



An overview of fast pyrolysis of biomass

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Abstract

Biomass fast pyrolysis is of rapidly growing interest in Europe as it is perceived to offer significant logistical and hence economic advantages over other thermal conversion processes. This is because the liquid product can be stored until required or readily transported to where it can be most effectively utilised. The objective of this paper is to review the design considerations faced by the developers of fast pyrolysis, upgrading and utilisation processes in order to successfully implement the technologies. Aspects of design of a fast pyrolysis system include feed drying; particle size; pretreatment; reactor configuration; heat supply; heat transfer; heating rates; reaction temperature; vapour residence time; secondary cracking; char separation; ash separation; liquids collection. Each of these aspects is reviewed and discussed. A case study shows the application of the technology to waste wood and how this approach gives very good control of contaminants. Finally the problem of spillage is addressed through respirometric tests on bio-oils concluding with a summary of the potential contribution that fast pyrolysis can make to global warming. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage and its contribution to the Greenhouse Effect. 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 or 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.

2. Fast pyrolysis principles

Biomass is a mixture of hemicellulose, cellulose, lignin and minor amounts of other organics which each pyrolyse or degrade at different rates and by different mechanisms and pathways. Lignin decomposes over a wider temperature range compared to cellulose and hemicellulose which rapidly degrade over narrower temperature ranges, hence the apparent thermal stability of lignin during pyrolysis. The rate and extent of decomposition of each of these components depends on the process parameters of reactor (pyrolysis) temperature, biomass heating rate and pressure. The degree of secondary reaction (and hence the product yields) of the gas/vapour products depends on the time-temperature history to which they are subjected before collection, which includes the influence of the reactor configuration.

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Although some research has been carried out on the individual components of biomass, most applied and larger scale work has focused on whole biomass as the cost of pre-separation is considered too high. In addition, the separation and recovery of pure forms of lignin and hemicellulose are difficult due to structural changes in their processing, although pure cellulose is relatively easy to produce.

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. Liquid production requires very low vapour residence time to minimise secondary reactions of typically 1 s, although acceptable yields can be obtained at residence times of up to 5 s if the vapour temperature is kept below 400°C. 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. Research has shown that maximum liquid yields are obtained with high heating rates, at reaction temperatures around 500°C and with short vapour residence times to minimise secondary reactions. A compilation of published data is shown in Fig. 1 for typical products from fast pyrolysis of wood (Toft, 1996). Fast pyrolysis processes have been developed for production of food flavours (to replace traditional slow pyrolysis processes which had much lower yields), speciality chemicals and fuels. These utilise very short vapour residence times of between 30 and 1500 ms and reactor temperatures around 500°C. Both residence time and temperature control is important to “freeze” the intermediates of most chemical interest in conjunction with moderate gas/vapour phase temperatures of 400–500°C before recovery of the product to maximise organic liquid yields.

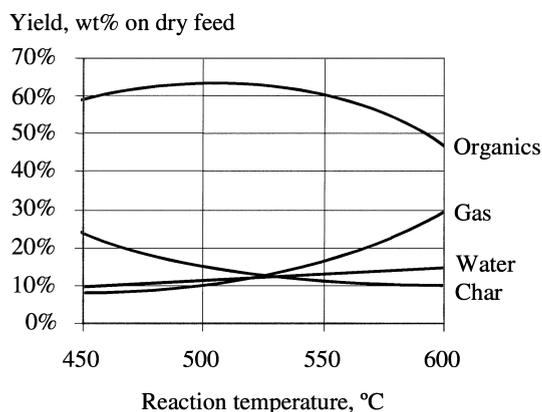


Fig. 1. Typical yields of organic liquid, reaction water, gas and char from fast pyrolysis of wood, wt% on dry feed basis.

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 500°C in the vapour phase, with 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 a miscible mixture of polar organics (about 75–80 wt%) and water (about 20–25 wt%). It is obtained in yields of up to 80 wt% in total (wet basis) on dry feed, together with by-product char and gas which are, or can be, used within the process so there are no waste streams.

