gives a higher quality product with lower char; however, the liquid yield is reduced by about 10–20% due to the char accumulating on the filter surface that cracks the vapours. There is limited information available on the performance or operation of hot-vapour filters, but they can be specified and perform similarly to hot-gas filters in gasification processes.

Diesel engine tests performed on crude and on hot-filtered oil showed a substantial increase in burning rate and a lower ignition delay for the latter, due to the lower average molecular weight for the filtered oil (Shihadeh 1998). Hot-gas filtration has not yet been demonstrated over a long-term process operation. A consequence of hot-vapour filtration to remove char is the catalytic effect of the accumulated char on the filter surface, which potentially cracks the vapours, reduces yield by up to 20%, reduces viscosity, and lowers the average molecular weight of the liquid product. A little work has been done in this area by NREL (Diebold et al. 1994a) and VTT and Aston University (Sitzmann and Bridgwater 2007), but very little has been published.

Liquid filtration to very low particle sizes of below around 5 μm is very difficult due to the physico-chemical nature of the liquid and usually requires very high pressure drops and self-cleaning filters.

3.7.1.2 Solvent Addition

Polar solvents have been used for many years to homogenise and reduce the viscosity of biomass oils. The addition of solvents, especially methanol, showed a significant effect on the oil stability. Diebold and Czernik (1997) found that the rate of viscosity increase (“ageing”) for the oil with 10 wt% of methanol was almost 20 times less than for the oil without additives.

3.7.1.3 Emulsions

Pyrolysis oils are not miscible with hydrocarbon fuels, but they can be emulsified with diesel oil with the aid of surfactants. A process for producing stable microemulsions with 5–30% of bio-oil in diesel has been developed at CANMET (Ikura et al. 1998). The University of Florence, Italy, has been working on emulsions of 5–95% bio-oil in diesel (Baglioni et al. 2001, 2003) to make either a transport fuel or a fuel for power generation in engines that does not require engine modification to dual-fuel operation. There is limited experience of using such fuels in engines or burners, but significantly higher levels of corrosion/erosion were observed in engine applications compared with bio-oil or diesel alone. A further drawback of this approach is the cost of surfactants and the high energy required for emulsification.

3.7.2 Catalytic Upgrading of Bio-oil

3.7.2.1 Natural Ash in Biomass

Before considering catalytic upgrading of bio-oil, it is important to appreciate first that biomass contains very active catalysts within its structure. These are the alkali metals that form ash and which are essential for nutrient transfer and growth of the biomass. The most active is potassium followed by sodium. These act by causing secondary cracking of vapours and reducing liquid yield and liquid quality.

Ash can be managed to some extent by selection of crops and harvesting time, but 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 both temperature and concentration, the more complete the ash removal. However, as washing conditions become more extreme, firstly hemicellulose and then cellulose are 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, which can reach levels in bio-oil where recovery becomes an interesting proposition, although commercially, markets need to be identified and/or developed.

3.7.2.2 Upgrading to Biofuels

Upgrading bio-oil to a conventional transport fuel such as diesel, gasoline, kerosene, methane and LPG requires full deoxygenation and conventional refining, which can be accomplished either by integrated catalytic pyrolysis, as discussed

