



Biomass Pyrolysis

IEA Bioenergy

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Cover picture

Dynamotive 100 t/d fluid bed fast pyrolysis, bio-oil plant in West Lorne, Ontario, Canada. (Courtesy Dynamotive and A. Bridgwater)

Biomass Pyrolysis

This feature article provides an overview based on the work of Task 34: Pyrolysis of Biomass. It was prepared by the Task Leader, Professor Tony Bridgwater, Bioenergy Research Group, Aston University, UK.

Introduction

Renewable energy is of growing importance in responding to concerns over the environment and security of energy supply. Biomass is unique in providing the only renewable source of fixed carbon, which is an essential ingredient in meeting many of our fuel and consumer goods requirements. It is also considered the renewable energy source with the highest potential to contribute to the energy needs of modern society for both the developed and developing economies worldwide.^{1,2} Wood, energy crops and agricultural and forestry residues are some of the main renewable energy resources available. The biodegradable components of municipal solid waste (MSW) and commercial and industrial wastes are also significant bioenergy resources, although, particularly in the case of MSW, they may require extensive processing before conversion.

Bioenergy could provide the major part of the projected renewable energy provisions of the future as biofuels in the form of gas, liquid or solid fuels, or electricity and heat. There are many ways of providing these biofuels, including thermal and biological conversion, of which pyrolysis, and particularly fast pyrolysis, forms the focus of this review.

Of the available biomass conversion technologies for production of more usable energy forms, fast pyrolysis is the least developed, but offers the benefits of a liquid fuel with concomitant advantages of easy storage and transport as well as higher power generation efficiencies than fossil fuelled systems at the smaller scales of operation that are likely to be realised from bioenergy systems. All the other thermal and biological biomass conversion processes are commercially available, usually with performance guarantees, and are steadily being implemented around the world.

Pyrolysis

Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is also always the first step in combustion and gasification, but in these processes it is followed by total or partial oxidation of the primary products. 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 times are optimum for producing liquids. Table 1 indicates the product distribution obtained from different modes of pyrolysis. Fast pyrolysis for liquids production is currently of particular interest because liquids can be stored and transported more easily and at lower cost than solid biomass.^{3,4,5,6}

Table 1: Typical product yields (dry wood basis) obtained by different modes of pyrolysis of wood

Mode	Conditions	Liquid	Char	Gas
Fast	moderate temperature, around 500°C, short hot vapour residence time ~ 1 second	75%	12%	13%
Intermediate	moderate temperature, around 500°C, moderate hot vapour residence time ~ 10-20 seconds	50%	20%	30%
Slow (carbonisation)	low temperature, around 400°C, very long solids residence time	30%	35%	35%
Gasification	high temperature, around 800°C, long vapour residence time	5%	10%	85%

Fast pyrolysis occurs in a few seconds or less. Therefore 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 intermediate (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 rapidly only to the particle surface that contacts the heat source, as applied in ablative pyrolysis. A critical technical challenge in every case is heat transfer to the reactor in commercial systems.

Principles of fast pyrolysis

In fast pyrolysis, biomass rapidly decomposes to generate vapours, aerosols, gases and some charcoal. After cooling and collection, a dark brown mobile liquid is formed that has a heating value of about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes for making charcoal (see Table 1), fast pyrolysis is an

advanced process that is completed in seconds, with carefully controlled parameters, to give high yields of liquid. The essential features of a fast pyrolysis process for producing liquids are:

- Very high heating and heat transfer rates at the reaction interface, which usually requires a finely ground biomass feed.
- Carefully controlled pyrolysis reaction temperature of around 500°C and vapour phase temperature of 400–450°C. The effect of temperature on yields and product spectrum is discussed in the section on pyrolysis liquid below.
- Short hot vapour residence times of typically less than two seconds.
- Rapid cooling of the pyrolysis vapours to give the bio-oil product.

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

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 around 2 mm particle size in the case of fluid bed reactors) to give sufficiently small particles to ensure rapid reaction, fast pyrolysis, separation of solids (char), and quenching and collection of the liquid product (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, nearly 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.

A typical fast pyrolysis process is depicted in Figure 1 showing the necessary preparation steps, alternative reactors, and product collection.