Liquids for use as fuels can be produced with longer vapour residence times (up to around 5 s) and over a wider temperature range although yields might be affected in two ways: secondary volatiles decomposition at temperatures above 500°C and condensation reactions at gas/vapour product temperatures below 400°C. Most woods give maximum liquid yields of up to 80 wt% dry feed basis at 500–520°C with vapour residence times not more than 1 s. Very short residence times result in incomplete depolymerisation of the lignin due to random bond cleavage and inter-reaction of the lignin macromolecule resulting in a less homogenous liquid product, while longer residence times can cause secondary cracking of the primary products, reducing yield and adversely affecting bio-oil properties. Evidence from SEC (selective exclusion chromatography) analysis of the liquids would suggest that the reactor configuration and the dominant mode of heat transfer strongly influences the average molecular weight of the products (McKinley, 1989). This is discussed further below.

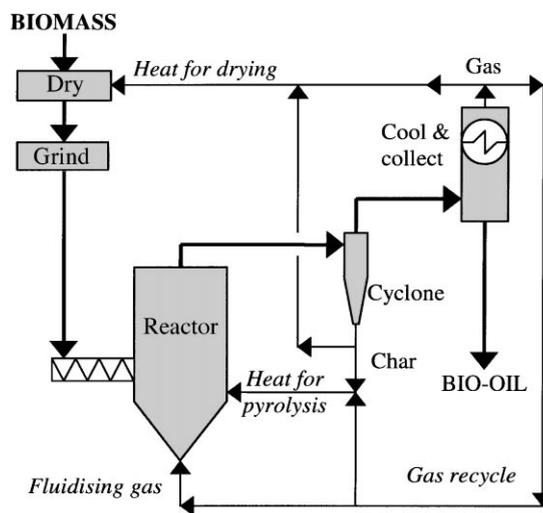


Fig. 2. Conceptual fluid bed fast pyrolysis process.

While a wide range of reactor configurations have been operated (Bridgwater, 1999), 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 Fig. 2 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 2 mm to give sufficiently small particles to ensure rapid reaction. This configuration is used below for processing waste wood.

Several reviews of processes that are advanced technically and/or commercially available have been published (Bridgwater and Evans, 1993; Whiting, 1997). A brief review of European activities (Bridgwater, 1998) and a comprehensive review of most of the current fast pyrolysis processes has recently been published (Bridgwater and Peacocke, 1999). Fast pyrolysis of biomass for liquids began in North America around 1980 and has seen significant RD&D effort since then with two commercial organisations offering plants with a performance guarantee and several demonstration and pilot scale processes.

3. Process characteristics and technology requirements

Although fast pyrolysis of biomass has achieved commercial status, there are still many aspects of the process which are largely empirical and require further study to improve reliability, performance, product consistency, product characteristics and scale-up. This section summarises these topics.

3.1. Reactor configuration

A variety of reactor configurations have been investigated as listed in Table 1. Pyrolysis, perhaps more than any other conversion technology, has received considerable creativity and innovation in devising reactor systems that provide the essential ingredients of high heating rates, moderate temperatures and short vapour product residence times for liquids. A thorough review of the technologies has recently been completed (Bridgwater and Peacocke, 1999). There are three main methods of achieving fast pyrolysis.

1. *Ablative pyrolysis* in which wood is pressed against a heated surface and rapidly moved during which the wood melts at the heated surface and leaves an oil film behind which evaporates. This process uses larger particles of wood and is typically limited by the rate of heat supply to the reactor. It leads to compact and intensive reactors that do not need a carrier gas, but with the penalty of a surface area controlled system and moving parts at high temperature.
2. *Fluid bed* and *circulating fluid bed pyrolysis* which transfers heat from a heat source to the biomass by a mixture of convection and conduction. The heat transfer limitation is within the particle, thus, requiring very small particles of typically not more than 3 mm to obtain good liquid yields. Substantial carrier gas is needed for fluidisation or transport.
3. *Vacuum pyrolysis* which has slow heating rates but removes pyrolysis products as rapidly as in the pre-

Table 1
Fast pyrolysis reactors and heating methods

Reactor type	Method of heating
Ablative coil	Reactor wall heating
Ablative mill	Reactor wall (disc) heating
Ablative plate	Reactor wall heating
Ablative vortex	Reactor wall heating
Circulating fluid bed	In-bed gasification of char to heat sand
Cyclone or vortex	Reactor wall heating
Entrained flow	Char combustion products Hot sand
Fluid bed	Heated recycle gas Hot inert gas Partial gasification Fire tubes
Horizontal bed	Fire tubes
Vacuum multiple hearth	Hearth heating
Rotating cone	Wall and sand heating
Stirred bed	Partial gasification of char
Transported bed	Recirculated hot sand heated by char combustion
Vacuum moving bed	Direct contact with hot surface

vious methods which thus simulates fast pyrolysis. Larger particles are needed and the vacuum leads to larger equipment and higher costs. Total liquid yields are typically lower at up to 60–65% compared to 75–80 wt% from the previous two methods.