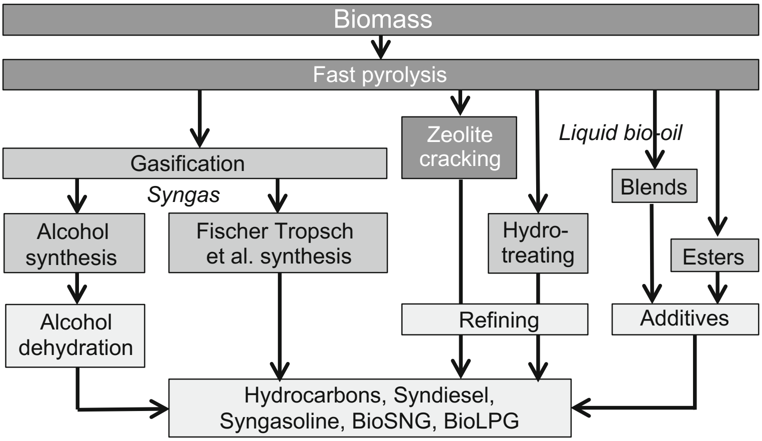

Fig. 3.5 Upgrading of bio-oil to biofuels and chemicals

above, or by decoupled operation, as summarised below and depicted in Fig. 3.5. There is also interest in partial upgrading to a product that is compatible with refinery streams in order to take advantage of the economy of scale and experience in a conventional refinery. Integration into refineries by upgrading through cracking and/or hydrotreating has been reviewed by Huber and Corma (2007):

- Hydrotreating;
- Catalytic vapour cracking;
- Esterification and related processes;
- Gasification to syngas followed by synthesis to hydrocarbons or alcohols.

3.7.2.3 Hydrotreating

Hydroprocessing rejects oxygen as water by catalytic reaction with hydrogen. This is usually considered as a separate and distinct process to fast pyrolysis that can, therefore, be carried out remotely. The process is typically high pressure (up to 200 bar) and moderate temperature (up to 400 °C) and requires a hydrogen supply or source (Elliott and Baker 1987). Full hydrotreating gives a naphtha-like product that requires orthodox refining to derive conventional transport fuels, however complete de-oxygenation is difficult to achieve and requires relatively extreme conditions. This refining would be expected to take place in a conventional refinery to take advantage of know-how, existing processes and economies of scale. A projected typical yield of naphtha equivalent from biomass is about 25% by weight or 55% in energy terms, excluding provision of hydrogen (Bridgwater 1966). Inclusion of hydrogen production by gasification of biomass reduces the yields to around 15 wt% or 33% in energy terms. The process can be depicted by the following conceptual reaction:

$$C_1H_{1.33}O_{0.43} + 0.77\,H_2 \rightarrow CH_2 + 0.43H_2O$$

The catalysts originally tested in the 1980s and 1990s were based on sulfided CoMo or NiMo supported on alumina or aluminosilicate and the process conditions are similar to those used in the desulfurisation of petroleum fractions. However, a number of fundamental problems arose including that the catalyst supports of typically alumina or aluminosilicates were found to be unstable in the high-water content environment of bio-oil and the sulfur was stripped from the catalysts requiring constant re-sulfurisation. The main activities were based at Pacific Northwest National Laboratory (PNNL), USA by Elliott and co-workers (e.g. Baker and Elliott 1988a, b; Elliott and Neuenschwander 1997) at UCL in Louvain la Neuve in Belgium by Maggi and co-workers (e.g. Maggi and Delmon 1994; Grange et al. 1996). This area has been thoroughly reviewed (Oasmaa et al. 1997). A recent design study of this technology for a biomass input of 2000 t/d (dry) for production of gasoline and diesel has been carried out by PNNL (Jones et al. 2009). A comprehensive review of unsupported metal sulphide hydrotreating catalysts was published in 2007 providing an up-to-date view (Eijsbouts et al. 2007).

More recently, attention turned to precious metal catalysts on less susceptible supports, and considerable academic and industrial research has been initiated in the last few years. Of note is the work by UOP in Chicago with (PNNL) in the USA to address the scientific and technical challenges and develop a cost-effective process (UOP 2008). Model compounds were used initially to understand the basic processes (Elliott and Hart 2009) and both whole oil and fractions have been evaluated. Tests have been carried out on both batch and continuous-flow processes and work to date has been based on relatively low-temperature (up to 380 °C) catalytic hydrogenation of bio-oil using different metal catalysts and processing conditions to give a range of products, including petroleum refinery feedstock.

Groningen University in the Netherlands is also active in fundamental research on hydrotreating bio-oils and model compounds using ruthenium on carbon (Wildschut et al. 2008, 2009). Different levels of upgrading are being studied from stabilisation with low levels of oxygen removal through mild hydrotreating to two-stage hydrotreatment with substantial oxygen removal (Ardiyanti et al. 2009).

