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Review of fast pyrolysis of biomass and product upgrading

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ABSTRACT

This paper provides an updated review on fast pyrolysis of biomass for production of a liquid usually referred to as bio-oil. The technology of fast pyrolysis is described including the major reaction systems. The primary liquid product is characterised by reference to the many properties that impact on its use. These properties have caused increasingly extensive research to be undertaken to address properties that need modification and this area is reviewed in terms of physical, catalytic and chemical upgrading. Of particular note is the increasing diversity of methods and catalysts and particularly the complexity and sophistication of multi-functional catalyst systems. It is also important to see more companies involved in this technology area and increased take-up of evolving upgrading processes.

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1. Introduction

Biomass fuels and residues can be converted to more valuable energy forms via a number of processes including thermal, biological, and mechanical or physical processes. While biological processing is usually very selective and produces a small number of discrete products in high yield using biological catalysts, thermal conversion often gives multiple and often complex products, in very short reaction times with inorganic catalysts often used to improve the product quality or spectrum. Pyrolysis has been applied for thousands of years for charcoal production but it is only on the last 30 years that fast pyrolysis at moderate temperatures of around 500 °C and very short reaction times of up to 2 s has become of considerable interest. This is because the process directly gives high yields of liquids of up to 75 wt.% which can be used directly in a variety of applications [1] or used as an efficient energy carrier.

Fig. 1 summarises the markets for the products from the three main thermal processes available for converting biomass to a more useful energy form - pyrolysis, gasification and combustion. Combustion is a well-established commercial

technology with applications in most industrialised and developing countries and development is concentrated on resolving environmental problems [2]. Gasification has been practiced for many years and while there are many examples of demonstration and pre-commercial activities [3,4] there are still surprisingly few successful operational units. This review focuses on the emerging advanced technology of fast pyrolysis both as an integrated process for production of a liquid fuel that can be used directly and as an intermediate pre-treatment step to convert solid biomass into a higher energy content transportable liquid for subsequent processing for heat, power, biofuels, and chemicals. This technology is widely expected to offer a considerable contribution in the short term in terms of versatility, improved efficiency and environmental acceptability.

2. Fast pyrolysis

Pyrolysis is thermal decomposition occurring in the absence of oxygen. Lower process temperatures and longer vapour

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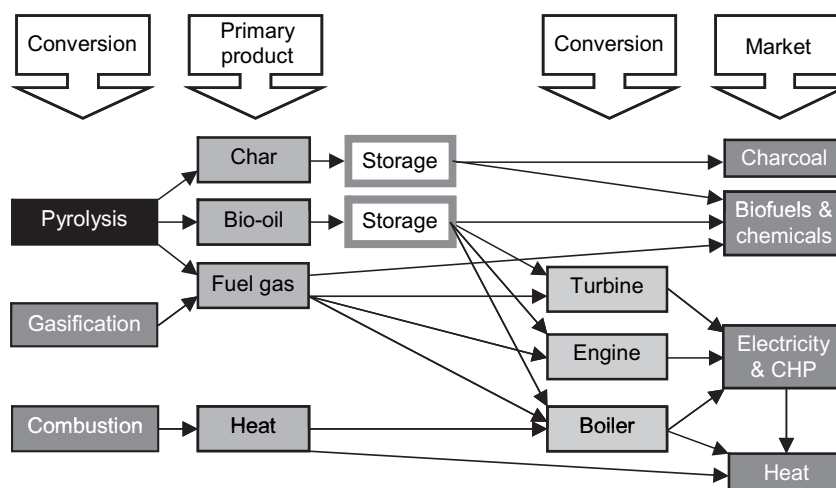


Fig. 1 – Products from thermal biomass conversion.

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. Three products are always produced, but the proportions can be varied over a wide range by adjustment of the process parameters. Table 1 and Fig. 2 indicate 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 as the liquid can be stored and transported, and used for energy, chemicals or as an energy carrier.

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 homogeneous 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 usually require a finely ground biomass feed of typically less than 3 mm as biomass generally has a low thermal conductivity,
- Carefully controlled pyrolysis reaction temperature of around 500 °C to maximise the liquid yield for most biomass,

- 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 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

Table 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%	12% char	13%
Intermediate	~500 °C, hot vapour residence time ~ 10–30 s	50% in 2 phases	25% char	25%
Carbonisation (slow)	~400 °C, long vapour residence hours → days	30%	35% char	35%
Gasification	~750–900 °C	5%	10% char	85%
Torrefaction (slow)	~290 °C, solids residence time ~ 10–60 min	0% unless condensed, then up to 5%	80% solid	20%

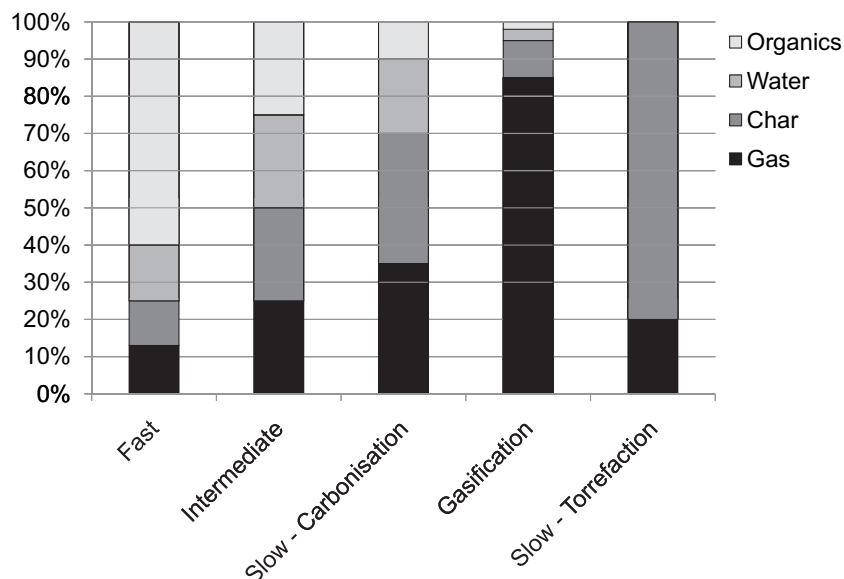


Fig. 2 – Product spectrum from pyrolysis.

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 can be considered for fast pyrolysis. While most work has been carried out on wood because of its consistency and comparability between tests, 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 pre-treatment;
- Conversion of solid biomass by fast pyrolysis to a more usable form of energy in liquid form which is known as bio-oil;
- Conversion of this primary liquid product by processing, refining or clean-up to a marketable end-product such as electricity, heat, biofuels and/or chemicals.

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. 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. Several comprehensive reviews of fast pyrolysis processes for liquids production are available such as [5–9].

Table 2 lists most of the known recent and current activities in fast pyrolysis arranged by reactor type and maximum known throughput. There has been considerable growth and expansion of activities over the last few years with more innovation in the types of reactor explored by academic institutions. It is disappointing to see so much re-invention and poor appreciation of the underlying fundamental requirements of fast pyrolysis as well as a reluctance to carry out basic reviews of past research publications.

There are increasing activities on fixed bed and related systems that are unlikely to give high liquid yields but are likely to give phase separated liquids. Phase separated liquid products may be desirable in some applications where fractionation is required, but it would seem preferable to control such separation rather than rely on poor design and process control.

2.2.1. Bubbling fluid beds

Bubbling fluid beds have the advantages of a well understood technology that is simple in construction and operation, good temperature control and very efficient heat transfer to biomass particles arising from the high solids density. Fig. 3 shows a typical configuration using electrostatic precipitators for coalescence and collection of what are referred to as 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.

2.2.1.1. *Heating.* Heating can be achieved in a variety of ways and scaling is well understood. However, heat transfer to bed at large scales of operation has to be considered carefully

Table 2 – Summary of fast pyrolysis reaction systems for liquids, recently and currently operational.