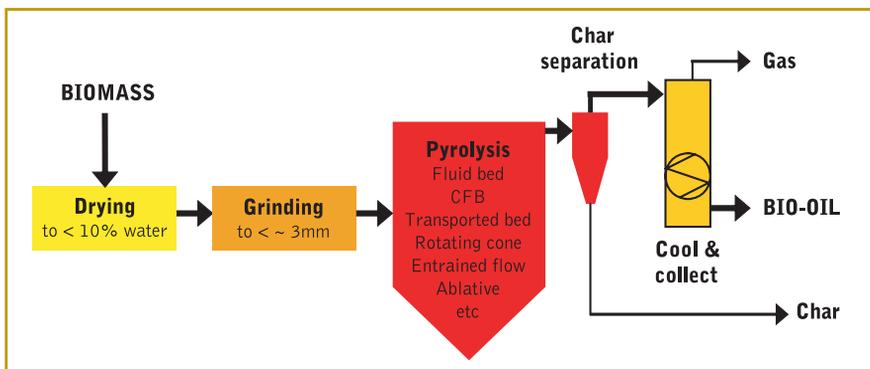


Figure 1: Conceptual fast pyrolysis process

Reactors

At the heart of a fast pyrolysis process is the reactor. Although it probably represents at most only about 10-15% of the total capital cost of an integrated system, most research and development projects have focused on the reactor. Increasing attention is now being paid to control and improvement of 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, liquid upgrading. The key aspects of these peripheral steps are described later. A comprehensive survey of fast pyrolysis processes for liquids production that have been built and tested in the last 10-15 years has already been published.⁴

Bubbling fluid beds

Bubbling fluid beds - usually referred to as just 'fluid beds' as opposed to 'circulating 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. 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.



Figure 2: Dynamotive 100 t/d fluid bed fast pyrolysis plant in West Lorne, Ontario, Canada

Lorne, Ontario, Canada, which has a 100 tonnes per day (t/d) dry biomass feed demonstration plant, with plans for further plants up to 400 t/d¹⁰ (Figure 2). A 2.5 MWe gas turbine is also provided on site for generation of power for local use and for export to the grid. There are research units at universities and research institutions around the world including State University of Iowa, USA, RTI Canada, IWC Germany, Aston University UK, VTT Finland, and the National Renewable Energy Laboratory (NREL), USA. A typical 1 kg/h laboratory unit is shown in Figure 3.

Residence times of solids and vapours are controlled by the fluidising gas flow rate and are 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 earliest pioneering work on fast pyrolysis was carried out at the University of Waterloo by Scott who published extensively.^{7,8,9} The largest plant currently operating is that of Dynamotive in West



Figure 3: Laboratory fluid bed fast pyrolysis units: Aston University 1 kg/h (left) and Iowa State University 5 kg/h (right)

Circulating fluid beds and transported bed

Circulating fluid beds (CFB) 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, which can lead to higher char contents in the collected bio-oil. An added advantage is that CFBs are potentially suitable for very large throughputs even though the hydrodynamics are more complex - this technology is widely used at very high throughputs in the petroleum and petrochemical industry. However, heat transfer at higher throughputs has not been demonstrated and offers some challenges.¹¹ 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 and heat flux match the process and feed requirements. VTT has a 20 kg/h process development unit shown in Figure 4.

A variation on the transported bed is the rotating cone reactor, invented at the University of Twente¹² and implemented by BTG in the Netherlands. In this configuration, the transport is effected by centrifugal forces rather than gas. A 50 t/d plant has been built in Malaysia and was commissioned in summer 2005 (Figure 5).



Figure 4: 20 kg/h fast pyrolysis process development unit at VTT

Ablative pyrolysis

Ablative pyrolysis is substantially different in concept from other methods of fast pyrolysis.¹³ In all the other methods, the rate of reaction is limited by the rate of heat transfer through the biomass particles, which is why small particles are required.

