

Review

Biomass for energy

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Abstract: Bio-energy is now accepted as having the potential to 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 three main routes to providing these biofuels – thermal conversion, biological conversion and physical conversion – all of which employ a range of chemical reactor configurations and designs. This review focuses on thermochemical conversion processes for their higher efficiencies, lower costs and greater versatility in providing a wide range of energy, fuel and chemical options. The technologies of gasification and fast pyrolysis are described, particularly the reactors that have been developed to provide the necessary conditions to optimise performance. The primary products that can be derived as gas, liquid and solid fuels are characterised, as well as the secondary products of electricity and/or heat, liquid fuels and a considerable number of chemicals.

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Keywords: biomass; bioenergy; pyrolysis; gasification; biofuels

INTRODUCTION

Renewable energy is of growing importance in responding to concerns over the environment and the security of energy supplies. 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. Wood and annual 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 bio-energy resources, although particularly in the case of MSW, they may require extensive processing before conversion. Biomass is 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} In addition, energy from biomass based on short rotation forestry and other energy crops can contribute significantly towards the objectives of the Kyoto Protocol in reducing greenhouse gas emissions and alleviating problems related to climate change.³

Biomass fuels and residues can be converted to energy via the thermal, biological and mechanical or physical processes summarised in Fig. 1.⁴ Thermal processing currently attracts the most interest in Europe and Canada while ethanol production is the focus of attention in the USA for security of supply reasons. Gasification has traditionally received the most RD&D support as it offers potentially higher efficiencies compared with combustion. Fast pyrolysis is still at a relatively early stage of development but offers the benefits of a liquid fuel with concomitant

advantages of easy storage and transport as well as comparable higher power generation efficiencies at the smaller scales of operation that are likely to be achieved from bio-energy systems compared to fossil-fuelled systems. Combustion systems are widely available at domestic, small industrial and utility scales; biological conversion processes (fermentation and digestion) and mechanical processing (e.g. vegetable oils) are well established and are all commercially offered with performance guarantees. This review therefore focuses on the thermal conversion processes of gasification and pyrolysis as they offer high conversion efficiencies, potentially competitive costs, and considerable flexibility in scale of operation and range of products.

The key difference between thermal and biological conversion is that biological conversion gives single or specific products such as ethanol or biogas (which contains up to 60% methane) and is a slow process, typically taking hours, days, weeks (anaerobic fermentation and farm digestion) or years (landfill gas by digestion) for reactions to be completed. Thermal conversion gives multiple and often complex products, with catalysts often used to improve the product quality or spectrum, and takes place in very short reaction times of typically seconds or minutes. Table 1 summarises some of the main products that can be obtained by processing biomass.

A commercial process for realisation of energy and fuel products from biomass comprises a biomass production system and five main stages in the conversion plant:⁴

- 1 Production of biomass as a short rotation coppice, such as willow; forest residues; annually harvested

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(Received 20 December 2005; revised version received 22 March 2006; accepted 23 June 2006)

Published online 31 July 2006; DOI: 10.1002/jsfa.2605

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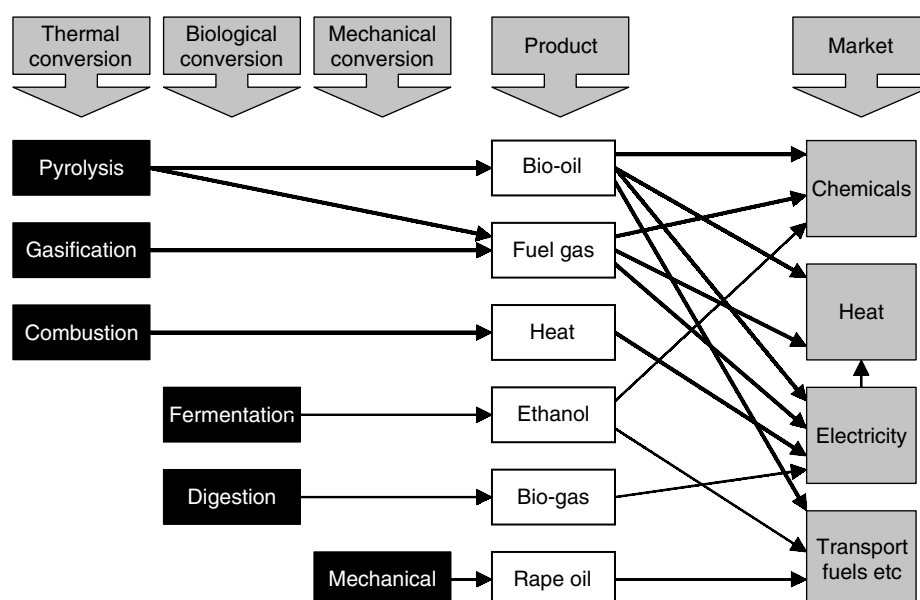


Figure 1. Conversion processes, products and applications.