Fast pyrolysis	Industrial	Units built	Max size kg/h	Research	Max size kg/h
Fluid bed	Agritherm, Canada	2	200	Adelaide U, Australia	1
	Biomass Engineering Ltd, UK	1	200	Aston U., UK	5
	Dynamotive, Canada	4	8000	Cirad, France	2
	RTI, Canada	5	20	Curtin U, Australia	2
				ECN, NL	1
				East China U. Science and Technology, Shanghai, China	nk
				Gent U., Belgium	0.3
				Guangzou Inst, China	10
				Harbin Institute of Technology	nk
				Iowa State U., USA	6
				Monash U. Australia	1
				NREL, USA	10
				PNNL, USA	1
				Shandong U. Technology	nk
				Shanghai JiaoTong U,	1
				Shenyang U., China	1
				South East U., China	1
				Texas A&M U., USA	42
				TNO, Netherlands	10
				U. Basque Country, Spain	nk
				U. Campinas, Brazil	100
				U. Maine, USA	0.1
				U. Melbourne, Australia	0.1
				U. Naples, Italy	1
				U. Science and Technology of China	650
				U. Seoul, Korea	nk
				U. Twente, Netherlands	1
			U. Western Ontario, Canada	nk	
			U. Zaragoza, Spain	nk	
			USDA, ARS, ERRC, USA	1	
			Virginia Tech. U., USA	0.1	
			VTT, Finland	1	
			vTI, Germany	6	
			Zhejiang U., China	3	
			Zhengzhou U., China	2	
Spouted fluid bed	Ikerlan, Spain	1	10	Anhui U. of Science & Technology, China	5
Transported bed & CFB	Ensyn, Canada	8	4000	U. Basque Country, Spain	nk
	Metso/UPM, Finland	1	400	CPERI, Greece	1
Rotating cone Integral catalytic pyrolysis	BTG, Netherlands BioEcon, Netherlands + Kior USA	4 nk	2000 nk	Guangzhou Inst. Energy Conversion, China	nk
				U. Birmingham, UK	nk
				U. Nottingham, UK	nk
				VTT, Finland	20
				BTG, Netherlands	10
				Battelle Columbus, USA	1
Vortex Centrifuge reactor Ablative	PyTec, Germany	2	250	PNNL, USA	1
				Technical U. of Munich	nk
				U. Massachusetts–Amhurst, USA	nk
				Virginia Tech. U., USA	3?
				TNO, Netherlands	30
Augur or Screw	Abritech, Canada Lurgi LR, Germany Renewable Oil Intl, USA	4 1 4	2083 500 200	Technical U. Denmark	nk
				Aston U., UK	20
				Institute of Engineering Thermophysics, Ukraine	15
				Latvian State Institute, Latvia	0.15
				Technical U. Denmark	1.5
				Auburn U. USA	1.0
				KIT (FZK), Germany	500
				Mississippi State U., USA	2
				Michigan State U. USA	0.5
				Texas A&M U., USA	30

Table 2 (continued)

Fast pyrolysis	Industrial	Units built	Max size kg/h	Research	Max size kg/h
Radiative-Convective Entrained flow,				CNRS – Nancy U., France	nk
				Dalian U. of Technology, China	nk
Microwave	Carbonscape New Zealand & UK Bioenergy 2020 + gmbh, Austria	nk	nk	Institute for Wood Chemistry, Latvia	nk
				Shandong University of Technology	0.05
				Chinese Academy of Sciences, Dalian 116023, P. R. China	nk
				National Inst. Advanced Industrial Sci. & Technol., Japan	<0.1
				Shandong U. China	<0.1
				Technical U. Vienna, Austria	nk
		1	nk	U. Malaysia Sarawak	<0.1
				U. Minnesota, USA	10
				U. Mississippi	nk
				U. Nottingham, UK and China	nk
				U. York, UK	nk
				Washington State U.-Tricities, USA	<1
Moving bed and fixed bed	Anhui Yineng Bio-energy Ltd., China	3	600	Anadolu University, Turkey	nk
				U. Autònoma de Barcelona, Spain	nk
Ceramic ball downflow Unspecified				U. Science & Technology of China	~0.5
				Shandong University of Technology, China	110
Vacuum	Pyrovac, Canada	1	3500	U. Kentucky, USA	nk
				U. Texas, USA	nk
				Technical U. Compiegne, France	nk
				None known	

because of the scale-up limitations of different methods of heat transfer. 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.

2.2.1.2. *Char*. 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.

2.2.1.3. *Background*. 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 (e.g. [10–12]). Bubbling fluid beds have been selected for further development by several companies, including Union Fenosa [13], who built and operated a 200 kg/h pilot unit in Spain based on the University of Waterloo process which was dismantled some years ago; Dynamotive, who operated a 75 kg/h and 400 kg/h pilot unit

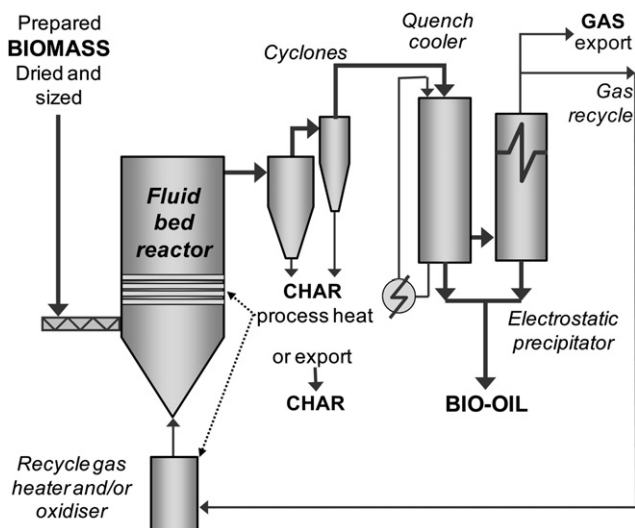


Fig. 3 – Bubbling fluid bed reactor with electrostatic precipitator.

[14] in Canada based on an RTI design and have subsequently built a 100 t/d and a 200 t/d plant in Canada; Wellman, who built a 250 kg/h unit [15] in the UK which has not operated; Biomass Engineering Ltd in the UK who are finalising construction of a 250 kg/h pilot unit and Fortum who built and extensively tested a 500 kg/h plant in Finland which has now been dismantled [16]. More recent activities include Ikerlan who are developing a spouted fluid bed in Spain [17], Metso who are working with UPM and VTT in Finland who have constructed and are operating a 4 MWth unit in Tampere Finland [18] and Anhui University of Science and Technology in China who are overseeing the construction of three demonstration plants in China up to 600 kg/h [19]. Many research units have also been built at universities and research institutions around the world, as they are relatively easy to construct and operate and give good results, and many are listed in Table 2.

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. 4. 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.

2.2.2.1. Heating. 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.

2.2.2.2. Char. 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.

2.2.2.3. Background. Larger scale examples include the 650 kg/h ENEL plant in Italy built by Ensyn [20,21] which has not operated for some years, several Ensyn units in the USA at Red Arrow in Wisconsin for production of food flavourings up to 1700 kg/h, and the Ensyn units at their R&D centre in Renfrew Canada up to 2000 kg/h with plans for units up to 1000 t d⁻¹ [22].

2.2.3. Rotating cone

The rotating cone reactor, invented at the University of Twente [23] and developed by BTG [24], is a relatively recent 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 120 t/d plant is at an advanced planning stage [25]. Fig. 5 shows an early prototype on the left and its role in an integrated fast pyrolysis process on the right. The key features are:

- centrifugation (at ~10 Hz) drives hot sand and biomass up a rotating heated cone;
- vapours are collected and processed conventionally;
- char and sand drop into a fluid bed surrounding the cone, whence they are lifted to a separate fluid bed combustor where char is burned to heat the sand, which is then dropped back into the rotating cone;
- char is burned in a secondary bubbling fluid bed combustor. The hot sand is recirculated to the pyrolyser;
- carrier gas requirements in the pyrolysis reactor are much less than for fluid bed and transported bed systems; however, gas is needed for char burn-off and sand transport;
- a more complex integrated operation of three subsystems is required: rotating cone pyrolyser, riser for sand recycling, and bubbling bed char combustor;
- liquid yields of 60–70% on dry feed are typically obtained.

As with CFB and transported beds all the char is burned so is not a byproduct, although the char could in principle be separated and recovered if an alternative heating source is provided.

2.2.4. 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

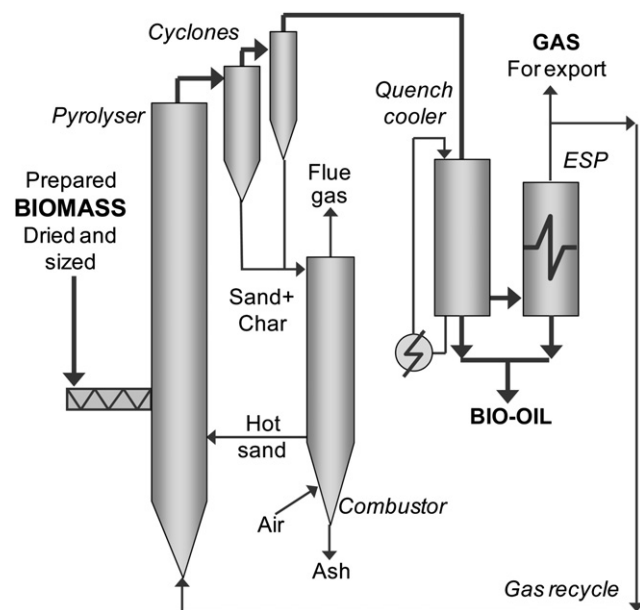


Fig. 4 – Circulating fluid bed reactor.

