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Renewable fuels and chemicals by thermal processing of biomass

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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. There are three main routes to providing these bio-fuels—biological conversion, physical conversion and thermal conversion—all of which employ a range of chemical reactors configurations and designs. This review concentrates on thermal conversion processes and particularly the reactors that have been developed to provide the necessary conditions to optimise performance. A number of primary and secondary products can be derived as gas, liquid and solid fuels and electricity as well as a considerable number of chemicals. The basic conversion processes are summarised with their products and the main technical and non-technical barriers to implementation are identified.

Keywords: Bio-fuels; Renewable energy; Thermal processing; Gasification; Pyrolysis

1. Introduction

Renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage. Wood and other forms of biomass including energy crops and agricultural and forestry wastes are some of the main renewable energy resources available. These can provide the only source of renewable liquid, gaseous and solid fuels. 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 world-wide [1,2]. Energy from biomass based on short rotation forestry and other energy crops can contribute significantly towards the objectives of the Kyoto Agreement in reducing the green house gases emissions and to the problems related to climate change [3].

Biomass fuels and residues can be converted to energy via thermal, biological and physical processes. Each process area is described with the greatest emphasis on the technologies that are attracting the most attention in the research, demonstration and commercial arenas. In the thermochemical conversion technologies, biomass gasification has attracted the highest interest as it offers higher efficiencies compared to combustion and fast pyrolysis is still at a relatively early stage of development.

There are three main thermal processes available for converting biomass to a more useful energy form—combustion, gasification and pyrolysis. Their products and applications are summarised in Fig. 1.

2. Combustion

Combustion of biomass and related materials is widely practised commercially to provide heat and power. The technology is commercially available and presents minimum risk to investors. The product is heat, which must be used immediately for heat and/or power generation as storage is not a viable option. Overall efficiencies to power tend to be rather low at typically 15% for small plants up to 30% for larger and newer plants. Costs are only currently competitive when wastes are used as feed material such as from pulp and paper, and agriculture. Emissions and ash handling remain technical problems. The technology is, however, widely available commercially and there are many successful working examples throughout North America and Europe, frequently utilising forestry, agricultural and industrial wastes.

3. Gasification

Fuel gas can be produced from biomass and related materials by either partial oxidation to give a mixture of carbon monoxide, carbon dioxide, hydrogen and methane or by steam or pyrolytic gasification as illustrated in Table 1.

Gasification occurs in a number of sequential steps:

- drying to evaporate moisture,
- pyrolysis to give gas, vaporised tars or oils and a solid char residue,

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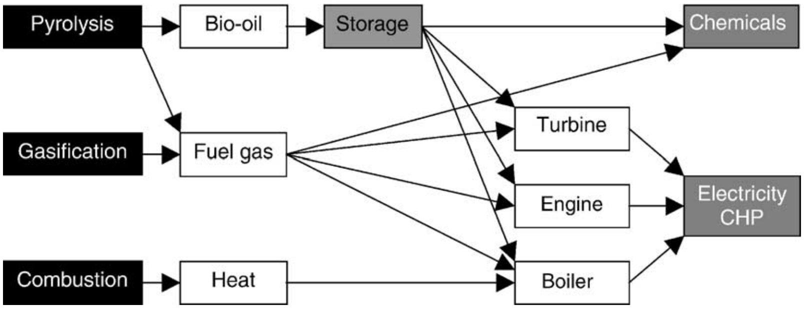

Fig. 1. Products from thermal biomass conversion.

Table 1
Modes of thermal gasification

Partial oxidation with air	Main products are CO, CO_2, H_2, CH_4, N_2, tar. This gives 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, tar (no N_2). This gives 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, tar. This gives a medium heating value gas of ∼15–20 MJ/m^3. The process has two stages with a primary reactor producing gas and char, and a second reactor for char combustion to reheat sand which is recirculated. 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

- gasification or partial oxidation of the solid char, pyrolysis tars and pyrolysis gases.

When a solid fuel is heated to 300–500 °C in the absence of an oxidising agent, it pyrolyses to solid char, condensable hydrocarbons or tar, and gases. The relative yields of gas, liquid and char depend mostly on the rate of heating and the final temperature. Generally in gasification, pyrolysis proceeds at a much quicker rate than gasification and the latter is thus the rate controlling step. The gas, liquid and solid products of pyrolysis then react with the oxidising agent—usually air—to give permanent gases of CO, CO_2, H_2, and lesser quantities of hydrocarbon gases. Char gasification is the interactive combination of several gas–solid and gas–gas reactions in which solid carbon is oxidised to carbon monoxide and carbon dioxide, and hydrogen is generated through the water gas shift reaction. The gas–solid reactions of char oxidation are the slowest and limit the overall rate of the gasification process. Many of the reactions are catalysed by the alkali metals present in wood ash, but still do not reach equilibrium. The gas composition is influenced by many factors such as feed composition, water content, reaction temperature, and the extent of oxidation of the pyrolysis products.

Not all the liquid products from the pyrolysis step are completely converted due to the physical or geometrical limitations of the reactor and the chemical limitations of the reactions involved, and these give rise to contaminant tars in the final product gas. Due to the higher temperatures involved in gasification compared to pyrolysis, these tars tend to be refractory and are difficult to remove by thermal, catalytic or physical processes. This aspect of tar cracking or removal in gas clean-up is one of the most important technical uncertainties in implementation of gasification technologies and is discussed below.

A number of reactor configurations have been developed and tested, with advantages and disadvantages as summarised in Table 2. A recent survey of gasifier manufacturers found that 75% of gasifiers offered commercially were downdraft, 20% were fluid beds (including circulating fluid beds), 2.5% were updraft and 2.5% were other types [4].

The fuel gas quality requirements, for turbines in particular, are very high. Tar is a particular problem and remains the most significant technical barrier. There are two basic ways of destroying tars [23], both of which have been and continue to be extensively studied:

- by catalytic cracking using, for example, dolomite or nickel,
- by 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 raw product gas divided by energy in 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 which reduces to 35% for smaller applications. A number of comprehensive reviews have been published such as [24,25].