The mode of reaction in ablative pyrolysis is like melting butter in a frying pan - the rate of melting can be significantly enhanced by pressing the butter down and moving it over the heated pan surface. In ablative pyrolysis, heat is transferred from the hot reactor wall to 'melt' wood that is in contact with it under pressure. The pyrolysis front thus moves uni-directionally 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. The rate of reaction is strongly influenced by pressure, the relative velocity of the wood and the heat exchange surface and the reactor surface temperature. The key features of ablative pyrolysis are therefore:

- High pressure of particle on hot reactor wall, achieved due to mechanical force (Aston University) or centrifugal force (NREL).
- High relative velocity 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, large 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 of potentially lower cost. However, the process is surface-area-controlled so scaling is a linear function of the heat transfer area and thus does not benefit from the economies of scale of other systems such as fluid beds. In addition, the reactor is mechanically driven and is thus more complex. PyTec has recently started operating a 50 t/d demonstration plant in north Germany¹⁴, (Figure 6); and a small research unit operates at Aston University¹³, (Figure 7).



Figure 5: BTG 50 t/d rotating cone fast pyrolysis plant in Malaysia



Figure 6: PyTec 50 t/d ablative pyrolysis demonstration plant

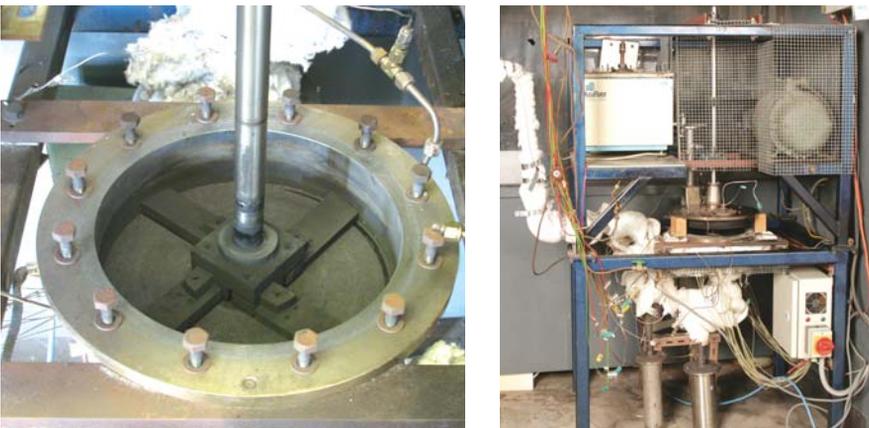


Figure 7: Aston University ablative plate fast pyrolysis reactor (left) and unit (right)

Entrained flow

Entrained flow fast pyrolysis is in principle a simple technology, but most developments have not been as successful as had been hoped, mostly because of the poor heat transfer between a hot gas and a solid particle. High relative gas velocities and high turbulence are required to effect sufficient heat transfer. This requires large plant sizes and high gas flow rates, which results in more difficult liquid collection from the low vapour partial pressure. Liquid yields have usually been lower than fluid bed and CFB systems.

By-products

Charcoal 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 by-products, only the char has sufficient energy to

provide this heat. The process heat requirement can be derived by burning the gas and/or the charcoal by-product. More advanced configurations could gasify the char to a lower heating value (LHV) gas and then burn the resultant gas more effectively to provide process heat, with the advantage that the alkali metals in the char can be much better controlled and avoid potential slagging problems from direct char combustion. There are many other ways of providing the heat.¹¹

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. The product spectrum from fast pyrolysis of aspen poplar wood, and the high dependence on temperature, are shown in Figure 8.