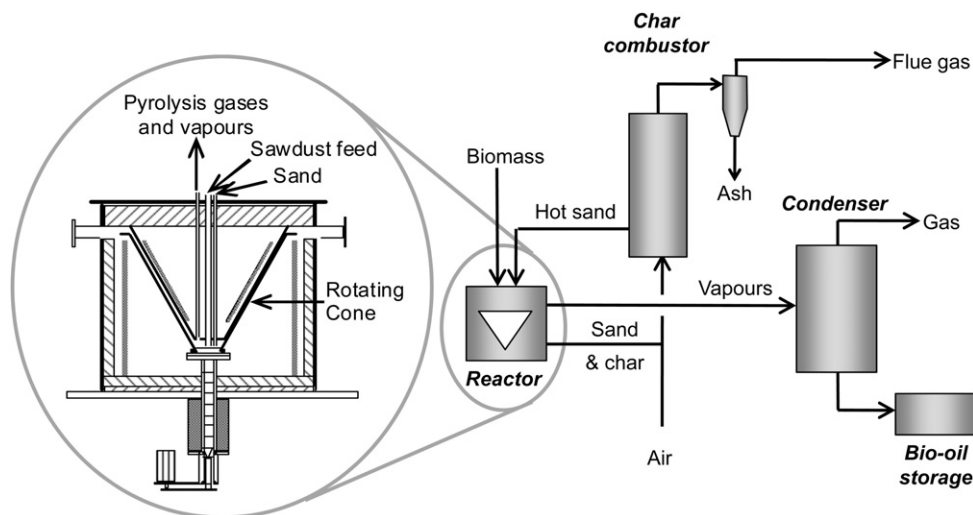


Fig. 5 – Rotating cone pyrolysis reactor and integrated process.

“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.

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 in the NREL, USA, concept, (no longer operational [26]) or mechanically at Aston University, UK which is described below and at PyTec in Germany;
- 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.

2.2.4.1. *Char*. The char is a fine powder which can be separated by cyclones and hot vapour filters as for fluid bed reaction systems.

2.2.4.2. *Background*. 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 [27]. 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 [26]. 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 [28] 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 [29] (Fig. 6).

Another configuration is the mechanically driven PyTec process in Germany [30]. 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 the other systems described above [30]. A 6 t/d unit has been built in north Germany in 2006 which is undergoing testing and designs are in progress for a 50 t/d unit. The liquid is used in an engine for power generation.

2.2.5. Other reaction systems

2.2.5.1. *Entrained flow*. 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 effect 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 [31] and Egemin [32] but neither is now operational. There is some basic research in this area in China.

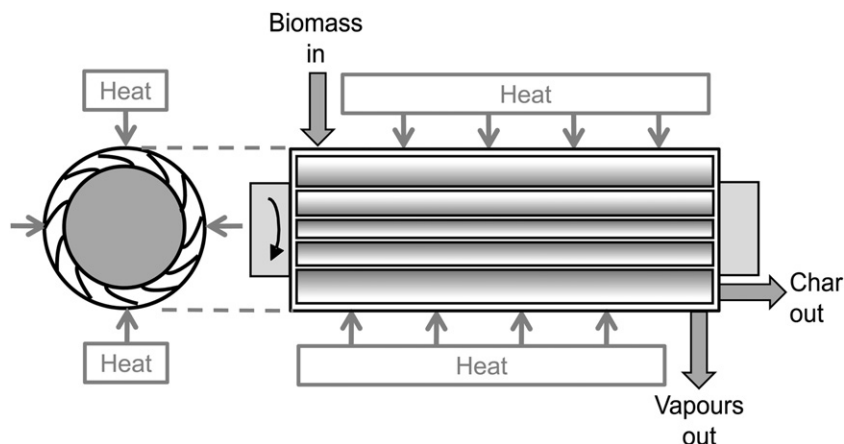


Fig. 6 – Aston University Mark 2 ablative fast pyrolysis reactor.

2.2.5.2. *Vacuum pyrolysis.* 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 [33]. 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.

2.2.5.3. *Screw and auger kilns.* There have been a number of developments that mechanically move biomass through a hot reactor rather than using fluids. These include screw and auger reactors. Heating can be with recycled hot sand as at the Bioliq plant at KIT (FZK until 2009) [34], with heat carriers such as steel or ceramic balls, 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 s depending on the design and size of reactor. Examples include screw reactors and more recently the Lurgi LR reactor at Karlsruhe Institute of Technology (KIT) [35] and the Bio-oil International reactors which have been studied at Mississippi State University [36]. Screw and auger reactors have also been developed as intermediate pyrolysis systems such as Haloclean also at KIT (e.g. [37]) and also as slow pyrolysis systems which are not included in this review.

Screw reactors are particularly suitable for feed materials that are difficult to handle or feed, or are heterogeneous. The liquid product yield tends to be somewhat 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 [35], but this would require an alternative energy source to provide heat for the process.

2.2.5.4. *Fixed bed fast pyrolysis.* 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.

2.2.5.5. *Microwave pyrolysis.* Some basic research has been carried out on microwave driven pyrolysis. Microwave heating is fundamentally different 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. Activities are included in Table 2.

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.

2.2.5.6. *Hydropyrolysis.* 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 [38] and a new patent has been applied for that includes hydrogen in the pyrolysis reactor with claims of producing hydrocarbons, alcohols and other oxygenates [39].

The concept has some contradictory requirements – high pressure in pyrolysis increases char yields e.g. Antal [40] and reduces liquid yields while high pressures are required to provide effective hydrogenation.

2.3. 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 by-product charcoal would typically be used in a commercial process by combustion of the char in air. The char typically contains about 25% of the energy of the feedstock, and about 75% of this energy is typically required to drive the process. The by-product 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 suitable positions in the reactor;
- 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 resulting in local overheating and reduced liquid yield, or alternatively very high gas flows are needed resulting in unstable hydrodynamics. 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 hot spots and increase cracking of the liquids to tars.

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 requires supplementation,
- 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 by-products have a sufficiently high value.

2.4. Char removal

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 aging 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 e.g. [41–44]. 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 $<5 \mu\text{m}$) 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. 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.

2.5. 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 exchanges. 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 [45].

2.6. By-products

Char and gas are by-products, 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 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 by-product 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.

3. Pyrolysis liquid – bio-oil

Crude 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. Typical organics yields from different feedstocks and their variation with temperature is shown in Figs. 7 and 8 shows the temperature dependence of the four main products from a variety of feedstocks [46]. Similar results are obtained for most biomass feedstocks, although the maximum yield can occur between 480 and 520 °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.

The liquid 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. Aging or instability is believed to result from a breakdown in this emulsion. In some ways it can be considered to be analogous to asphaltenes found in petroleum.

3.1. Bio-oil characteristics

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. While the liquid is widely referred to as

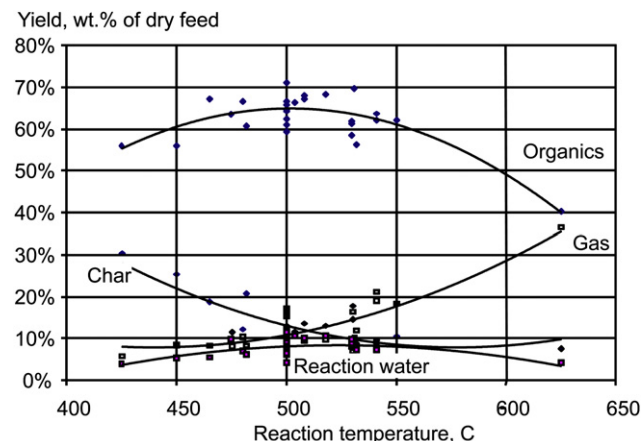


Fig. 7 – Variation of products from Aspen Poplar with temperature [46].