3.1. Status

There is still very little information on costs, emissions, efficiencies, turn-down ratios and actual operational

Table 2
Gasifier reactor types and characteristics

- Downdraft-fixed bed reactor (Fig. 2)
  - Solid moves slowly down a vertical shaft and air is introduced and reacts at a throat that supports the gasifying biomass
  - Solid and product gas move downward in co-current mode
  - The technology is simple, reliable and proven for fuels that are relatively uniform in size and have a low content of fines (below 5 mm)
  - A relatively clean gas is produced with low tar and usually with high carbon conversion
  - There is limited scale-up potential to about 500 kg/h feed rate
  - There is a maximum feed moisture content of around 35% wet basis

Examples: Biomass Engineering [5], Rural Energy [6], BTG&KARA [7], Fluidyne [8], Johanssen [9]

- Updraft-fixed bed reactor (Fig. 2)
  - Solid moves down a vertical shaft and contacts a counter-current upward moving product gas stream,
  - The technology is simple, reliable and proven for fuels that are relatively uniform in size and have a low content of fines (below 5 mm)
  - The product gas is very dirty with high levels of tars, although tar crackers have been developed
  - Scale up limited to around 4 dry t/h feed rate
  - There is high thermal efficiency and high carbon conversion
  - Intolerant of high proportion of fines in feed
  - The gas exit temperature is low
  - Good turn-down capability

Examples: Wellman [10], Volund [11], Bioneer [12]

- Bubbling fluid bed (Fig. 3)
  - Good temperature control & high reaction rates
  - Higher particulates in the product gas and moderate tar levels in product gas
  - Good scale-up potential to 10–15 dry t/h with high specific capacity and easily started and stopped
  - Greater tolerance to particle size range
  - Good temperature control
  - Tar cracking catalyst can be added to bed
  - Limited turn-down capability
  - There is some carbon loss with ash

Examples: EPI [13], Carbona [14], Dinamec [15]

- Circulating Fluid Bed (Fig. 4)
  - All the features of bubbling beds PLUS
  - Large minimum size for viability, above around 15 t/h dry feed rate
  - High cost at low capacity
  - In-bed catalytic processing not easy

Examples: Technical University of Vienna (development) [16], TPS [17], Lurgi [18], Foster Wheeler [19]

- Entrained flow
  - Inherently simple reactor design, but only potentially viable above around 20 dry t/h feed rate and with good scale-up potential
  - Costly feed preparation needed for woody biomass
  - Carbon loss with ash
  - Little experience with biomass available

Examples: Texaco R&D

- Twin fluid bed (Fig. 5)
  - Complex process with two close-coupled reactors with difficult scale-up and high cost
  - The gasifier is usually a circulating fluid bed, while the char combustor can be either a bubbling bed or a second circulating fluid bed
  - Complexity requires capacities of >10 t/h for viability
  - MHV gas produced with air and without requiring oxygen
  - Low carbon conversion to gas as carbon in char is lost to reheat sand for recycling
  - High tar levels in gas
  - Tar cracking catalyst can be added to bed

Examples: Ferco, Vermont USA [20]

- Other reactors
  - Moving bed with mechanical transport of solid; usually lower temperature processes. Includes: Multiple hearth; Horizontal moving bed; Sloping hearth; Screw/auger kiln
  - Rotary kiln: good gas–solid contact; careful design needed to avoid solid carry over
  - Multi-stage reactors with pyrolysis and gasification separated for improved process control and better quality gas
  - Cyclonic and vortex reactors: high particle velocities give high reaction rates

Examples: Rotary kiln [21], Two-stage pyrolysis + gasification − *Thermoselect* [21], Compact Power [21]

Table 2 (*Continued*)

Use of oxygen
Gives better quality gas
High cost of providing oxygen and high cost of meeting extra process requirements
No evidence that benefits exceed costs
Examples: There are no known current or recent examples of oxygen fuelled gasifiers
High pressure gasification
Significant efficiency and cost advantage in IGCC applications, but large sizes are needed
Significant additional cost for pressure with smaller savings from reduced vessel and piping sizes
Examples: The most recent example is at Varnamo (Foster Wheeler and Sydkraft) which finished operation in 2000 [22], Carbona [14]
All biomass fuelled gasifiers
Feeding can give problems
Ash slagging and clinkering potential

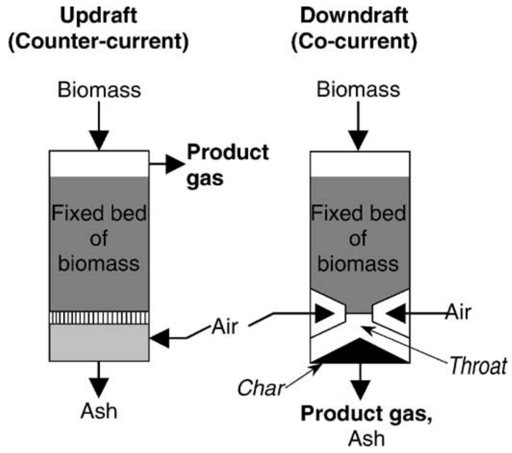

Fig. 2. Fixed bed gasifiers.

experience. In particular, no manufacturer is willing to give full guarantees for technical performance of their gasification technology. This confirms the limited operating experience and the limited confidence in the technology. Fig. 6 suggests a relationship between gasification technologies in terms of their strength and their market attractiveness for power generation (derived from) [24].

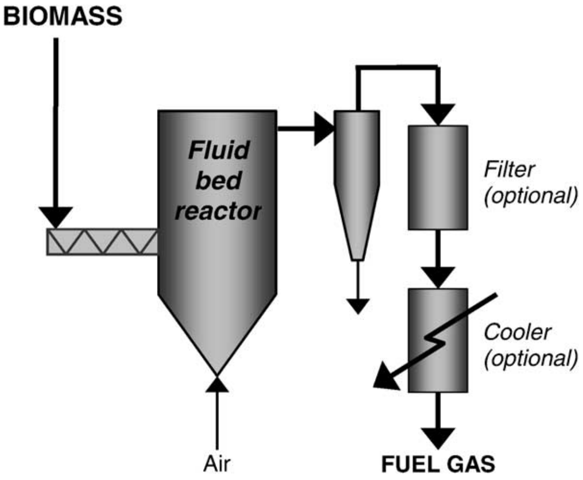

Fig. 3. Fluid bed gasifier.