Table 1. Major products from biomass conversion⁴

Product	Biological processing	Physical processing	Thermal processing
<i>Fuels</i>			
Additives	✓	✓	✓
Alcohols	✓		✓
Charcoal			✓
Diesel-type fuels		✓	
Fischer–Tropsch liquids			✓
Fuel oil			✓
Gas	✓		✓
Gasoline			✓
Hydrogen	✓		✓
<i>Chemicals</i>			
Acetone	✓		
Activated carbon			✓
Butanol	✓		
Ethanol	✓		✓
Fertilisers	✓		✓
Fine chemicals	✓	✓	✓
Food additives	✓		✓
Hydrogen	✓		✓
Methane	✓		✓
Methanol			✓
Resins			✓

crops, such as miscanthus; and agricultural residues, such as straw. This includes harvesting, in-field processing such as chipping, and transport to the conversion plant

- 2 Feed reception, storage, handling and pre-treatment to prepare the biomass for the subsequent conversion process
- 3 Conversion of solid biomass to a more usable form of energy by means such as gasification or pyrolysis
- 4 Primary product refining or clean-up

- 5 Conversion of the primary product to a marketable end-product such as electricity, heat, liquid biofuels or chemicals

BIOMASS RESOURCES

Biomass is a diffuse resource, arising over very large areas, and thus requiring large areas of land with substantial logistical problems in collection and transport as well as high costs. Typically, a sustainable crop of 10 dry t ha⁻¹ y⁻¹ of woody biomass can be produced in northern Europe, rising to perhaps 15 or maybe 20 dry t ha⁻¹ y⁻¹ for energy crops in southern Europe. Thus an area of 1 km² or 100 ha will produce 1000 dry t y⁻¹, enough for a power output of 150 kW_e at low conversion efficiencies, or 300 kW_e at high conversion efficiencies. It is therefore difficult to visualise power generation plants based on indigenous biomass production much bigger than around 30–40 MW_e anywhere in Europe and even these will require a planted area of around 100 km².

A further complication with almost all forms of biomass is their seasonality: forestry and coppiced crops can only be harvested during the winter months, and energy crops and agricultural residues are even more seasonal, typically growing for a only few months a year. Extensive provision for storage thus has to be made. One solution to this problem is a multi-fuel system and increasing efforts are under way to develop processes that can handle a number of different fuels, either mixed or separately.⁵ The current view is that even these plants are limited in size, with a typical plant size of 5–15 MW_e likely to dominate the market in the short term. However, in locations where extensive industrial operations are located close to managed forests, it is technically feasible and economically attractive to install large-scale bio-energy combined heat and power (CHP) plants and burn the process

residues to provide heat for the local industry. Biomass and agricultural wastes are very similar in their arisings, with most European industries individually producing comparable quantities of material, although overall regional and national totals may be substantial.

THERMAL CONVERSION PROCESSES

There are three main thermal processes – pyrolysis, gasification and combustion – available for converting biomass to a more useful energy form. Figure 2 summarises their products and applications. Combustion is already a well-established commercial technology with applications in most industrialised and developing countries and development is concentrated on resolving environmental problems. Combustion is well established and widely practised with many examples of dedicated plant and co-firing applications.⁶

Gasification

Fuel gas can be produced from biomass and related materials either by partial oxidation to give a mixture of carbon monoxide, carbon dioxide, hydrogen and methane with nitrogen if air is used as the oxidant, or by steam or pyrolytic gasification. Table 2 summarises the main products in each case.

The process of gasification is a sequence of interconnected reactions: the first step, drying, is a relatively fast process. The second step, pyrolysis, is also relatively fast but it is a complex process that gives rise to the tars that cause so many problems in gasification processes. Pyrolysis occurs when a solid fuel is heated to 300–500 °C in the absence of an oxidising agent, giving a solid char, condensable hydrocarbons or tar and gases. The relative yields of char, liquid and gas mainly depend on the rate of heating and the final temperature, and this is discussed

later in the section on fast pyrolysis. In gasification by partial oxidation, both the gas and liquid and solid products of pyrolysis then react with the oxidising agent – usually air, although oxygen can be used – to give the permanent gases CO, CO₂, H₂, and lesser quantities of hydrocarbon gases. In steam or pyrolytic gasification, the char is burned in a secondary reactor to reheat the hot sand which provides the heat for the gasification.⁴

The composition of the gas from char gasification and partial oxidation of the other pyrolysis products is influenced by many factors, including feed composition, water content, reaction temperature and the extent of oxidation of the pyrolysis products. However, the overall composition is essentially the equilibrium composition of the C–H–O system at the temperature of gasification. The alkali metals in the biomass act an effective catalyst to promote the gasification reactions.

Status of biomass gasification technology

A number of gasifier configurations have been developed. A recent survey of gasifier manufacturers found that 75% of gasifiers offered commercially were

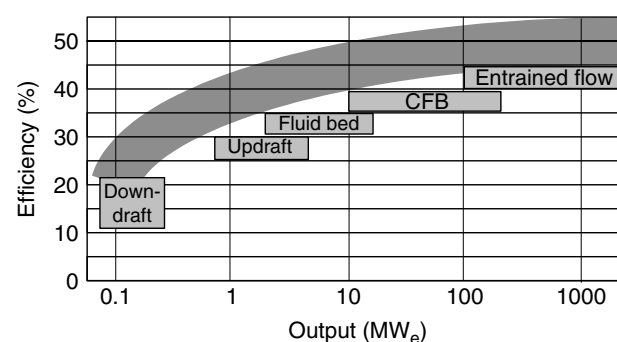


Figure 3. Relationship between technology, scale and efficiency for electricity production.