Organics yield, wt.% of dry feed

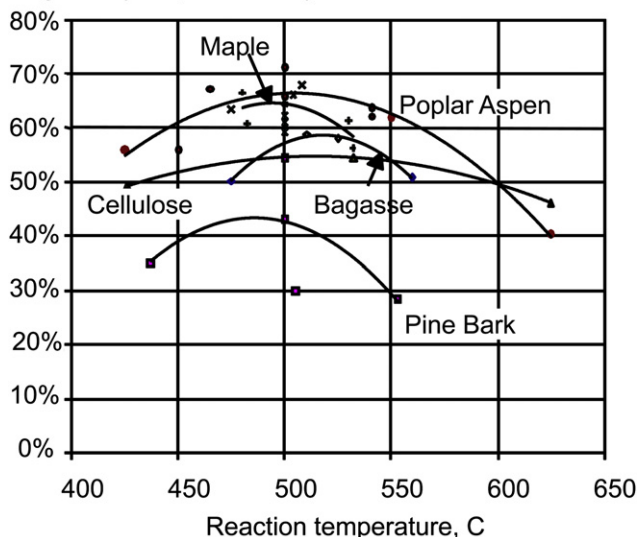


Fig. 8 – Organics yield from different feedstocks [46].

‘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 3.

Pyrolysis oil typically is a dark brown, free-flowing liquid. 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.

There are many particular characteristics of bio-oil that require consideration for any application. These are summarised in Table 4 with causes, effects and solutions. Oasma and Peacocke have reviewed physical property characterisation and methods [47]. The more significant characteristics are discussed below.

Table 3 – 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
Viscosity (40 °C and 25% water)	40–100 mpa s
Solids (char)	0.1%
Vacuum distillation residue	up to 50%

Table 4 – Characteristics of bio-oil.

Characteristic	Cause	Effects
Acidity or Low pH	Organic acids from biopolymer degradation	Corrosion of vessels and pipework
Aging	Continuation of secondary reactions including polymerisation	Slow increase in viscosity from secondary reactions such as condensation Potential phase separation
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
Char	Incomplete char separation in process	Aging of oil Sedimentation Filter blockage Catalyst blockage Engine injector blockage Alkali metal poisoning
Chlorine Colour Contamination of feed	Contaminants in biomass feed Cracking of biopolymers and char Poor harvesting practice	Catalyst poisoning in upgrading Discolouration of some products such as resins Contaminants notably soil act as catalysts and can increase particulate carry over.
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
High viscosity		Gives high pressure drop increasing equipment cost High pumping cost Poor atomisation
Low H:C ratio Materials incompatibility Miscibility with hydrocarbons is very low Nitrogen	Biomass has low H:C ratio Phenolics and aromatics Highly oxygenated nature of bio-oil Contaminants in biomass feed High nitrogen feed such as proteins in wastes	Upgrading to hydrocarbons is more difficult Destruction of seals and gaskets Will not mix with any hydrocarbons so integration into a refinery is more difficult Unpleasant smell Catalyst poisoning in upgrading NO _x in combustion
Oxygen content is very high	Biomass composition	Poor stability, Non-miscibility with hydrocarbons
Phase separation or In-homogeneity	High feed water, High ash in feed, Poor char separation,	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
Solids	See also Char Particulates from reactor such as sand Particulates from feed contamination	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 aging such as viscosity increase and phase separation
Sulphur Temperature sensitivity	Contaminants in biomass feed Incomplete reactions	Catalyst poisoning in upgrading Irreversible decomposition of liquid into two phases above 100 °C Irreversible viscosity increase above 60 °C Potential phase separation above 60 °C
Toxicity	Biopolymer degradation products	Human toxicity is positive but small Eco-toxicity is negligible
Viscosity	Chemical composition of bio-oil.	Fairly high and variable with time Greater temperature influence than hydrocarbons
Water content	Pyrolysis reactions, Feed water	Complex effect on viscosity and stability: Increased water lowers heating value, density, stability, and increase pH Affects catalysts

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 30–50 wt.% water, depending on the feed material, 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. 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. It is miscible with polar solvents such as methanol, acetone, etc. 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 below.

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 . 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 [48]. The viscosity of the bio-oil as produced can vary from as low as $25 \text{ m}^2 \text{ s}^{-1}$ to as high as $1000 \text{ m}^2 \text{ s}^{-1}$ (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 and some distillate containing volatile organic 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.

Aging 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 [49].

3.2. 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 [50]. The study includes a comprehensive evaluation of transportation requirements as an update of an earlier study [51] and an assessment of the biodegradability [52]. 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.

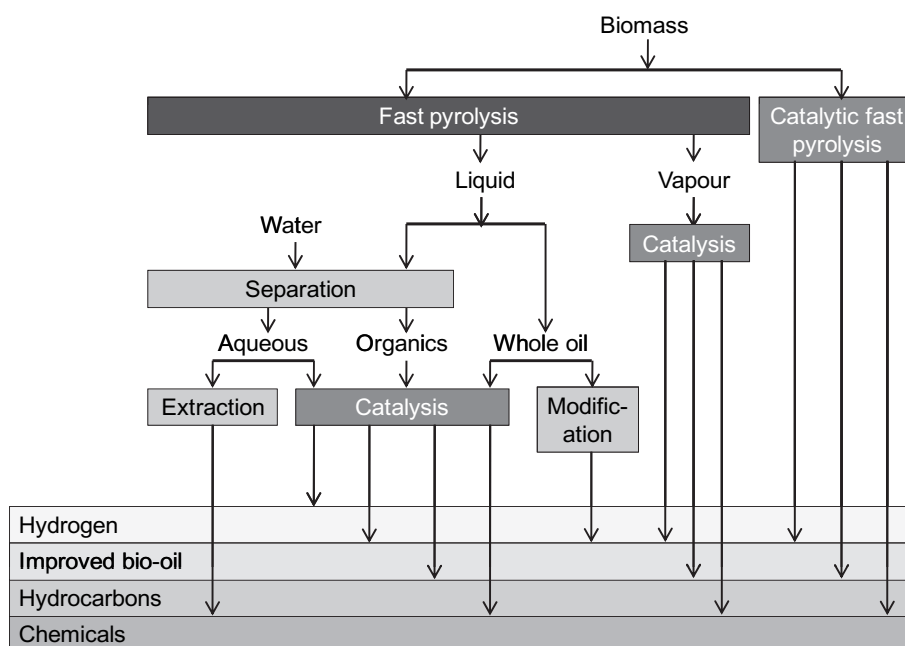


Fig. 9 – Overview of fast pyrolysis upgrading methods.

4. Bio-oil upgrading

Bio-oil can be upgraded in a number of ways – physically, chemically and catalytically. This has been extensively reviewed [1,53–56] and only the more significant features and recent developments are reported here. A summary of the main methods for upgrading fast pyrolysis products and the products is shown in Fig. 9.

4.1. 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.

4.1.1. 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 [57], however char is catalytically active and potentially cracks the vapours, reduces yield by up to 20%, reduces viscosity and lowers the average molecular weight of the liquid product. 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.

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 [58]. Hot gas filtration has not yet been demonstrated over a long-term process operation. A little work has been done in this area by NREL [56], VTT and Aston University [59], and very little has been published.

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

4.1.2. 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 [60] found that the rate of viscosity increase (“aging”) for the oil with 10 wt.% of methanol was almost twenty times less than for the oil without additives.

4.1.3. 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 micro-emulsions with 5–30% of bio-oil in diesel has been developed at CANMET [61]. The University of Florence, Italy, has been working on emulsions of 5–95% bio-oil in diesel [62,63] 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 high energy required for emulsification.

4.2. Catalytic upgrading of bio-oil

4.2.1. Natural ash in biomass

Before considering catalytic upgrading of bio-oil, it is important to appreciate firstly 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, and depending on the concentration the effect can be more severe than char cracking.

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 temperature or concentration respectively, the more complete the ash removal. 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 which can reach levels in bio-oil where recovery becomes an interesting proposition, although commercially markets need to be identified and/or developed.

4.2.2. 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 above or by decoupled operation as summarised below and depicted in Fig. 10. 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 [64].

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

4.2.3. Hydrotreating

Hydro-processing 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

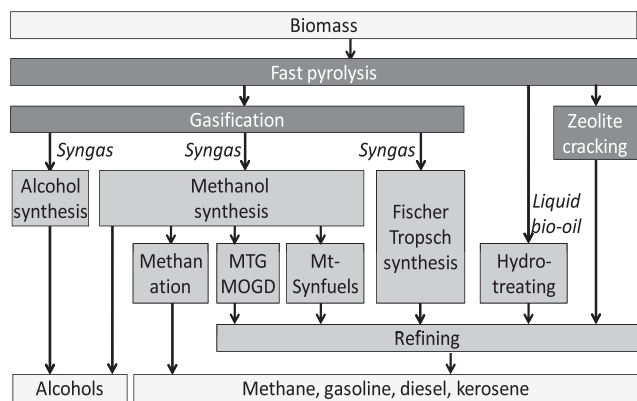
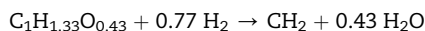


Fig. 10 – Upgrading of bio-oil to biofuels and chemicals.

carried out remotely. The process is typically high pressure (up to 20 MPa) and moderate temperature (up to 400 °C) and requires a hydrogen supply or source [65]. Full hydrotreating gives a naphtha-like product that requires orthodox refining to derive conventional transport fuels. This would be expected to take place in a conventional refinery to take advantage of know-how and existing processes. A projected typical yield of naphtha equivalent from biomass is about 25% by weight or 55% in energy terms excluding provision of hydrogen [54]. 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:



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 sulphur was stripped from the catalysts requiring constant re-sulfurisation. The main activities were based at PNNL, USA by Elliott (e.g. [66–68]) and at UCL in Louvain la Neuve in Belgium by Maggi et al. (e.g. [69,70]). This area has been thoroughly reviewed [52]. A recent design study of this technology for a biomass input of 2000 dry t/d for production of gasoline and diesel has been carried out by PNNL [71].

