ASTON UNIVERSITY

MARCH 1999 PyNe GUIDE 1

PyNe

Special Review
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A Guide to Fast Pyrolysis of Biomass for Fuels and Chemicals

Introduction

Renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage. Wood and other forms of biomass are some of the main renewable energy resources available and provide the only source of renewable liquid, gaseous and solid fuels. Wood and biomass can be used in a variety of ways to provide energy:

- By direct combustion to provide heat for use in heating, for steam production and hence electricity generation.
- By gasification to provide a fuel gas for combustion for heat, or in an engine or turbine for electricity generation.
- By fast pyrolysis to provide a liquid fuel that can substitute for fuel oil in any static heating of electricity generation application. The liquid can also be used to produce a range of speciality and commodity chemicals.

Fast pyrolysis can directly produce a liquid fuel from biomass which can be readily stored or transported.

Fast Pyrolysis

Fast pyrolysis is a high temperature process in which biomass is rapidly heated in the absence of oxygen. As a result it 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 which is carefully controlled to give high yields of liquid.

Fast Pyrolysis Processes

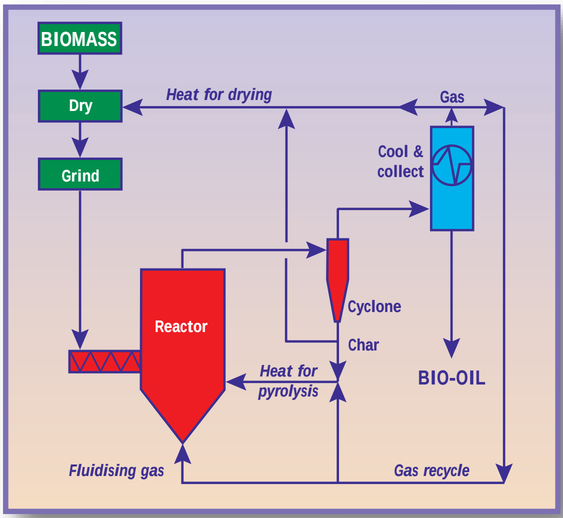

Figure 1: Conceptual fluid bed fast pyrolysis process

Figure 2: Dynamotive, Canada, 50 kg/h fluid bed fast pyrolysis unit

Features

The essential features of a fast pyrolysis process are:

- Very high heating and heat transfer rates, which usually requires a finely ground biomass feed.
- Carefully controlled pyrolysis reaction temperature of around 500ºC in the vapour phase, with short vapour residence times of typically less than 2 seconds.
- Rapid cooling of the pyrolysis vapours to give the bio-oil product.

The main product, bio-oil, is obtained in yields of up to 80% wt on dry feed, together with by-product char and gas which are used within the process so there are no waste streams. While a wide range of reactor configurations have been operated, fluid beds are the most popular configurations due to their ease of operation and ready scale-up. A typical bubbling fluid bed configuration is depicted in Figure 1 with utilisation of the by-product gas and char to provide the process heat. The figure includes the necessary steps of drying the feed to less than 10% water to minimise the water in the product liquid oil, and grinding the feed to around 2mm to give sufficiently small particles to ensure rapid reaction.

Reactors

Fluid beds

Bubbling fluid beds have been selected for further development by several companies including Union Fenosa who have a 200 kg/h pilot unit in Spain (Figure 3), Dynamotive who have a 50 kg/h unit in Canada based on a RTI design (Figure 2), and Wellman who are building a 200 kg/h unit in the UK.

Circulating fluid beds and transported bed reactors have been developed to commercial status and are used in the USA for food flavourings and related products in several plants of 1 to 2 t/h. Figure 4 shows the 650 kg/h unit supplied by Ensyn to ENEL in Italy.