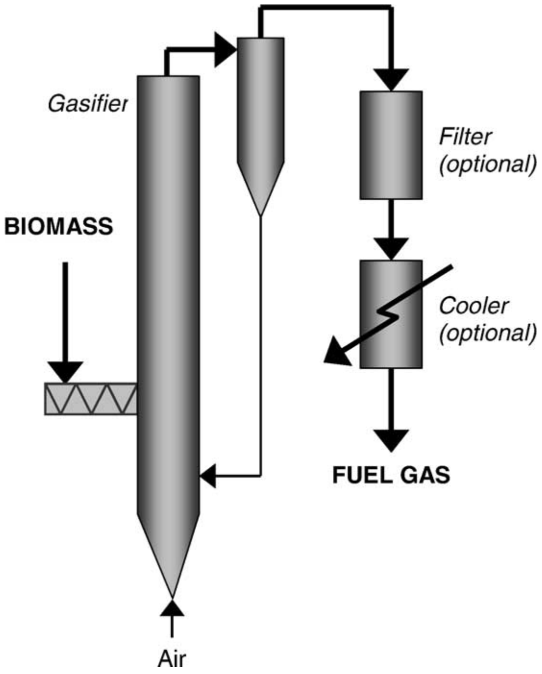

Fig. 4. Circulating fluid bed gasifier.

Atmospheric circulating fluidised bed gasifiers have proven very reliable with a variety of feedstocks and are relative easy to scale up from a few MWth up to 100 MWth. Even for capacities above 100 MWth, there is confidence that the industry would be able to provide reliable gasifiers. This appears to be the preferred system for large-scale applications and is used by most industrial companies and these systems therefore have high market attractiveness and are technically well proven.

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 MWth. They are limited in their capacity size range as they have not been scaled up significantly and the gasifier

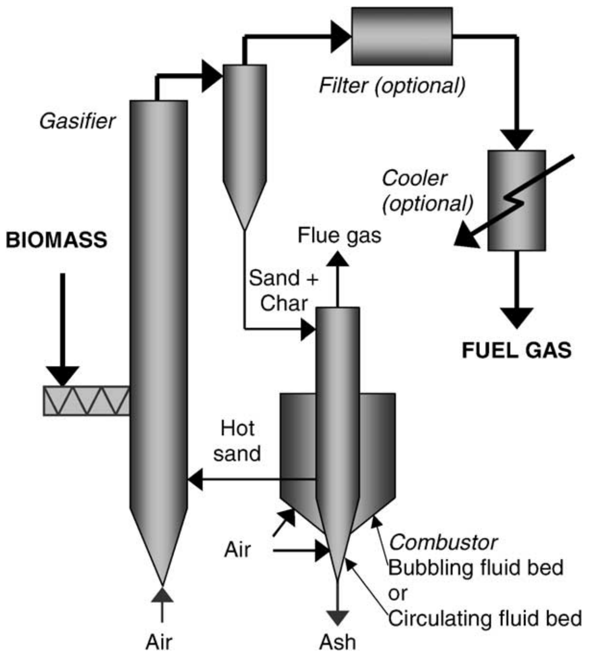

Fig. 5. Twin fluid bed gasifier with char combustor as a CFB or bubbling bed.

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 is thus relative high as well as their technology strength.

Pressurised fluidised bed systems either circulating or bubbling are considered of more limited market attractiveness due to the more complex operation of the installation and the additional costs related to the construction of pressurised vessels. However, pressurised fluidised bed systems have the advantage in integrated combined cycle applications as the need to compress the fuel gas prior its utilisation in the combustion chamber of the gas turbine is avoided.

Atmospheric downdraft gasifiers are attractive for small-scale applications up to about 1.5 MWth as there is a very big market in both developed and developing economies [26]. However, the problem of efficient tar removal is still a major problem and a higher level of automation is needed especially for small-scale industrial applications. Nevertheless, recent progress in catalytic conversion of tar gives more credible options and these systems can therefore be considered of average technical strength.

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 [10,27]. Another possible reason is that the upper size of a single unit is around 2.5 MWe so larger plant capacities require multiple units.

Atmospheric cyclonic gasifiers have only recently been tested for biomass feedstocks and although they have medium market attractiveness due to their simplicity, they are still unproven. Finally, atmospheric entrained bed gasifiers are still at a very early stage of development and since they require feedstock of a very small particle size, their market attractiveness is very low. No company is known to be developing pressurised systems for downdraft, updraft, cyclonic or entrained bed gasifiers for biomass feedstocks and it is difficult to imagine that such a technology could ever be developed into a commercial product due to the inherent problems of scale, tar removal and cost.

In conclusion, for large-scale applications the preferred and most reliable system is the circulating fluidised bed gasifier while for the small-scale applications the downdraft gasifiers are the most extensively studied. Bubbling fluidised bed gasifiers can be competitive in medium scale applications. Large-scale fluidised bed systems have become commercial due to the successful co-firing projects (see below), while moving bed gasifiers are still trying to achieve this.

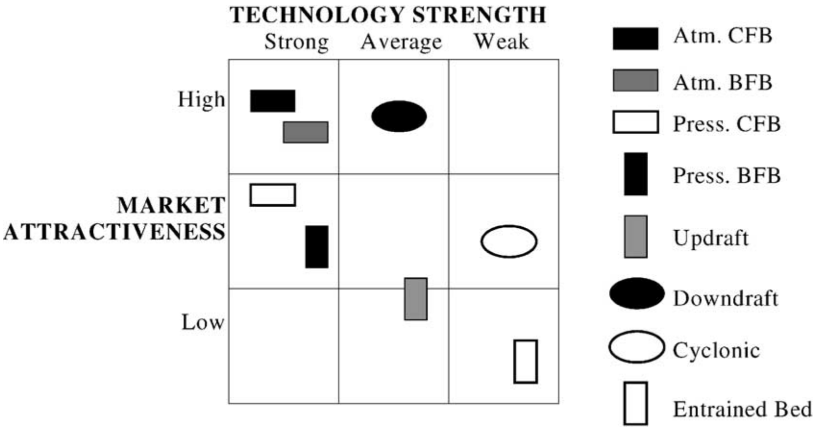

Fig. 6. Technology status of biomass gasification (derived from).

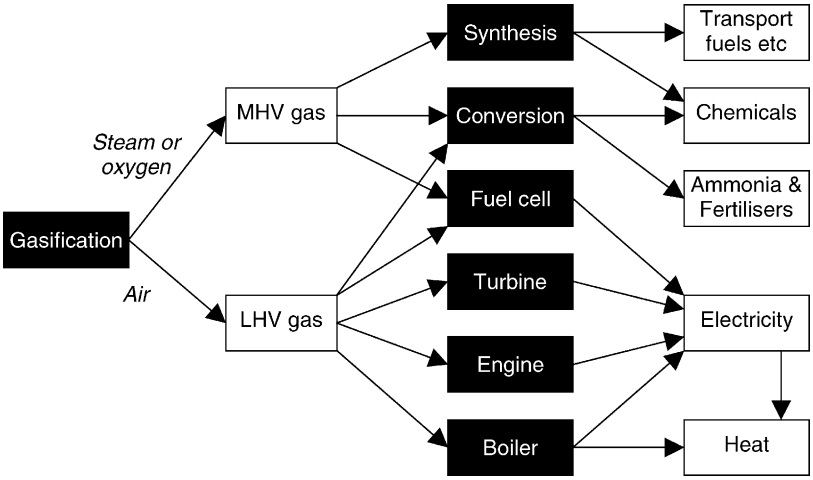

Fig. 7. Applications for gas from biomass gasification.