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 Pacific Northwest National Laboratory (PNNL) in the USA to address the scientific and technical challenges and develop a cost effective process [72]. Model compounds were used initially to understand the basic processes [73] 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 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 [74,75]. 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 [76].

At the Technical University of Munich Lercher proposes a “one pot” approach which is based on aqueous-phase hydrodeoxygenation of phenolic monomers using bifunctional catalysis that couples precious metal catalyzed hydrogenation and acid-catalyzed hydrolysis and dehydration [77]. 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 [78]. A significant improvement in many properties was reported.

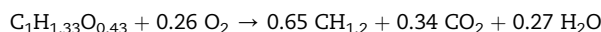
A number of other organisations are active in hydrotreating as summarised in Table 5.

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 for example by gasification. This is about 80% of that required to produce the bio-oil. The process is thus less efficient than simple performance figures often presented. If only the organic fraction of bio-oil after phase separation is hydrotreated, 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 [69,97]. Catalyst deactivation remains a concern from coking due to the poor C:H ratio.

In all cases the upgraded product needs conventional refining to produce marketable products and this would be expected to take place in a conventional refinery.

4.2.4. Zeolite cracking

Zeolite cracking rejects oxygen as CO₂, as summarised in the conceptual overall reaction below:



There are several ways in which this can be carried out as summarised in Fig. 11. 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. All these have been examined as summarised in Table 6.

A report by hydrocarbon processing for the future of 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

Table 5 – Organisations involved in catalytic upgrading of pyrolysis by hydrotreatment and related processes since 2000.

Organisation	Catalyst	Latest known activity	Reference example
Dynamotive, Canada	nk	2009	[79]
East China U. Science and Technology, Shanghai, China	CoMo–P sulfided	2004	[80,81]
East China U. Science and Technology, Shanghai, China	Pd on ZrO ₂ with SBA1 ₅	2009	[78]
Guangzhou Institute of Energy Conversion, China	NiMo on Al ₂ O ₃	2009	[82]
Groningen University, Netherlands	Ru and homogeneous Ru	2010	[73,83]
IRCELYON CNRS Université Lyon 1,	CoMo/Al ₂ O ₃	2008	[84]
Mississippi State U., USA	NiMo/γ Al ₂ O ₃	2009	[85,86]
	CoMo/γ Al ₂ O ₃		
	HZSM-5, SUZ-4		
	Precious metal		
Pacific Northwest Laboratory (PNNL), USA	Pd, Ru	2010	[72,87,88]
REHydrogen, UK	nk	2010	[89]
State U. Iowa, USA	nk	2009	
Technical U. of Munich, Germany	Pd on C	2009	[76,77]
U. Jyväskylä, Finland/VTT, Finland	Ru on C	2003	[90]
U. Kentucky, USA	Pt	2008	[91]
U. Maine, USA	nk	2007	[92]
U. Oklahoma, USA	Pd on carbon nanotubes	2010	[93]
U. Twente, Netherlands	Precious metal	2006	[94]
UOP, USA	Precious metal	2010	[95,96]

coke easily, and high TANs (Total Acid Number) and undesirable byproducts such as water and CO₂ are additional challenges.” [98].

4.2.4.1. Integrated catalytic pyrolysis. There is increasing interest in improving the quality of bio-oil 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.

Huber from University of Massachusetts Amhurst has also worked 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 [109,123]. High heating rates and catalyst-to-feed ratios are necessary to ensure that the pyrolysis vapours enter the catalyst pores and that thermal decomposition is avoided. The entire process was completed in under 2 min using relatively moderate amounts of heat [101]. The compounds that formed in the single step, such as naphthalene and toluene, make up 25% of the suite of chemicals found in gasoline. The product is referred to as Grassoline and a spin out company has been formed – Anellotech [124]. Anellotech already has demonstrated commercially relevant production not only of gasoline and biofuel precursors, but also of benzene, toluene, and xylene in milligram and gram-scale bench-top reactors. The “one pot” concept has also been developed by the Technical University of Munich which is described above in the hydro-treating section.

BioECon has formed a joint venture with KIOR [125] to exploit their technology. 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 [126]. Success is claimed at temperatures as low as 230 °C [99]. CPERI in Greece has carried out a number of projects on catalytic pyrolysis of biomass in

a circulating fluid bed reactor using zeolites and mesoporous catalysts. There was clear evidence of upgrading but incomplete de-oxygenation [100,101].

Aglevor at Virginia Polytechnic Institute & State University has developed a fractional pyrolysis process based on in-bed catalysis [111], which has been patented [112].

Exelus claims a low temperature (ca 200 °C) long residence time (ca 20 min) catalytic thermochemical process to convert biomass into gasoline [127]. While it is unlikely to be considered pyrolysis, it well illustrates the increasing innovation being applied to this field.

Other work on integrated catalytic pyrolysis has been carried out by a number of laboratories with limited success. One problem often encountered is the declared objective of improving bio-oil quality without defining what this means and what characteristic(s) is being addressed.

Integration of catalysis and pyrolysis requires operation at a single temperature and sufficiently robust catalyst to withstand the temperature and mechanical environment. There is therefore less flexibility in operating conditions suggesting

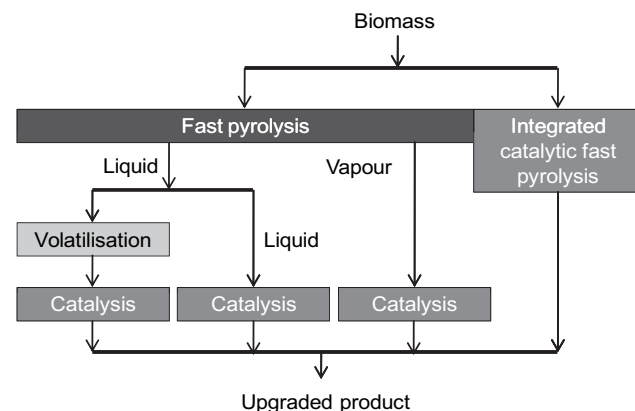
**Fig. 11 – Methods of upgrading fast pyrolysis products with cracking catalysts.**

Table 6 – Organisations involved in catalytic upgrading of pyrolysis since 2000 by zeolite based cracking processes.

Organisation	Catalyst	Latest known activity	Reference example
Integrated catalytic pyrolysis			
Anadolu University	clinoptilolite (natural zeolite, NZ), ZSM-5, H-Y	2009	[99]
Aston U. UK	ZSM-5	2010	
BioECon Netherlands, and Kior USA	nk	2009	[100]
CPERI, Geece	MCM-41	2008	[101,102]
East China U. Science and Technology, Shanghai, China	HZSM-5	2009	[80,81,103]
Exelus	nk	2010	[104]
Georgia Institute of Technology, USA	H-Y zeolites	2009	[105]
Michigan State U. USA	nk	2009	[106]
Sichuan U. China	Na/Y zeolite	2006	[107]
Southeast U. Nanjing, China	FCC	2009	[108]
U. Leeds, UK	ZSM-5	2000	[109]
U. Massachusetts USA	ZSM-5	2009	[110,111]
Virginia Tech USA	H-ZSM-5 Zr based superacids	2009	[112,113]
Close coupled vapour upgrading			
Aston U. UK	ZSM-5	2010	
East China University of Science and Technology, Instituto Superior Técnico, Portugal + Kior + Petrobras	HZSM-5 FCC and FCC+ZSM-5	2008 2009	[103] [114]
Norwegian U. Science and Technology + CPERI (Greece) + SINTEF (Norway)	Al-MCM-41, FCC, SBA-15	2006	[115]
U. Science and Technology of China, Anhui, China	HZSM-5, HY, ZrO ₂ &TiO ₂ , SBA-15, Al/SBA-15.	2009	[116,117]
University of Seoul, Kongju National University, Kangwon National University, Korea	Spent HZSM-5	2010	[118,119]
Decoupled vapour upgrading by volatilisation of bio-oil and Decoupled liquid bio-oil upgrading			
U. of the Basque Country, Spain	H ZSM-5, Ni-HZSM-5	2004	[116,120]
U. Pisa, Italy	H-ZSM-5	2000	[121]
Other approaches			
Zhejiang U. China	HZSM-5 in sub- and supercritical ethanol	2009	[122]

that catalytic systems will need to be quite sophisticated. Since coking is a recognised problem and is the mechanism by which oxygen is rejected from the bio-oil, catalyst regeneration is an essential aspect of a reactor design.