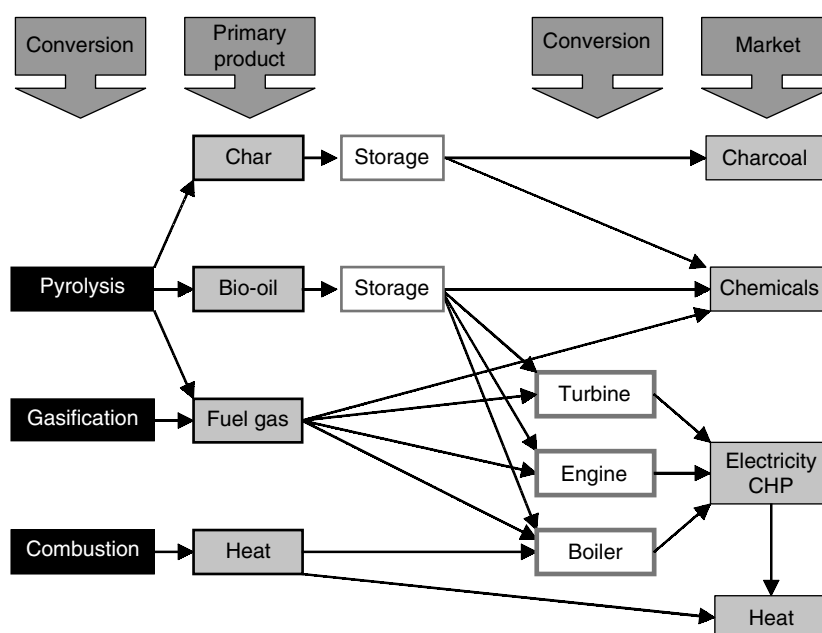


Figure 2. Thermal biomass conversion processes.

Table 2. Modes of thermal gasification⁴

Method	Comments
Partial oxidation with air	The main products are CO, CO ₂ , H ₂ , CH ₄ , N ₂ and tar, giving a low heating value gas of ~5 MJ m ⁻³ . Utilisation problems can arise in combustion, particularly in gas turbines.
Partial oxidation with oxygen	The main products are CO, CO ₂ , H ₂ , CH ₄ and tar (no N ₂), giving a medium heating value gas of ~10–12 MJ m ⁻³ . The cost of providing and using oxygen is compensated by a better quality fuel gas. The trade-off is finely balanced.
Steam (pyrolytic) gasification	The main products are CO, CO ₂ , H ₂ , CH ₄ and tar giving a medium heating value gas of ~15–20 MJ m ⁻³ . The process has two stages: the primary reactor produces gas and char, and the sand and char is passed to a second reactor where the char is burned with air to reheat the sand, which is then re-circulated to the first reactor to provide the heat for reaction. The gas heating value is maximised due to a higher methane and higher hydrocarbon gas content, but at the expense of lower overall efficiency due to loss of carbon in the second reactor.
Pressure	Pressurised gasifiers operate under pressures of typically 15–50 bar. Both capital and operating costs are significantly higher for pressurised operation, although these are to some extent balanced by savings from reduced vessel and piping sizes, the avoidance of a gas compressor for the gas turbine and higher efficiencies. Liquid feeding as bio-oil or slurry has significant operational and economic advantages over solid biomass feeding. Pressurised operation is often carried out with oxygen.
Oxygen	Use of oxygen, usually with pressure operation, gives higher reaction temperatures and hence lower tar levels; smaller and hence lower cost equipment from the absence of nitrogen; and higher quality gas for both power generation and liquid fuel synthesis. There is, however, a significant energy and financial cost associated with the use and supply of oxygen, from both its procurement and the additional measures needed to mitigate hazards in handling and use.

downdraft, 20% were fluid beds (including circulating fluid beds), 2.5% were updraft and 2.5% were other types.⁷ The range of gasifier technologies and their advantages and disadvantages are summarised below^{4,7} and in Fig. 3.

Atmospheric downdraft gasifiers are attractive for small-scale applications up to about 1.5 MW_{th} as there is a large market in both developed and developing economies. While some configurations still have problems with the effective removal of tar and particulates, considerable progress has been made and performance guarantees are increasingly offered.⁸ Biomass Engineering is one company that has made considerable progress in this area with successful operation of engines and microturbines.⁹

Atmospheric updraft gasifiers seem to have little market attractiveness for power applications. While this may be due to the high tar levels in the fuel gas, recent developments in tar cracking have shown that very low levels can be achieved from dedicated thermal/catalytic cracking reactors downstream of the gasifier. Another possible reason is that the upper size of a single unit is around 2.5 MW_e so larger plant capacities require multiple units. There are typically used for heat applications to maximise energy efficiency.¹⁰

Atmospheric bubbling fluidised bed gasifiers have proven to be reliable with a variety of feedstocks at pilot scale and commercial applications in the small to medium scale, up to about 25 MW_{th}. They are limited in their capacity size range as they have not been significantly scaled up and the gasifier diameter is significantly larger than that of circulating fluid beds for the same feedstock capacity. On the other hand, they are more economic for small to medium range

capacities. Their market attractiveness and technology strength are thus relatively high, although there are few operational examples.

Atmospheric circulating fluidised bed gasifiers have proved very reliable with a variety of feedstocks and are relatively easy to scale up from a few MW_{th} to 100 MW_{th}. Even for capacities above 100 MW_{th}, there is confidence that the industry would be able to provide reliable gasifiers. These gasifiers appear to be the preferred system for large-scale applications and these systems therefore have high market attractiveness and are technically well proven. Examples include the TPS (Termiska Processer AB) atmospheric process,¹¹ and the Varnamo pressurised system.¹²

The most successful biomass gasifier currently operating for power generation is the Güssing gasifier in Austria which is an indirect gasification system based on high temperature pyrolysis to generate a medium heating value gas which is burned in an engine to generate 2 MW_e.¹³ This has completed more than 15 000 h of operation at the time of writing and has an availability in excess of 90%.