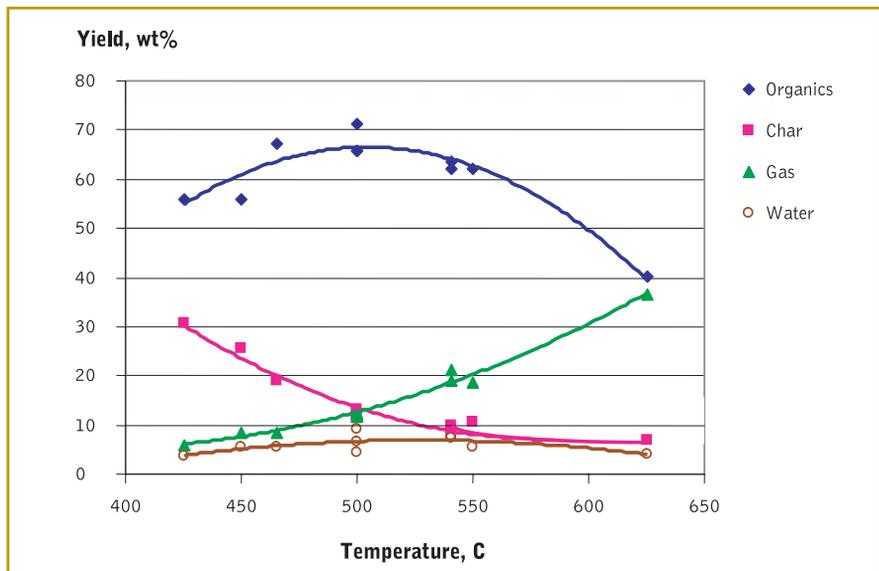


Figure 8: Variation of products from aspen poplar with temperature ¹⁵

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 chemicals, 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 macro-molecules through mechanisms such as hydrogen bonding.

Bio-oil has a higher heating value (HHV) of about 16-17 MJ/kg as produced with about 25% wt water that cannot readily be separated. It is composed of a complex mixture of oxygenated compounds that provide both the potential and challenge for utilisation. There are some important characteristics of this liquid that are summarised in Table 2 and discussed briefly below, of which the most significant is that it will not mix with any

conventional hydrocarbon-based fuels. Typically it 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.

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

Table 2: 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	6.5%
	O	37.5%
	N	0.1%
	Ash	0%
HHV* as produced		17 MJ/kg
Viscosity (40°C and 25% water)		50cp
Solids (char)		0.1%
Vacuum distillation residue		up to 50%
<i>*HHV: Higher Heating Value</i>		
Characteristics		
<ul style="list-style-type: none"> • Liquid fuel • Ready substitution for conventional fuels in many stationary applications such as boilers, furnaces, engines, turbines • Heating value of 17 MJ/kg at 25% wt water, is about 40% that of fuel oil/diesel • Does not mix with hydrocarbon fuels • Quality needs definition for each application 		

The liquid usually forms a stable single-phase mixture when the feedstock is clean wood. It contains varying quantities of water ranging from about 15% by weight (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 end

up in the liquid product. This results in a liquid with around 25% water. Water levels above 35-40% from high feed moisture or vapour cracking can result in instability and phase separation. 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 substantially immiscible with petroleum-derived fuels.

The density of the liquid is very high at around 1.2 kg/litre, compared with light fuel oil at around 0.85 kg/litre. 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.

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 reacts firstly by polymerisation followed by thermal cracking and eventually produces a solid residue of around 50 wt% of the original liquid and some distillate containing volatile organic compounds and water. 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. However, there is a gradual increase in viscosity over time and in extreme cases of wide temperature fluctuation, phase separation can occur.

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.¹⁶ Figure 9 summarises the possibilities. A range of chemicals including food flavourings, specialities such as

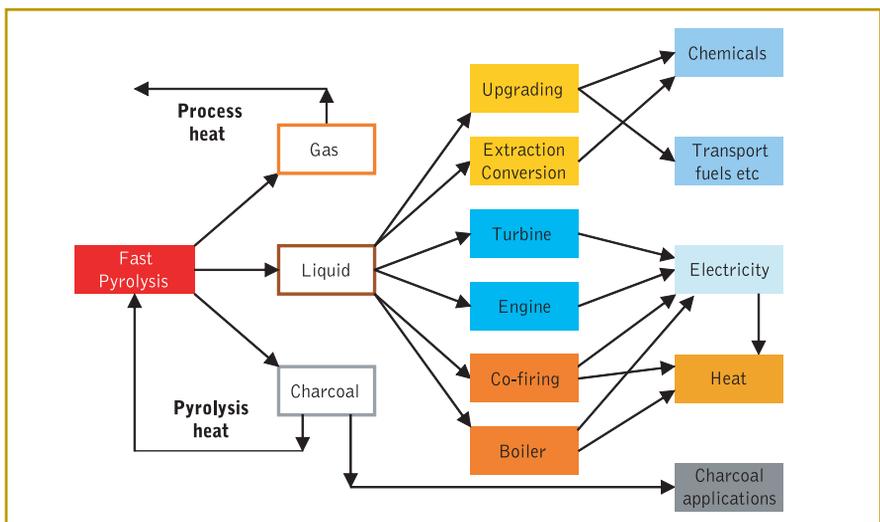


Figure 9: Applications for products of fast pyrolysis

hydroxyacetaldehyde¹⁷, resins¹⁸, agri-chemicals, fertilisers, and emissions control agents can also be extracted or derived from bio-oil. For power generation, at least 400 hours operation has been achieved on a 250 kW_e specially modified dual fuel engine¹⁹ and substantial experience has been gained on a modified 2.5 MW_e industrial gas turbine.