4.2.4.2. *Close coupled vapour upgrading.* Catalytic vapour cracking over acidic zeolite catalysts provides deoxygenation by simultaneous dehydration–decarboxylation producing mostly aromatics [128] at 450 °C and atmospheric pressure.

Table 7 – Organisations involved in other methods for chemical upgrading of pyrolysis liquid since 2000.

Organisation	Method	Latest known activity	Reference example
Groningen U. Netherlands	Reactive distillation and acid catalyst	2007	[138]
Guangzhou Institute of Energy Conversion, China	Solid acid 40SiO ₂ /TiO ₂ –SO ₄ ²⁻ solid base 30K ₂ CO ₃ /Al ₂ O ₃ –NaOH	2009	[139,140]
Helsinki U. Technology	Zinc oxide	2000	[137]
Institute of Chemical Industry of Forest Products, Nanjing China	Reactive distillation	2008	[141]
South China U. Technology	Solid acid and solid base catalysts	2008	[142]
U. Georgia, USA	Esterification of pyrolysis vapor	nk	[143]
U. Kentucky USA	ZnO, MgO and Zn-Al and Mg-Al mixed oxides;	2007	[136]
U. Science and Technology of China, Hefei	Dicationic ionic liquid C ₆ (mim) ₂ –HSO ₄	2009	[144,145]
U. Science and Technology of China Hefei	C ₁₂ A ₇ –O	2006	[146]
U. Wisconsin and U. Massachusetts USA	Aqueous phase reforming + dehydration + hydrogenation	2009	[135,147]
Zhejiang University	Acid cracking in supercritical ethanol	2008	[148]
Zhejiang University	Hydrogenation–Esterification over Bifunctional Pt Catalysts	2008	[149]

Oxygen is ultimately rejected as CO₂ 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. A projected typical yield of aromatics suitable for gasoline blending from biomass is about 20% by weight or 45% in energy terms [129]. The crude aromatic product would be sent for refining in a conventional refinery.

A key feature of this route is the absence of a hydrogen requirement and operation at atmospheric pressure. Some of the earlier work was carried out at NREL in a close coupled reactor with their ablative fast pyrolysis process [130]. The process was modelled technically and economically by an IEA Bioenergy Task [119].

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 [131]. The processing costs are high and the products are not competitive with fossil fuels [132]. Approach has only been studied at the basic research level and considerably more development is necessary.

4.2.4.3. 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 (e.g. [44,45]).

4.2.4.4. Decoupled liquid bio-oil upgrading. The University of the Basque Country has investigated a close coupled liquid bio-oil preheated fluid bed zeolite cracking reactor [108]. Separation of thermal pre-treatment from catalytic upgrading was found to reduce coking but then proposal for secondary upgrading of thermally degraded products in the pre-treatment section suggest potential for blockage. This is analogous to the work at Saskatchewan.

4.3. 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. Research activities are summarised in Table 7 and the main areas are described below.

4.3.1. Aqueous phase processing

This is a relatively new approach that was first proposed by Dumesic et al. who produced hydrogen and alkanes from aqueous solutions of oxygenated hydrocarbons through aqueous phase reforming and dehydration/hydrogenation [133–135]. A large fraction of bio-oil is water soluble and the compounds present in its aqueous fraction are mainly oxygenated hydrocarbons.

4.3.2. Mild cracking

An alternative to orthodox zeolite based cracking is mild cracking over base catalysts that address only the cellulose and hemicellulose derived products and aim to minimise coke

and gas formation. Crofcheck at University of Kentucky [136] has explored ZnO and freshly calcined Zn/Al and Mg/Al layered double hydroxides to upgrade a synthetic bio-oil based on earlier work in Finland [137]. These are summarised in Table 7.

4.3.3. Esterification and other processes

An increasing number of methods are being investigated and developed for improving the quality of bio-oil without substantial de-oxygenation which are summarised in Table 7. Properties that are mostly addressed are water content, acidity, stability, and reactivity.

4.3.4. Aqueous phase reforming

The concept was first proposed by Dumesic at the University of Wisconsin for upgrading the aqueous fraction of bio-oil for hydrogen and alkanes [147], and was subsequently supported by others [135].

4.3.5. 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 steam reforming both 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 summary of known research since 2000 is given in Table 8.

As referred to above, the water-soluble (carbohydrate-derived) fraction of bio-oil can be processed to hydrogen [150,151] by steam reforming. This has been accomplished in a fluidized 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 [152] or for upgrading this organic fraction.

4.3.6. Gasification for synfuels

A recent concept that has attracted much interest is the decentralised production of bio-oil or bio-oil-char slurries for transportation to a central process plant for gasification and synthesis of hydrocarbon transport fuels, by for example Fischer Tropsch synthesis, or alcohols. This is depicted above in Fig. 10. Although there is a small energy penalty from the lower pyrolysis energy efficiency, transportation energy and additional bio-oil gasification stage, this is more than compensated by the economies of scale achievable on a commercial sized gasification and transport fuel synthesis plant [187].

Although the concept of very large gasification plants of 5 GW or more has been promoted [188] based on importation of biomass on a massive scale to an integrated plant, based for example at Rotterdam, there are significant obstacles to be overcome. Decentralised fast pyrolysis plants of up to 100,000 t/y or 12 t/h are currently feasible and close to being commercially realised. Bio-oil gasification in an entrained flow oxygen blown pressurised gasifier is also feasible such as a Texaco or Shell system, with the added advantage that feeding a liquid at pressure is easier than solid biomass, offers

Table 8 – Organisations involved in reforming bio-oil for hydrogen since 2000.

Organisation	Catalyst	Model compounds	Latest known activity	Reference example
Non-catalytic partial oxidation				
Colorado School of Mines, USA and NREL, USA	None		2008	[153]
Siemens (Future Energy), Germany	None		2007	[154,155]
Aqueous phase reforming				
U. Pittsburgh, USA	Pt/Al ₂ O ₃	M glycerol, sorbitol, glucose	2008	[156]
U. Wisconsin, USA	Pd, Pt, Ni, Ru, Rh	M ethanol	2005	[147]
Catalytic steam reforming				
Aristotle U. Thessaloniki, Greece	Ni/olivine	M acetic acid, acetone, ethylene glycol	2009	[157,158]
Aristotle U. Thessaloniki, Greece	Nickel (5 wt.%) and noble metal (0.5 wt.% Rh or Ir) catalysts on CaO/Al ₂ O ₃ and 12CaO/Al ₂ O ₃	M acetic acid, acetone	2008	[159]
East China U. Science and Technology, Shanghai, China	Ni/MgO		2008	[160]
East China U. Science and Technology, Shanghai, China	Ni/Al ₂ O ₃		2007	[161]
Guangzhou Institute of Energy Conversion, China	Nk		2008	[162]
NREL, USA	Ni/Mg/K on Al ₂ O ₃		2002	[163]
NREL, USA	Ni – C11-NK from Süd-Chemie; Ni/Cr Al ₂ O ₃		2004	[151,164,165]
Queens U, Belfast UK	Noble metals	M	2005	[166]
Tokyo Institute of Technology Japan and U. Twente Netherlands	Pt/ZrO ₂	M acetic acid	2006	[167,168]
U. Basque Country, Spain	NiG-90, Rh-ZDC, 20NiSi, Ni/ α Al ₂ O ₃ , Ni-La ₂ O ₃ / α Al ₂ O ₃ , Ni-Co-La ₂ O ₃ / α Al ₂ O ₃ and Co/ZnO.	M acetic acid	2009	[169]
U. Kentucky, USA	Pt/Al ₂ O ₃ , Pt/TiO ₂ , Pt/ZrO ₂ , Pt/CeO ₂ , Pt/Ce _{0.7} Zr _{0.3} O ₂ , Rh/Al ₂ O ₃ , Rh/SiO ₂ -Al ₂ O ₃ and Rh/ZrO ₂ ,		2007	[170]
U. Patras, Greece	Ru/MgO/Al ₂ O ₃	M acetic acid	2007	[171]
U. Science & Technology of China, Hefei; U. Tokyo; Oxy Japan Corporation	CNTs-supported Ni		2009	[172]
U. Science & Technology of China, Hefei, Oxy Japan Corporation, Japan	C12A7/15%Mg, 12%Ni/ γ -Al ₂ O ₃ , 1%Pt/ γ -Al ₂ O ₃		2007	[173]
U. Science and Technology of China, Hefei, China	(Ca ₂₄ Al ₂₈ O ₆₄) ⁴⁺ ·4O ⁻ /Mg (C ₁₂ A ₇ -Mg)		2006	[146]
U. Science and Technology of China, Hefei, China	Ni-Cu-Zn-Al ₂ O ₃		2009	[174]
U. Twente Netherlands	Pd, Rh, Ru, Pt, Ni Al ₂ O ₃ , CeZrO ₂ , La ₂ O ₃		2004	[175]
U. Zaragoza, Spain	Coprecipitated Ni-Al catalysts	M acetic acid	2005	[176,177]
2 stage catalytic steam reforming				
East China U. Science and Technology, Shanghai 200237, China	Dolomite + Ni/MgO		2008	[178]
Combined non-catalytic partial oxidation and catalytic steam reforming				
Colorado School of Mines USA and NREL, USA	POx + 0.5% rhodium, ruthenium, platinum, and palladium (all supported on alumina) and alumina.		2007	[153,179]
Combined reforming processes				
U. Hawaii, USA	Steam reforming + CO ₂ removal with CaO		2003	[180]
U. Science & Technology of China, Hefei; Oxy Japan Corporation, Japan; U. Tokyo Japan	Electrochemical + NiO-Al ₂ O ₃		2009	[181–183]
Washington State U. USA	Plasma + Ni		2009	[184]
Cracking and steam reforming				
IRCELYON, UMR-CNRS, France	Rh/Ce _{0.5} Zr _{0.5} O ₂ and Pt/Ce _{0.5} Zr _{0.5} O ₂		2008	[185]
Aqueous phase reforming and hydrodeoxygenation				
Auburn U. USA				[186]