Pressurised fluidised bed systems, either circulating or bubbling, are considered of more limited market attractiveness in the short term because of their more complex installation and the additional costs of construction of pressurised vessels. However, pressurised systems have an advantage in integrated combined cycle applications as the need to compress the fuel gas prior to utilisation in the combustion chamber of the gas turbine is avoided. Pressurised systems are often used with oxygen as the oxidant to improve the gas quality. There is, however, a significant energy and financial cost associated with the use and supply of oxygen, from both its procurement

and the additional measures needed to mitigate hazards in handling and use.

Very large scale gasification systems currently being considered for processing millions of tonnes of biomass a year would probably be pressurised oxygen blown systems. There are logistical problems of biomass supply that require resolution, but are essential for economic synthesis of transport fuels. These technologies would also be applied to pyrolysis liquid gasification, when liquefaction of biomass would reduce the handling and transport costs of solid biomass and simply the gasification process. Consideration is also being given to co-gasification of biomass with coal and extensive trials have already demonstrated the feasibility of this approach.

Fuel gas quality

The fuel gas quality requirements, for turbines and liquid fuel synthesis in particular, are very high; Table 3 gives some suggested figures for common gasifiers.¹⁴ Tar is a particular problem and remains the most significant technical barrier. There are two basic ways of destroying tars, both of which have been and continue to be extensively studied:¹⁵

- Catalytic cracking using, for example, dolomite or nickel
- Thermal cracking, for example by partial oxidation or direct contact

The gas is very costly to store or transport so it has to be used immediately. Hot gas efficiencies for the gasifier (total energy in the raw product gas as a fraction of

the energy in the feed) can be as high as 95–97% for close-coupled turbine and boiler applications, and up to 85% for cold gas efficiencies. In power generation using combined cycle operation, efficiencies of up to 50% for the largest installations have been proposed, reducing to 35% for smaller applications.

Gas clean-up

Gases formed by gasification will be contaminated by some or all of the constituents listed in Table 4. The level of contamination will vary depending on the gasification process and the feedstock. Gas cleaning must be applied to prevent erosion, corrosion and environmental problems in downstream equipment.⁴

Applications of product gas

Figure 4 summarises the range of fuel, electricity and chemical products that can be derived from the product gas. Medium heating value gas from steam or pyrolytic gasification, or from oxygen gasification, is better suited to synthesis of transport fuels and commodity chemicals because of the absence of diluent nitrogen, which would pass through unchanged but reduce process efficiency and increase costs. The exception is ammonia synthesis, where the nitrogen content derived from air gasification can be utilised in the ammonia synthesis process.

Transport fuels and other chemicals

As biomass is the only renewable source of fixed carbon, there is considerable interest in the production of transport fuels and other commodity chemicals

Table 3. Typical product gas characteristics from different gasifiers¹⁴

	Gas composition, dry, vol%					HHV* (MJ N ⁻¹ m ³)	Gas quality	
	H ₂	CO	CO ₂	CH ₄	N ₂		Tars	Dust
Fluid bed air-blown	9	14	20	7	50	5.4	Fair	Poor
Updraft air-blown	11	24	9	3	53	5.5	Poor	Good
Downdraft air-blown	17	21	13	1	48	5.7	Good	Fair
Downdraft oxygen	32	48	15	2	3	10.4	Good	Good
Twin fluid bed	31	48	0	21	0	17.4	Fair	Poor
Pyrolysis for comparison	40	20	18	21	1	13.3	Poor	Good

* HHV: higher heating value.

Table 4. Fuel gas contaminants and their problems¹⁴

Contaminant	Examples	Problems	Solution
Tars	Refractive aromatics	Clogs filters Difficult to burn Deposits internally	Tar cracking thermally or catalytically, or tar removal by scrubbing
Particulates	Ash, char, fluidised bed material	Erosion	Filtration, scrubbing
Alkali metals	Sodium, potassium compounds	Hot corrosion	Cooling, condensation, filtration, adsorption
Fuel-bound nitrogen	Mainly ammonia and HCN	NO _x formation	Scrubbing, Selective catalytic removal (SCR)
Sulfur, chlorine	HCl, H ₂ S	Corrosion emissions	Lime or dolomite, scrubbing, absorption

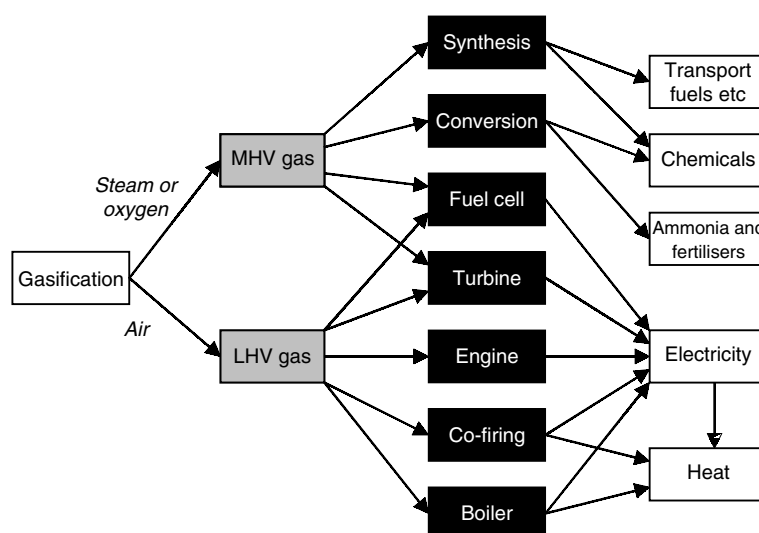


Figure 4. Applications for biomass gasification systems. MHV, medium heating value, typically 15 MJ/Nm³; LHV, low heating value, typically 5 MJ/Nm³.