3.2. Applications for gas

Fig. 7 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 due to the absence of diluent nitrogen, which would pass through unchanged, but reduce process efficiency and increase costs. The exception is ammonia synthesis when the nitrogen content derived from air gasification can be utilised in the ammonia synthesis process. In electricity generation, there is no evidence that the benefits of producing higher heating value gas with oxygen gasification justifies the cost of providing and using oxygen, which explains the low level of interest in oxygen gasification. The technology for synthesis of commodity chemicals is commercially available but requires a very high gas quality, which is still elusive as well as a very large scale of operation, which for biomass systems is difficult to locate.

The major interest currently is in electricity generation due to the ease of distributing the product and absence of product quality requirements concerning compatibility in the market place, which remains a significant problem with many fuel and chemicals products. This attraction is enhanced by the widespread incentives for electricity generation from renewable resources throughout Europe.

Co-firing is a particularly attractive option since most bio-fuels including gases, liquids and solids can be readily introduced into conventional power stations and this takes advantage of the economies of scale, contributes comparable fossil fuel savings and reduces risks and uncertainties. There has been little commercial activity in this area.

3.3. Summary

Although biomass gasification technologies have been successfully demonstrated at large-scale and several demonstration projects are in operation or at an advanced stage of construction [28,29], they are still relatively expensive compared to fossil based energy and thus face economic and other non-technical barriers when trying to penetrate the energy markets [30,31,32].

Biomass gasification will only be able to penetrate energy markets if it is completely integrated into a biomass system. Thus the innovation in practically all demonstration projects under implementation lies not only in the technical aspects of the various processes but also in the integration of the gasification technologies in existing or newly developed systems where it can be demonstrated that the overall system offers better prospects for economic development [33].

4. Pyrolysis

Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is always also the first step in combustion and gasification processes where it is followed by total or partial oxidation of the primary products. Lower process temperature and longer vapour residence times favour the production of charcoal. High temperature and longer residence time increase the biomass conversion to gas and moderate temperature and short vapour residence time are optimum for producing liquids. Table 3 indicates the product distribution obtained from different modes of pyrolysis process. Fast pyrolysis for liquids production is of particular interest currently.

Fast pyrolysis occurs in a time of few seconds or less. Therefore, not only chemical reaction kinetics but also heat and mass transfer processes, as well as phase transition phenomena, play important roles. The critical issue is to bring the reacting biomass particle to the optimum process temperature and minimise its 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

Table 3
Typical product yields (dry wood basis) obtained by different modes of pyrolysis of wood

		Liquid (%)	Char (%)	Gas (%)
Fast pyrolysis	Moderate temperature, short residence time particularly vapour	75	12	13
Carbonisation	Low temperature, very long residence time	30	35	35
Gasification	High temperature, long residence times	5	10	85

later. Another possibility is to transfer heat very fast only to the particle surface that contacts the heat source (this second method is applied in ablative processes that are described later).

In order to illustrate the science and technology of thermal conversion in sufficient detail to appreciate the potential, fast pyrolysis is described at length.

4.1. Principles

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,
- short 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 dry feed basis, together with by-product char and gas which are used within the process 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 in the case of fluid bed reactors) to give sufficiently small particles to ensure rapid reaction, pyrolysis reaction, separation of solids (char), and collection of the liquid product (bio-oil).

Any form of biomass can be considered for fast pyrolysis. While most work has been carried out on wood due to 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 and solid wastes such as sewage sludge and leather wastes.

4.2. 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, almost all research and development has focused on the reactor. The rest of the process consists of biomass reception, storage and handling, biomass drying and grinding, product collection, storage and, when relevant, upgrading (Table 4). The key aspects of these peripheral steps are described later. A comprehensive survey of fast pyrolysis processes has been published that describes all the pyrolysis processes for liquids production that have been built and tested in the last 10–15 years [34].

4.3. 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 ageing and exacerbate the instability problem, which is described below. Hot vapour filtration, analogous to hot-gas filtration in gasification processes, gives a high-quality char free product [49], however the liquid yield is reduced by about 10–20% due to the char accumulating on the filter surface that cracks the vapours.

Pressure filtration of the liquid is very difficult due to 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 micro-structure by addition of solvents such as methanol or ethanol that solubilise the less soluble constituents will improve this problem and also contribute to improvements in liquid stability as described below.

4.4. Liquid 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 to condense the true vapours, while the aerosols require coalescence or agglomeration. Simple heat exchange can cause

Table 4
Fast pyrolysis reactor types and characteristics

Bubbling fluid beds (Fig. 8)

- Simple construction and operation
- Good temperature control
- Very efficient heat transfer to biomass particles due to high solids density
- Easy scaling
- Well-understood technology
- Good and consistent performance with high liquid yields: of typically 70–75 wt.% from wood on a dry feed basis
- Heating can be achieved in a variety of ways as shown in Fig. 10
- Residence time of solids and vapours is controlled by the fluidising gas flow rate and is higher for char than for vapours
- Char acts as an effective vapour cracking catalyst at fast pyrolysis reaction temperatures so rapid and effective char separation/elutriation is important
- Small biomass particle sizes are needed to achieve high biomass heating rates of less than 2–3 mm
- Good char separation is important—usually achieved by ejection and entrainment followed by separation in one or more cyclones
- Heat transfer to bed at large scale has to be considered carefully due to scale-up limitations.