lower costs and the gas quality under such conditions is likely to be higher than from solid biomass. Finally transport fuel synthesis at 50,000 to 200,000 t/d is also commercially realisable from the extensive gas-to-liquid plants currently operational around the world. Future Energy (now Siemens) has successfully conducted pressurised oxygen blown gasification tests on both bio-oil and bio-oil/char slurries [189,190].

Synthetic hydrocarbons include diesel, gasoline, kerosene, LPG (liquefied Petroleum Gas) and methane (synthetic natural gas – SNG). These liquid fuels are entirely compatible with conventional fuels in all proportions, but are much cleaner. At least in the medium term, these are likely to be the biofuel of choice due to the ease of assimilation into the market place. It is also important that consumers have confidence in transport fuels, and conventional but synthetic hydrocarbon fuels are likely to cause least consumer resistance, particularly since there are well established and well defined quality requirements that would normally be applied in existing refineries if these are used for finishing products prior to marketing.

4.3.7. Model compounds and model bio-oil

Many new and interesting techniques for upgrading bio-oil are being investigated and this is very encouraging and interesting. But some of the laboratory work and particularly newer methods are based on model compounds or a selection of model compounds that purports to represent bio-oil. 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 of fast pyrolysis liquid.

5. Applications of bio-oil

Bio-oil can substitute for fuel oil or diesel in many static applications including boilers, furnaces, engines and turbines for electricity generation which was been thoroughly reviewed

in 2004 [1] and many aspects have not changed very much. The most significant changes since then are:

- An appreciation of the potential for fast pyrolysis to be a pre-treatment method i.e. for bio-oil to be an effective energy carrier
- Greater interest in bio-oil as a precursor for second-generation biofuels for transport
- Greater awareness of the potential for fast pyrolysis and bio-oil to offer more versatile processes routes to a wider range of products and contribute to biorefinery concept development.
- Considerably greater interest in upgrading bio-oil sufficiently for it to be used for heat, power and other applications with greater confidence by users

Fig. 12 summarises the possibilities for applications for bio-oil and the main developments are expanded below.

5.1. Pretreatment method for energy carrier

Biomass is a widely dispersed resource that has to be harvested, collected and transported to the conversion facility. The low bulk density of biomass, which can be as low as 150 kg/m^3 , means that transport costs are high and the number of vehicle movements for transportation to a large scale processing facility are also very high, with consequent substantial environmental impacts. Conversion of biomass to a liquid by fast pyrolysis at or near the biomass source will reduce transport costs and reduce environmental concerns as the liquid has a density of 1.2 kg/m^3 – nearly 10 times higher than low density crops and residues. This not only reduces the number of vehicle movements and costs by up to 87%, it also reduces costs of handling and transportation by virtue of it being a liquid that can be pumped. This leads to the concept of small decentralised fast pyrolysis plants of 100,000–300,000 t/y for production of liquids to be transported to a central processing plant. It is

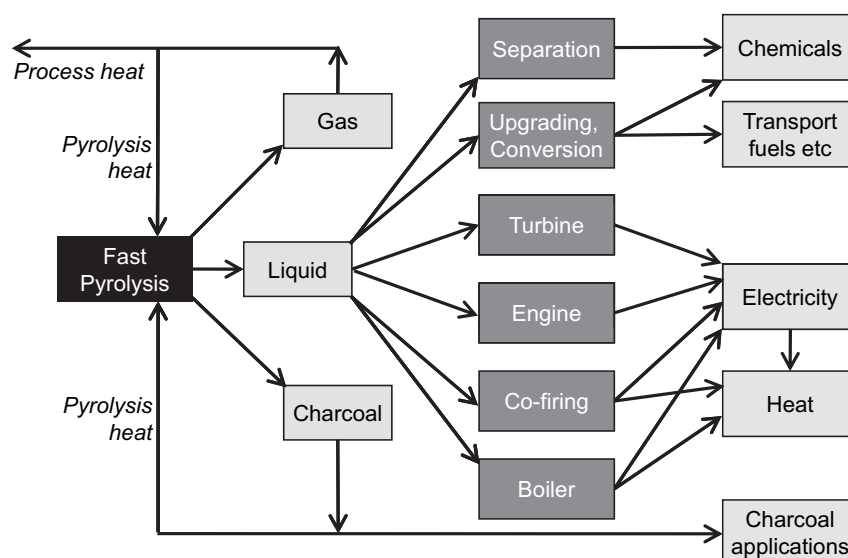


Fig. 12 – Applications for fast pyrolysis products.

Table 9 – Comparison of solid biomass gasification vs bio-oil gasification [183].

Impact from using liquid bio-oil	Capital cost	Performance	Product cost
Transport costs	Lower	Higher	Lower
Very low alkali metals	Lower	Higher	Lower
Handling and transporting costs	Lower	None	Lower
Liquid feeding to a gasifier particularly pressurised	Lower	Higher	Lower
Lower gas cleaning requirements	Lower	Higher	Lower
Higher costs for fast pyrolysis	Higher	Lower	Higher
Lower efficiency from additional processing step	Higher	Lower	Higher

also possible to consider mixing the byproduct char with the bio-oil to make a slurry to improve the energy content of the product as advocated by KIT and Dynamotive, but the pyrolysis process will then require that its process energy needs are met from another source.

Adoption of decentralised fast pyrolysis with transportation of the resultant liquid to a central gasification and fuel synthesis plant has both technical and economic advantages and disadvantages as summarised in Table 9. The impact of inclusion of fast pyrolysis as a pre-treatment step on BTL cost and performance has been analysed [178].