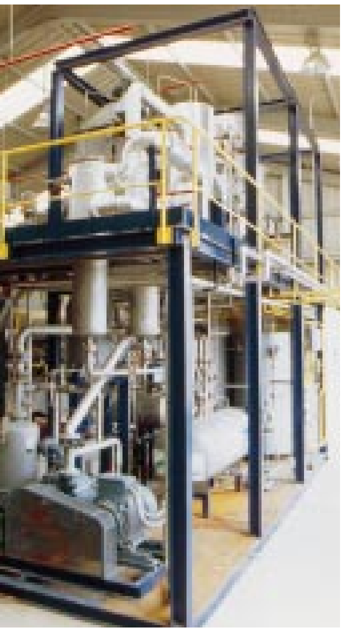

Figure 3: 200 kg/h Fast pyrolysis pilot plant at Union Fenosa, Spain

Figure 4: External view of the 650 kg/h unit at ENEL, Italy, supplied by Ensyn

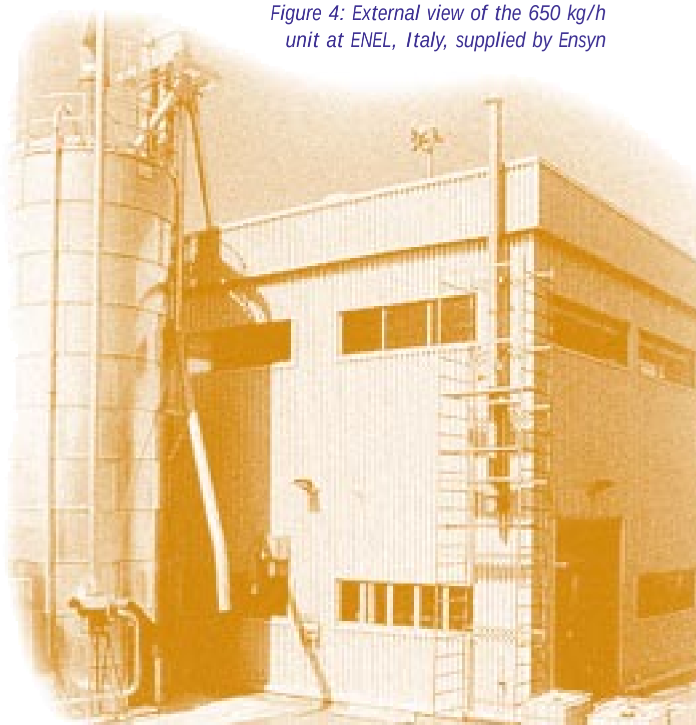

Figure 5: 10 kg/h Ablative reactor at Aston University, UK

Entrained flow reactor
Entrained flow fast pyrolysis was developed at Georgia Tech Research Institute and scaled up by Egemin. However, probably because of the difficulties that have been encountered in achieving good heat transfer from a gaseous heat carrier to solid biomass, the Egemin process is no longer operational or being further developed.

Rotating cone reactor
The rotating cone reactor, invented at the University of Twente and being developed by BTG, is a recent development and effectively operates as a transported bed reactor, but with transport effected by centrifugal forces rather than gas (PyNe Newsletter 3). The 200 kg/h unit is shown in Figure 7.

Ablative pyrolysis
Ablative pyrolysis is interesting as much larger particle sizes can be employed than in other systems and the process is limited by the rate of heat supply to the reactor rather than the rate of heat absorption by the pyrolysing biomass. Much of the pioneering work on ablative pyrolysis reactors has been carried out by NREL in their vortex reactor (Figure 6) and by CNRS at Nancy. More recent developments have been carried out at Aston University and the second version of their reaction system is shown in Figure 5. This fast pyrolysis route offers a more intensive and potentially compact reaction system.

Vacuum pyrolysis
Vacuum pyrolysis is unique in that the rate of heating is very low compared to the other systems described above, but the effect (in terms of liquid product yield and quality) of fast pyrolysis is achieved by removing the vapours as soon as they are formed by operating under a vacuum (PyNE Newsletter 3).

Research and development
Research and development is underway in many centres in Europe and North America such as the fluid bed at IWC (Figure 8) and the ablative reactor at Aston University (Figure 5) but there is insufficient space to include all of them.

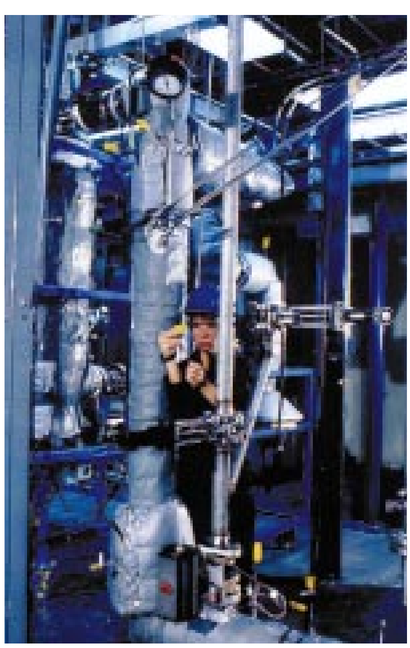

Figure 6: NREL, USA, 20kg/h Ablative vortex fast pyrolysis unit

Figure 7: 200 kg/h Rotating cone pilot plant, BTG, The Netherlands

Figure 8: 6 kg/h Fluid bed unit at IWC, Hamburg, Germany

Pyrolysis Liquid – Bio-oil

Pyrolysis liquid is referred to by many names including pyrolysis liquid, 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. It is combustible and renewable hence the use of the term 'bio' Pyrolysis liquid has a heating value of nearly half that of a conventional fuel oil – typically 16–18 MJ/kg. The main characteristics are summarised in Table 1.