Transport fuels

As biomass is the only renewable source of fixed carbon, there is considerable interest in the production of transport fuels and other commodity chemicals via synthesis gas or syngas as it is usually known. Syngas provides the raw material for production of virtually every fuel and chemical in use today, including conventional and unconventional transport fuels, commodity chemicals and speciality chemicals. Some of the possibilities of considerable topical significance for production of hydrocarbon transport fuels are shown in Figure 10.

There are two main routes to transport fuels that are currently being considered: gasification of bio-oil followed by synthesis; and hydro-processing of bio-oil or separated bio-oil. These are shown in Figure 10.

Gasification and fuel synthesis

Syngas is a mixture of carbon monoxide (CO) and hydrogen (H₂). There are usually other components arising from gasification such as carbon dioxide (CO₂), methane (CH₄), higher hydrocarbons such as ethylene and ethane, propane and propylene, and nitrogen from air gasification. Generally these act as diluents, but different generic and specific processes have different levels of tolerance for each component. There will also be trace contaminants containing sulphur (e.g. H₂S), chlorine (e.g. HCl, COCl) and nitrogen (e.g. ammonia NH₃) in a range of compounds. The concentrations of these trace components will usually require reduction to a few parts per million for most catalyst systems used in synthesising alcohols and hydrocarbons, and each catalyst has its own limitations and tolerances.

Figure 10 includes gasification of solid biomass as well as bio-oil from fast pyrolysis. The dispersed nature of biomass in Europe and the environmental cost of collection and transport are often considered to limit the size of solid feed processes to around 100,000 t/y or 20 MW_e, except in Scandinavia. However, in North and South America this upper limit is usually considered to be much higher. Transport fuel synthesis becomes uneconomic at such small scales of operation, but a decentralised fast pyrolysis network feeding bio-oil as an energy carrier is not limited, and commercially viable scales of operation can then become feasible, even with the small loss of efficiency in the pyrolysis step. In addition, a liquid feed to a pressurised oxygen blown gasifier is less complex and thus lower cost than solid biomass. Partial upgrading of bio-oil into a conventional refinery feedstock is another option that is being widely considered.