Examples: Waterloo (basic research, extensive publications such as [35]); Union Fenosa [36]; Dynamotive [37]; Wellman [38]

Circulating fluid beds and transported bed (Fig. 9)

- Good temperature control can be achieved in reactor
- Residence time for the char is almost the same as for vapours and gas
- CFBs are suitable for very large throughputs
- Well-understood technology
- Hydrodynamics more complex
- Char is more attrited due to higher gas velocities; char separation is by cyclone
- Closely integrated char combustion in a second reactor requires careful control
- Heat transfer at large scale has to be proven

Examples: Ensyn [39]; CRES [40]

Ablative pyrolysis (Fig. 10)

- High pressure of particle on hot reactor wall, achieved due to centrifugal force (NREL) or mechanically (Aston)
- High relative motion between particle and reactor wall
- Reactor wall temperature should be less than 600 °C
- Large feed sizes can be used
- Inert gas is not required, so the processing equipment is smaller (in case of mechanically applied pressure)
- The reaction system is more intensive
- Reaction rates are limited by heat transfer to the reactor, not to the biomass
- The process is surface area controlled so scaling is more costly
- The process is mechanically driven so the reactor is more complex

Examples: CNRS Nancy (basic research) [41]; NREL [42]; Aston University [43]

Entrained flow

- Simple technology
- Poor heat transfer
- High gas flows give large plant and cause difficult liquid collection
- Good scale-up
- Lower liquid yields

Examples: GTRI [44]; Egemin [45]

Rotating cone (Fig. 11)

- Centrifugation (at around 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 from where 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 for sand transport
- 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

Examples: Twente University [46]; BTG [47]

Vacuum pyrolysis

- Not a true fast pyrolysis process as solids residence time is very high
- It can process larger particles than most fast pyrolysis reactors
- There is less char in the liquid product due to lower gas velocities
- There is no requirement for a carrier gas
- Liquid yields of 35–50% on dry feed are typically obtained with higher char yields than fast pyrolysis systems; conversely, the liquid yields are higher than in slow pyrolysis technologies because of fast removal of vapours from the reaction zone
- The process is relatively complicated mechanically

Example: Pyrovac [48]

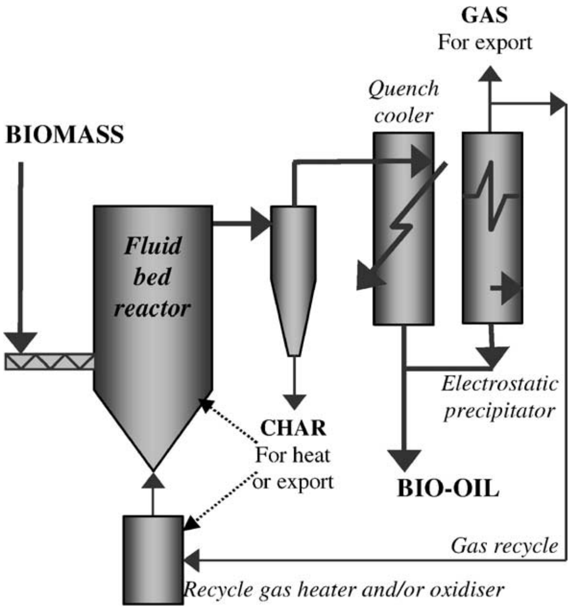

Fig. 8. Bubbling fluid bed reactor.

preferential deposition of lignin derived components leading to liquid fractionation and eventually blockage. Quenching in product 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 very effective and electrostatic precipitation is currently the preferred method at smaller scales up to pilot plant. The vapour product from fluid bed and transported bed reactors has a low partial pressure of collectible products due to the large volumes of fluidising gas, and this is an important design consideration in liquid collection.

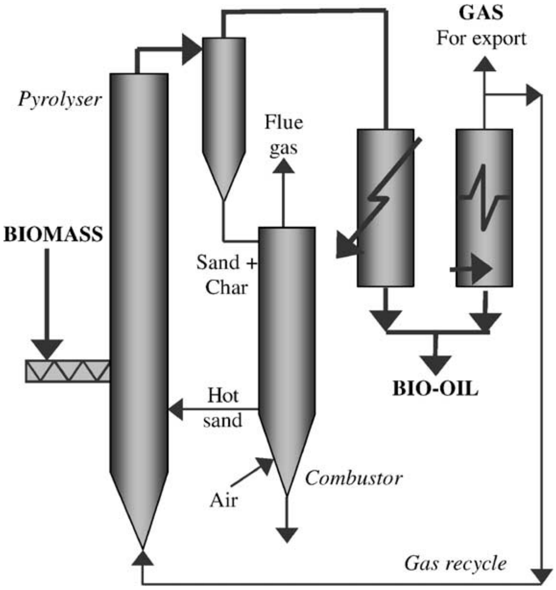

Fig. 9. Circulating fluid bed reactor.

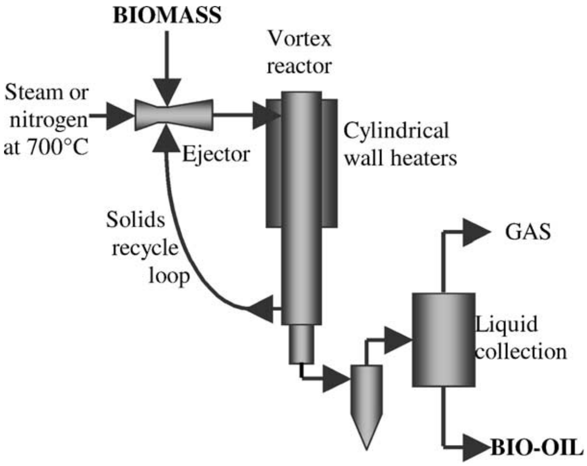

Fig. 10. NREL Vortex ablative reactor.

4.4.1. Pyrolysis liquid—bio-oil

Pyrolysis liquid is referred to by many names including pyrolysis oil, bio-oil, bio-crude-oil, bio-fuel-oil, wood liquids, wood oil, liquid smoke, wood distillates, pyroligneous tar, pyroligneous acid, and liquid wood. The crude pyrolysis liquid 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 and dissolved alkali metals from ash [50] may also be present. The product spectrum from aspen wood and the dependence on temperature is shown in Fig. 12.

4.4.2. Liquid product characteristics

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. Ageing or instability is believed to result from a breakdown in this

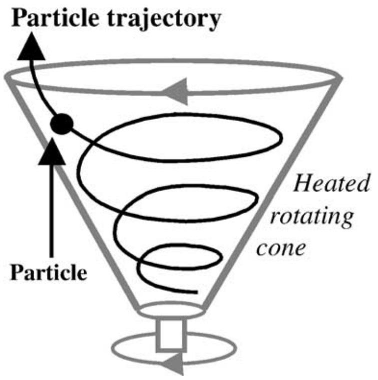

Fig. 11. Principle of rotating cone pyrolysis reactor.