At the Technical University of Munich, Lercher proposed a “one-pot” approach which is based on aqueous-phase hydro-deoxygenation of phenolic monomers using bifunctional catalysis that couples precious-metal-catalysed hydrogenation and acid-catalysed hydrolysis and dehydration (Zhao et al. 2009). There is still a significant hydrogen requirement which could, in principle, be derived from the aqueous phase after hydrotreatment. A more complex process involving hydrotreatment, esterification and cracking in supercritical ethanol using a palladium on zirconium with a SBA15 catalyst, has been researched in China (Tang et al. 2009). A significant improvement in many properties was reported. Many other organisations are active in hydrotreating, which were listed in Bridgwater (2012) although there has been a rapid increase in activity in this area around the world.

There is a substantial hydrogen requirement in all hydrotreating processes to hydrogenate the organic constituents of bio-oil and remove the oxygen as water. The hydrogen requirement can be represented by processing an additional amount of biomass to provide the hydrogen, by gasification for example. This is about 70–80% of that required to produce the bio-oil. The process is thus less efficient than the simple performance figures often presented. If only the organic fraction of bio-oil after phase separation is hydrotreated, then the hydrogen required can be produced by steam reforming the aqueous phase. There has been extensive research on reforming the aqueous fraction of bio-oil as discussed below. There is also a high cost from the high-pressure requirement (Jones et al. 2009; Cottam and Bridgwater 1994). Catalyst deactivation remains a concern from coking due to the poor C/H ratio.

In all cases the upgraded product will almost certainly require conventional refining to produce marketable products, and this would be expected to take place in a conventional refinery.

3.7.2.4 Zeolite Cracking

Zeolite cracking rejects oxygen as CO_2, as summarised in the conceptual overall reaction below:

$$C_1H_{1.33}O_{0.43} + 0.26\,O_2 \rightarrow 0.65\,CH_{1.2} + 0.34\,CO_2 + 0.27\,H_2O$$

Catalytic vapour cracking over acidic zeolite catalysts provides deoxygenation by simultaneous dehydration-decarboxylation producing mostly aromatics (Chang and Silvestri 1977) at 450 °C and atmospheric pressure. Oxygen is ultimately rejected as CO_2 and CO from a secondary oxidising reactor to burn off the coke deposited on the catalyst. This would operate much as an FCC in a refinery. The low H/C ratio in the bio-oils imposes a relatively low limit on the hydrocarbon yield. A projected typical yield of aromatics suitable for gasoline blending from biomass is about 20% by weight or 45% in energy terms (Diebold et al. 1994b). This publication also reported on technical and economic modelling by an IEA Bioenergy Task (Diebold et al. 1994b). The crude aromatic product would be sent for refining in a conventional refinery.

Catalyst deactivation remains a concern for both routes, although the coking problem with zeolites can in principle be overcome by a conventional FCC arrangement with continuous catalyst regeneration by oxidation of the coke. Some concern has been expressed over the poor control of molecular size and shape with orthodox zeolites and the propensity for formation of more noxious hydrocarbons

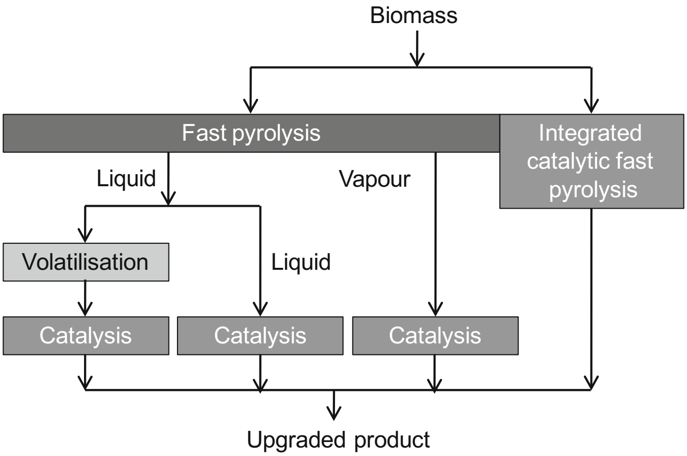

Fig. 3.6 Methods of upgrading fast pyrolysis products with cracking catalysts

(Williams and Horne 1994). The processing costs are high and the products are not competitive with fossil fuels (Bridgwater and Cottam 1992). The approach has only been studied at a relatively basic research level and considerably more development is necessary. Recently, some research is known to have taken place commercially in the USA and Brazil with limited success.