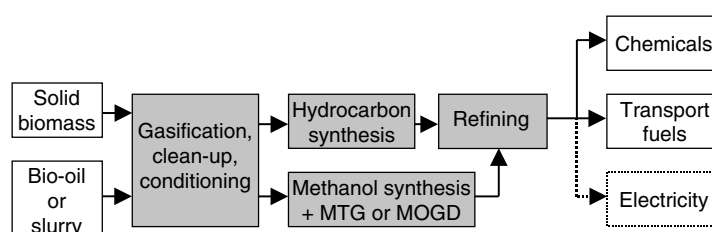


Figure 5. Transport fuels via biomass gasification. MTG, methanol to gasoline; MOGD, methanol to olefins, gasoline and diesel.

through synthesis gas or syngas, as it is usually known. 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 sulfur (e.g. H₂S), chlorine (e.g. HCl, COCl) and nitrogen (e.g. 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.

Either solid biomass can be gasified, which for European-derived biomass will tend to limit the size of plant to the availability of biomass unless considerable

biomass is imported, or bio-oil from fast pyrolysis can be gasified which has a lower overall efficiency but enables the necessary economies of scale to be realised in the downstream synthesis of transport fuels and chemicals. Gasification of bio-oil is also potentially lower cost as it is easier to feed a liquid into a pressurised gasifier than solid biomass.

Syngas provides the raw material for the 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 for production of hydrocarbon transport fuels are shown in Fig. 5, which are of considerable topical significance.

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

Table 5. 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 s	75	12	13
Intermediate	Moderate temperature, around 500 °C, Moderate hot vapour residence time ~10–20 s	50	20	30
Slow (carbonisation)	Low temperature, around 400 °C, very long residence time	30	35	35
Gasification	High temperature, around 800 °C, long residence times	5	10	85

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 time are optimum for producing liquids. Table 5 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. A number of reviews have been published to which reference should be made for detailed information.^{16–19}

Fast pyrolysis occurs in a time of 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 fast 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 decomposes to generate mostly vapours and aerosols and some charcoal. After cooling and condensation, a dark brown mobile liquid is formed which has a heating value about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes for making charcoal, fast pyrolysis is an advanced process, 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 2 s
- 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% 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 (although up to 15% can be acceptable), 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, pyrolysis reaction, 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 Fig. 6 showing the necessary preparation steps, alternative reactors and product collection.

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 has focused on the reactor, although 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, upgrading. The key aspects of these peripheral steps are described later. A comprehensive survey of fast pyrolysis processes for

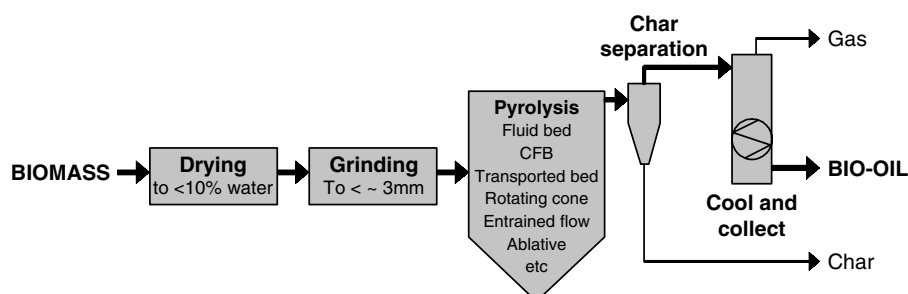


Figure 6. Conceptual fast pyrolysis process.

liquids production that have been built and tested in the last 10–15 years has been published.¹⁷

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.

Residence time of solids and vapours 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/elutriation 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 and colleagues^{20–22} who published extensively. The largest plant currently operating is that by Dynamotive in West Lorne, Ontario, Canada, which has a demonstration plant that produces 100 t d⁻¹ of dry biomass feed, with plans for further plants up to 400 t/d.²³ A 2.5 MW_e gas turbine is also provided on site for generation of power locally and for export to the grid.

Circulating fluid beds and transported bed

Circulating fluid beds (CFBs) 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 industries. However, heat transfer at higher throughputs has not been demonstrated and offers some challenges.⁴ 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.

A variation on the transported bed is the rotating cone reactor, invented at the University of Twente²⁴

and implemented by BTG in the Netherlands. In this configuration, the transport is effected by centrifugal forces rather than gas. A 50 t d⁻¹ plant has been built in Malaysia and was commissioned in summer 2005.

Ablative pyrolysis

Ablative pyrolysis is substantially different in concept compared with other methods of fast pyrolysis.⁴ 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 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. 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 as follows:

- High pressure of particle on hot reactor wall, achieved due to centrifugal force
- 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, large particles can be used and, in principle, there is no upper limit to the size that can be processed. In fact, the process 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 potentially lower cost. However, the process is surface-area-controlled so scaling is more costly and the reactor is mechanically driven, and is thus more complex. A 50 t d⁻¹ demonstration plant has recently started operating in north Germany²⁵ and a small research unit operates at Aston University.²⁶

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 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.