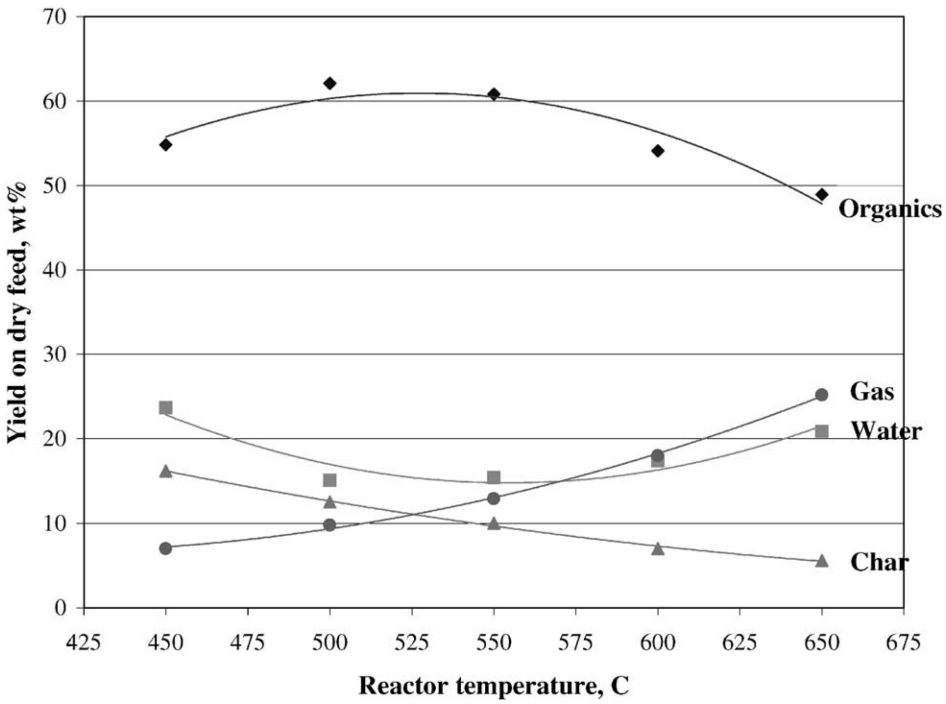

Fig. 12. Variation of products from Aspen Poplar with temperature [51].

emulsion. In some ways, it is analogous to asphaltenes found in petroleum.

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. The liquid is often referred to as ‘oil’ or ‘bio-oil’ or ‘bio-crude’, although 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 characteristics of this liquid that are summarised in Table 5 and discussed briefly in Table 6.

4.4.3. *Upgrading pyrolysis liquid*

The most important properties that adversely affect bio-oil fuel quality are incompatibility with conventional fuels, solids content, high viscosity, and chemical instability. The field of chemical and physical upgrading of bio-oil has been thoroughly reviewed [52]. Hot-gas 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.

A process for producing stable micro-emulsions with 5–30% of bio-oil in diesel has been developed at CANMET [54] and the University of Florence, Italy, has been working emulsions of 5–95% bio-oil in diesel [55]. The addition of polar solvents, especially methanol, gave a significant positive effect on the oil stability [56].

Chemical/catalytic upgrading processes to produce hydrocarbon fuels that can be conventionally processed are more complex and costly than physical methods, but of-

Table 5
Typical properties of wood derived crude bio-oil

Physical property	Typical value	Characteristics
Moisture content	15–30%	Liquid fuel
pH	2.5	Ready substitution for conventional fuels in many static applications such as boilers, engines, turbines
Specific gravity	1.20	Heating value of 17 MJ/kg at 25 wt.% water, is about 40% that of fuel oil diesel
Elemental analysis C	55–58%	Does not mix with hydrocarbon fuels
H	5.5–7.0%	Not as stable as fossil fuels
O	35–40%	Quality needs definition for each application
N	0–0.2%	
Ash	0–0.2%	
HHV as produced	16–19 MJ/kg	
Viscosity (at 40 °C and 25% water)	40–100 cp	
Solids (char)	1%	
Vacuum distillation residue	up to 50%	

Table 6
Typical properties and characteristics of wood derived crude bio-oil

Appearance	Pyrolysis oil typically is a dark brown free flowing liquid. Depending upon 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 by the chemical composition. Hot vapour filtration gives a more translucent red-brown appearance due to the absence of char. High nitrogen contents in the liquid can give it a dark green tinge
Odour	The liquid has a distinctive odour—an acrid smoky smell, which can irritate the eyes if exposed for a prolonged period to the liquids. The cause of this smell is due to the low molecular weight aldehydes and acids. 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
Miscibility	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 how it was produced and subsequently collected. 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. It is miscible with polar solvents such as methanol, acetone, etc. but totally immiscible with petroleum-derived fuels
Density	The density of the liquid is very high at around 1.2 kg/l compared to 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 on the design and specification of equipment such as pumps
Viscosity	The viscosity of the bio-oil as produced can vary from as low as 25 cSt to as high as 1000 cSt (measured at 40 °C) or more depending on the feedstock, the water content of the oil, the amount of light ends that have been collected and the extent to which the oil has aged. Viscosity is important in many fuel applications [53]
Distillation	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. The liquid is, therefore, chemically unstable, and the instability increases with heating, so it is preferable to store the liquid at room temperature. These changes do also occur at room temperature, but much more slowly and can be accommodated in a commercial application
Ageing of pyrolysis liquid	The complexity and nature of bio-oil causes some unusual behaviour, specifically that the following properties tend to change with time: viscosity increases, volatility decreases, phase separation and deposition of gums can occur

fer significant improvements ranging from simple stabilisation to high-quality fuel products [57]. Full deoxygenation to high-grade products such as transportation fuels can be accomplished by two main routes: hydrotreating and catalytic vapour cracking over zeolites, both of which have been reviewed [58,59].

4.4.4. Applications for bio-oil

Bio-oil can substitute for fuel oil or diesel in many static applications including boilers, furnaces, engines and turbines for electricity generation. The possibilities are summarised in Fig. 13. There is also a range of chemicals that can be extracted or derived including food flavourings, specialities, resins, agri-chemicals, fertilisers, and emissions control agents. Upgrading bio-oil to transportation fuels is feasible but currently not economic. At least 400 h operation has been achieved on a 250 kWe specially modified dual fuel engine and limited experience has been gained on a modified 2.5 MWe gas turbine.