There are several ways in which this can be carried out as summarised in Fig. 3.6. The zeolite upgrading can operate on the liquid or vapours within or close-coupled to the pyrolysis process, or they can be decoupled to upgrade either the liquids or re-vapourised liquids.

A report by hydrocarbon processing for the future of fluid catalytic cracking (FCC) and hydroprocessing in modern refineries states that.

Biomass-derived oils are generally best upgraded by HZSM-5 or ZSM-5, as these zeolitic catalysts promote high yields of liquid products and propylene. Unfortunately, these feeds tend to coke easily, and high TANs [total acid numbers] and undesirable byproducts, such as water and CO_2 are additional challenges. Interestingly, the most recent attempts to use orthodox technology in conventional refineries for deoxygenating bio-oil is co-feeding bio-oil into an FCC unit which has been addressed by several organisations with limited success so far. This approach offers considerable technical and economic potential.

Many other organisations are active in deoxygenation by zeolites, which were listed in (Bridgwater 2012) although there has subsequently been a rapid increase in activity in this area around the world due to the relative lack of success in hydro-deoxygenation.

Integrated Catalytic Pyrolysis

There is increasing interest in improving the quality of bio-oil, often without defining what quality means, and there have been a number of developments in the last few years that integrate or combine catalysis with pyrolysis. These combined pyrolysis—catalysis reaction systems have been studied by a number of organisations including several commercial developments. There is a rapidly expanding research community on catalytic (fast) pyrolysis but with little evidence of the necessary breakthroughs. Two notable commercial developments are included for special mention:

Huber from the University of Massachusetts Amhurst (now at the University of Wisconsin Madison) has also worked extensively in this area and developed a process that pyrolyses biomass in the presence of ZSM-5 into gasoline, and also diesel fuel, heating oil and renewable chemicals including benzene, toluene and xylenes in a one-step process. The product is referred to as Grassoline, and a spin out company has been formed—Anellotech (Huber and Bale 2009).

BioECon from the Netherlands formed a joint venture with KIOR (2010) to exploit their respective technologies. Little information is available other than modified clays are some of the materials studied and that one approach is impregnation of the biomass with nano-catalysts prior to reaction (Jonietz 2007). Success was claimed at temperatures as low as 230 °C (O'Connor et al. 2007). Unfortunately, in spite of considerable investment KIOR was unable to create a commercially viable venture and went into liquidation at the end of 2014 after investments totalling over USD 600 million.

Integration of catalysis and pyrolysis requires operation at a single temperature and sufficiently robust catalyst to withstand the temperature and mechanical environment and with sufficient residence for the catalyst to be effective, which is a challenging requirement. There is, therefore, less flexibility in operating conditions, suggesting that catalytic systems will need to be quite sophisticated and/or sequential with carefully chosen processes and conditions that do not rely on single reactors and catalysts. Since coking is a recognised problem and is the mechanism by which oxygen is rejected from the bio-oil and CO_2, catalyst regeneration is an essential aspect of a reactor design.

Decoupled Vapour Upgrading from Volatilisation of Bio-oil

This approach was extensively investigated at the University of Saskatchewan in the 1990s and widely reported and reviewed (Bridgwater 1966; Valle et al. 2007). Devolatilisation of bio-oil suffers from the temperature sensitivity of bio-oil and the highest yield of vapours would not be expected to be greater than 50 wt%. Data on analyses of the re-volatised bio-oil prior to catalytic conversion are not known to be available. The University of the Basque Country has investigated a close-coupled liquid bio-oil preheated fluid bed zeolite cracking reactor (Cortright et al. 2002). Separation of thermal pretreatment from catalytic upgrading was found to reduce coking, but then the proposal for secondary upgrading of thermally degraded products in the pretreatment section suggest potential for blockage. This is analogous to the work at Saskatchewan.