5.1.1. Co-firing

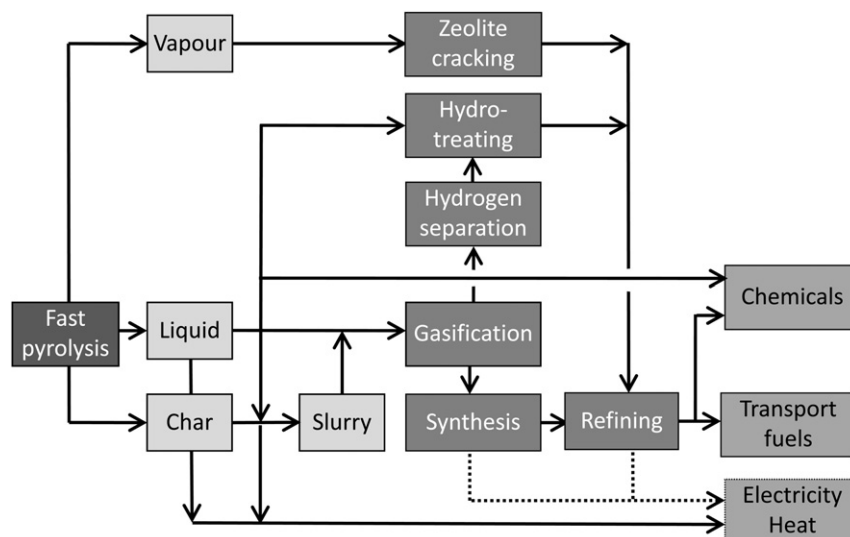
Co-processing of biomass with conventional fuels is potentially a very attractive option that enables full economies of scale to be realised as well as reducing the problems of product quality and clean up. Most current co-firing applications are those where the biomass fuels are added to the coal feed and this is widely practised at up to 5% on the energy demand of the power station. A few applications involve

conversion to a fuel gas via gasification followed by close coupled firing to the power station boiler. There are also some examples of co-firing fast pyrolysis liquids including a coal fired power station at Manitowac in the USA using the byproduct from liquid smoke production [191]. Large-scale tests have been carried out, where pyrolysis liquids from the Red Arrow operation were co-fired with coal for the commercial production of electricity [192]. The combustion of bio-oil was clean and efficient with no adverse changes on the boiler operation or on the emission levels. There is also some limited experience of successfully firing bio-oil in a natural gas fired power station in the Netherlands.

5.2. Biorefinery

The large majority of chemicals are manufactured from petroleum feedstocks. Only a small proportion of the total oil production, around 5%, is used in chemical manufacture but the value of these chemicals is high and contributes a comparable revenue to fuel and energy products. There is a clear economic advantage in building a similar flexibility into the biofuels market by devoting part of the biomass production to the manufacture of chemicals. In fact, this concept makes even more sense in the context of biomass because it is chemically more heterogeneous than crude oil and conversion to fuels, particularly hydrocarbons, is not so cost effective. Fig. 13 shows fast pyrolysis at the heart of a biorefinery.

A key feature of the biorefinery concept is the co-production of fuels, chemicals and energy. As explained earlier, there is also the possibility of gasifying biomass to make syngas, a mixture of hydrogen and carbon monoxide for subsequent synthesis of hydrocarbons, alcohols and other chemicals. However, this route is energy intensive so much of the energy content of the biomass is lost in the processing so electricity generation may be the most efficient use of biomass [193].

**Fig. 13 – Fast pyrolysis based biorefinery.**

Since the empirical chemical composition of biomass, approximately $(\text{CH}_2\text{O})_n$, is quite different from that of oil $(\text{CH}_2)_n$, the range of primary chemicals that can be easily derived from biomass and oil are quite different. Hence, any biomass chemical industry will have to be based on a different selection of simple ‘platform’ chemicals than those currently used in the petrochemical industry. 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. Fig. 14 shows schematically how an integrated pyrolysis based biorefinery might operate by integrating several of the different conversion technologies discussed above to create a single processing facility.

It is currently envisaged that biorefineries should focus on a limited number of platform chemicals for earlier implementation. Evolution will enable non-edible feedstock such as cellulose or lignin into well defined, useful carbon sources at high purity but at a lower cost than with starch or sugar feedstocks. For example vegetable oils can be transformed into a variety of high-value chemicals, particularly surface active chemicals, therefore it is wasteful merely to burn them as biodiesel, which should be derived from less valuable bio-feedstocks [194].

While biorefineries are not new, the recognition of their strategic and economic potential is recent. A biorefinery can be defined as the optimised performance of the use of biomass for materials, chemicals, fuels and energy applications, where performance relates to costs, economics, markets, yield, environment, impact, carbon balance and social aspects. In other words, there needs to be optimised use of resources, maximised profitability, maximised benefits and minimised wastes.

6. Economics

The total installed capital cost of a fast pyrolysis system from prepared and dried feed material to liquid bio-oil product in storage tanks is given by the following equation:

Bio-oil production cost, 2011, euros t^{-1}

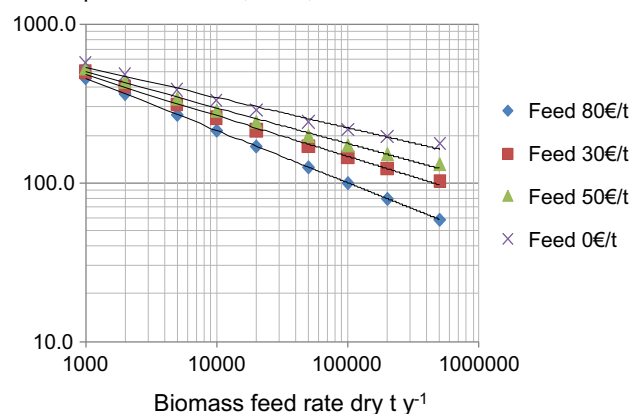


Fig. 15 – Bio-oil production costs.

Capital cost fast pyrolysis plant, euros million
 $_{2011} = 6.98 \times (\text{biomass feed rate dry t h}^{-1})^{0.67}$

The cost of production of bio-oil is given by the following equation:

$$\text{Production cost euros t}^{-1} \text{ bio-oil}_{2011} = 1.1 \times [(B) + (H \times 16,935 \times F^{-0.33})] Y^{-1}$$

B = Biomass cost € dry t^{-1} ,

H = Capital and capital related charges, default value = 0.18

F = Biomass feed rate dry t y^{-1} ,

Y = Fractional bio-oil yield, wt., default value = 0.75 for wood, 0.60 for grasses

The effect of scale for four dry basis feed costs from 0 to 80 euros t^{-1} is shown in Fig. 15

Fast pyrolysis technologies for the production of liquid fuel have been successfully demonstrated on a small scale, and several demonstration and commercial plants are in operation, but they are still relatively expensive compared with fossil-based energy, and thus face economic and other non-

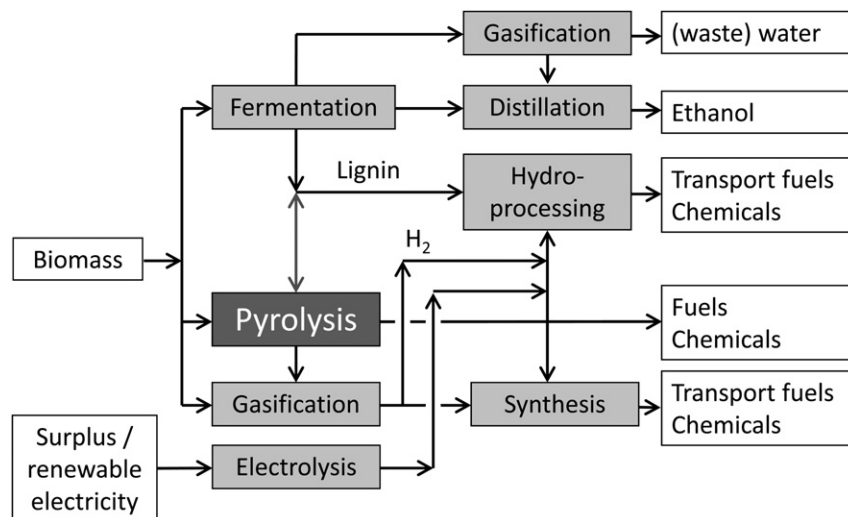


Fig. 14 – A biorefinery concept based on integrated biological and thermal processing for transport fuels and chemicals.

technical barriers when trying to penetrate the energy markets [195,196].

7. Conclusions

The liquid bio-oil produced by fast pyrolysis has the considerable advantage of being storable and transportable, as well as having the potential to supply a number of valuable chemicals. In these respects it offers a unique advantage. It is however disappointing to see that the lessons of past work are either not considered or forgotten in the rush to get new research underway. Fast pyrolysis has some basic and essential requirements if good yields of good quality bio-oil are to be derived.

The potential of bio-oil is increasingly being recognised, with a rapid growth in research into improving bio-oil properties particularly for dedicated applications and for biofuel production. Much of the research is still at a fundamental scale even to the use of model compounds and mixtures of model compounds that purport to represent whole bio-oil. It is doubtful if a limited component mixture can adequately represent the complexity of bio-oil. Some of the most interesting and potentially valuable research is on more complex and more sophisticated catalytic systems and these will require larger scale development to prove feasibility and viability.

Biorefineries offer considerable scope for optimisation of fast pyrolysis based processes and products, and these will require development of component processes in order to optimise an integrated system. They will necessarily include provision of heat and power for at least energy self sufficiency.

There is an exciting future for both fast pyrolysis and bio-oil upgrading as long as these are focussed on delivering useful and valuable products.

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