By-products

Charcoal and gas are by-products, typically containing about 25 and 5%, respectively, of the energy in the feed material. 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 heat can be derived by burning the gas and/or the charcoal byproduct. 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 and avoid potential slagging problems from direct char combustion.

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 aspen wood and the high dependence on temperature is shown in Fig. 7.

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, which stabilises the discontinuous phase of pyrolytic lignin macromolecules through mechanisms such as hydrogen bonding.

Fast pyrolysis liquid has a higher heating value of about $16\text{--}17\text{ MJ kg}^{-1}$ 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 Tables 6 and 7 and are discussed briefly below, of which the most

Table 6. 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^{-1}
Viscosity (40 °C and 25% water)	50 cP
Solids (char)	0.1%
Vacuum distillation residue	up to 50%

* HHV: higher heating value.

Table 7. Characteristics of wood-derived crude bio-oil

- Liquid fuel
- Ready substitution for conventional fuels in many stationary applications such as boilers, engines, turbines
- Heating value of 17 MJ kg^{-1} at 25% wt water, is about 40% that of fuel oil/diesel
- Does not mix with hydrocarbon fuels
- Not as stable as fossil fuels
- Quality needs definition for each application

significant is that it will not mix with any conventional hydrocarbon-based fuels.

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.

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.

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

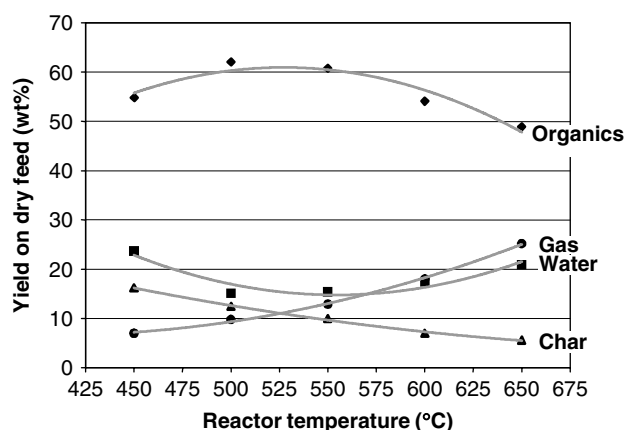


Figure 7. Variation of products from aspen poplar with temperature.²⁷

cannot be dissolved in water. The addition of water 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 and acetone, but is totally immiscible with petroleum-derived fuels.

The density of the liquid is very high at around 1.2 kg L^{-1} , compared with light fuel oil at around 0.85 kg L^{-1} . This means that the liquid has about 42% of the energy content of fuel oil on a weight basis, but 61% on a volumetric basis. This has implications for the design and specification of equipment such as pumps and atomisers in boilers and engines.

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. Recent samples that have been distributed for testing have shown substantial improvements in consistency and stability.

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.²⁸ Figure 8 summarises the possibilities. A range of chemicals including food flavourings, specialities, resins,²⁹ agri-chemicals, fertilisers, and emissions control agents can also be extracted or derived from bio-oil. At least 400 h operation has been achieved on a 250 kW_e specially

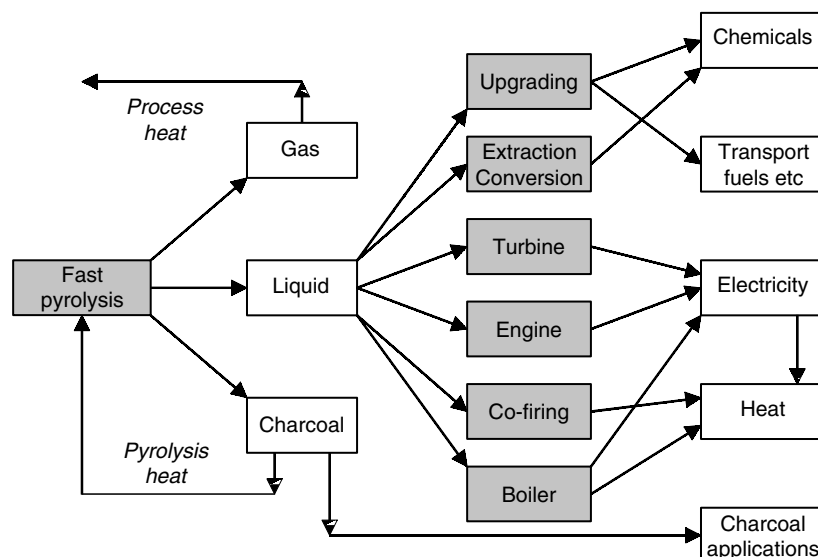


Figure 8. Applications for products of fast pyrolysis.

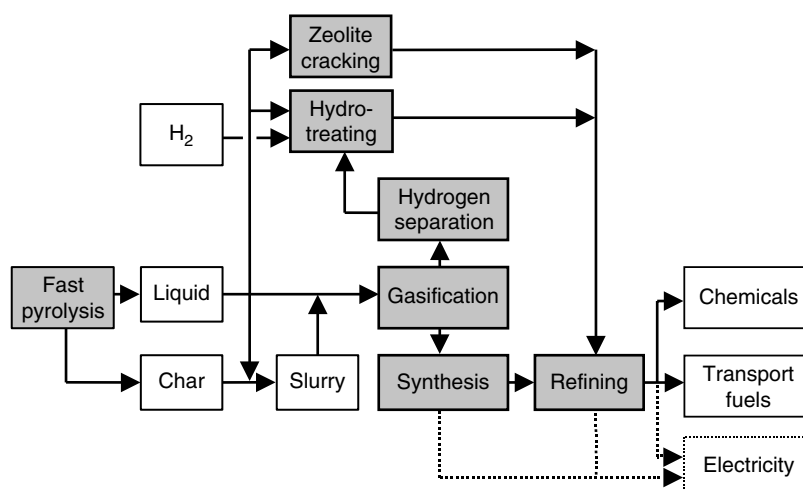


Figure 9. Transport fuels via biomass pyrolysis.