3.7.3 Other Methods for Chemical Upgrading of Bio-oil

This section includes non-physical methods and those catalytic processes not covered in hydrotreating and zeolite-related processes. A list of known research activities was published in 2011 (Bridgwater 2012), but subsequently there has been considerable growth in this area.

Aqueous-phase processing is a relatively new approach that was first proposed by Dumesic and co-workers, who produced hydrogen and alkanes from aqueous solutions of oxygenated hydrocarbons through aqueous-phase reforming and dehydration/hydrogenation (Cortright et al. 2002; Huber and Dumesic 2006). A large fraction of bio-oil is water soluble and the compounds present in its aqueous fraction are mainly oxygenated hydrocarbons. This shows that the concept of aqueous-phase processing can be used to produce hydrogen and alkanes from the aqueous fraction of bio-oil.

Mild cracking is an alternative to orthodox zeolite-based cracking is mild cracking over base catalysts that address only the cellulose-and hemicellulose-derived products and aims to minimise coke and gas formation. Crofcheck at the University of Kentucky (Fisk et al. 2006) has explored ZnO and freshly calcined Zn/Al and Mg/Al layered double hydroxides to upgrade a synthetic bio-oil based on the earlier work in Finland (Nokkosmaki et al. 2000).

Esterification with alcohols up to butanol is being investigated and developed for improving the quality of bio-oil without substantial deoxygenation. Properties that are mostly addressed are water content, acidity, stability and reactivity.

Steam reforming provides a route to convert the water-soluble (carbohydrate-derived) fraction of bio-oil to hydrogen (Wang et al. 1997; Czernik et al. 2002) by steam reforming. This has been accomplished in a fluidised-bed process by several researchers using commercial, nickel-based catalysts under conditions similar to those for reforming natural gas. The process depends on a viable use for the organic lignin-derived fraction of bio-oil; for example use as a phenol replacement in phenol-formaldehyde resins (Mann et al. 1996) or for upgrading this organic fraction.

Model compounds and model bio-oil are often used to better understand the underlying chemical processes. While scientifically credible and providing a consistent and well-characterised feed material, there are dangers in relying too much on synthetic bio-oil, since no mixture can adequately represent the complex composition and behaviour of fast pyrolysis liquid.

3.7.4 Hydrogen

Hydrogen is produced in the syngas from gasification of bio-oil and bio-oil/char slurries as described above. There are also activities in both non-catalytic partial oxidation and catalytic partial oxidation and catalytic steam reforming of the whole bio-oil and the aqueous fraction after phase separation, particularly to meet the hydrogen demands of a hydrotreating process as described above. Catalysts are usually based on nickel or precious metals. A comprehensive list of activities in 2011 has been published (Bridgwater 2012) but as with other catalytic methods, there has been rapid expansion of research in this area.

3.7.5 Chemicals

Since the empirical chemical composition of biomass, approximately $(CH_2O)_n$, is quite different from that of petroleum $(CH_2)_n$, the range of primary chemicals that can be easily derived from biomass and oil are quite different. Hence, any biomass-based chemical industry will necessarily be constructed on quite a different selection of simple 'platform' chemicals than those currently used in the petrochemical industry. Given the chemical complexity of biomass, there is some choice of which platform chemicals to produce, since, within limits, different processing strategies of the same biomass can lead to different breakdown products. However, once a set of platform chemicals has been chosen for bio-based chemical production and the appropriate network of production plants is established, it will become be increasingly difficult to change that choice without disrupting the whole manufacturing infrastructure. Since the available biomass will inevitably show major regional differences, it is quite possible that the choice of platform chemicals derived from biomass will show much more geographical variation than in petrochemical production. Examples of chemicals derived from bio-oil are listed in Table 3.4 (Bridgwater 2012).