Figure 9: Bio-oil

Appearance
Pyrolysis liquid 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 (Figure 9). 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 liquid contains several hundred different chemicals in widely varying proportions, ranging from low molecular weight and volatile formaldehyde and acetic acid to complex high molecular weight phenols and anhydrosugars.

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 40 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 immiscible with petroleum-derived fuels.

Density
The density of the liquid is very high at around 1.2 kg/litre compared to light fuel oil at around 0.85 kg/litre. This means that the liquid has about 42% of the energy content of fuel oil on a weight basis, but 61% on a volumetric basis. This has implications 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 cS to as high as 1000 cS or more depending on the water content, 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.

Distillation
Pyrolysis liquids cannot be completely vapourised once they have been recovered from the vapour phase. If the liquid is heated to 100°C or more to try to remove water or distil off lighter fractions, it rapidly reacts and produces a char residue of around 50 wt% of the original liquid and some distillate containing primary and secondary products and water. The liquid is, therefore, chemically unstable, and this effect increases with heating, so it is preferable to store the liquid at room temperature. These changes do occur at room temperature, but much more slowly and can be accommodated in a commercial application.

Table 1: Typical properties and characteristics of wood derived pyrolysis oil

Physical Properties		***Typical Value***
Moisture content		15–30%
pH		2.5
Specific gravity		1.20
Elemental analysis, dry basis	C	56.4%
	H	6.2%
	O *(by difference)*	37.3%
	N	0.1%
	Ash	0.1%
HHV as produced (depends on moisture)		16–19 MJ/kg
Viscosity (at 40°C and 25% water)		40–100 cp
Solids (char)		0.5%
Distillation		max. 50% as liquid degrades

Characteristics

- Liquid fuel.
- Easy substitution for conventional fuels in many static appliances – boilers, engines, turbines.
- Heating value is about 40% that of fuel oil or diesel on a weight basis and 60% on a volume basis.
- Does not mix with hydrocarbon fuels.
- Not as stable as fossil fuels.

Applications for Bio-oil

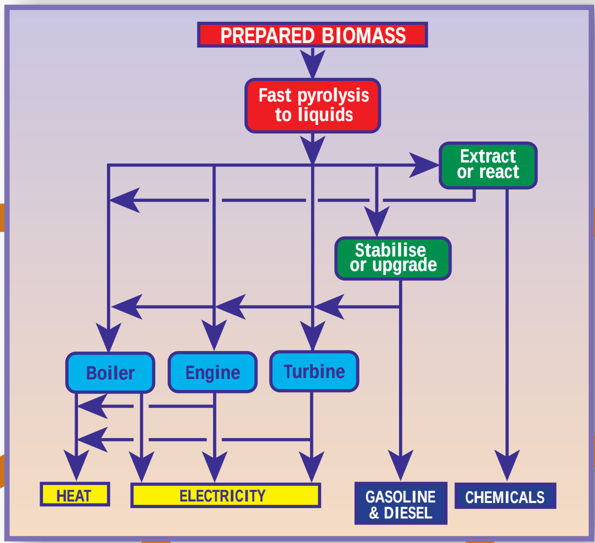

Figure 10: Applications for bio-oil

Figure 11: 250 kWe Dual fuel diesel engine modified by Ormrod Diesels, UK, to run on bio-oil

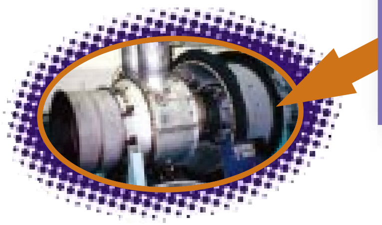

Figure 12: 2.5 MWe Gas turbine modified by Orenda, Canada

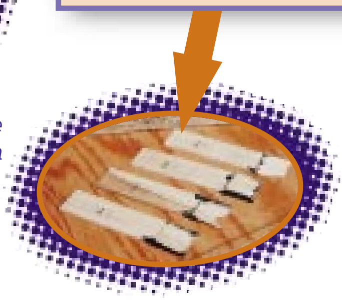

Figure 13: Wood products made from phenol-formaldehyde resins derived from bio-oil at NREL, USA

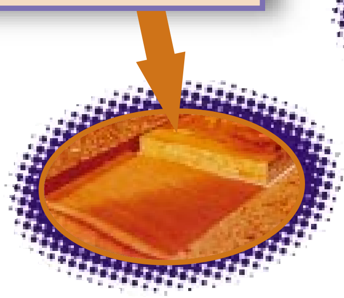

Figure 14: Products produced with phenol-formaldehyde resins made with bio-oil at ARI, Greece

Figure 15: Fine chemicals

Figure 16: Slow release fertiliser from whole 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 Figure 10. There are 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.