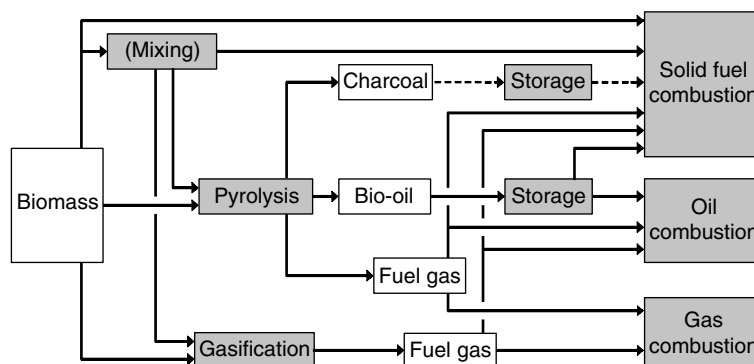


Figure 10. Opportunities for co-processing biomass and biofuels in conventional heat and power applications.

modified dual-fuel engine and experience has been gained on a modified 2.5 MW_e industrial gas turbine.³⁰ As noted above, upgrading bio-oil to transportation fuels is feasible but not currently economic. A possible route is shown in Fig. 9.

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.⁶ The opportunities are summarised in Fig. 10. 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.

Almost all co-firing is based on addition of solid biomass to the coal prior to combustion in the boilers. There are a number of examples where the biomass is first converted to a fuel gas via gasification, which is directly burned in an existing coal-fired boiler. Trials have also taken place of combustion of fast pyrolysis liquids in both coal fired and gas fired power stations. These latter options have the advantage that the biomass residual ash is not mixed with the coal ash, which has an existing market as a construction material and can thus be recycled back to the forest or field. In re-burning applications, (where the fuel gas is introduced almost at the top of the coal boiler), the environmental performance of the power station is significantly improved, in addition to the replacement of fossil fuels by renewable biomass fuels.

BIOLOGICAL CONVERSION PROCESSES

Ethanol

In order to produce ethanol by fermentation, the cellulose and hemicellulose in lignocelluloses need to be hydrolysed to sugars prior to fermentation, and both enzyme and acid hydrolysis are employed for this purpose.^{31,32} Carbohydrates such as starch also require hydrolysis. Only the cellulose in biomass is conventionally converted to ethanol, although increasing success is being obtained with conversion

of hemicellulose, which will improve conversion efficiency and reduce costs. The lignin is a residue that can be burned for process heat, particularly for ethanol concentration, or further processed for production of refinery feedstocks or aromatic chemicals. It is this integration of energy, fuels and chemicals that is increasingly considered as a biorefinery, which can be simply explained as an optimised system of utilising biomass in technical, economic, environmental and social terms.

The overall efficiencies of ethanol production are rather low, owing to the loss of about half the carbon in holocellulose as carbon dioxide; the loss of the carbon in lignin, which is not converted; and the need to concentrate the dilute ethanol solution.

Fermentation is particularly suitable for materials with high moisture content, as drying is not required. Ethanol can be readily converted to ethyl tertiary butyl ether (ETBE), which can be directly used as a gasoline additive. Fermentation technology is commercial and tends to be high cost unless subsidies are applied and low efficiency unless credits are applied to the by-products. After a lull in RD&D, there is now renewed interest in bio-ethanol, with enzyme hydrolysis in particular attracting more attention. A substantial demonstration plant can be expected soon. Currently there is little RD&D because the technology is established and viability relies on financial support.

BP and DuPont announced an initiative in June 2006 to develop bio-butanol from fermentation of suitable biomass feedstocks as an additive for transport fuels, which offers improved properties compared to ethanol.³³

Biodiesel

Biodiesel is the ester formed by reacting vegetable oils or animal fats with methanol or ethanol. Vegetable oil can be recovered from oil seeds such as rape (canola or colza), or other crops such as linseed, sunflower, soy etc. The product in its raw form is unsuitable for many applications because it is highly viscous and has other deleterious properties, so the methyl or ethyl ester is formed by esterification. However, there have been limited attempts to use the cold-pressed oil as transport fuel.

The most common product is rape methyl ester (RME). The raw oil is recovered by pressing, usually accompanied by solvent extraction to improve yields. This raw oil is then subjected to esterification with methanol or ethanol over a catalyst giving a lower viscosity and more stable product and glycerine as a by-product. The ester is entirely compatible with diesel in use and applications and biodiesel is thus an attractive renewable transport fuel.

The yield of vegetable oil per unit land area is, however, very low at around $1\text{--}2\text{ t ha}^{-1}\text{ y}^{-1}$ and is accompanied by around $5\text{--}8\text{ t ha}^{-1}\text{ y}^{-1}$ of solid residues such as rape straw, which is not usually utilised. The product cost is therefore high. The conventional conversion technology is semi-batch but simple and proven, but there have been a number of recent developments of fully continuous processes that can handle vegetable oils and waste oils and fats. Animal fats and waste cooking oils can also be processed in an analogous way and, while the scope is limited due to limited raw material availability, this route offers significant economic opportunities while the waste materials continue to be available at low cost.