Table 3.4 Some chemicals recovered from bio-oil

Acetic acid
Alcohols
Aldehydes
Anhydrosugars
Asphalt
Biolime
Formic acid
Furfural
Hydrogen
Hydroxyacetaldehyde
Ketones
Levoglucosan
Levoglucosenone
Liquid smoke and related products
Non-aromatic alcohols
Organic acids
Pharmaceuticals
Phenol and phenolics
Plastics and polymers
Preservative
Resins and adhesives
Slow release fertilisers
Synthesis gas
Wood preservative

3.7.5.1 Chemical Composition of Bio-oil

The chemicals in bio-oil are derived from random thermal decomposition of hemicellulose, cellulose and lignin. Over 400 individual chemicals have been identified in bio-oil, and this area has been reviewed by Diebold (2002). There are many papers that provide details of bio-oil analyses, as analytical techniques have rapidly developed.

Strategies for separation or recovery of any of these chemicals need to consider market, value, costs and process. The natural first step is to evaluate components with the highest concentration, since the processing will be easier and the costs lower. However, this may not prove the best strategy, and methodologies need to carefully consider capital and operating costs, product values and residue or waste utilisation or disposal. The opportunities for optimisation are considerable and challenging, and are likely to involve a range of process generation, evaluation and optimisation tools including process synthesis and linear programming.

3.7.5.2 Production of Chemicals

For many centuries wood pyrolysis liquids were a major source of chemicals, such as methanol, acetic acid, turpentine, tars etc. At present, most of these compounds can be produced at a lower cost from fossil fuel feedstocks. Although over 300 compounds have been identified in wood fast pyrolysis oil, their concentrations are usually too low to consider separation and recovery. Up to now, therefore, the development of technologies for producing products from the whole bio-oil or from its major, relatively easy separable fractions is the most developed. A more detailed review on this subject, including consideration of higher value products, was published by Radlein (1999) and a thorough review of the literature on production of chemicals utilising whole oil, fractions of bio-oil, and specific chemicals was published in 2004 (Diebold 2002). A comprehensive review of phenolics recovery and utilisation has been published by Amen Chen et al. (2001).

Chemicals are always attractive commercial possibilities owing to their much higher added value compared to fuels and energy products. This suggests a bio-refinery concept in which the optimum combinations of fuels and chemicals are produced.

3.8 Conclusions

There has been a very considerable expansion of activity in fast pyrolysis in the last 15 years exploring novel processes for production of more useful and valuable products from bio-oil. This is due to the recognition of the value of a crude liquid that can be more easily handled, stored and transported than solid or gas with the potential for enhanced bioenergy and biofuel chains.

Attention has focused on two main areas:

- improving the quality of bio-oil to reduce or avoid problems in direct use, which requires identification and specification of the qualities concerned;
- upgrading to a more conventional product that can be more readily assimilated into existing fuel infrastructures. This includes transport fuels, synthesis gas for transport fuels and chemicals, hydrogen and commodity and speciality chemicals.

Quality can be defined as any one or combination of over 25 characteristics of bio-oil that affect its usage, so it is important to identify which characteristic or characteristics require modification and then address those properties.

There is increasing interest in higher value and more orthodox products, such as transport fuels and hydrogen, which has seen considerable growth of R&D activity. The latter can be partly explained by the requirement for significant amounts of hydrogen for some upgrading processes for production of hydrocarbon fuels and also for decentralised production of hydrogen for fuels cells, as hydrogen is costly to store and transport.

The relatively low hydrogen content of bio-oil invariably results in coking of catalysts in catalytic upgrading processes. Some solutions have been sought in more sophisticated catalyst systems that require less severe conditions and also in multi-stage upgrading, where bio-oil is processed in a series of steps to give a progressively upgraded product. Liquid processing is generally preferred to avoid problems of vapourising bio-oil with consequent loss of carbon as coke unless oxidative processing is included to oxidise any carbon that is formed.

The use of model compounds makes for easier fundamental science, but it is doubtful if any single chemical or even small number of chemicals can adequately reproduce the complexity of whole bio-oil with interactions between the constituent chemicals.

The considerable growth in activity around the world demonstrates the exciting opportunities and future for fast pyrolysis which will move from laboratory to commercial reality in a surprisingly short time.

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