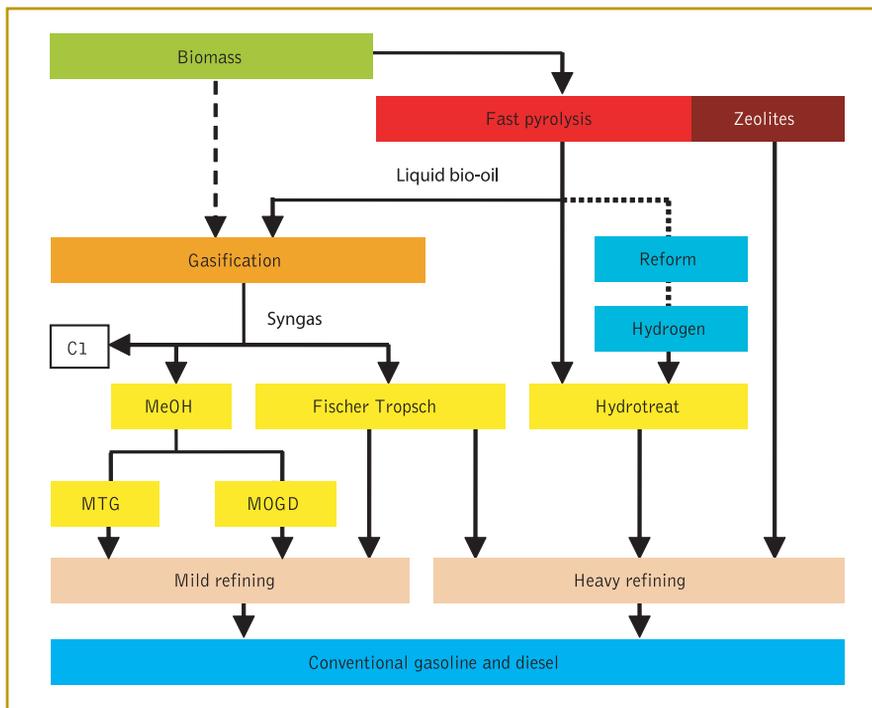


Figure 10: Transport fuels via bio-oil and biomass gasification (MTG: Methanol To Gasoline; MOGD: Methanol to Olefins, Gasoline and Diesel)

Hydro processing of bio-oil and other upgrading methods

Conversion of bio-oil into hydrocarbons requires removal of oxygen. Oxygen rejection from bio-oil can be as water by reaction with hydrogen or as carbon dioxide.

Hydroprocessing or hydrotreatment was extensively studied at Pacific Northwest National Laboratory (PNNL) in the USA and the University of Louvain in Belgium in the 1990s, and a comprehensive review of this work has been published.²⁰ This early work focused on conventional hydro-treating catalysts as used for hydrodesulphurization based typically on Co/Mo or Ni/Mo. While some success was obtained in producing a naphtha-type product in a two-stage high pressure process, catalyst instability problems in the high water content bio-oil and poor economics with low crude oil prices caused interest to wane.²¹

More recently, high oil prices and other pressures have led to a resurgence in interest and hydroprocessing optimization is being carried out at the PNNL on a bench-scale fixed-bed continuous-flow reactor to produce partially upgraded petroleum refinery feedstock with the intent to displace imported petroleum. This is funded by the US Department of Energy as part of a cooperative project with UOP LLC and the NREL.

The alternative of rejection of oxygen as carbon dioxide is based on atmospheric cracking of pyrolysis vapours over zeolite catalysts, which was pioneered at NREL.²² The inherent attraction is that it is a low pressure process that is integrated into the fast pyrolysis process, and thus offers potential cost savings. However the lower yields

and complexity from the requirement to constantly regenerate the coked zeolite catalysts has inhibited interest in this route. The two routes summarized here have been compared technically and economically.^{23,24} Other possibilities for upgrading bio-oil have been reviewed.¹⁶

Co-firing and co-processing

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 requirements for product quality and clean up. The opportunities are summarised in Figure 11. At present, co-firing offers the best opportunities for market penetration of biomass as the overall costs are relatively low because the power cycle in the coal-fired power plant is already there. Bio-oil is particularly attractive for co-firing because it can be more readily handled and burned than solid fuel, and is cheaper to transport and store. Limited trials of co-firing bio-oil in gas fired power stations²⁵ and a coal-fired power station²⁶ have also taken place.

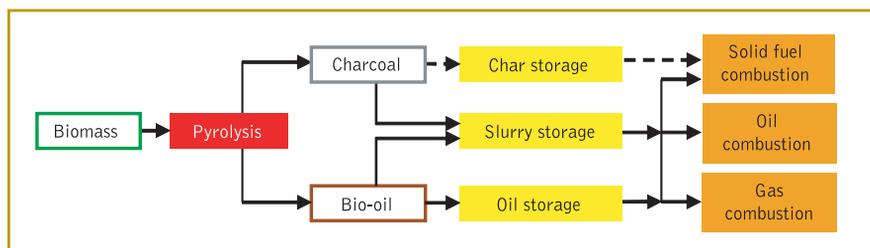


Figure 11: Opportunities for co-processing biomass and biofuels in conventional heat and power applications.

Biorefinery

After many years of production of chemicals from bio-oil, the concept of the biorefinery has suddenly become recognised and accepted. A biorefinery is where fuels and chemicals are produced optimally according to technical, economic, environmental and social criteria.²⁷ Other similar definitions and explanations have been reported, and Task 34 of IEA Bioenergy has recently produced the definition in Table 3.

Table 3: Definition of a biorefinery²⁸

A biorefinery processes and upgrades a renewable raw material (i.e. biomass^a) into several marketable products^b, emphasising fuels and chemicals.