Anaerobic digestion

Anaerobic digestion is microbial conversion of organic materials to methane and carbon dioxide in the absence of oxygen. The product gas from farm digesters is typically around 60% methane, although higher levels have been reported. The typical methane content from landfill sites is lower at 50–55%. Digestion is particularly suitable for residues with high moisture contents, as drying is not required. The biogas can be used for heat with minimal processing, or for power generation in engines or turbines and (after upgrading to methane quality by removal of carbon dioxide and other components) in fuel cells or as gaseous fuel for transport applications. This requires increasingly stringent quality specifications. Landfill sites tend to be very large and typically produce gas over a 20–25 year life. Gas is collected through a system of wells, which collect and pipe the gas to the user.

The gas is wet and contains acid components which require careful management to avoid or minimise problems in using the gas for heat and/or power production. As landfill gas collection is required in many countries to comply with legislation to minimise hazards, the additional costs of distributing gas to users is very small, so landfill gas is an economically attractive renewable energy resource. However, as pressure grows to reduce land filling by legislation in the European Union, this resource is expected to reduce in the long term. On-farm or industrial digesters using farm wastes, industrial food wastes and household wastes are becoming more widely used for smaller scale applications. The wastewater industry, in particular, has successfully and effectively used digestion for in-plant power generation for many years.

Dedicated digesters tend to be costly and inefficient as well making a significant amount of solid residues that must be disposed of. Thus small-scale digestion is not often cost-effective. Although there is widespread interest in anaerobic digestion for both waste disposal and energy generation, economic opportunities are limited to niche applications.

New developments in solid-state fermentation have allowed the content of the dry solids of the substrate to be as high as 30–35 wt%, compared with only 3–10 wt% for traditional liquid phase fermentation. This increases biogas productivity by a factor of about 3, and reduces digester volumes. This technology has found applications in the processing of the biodegradable fraction of MSW or source-separated waste. In all types of digestion, the carbon dioxide component can be reduced or removed to give higher quality gas, up to natural gas qualities. There is a range of available technologies, including membrane processes and conventional scrubbing processes, according to the scale of operation. All are costly, and careful assessment of the added value of the resultant higher quality gas is needed. The purified methane can either be used as transport fuel or added to a natural gas pipeline.

BIOREFINERY

After many years of production of chemicals from bio-oil, there is rapidly growing interest in the biorefinery concept in which fuels and chemicals are optimally produced by technical, economic, environmental and social criteria.³⁴ Recent examples of a biorefinery 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. The key feature and objective is optimum utilisation of products, by-products and wastes as shown in Fig. 11. Some of the alternatives for achieving this optimum for production of transport fuels and chemicals are shown in Fig. 12.

CONCLUSIONS

There is substantial and growing interest in thermal processing of biomass for biofuels, to make both energy and chemicals. Gasification and pyrolysis are complementary processes that have different market opportunities and should not be viewed as competitors. In both technologies, there is

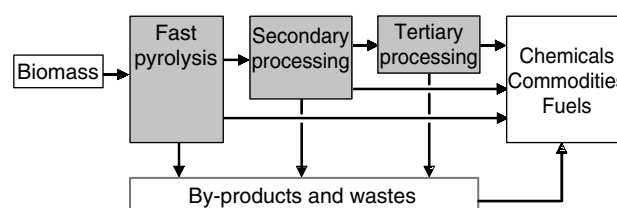


Figure 11. Biorefinery concept.

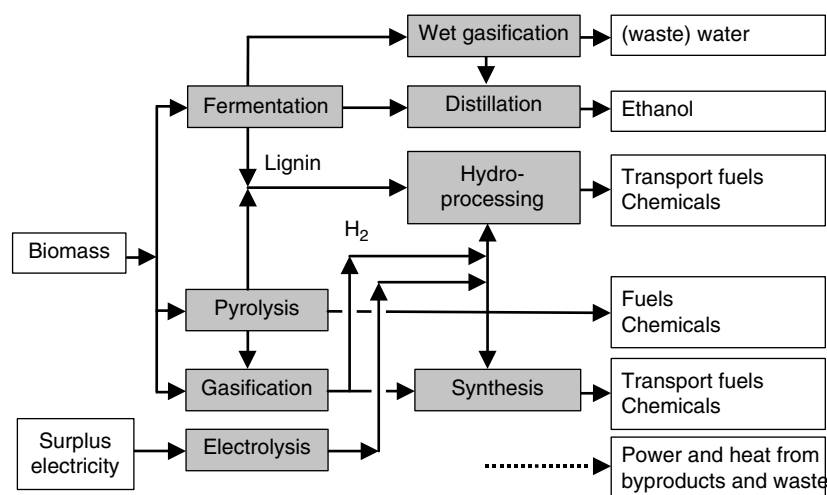


Figure 12. A biorefinery system with processing options for fuels and chemicals.

still considerable progress to be made in optimal interfacing of conversion and utilisation of the primary products from conversion, as well as the important interface between biomass production and conversion that has been largely left to market forces.

The main challenges lie first in bringing the thermal conversion technologies closer to the power generation or chemicals production processes, with both sides of the interface moving to an acceptable middle position, and second, in fully appreciating that, with rare exceptions, bio-energy systems will always be relatively small 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.

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