A range of chemicals can also be produced from specialities such as levoglucosan to commodities such as resins and fertilisers as summarised in Table 7. Food flavourings

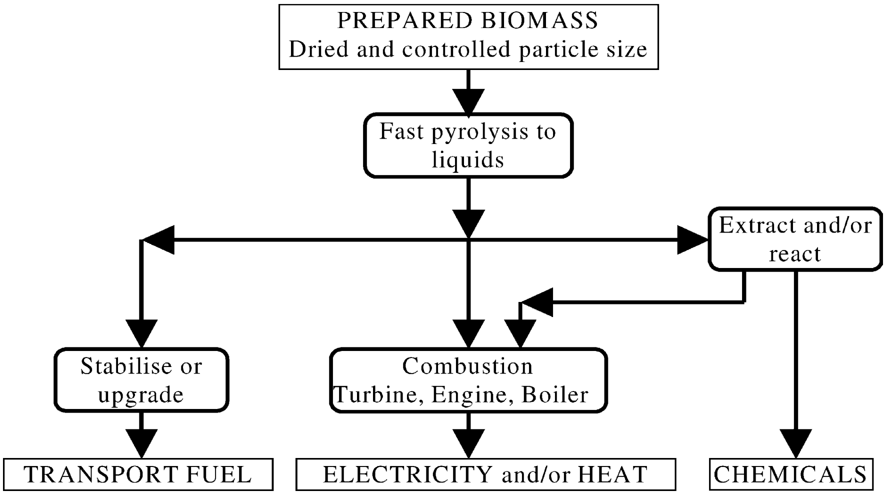

Fig. 13. Applications for Bio-oil.

Table 7
Chemicals from fast pyrolysis

Acetic acid	Adhesives	Calcium enriched bio-oil	Food flavourings
Hydrogen	Hydroxyaceladehyde	Levoglucosan	Levoglucosenone
Preservatives	Resins	Slow release fertilisers	Sugars

are commercially produced from wood pyrolysis products in many countries. All chemicals are attractive possibilities due to their much higher added value compared to fuels and energy products, and lead to the possibility of a bio-refinery concept in which the optimum combinations of fuels and chemicals are produced.

4.5. Summary

The liquid bio-oil product from fast pyrolysis has the considerable advantage of being storable and transportable as well as the potential to supply a number of valuable chemicals, but there are many challenges facing fast pyrolysis that relate to technology, product and applications. The problems facing the sector include the following:

- Cost of bio-oil, which is 10 to 100% more than fossil fuel.
- Availability: there are limited supplies for testing.
- There is a lack of standards for use and distribution of bio-oil and inconsistent quality inhibits wider usage; considerable work is required to characterise and standardise these liquids and develop a wider range of energy applications.
- Bio-oil is incompatible with conventional fuels.
- Users are unfamiliar with this material.
- Dedicated fuel handling systems are needed.
- Pyrolysis as a technology does not enjoy a good image.

The most important issues that need to be addressed seem to be:

- Scale-up.
- Cost reduction.
- Improving product quality including setting norms and standards for producers and users.
- Environment health and safety issues in handling, transport and usage.
- Encouragement for developers to implement processes; and users to implement applications.
- Information dissemination.

5. Economics of thermal conversion systems for electricity production

Comparisons for electricity production between combustion (Combust), atmospheric pressure gasification (GasEng), pressurised gasification in combined cycle (IGCC) and fast pyrolysis with an engine (PyrEng) are shown in Figs. 14–16 below. Capital costs for plants constructed now (i.e. first plant costs for gasification and pyrolysis and *n*th plant costs

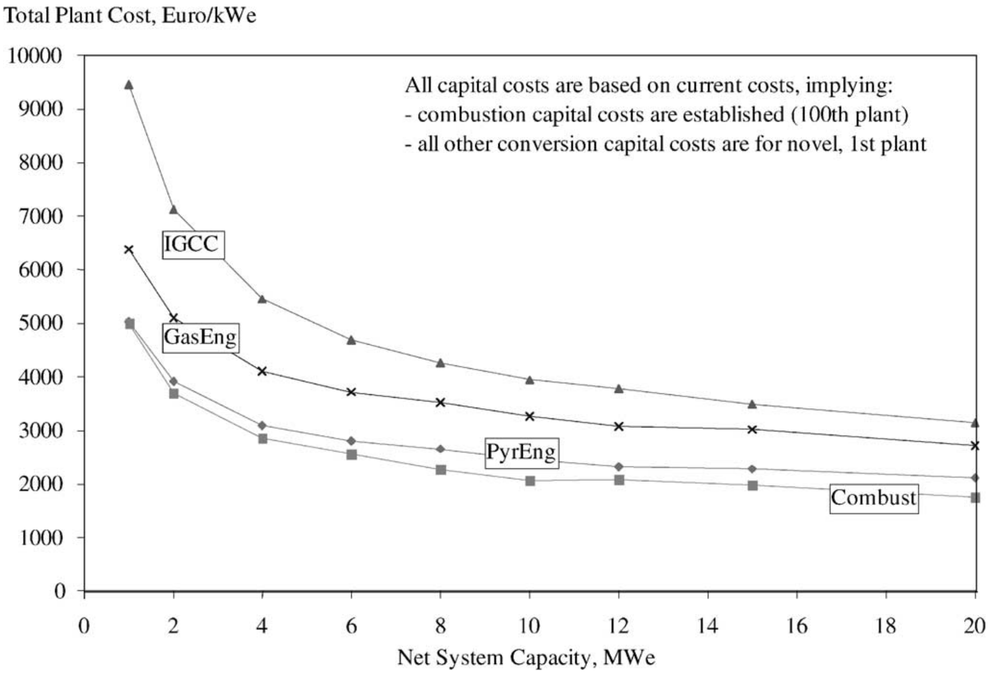

Fig. 14. Comparison of total plant costs for four biomass to electricity systems.