Electricity production

At least 500 hours operation has been achieved in the last few years on various engines from laboratory test units to 1.4 MWe modified dual fuel diesel engines. One such engine is shown in Figure 11. This is a 250 kWe dual fuel engine on which over 400 hours have been logged in total, including several runs of over 9 hours, and with electricity being generated for 320 hours. A 2.5 MWe gas turbine has also been modified and successfully run on bio-oil (Figure 12).

Chemicals

A range of chemicals can also be produced from specialities such as levoglucosan (Figure 15 and PyNe Newsletters 4 and 5) to commodities such as resins (see Figures 13 and 14 and PyNe Newsletters 6 and 7) and fertilisers (Figure 16). Food flavourings 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 (PyNe Newsletter 4 and 5).

Economics

The projected cost of bio-oil is related to feed cost and size of unit. Detailed cost analyses have been carried out over a range of plant sizes and feed costs to give the results shown in Figure 17. The cost includes all plant and processing from reception of wet whole tree chips through all necessary preparation and pyrolysis to storage of cold bio-oil.

The data in Figure 17 has been reduced to a simple equation shown below which can be used to estimate the cost of bio-oil for a range of feed costs and plant sizes with adjustments possible for plant efficiency and feed heating value.

$$\text{Bio-oil cost, (ECU/GJ[LHV])} = 8.87 * (\text{Wood Capacity, dry t/h})^{-0.3407} + \frac{\text{Feed cost ECU/dry t}}{0.625 * \text{Wood LHV GJ/t}}$$

The bio-oil cost is expressed in LHV terms and in ECU 1998 costs. The bio-oil energy yield is assumed to be 62.5% and the wood higher heating value is taken as 19 GJ/t. The exchange rate to US dollars is US$1.15/ECU.

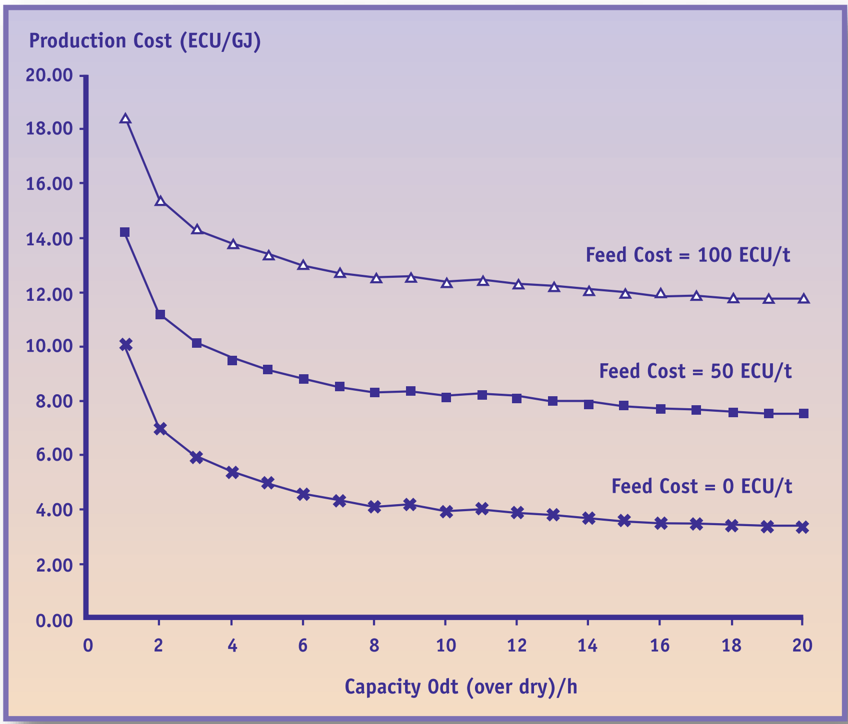

Figure 17: Bio-oil production costs versus capacity at different feed costs, 1998

Summary

There is still not a well defined 'best' fast pyrolysis process and much potential remains for further development and optimisation. The liquid bio-oil product has the considerable advantage of being storable and transportable as well as the potential to supply a number of valuable chemicals. Considerable work is required to characterise and standardise this liquid and develop a wider range of energy applications. Chemicals offer more interesting commercial opportunities and are likely to be a major focus of continuing R&D effort.

Acknowledgments

The assistance of the PyNe Subject Group Convenors in compiling this document is much appreciated.

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The PyNe Guide is published by the Bio-Energy Research Group, Aston University, UK and is sponsored by the FAIR Programme of the European Commission DGXII and IEA Bioenergy.

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