- It is important to consider complete use of raw material, optimisation, efficiency, effectiveness, economics and environment.
- The term 'marketable' includes value, standards, usefulness, environmental acceptability, economics, sustainability and legislation.

Examples of a biorefinery with fast pyrolysis include utilisation of heavy residues from liquid smoke production for co-firing in a power station and production of hydrogen by steam reforming of the aqueous residues from recovery of phenolics for resin production.²⁹ The key feature and objective is optimum utilisation of products, by-products and wastes as shown in Figure 12. Some of the alternatives for achieving this optimum for production of transport fuels and chemicals are shown in Figure 13.

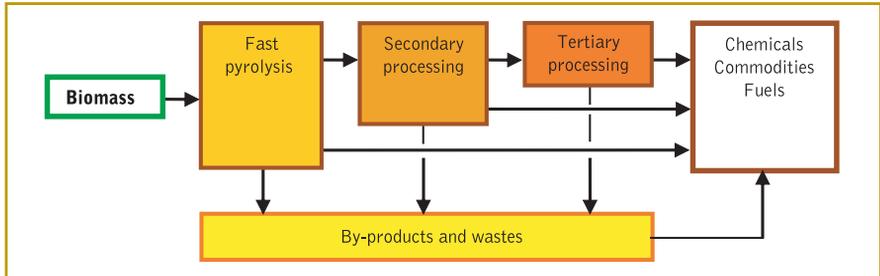


Figure 12: Biorefinery concept

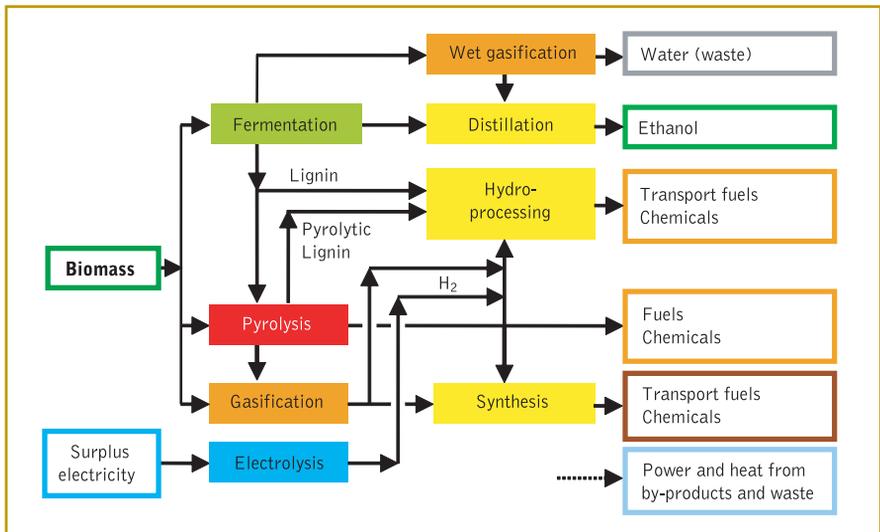


Figure 13: One biorefinery system with processing options for fuels and chemicals

Conclusions

There is substantial and growing interest in thermal processing of biomass for biofuels, to make both energy and chemicals. Fast pyrolysis is a relatively new thermal conversion technology for biomass that has benefited from extensive development in the last 30 years. It offers the key advantage of directly producing a liquid fuel in high yield that can be stored and/or transported to the point of use. This provides considerably more flexibility and allows greater use to be made of economies of scale for power generation, and transport fuel synthesis.

There are technical and economic challenges. Technical challenges lie in scaling up the endothermic pyrolysis reactor, particularly concerning heat transfer, and in improving the quality and consistency of the bio-oil. Economic challenges lie in reducing the capital cost, partly from scaling up and partly by developing and improving the technology. Scaling must consider that, with a few exceptions, bioenergy systems will always be small relative to fossil fuel options and must therefore be technically and economically competitive at much smaller scales of operation than the process and power generation industries are used to handling. It is this ability to improve economies of scale in applications for bio-oil that provides one of the best justifications of fast pyrolysis, whereby bio-oil from decentralised fast pyrolysis plants can be readily transported to central process plants.

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This paper was produced by the Implementing Agreement on Bioenergy, which forms part of a programme of international energy technology collaboration undertaken under the auspices of the International Energy Agency.