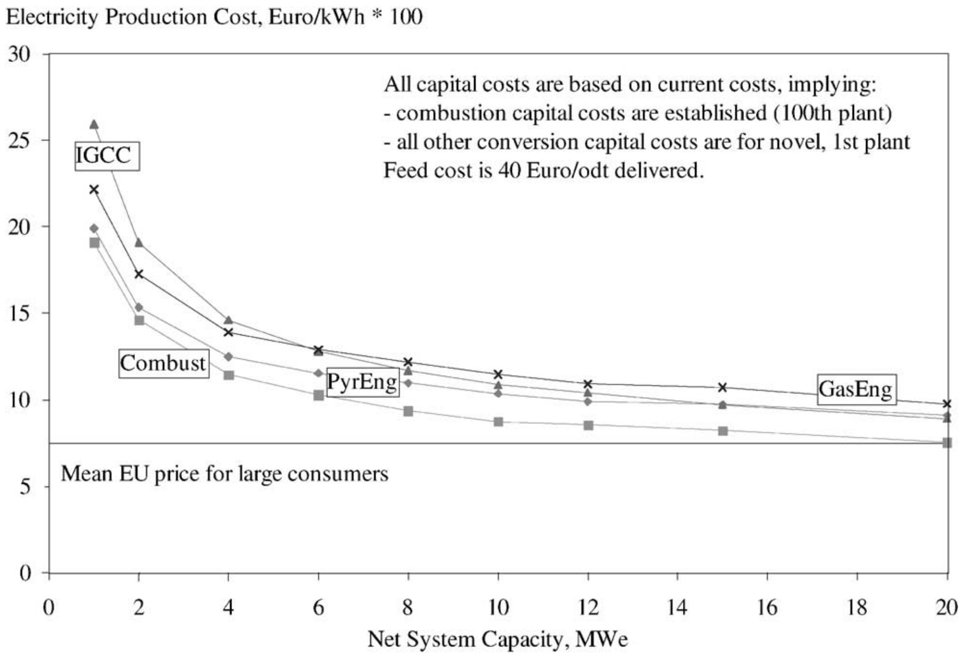

Fig. 15. Comparison of electricity production costs for four biomass to electricity systems.

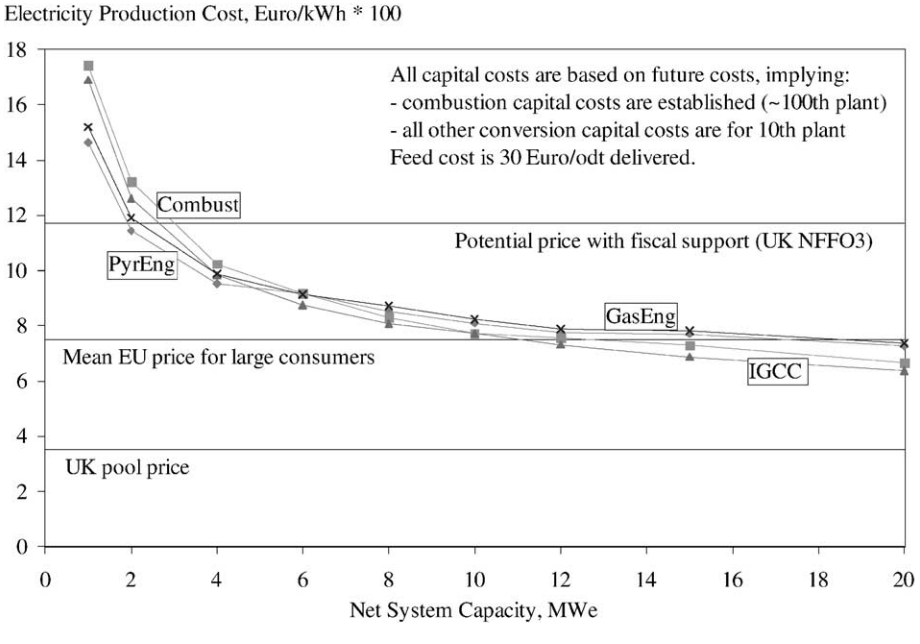

Fig. 16. Potential electricity production costs using future system conditions.

for combustion, all costs in Euros 2000) are shown in Fig. 14. The resultant electricity production costs for the four systems are shown in Fig. 15, while the benefits of learning in reducing capital costs as more plants are built, i.e. longer term costs, are shown in Fig. 16. Processes start with wood delivered as wet chips and include all steps and costs needed to produce electricity by turbine (Combust and IGCC) or engine (GasEng and PyrEng). Full details of the methodology can be found in [60] from which this data is derived.

6. Barriers

The technologies have to overcome a number of technical and non-technical barriers before industry will implement their commercialisation. The technical barriers have been described above, while some of the more important non-technical barriers are summarised below.

6.1. *Economics*

All bio-fuels have to compete with fossil fuels. For those countries who have made commitments to reduce fossil fuel derived carbon emissions, the current disincentive to implementation of bio-energy on simple cost grounds will have to be overcome—no company is going to invest in ventures that are guaranteed to lose money, regardless of the environmental benefits that may accrue. Industry will only invest in technology that has an acceptable return at an acceptable risk [61]. Acceptable returns will come from incentives to capital expenditure of product purchase, or to disincentives to orthodox options by, for example taxation on fossil fuels or legislation, etc. This is one of the major roles that governments have to play.

6.2. *Perception*

There is widespread approval of the interest in, and move towards, renewal energy and bio-energy—as long as it is not near me! Increasing attention will need to be placed on “selling” the idea to the populace where the plant is to be built, and this problem could be exacerbated by the need to build smaller plants and thus many more plants than conventional power stations and refineries. Early plants will have the curiosity factor and may enjoy popularity as an attraction by itself or as part of an attraction of a “green” site.

6.3. *Politics*

For industry to implement renewable energy technologies in order that commitments made to mitigate greenhouse gases can be met, investment has to be attractive. Without some fiscal incentives (or disincentives against fossil fuels), companies will only invest in those projects that are sufficiently profitable and most of these will be in niche markets and special opportunities. As commented above, only governments can create the necessary instruments.

6.4. *Scale*

Economies of scale are a vital feature of the development of industry and technology in which the larger a process can be built, the cheaper it becomes. This is particularly important in the energy and process industries that will shoulder the responsibility for technology development and implementation. However in the bio-energy industry, biomass is a diffuse resource which has to be harvested over large areas. A modest 10 MWe power station operating at a modest efficiency of 35% will require about 40,000 t per year of wood on a dry basis which will require about 4000 ha of land or 40 km^2. This could reduce to 2000 ha or 20 km^2 if the promise of high yielding short rotation forestry is realised. Neither figure makes any allowance for non-productive land. There are therefore finite sizes that bio-energy processes can be built in considering the costs and logistics of transporting biomass to a processing plant. The maximum size that has been suggested in Europe ranges from 30 to 80 MWe in the short to medium term, and 100 to 150 MWe in North America. This places a practical upper limit on the benefits of scale.

6.5. *Risk*

Investors are generally risk averse and always prefer low risk investments, but if risks have to be accepted, then an appropriately higher return is expected. Technology developers can do much to minimise technical risk and this topic has been thoroughly described and discussed [61].

6.6. *Vested interests*

The established energy suppliers and providers have considerable investments in orthodox energy systems and will always seek to maximise their returns and maintain their competitive edge. Most major energy companies have their own programmes of supporting renewable energy, but there have always been concerns over the extent to which they will seek to protect their interests.

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