It is important to remember that pyrolysis always gives three products — gas, liquid and solid — of which the liquid is a homogenous hydrophilic (oleophobic) mixture of polar organics and water from both the pyrolysis reaction and the original water in the feedstock. A sound understanding of the inherent processes will allow any of these products to be maximised and it is the engineer's challenge to optimise the process by maximising product quantity and quality while paying proper attention to minimising costs and environmental concerns.

3.2. Heat transfer

There are two important requirements for heat transfer in a pyrolysis reactor:

1. to the reactor heat transfer medium (solid reactor wall in ablative reactors, gas and solid in fluid and transport bed reactors, gas in entrained flow reactors);
2. from the heat transfer medium to the pyrolysing biomass.

Two main ways of heating biomass particles in a fast pyrolysis system can be considered: gas–solid heat transfer as in an entrained flow reactor where heat is transferred from the hot gas to the pyrolysing biomass particle by primarily convection [for example the Ege-min (Maniatis et al., 1994), or GTRI (Kovac and O'Neil, 1989) processes], and solid–solid heat transfer with mostly conductive heat transfer as in ablative pyrolysis such as NREL (Diebold and Scahill, 1987) and Aston (Peacocke and Bridgwater, 1994). Fluid bed pyrolysis utilises the inherently good solids mixing to transfer approximately 90% of the heat to the biomass by solid–solid heat transfer with a probable small contribution from gas–solid convective heat transfer of up to 10%. Circulating fluid bed [e.g. CRES (Boukis et al., 1993)] and transport reactors [e.g. Ensyn (Graham, 1991)] also rely on both gas–solid convective heat transfer from the fluidising gas and solid–solid heat transfer from the hot fluidising solid although the latter may be less significant than fluid beds due to the lower solids bulk density. Some radiation effects occur in all reactors.

The important feature of ablative heat transfer is that the contact of the biomass and the hot solid abrades the product char off the particle exposing fresh biomass for reaction. This removes particle size limitations in certain ablative reactors (e.g. the NREL vortex reactor), but at the expense of producing microcarbon which is difficult to remove from the vapour phase and reports to the

liquid product. Attrition of the char from the pyrolysing particle can also occur in both fluid and circulating fluid beds, due to contact of the biomass with in-bed solids where solids mixing occurs. In fluid bed reactors, however, attrition of the product char is relatively low and it has been observed that the char particles have the original particle shape, but are slightly reduced in size by char layer shrinkage and attrition.

Char removal is an essential requirement for large particles (>2 mm) to avoid slow pyrolysis reactions. The low thermal conductivity of biomass gives low heating rates through larger particles which leads to increased char formation and hot char is known to be catalytically active. It cracks organic vapours to secondary char, water and gas both during primary vapour formation and in the reactor gas environment. Therefore, its rapid removal from the hot reactor environment and minimal contact with the pyrolysis vapour products is essential.

Since the thermal conductivity of biomass is very poor (0.1 W/mK along the grain, ca 0.05 W/mK cross grain), reliance on gas–solid heat transfer means that biomass particles have to be very small to fulfil the requirements of rapid heating to achieve high liquid yields. Claimed temperature increases of 10,000°C/s may be achieved at the thin reaction layer but the low thermal conductivity of wood will prevent such temperature gradients throughout the whole particle. As particle size increases, liquid yields reduce as secondary reactions within the particle become increasingly significant (Scott and Piskorz, 1984).

A consistent method of expressing product yields is required to remove ambiguities in the comparison of product yields. It is recommended that the water in the feed should be discounted in the final pyrolysis products with only the water of pyrolysis being quoted and the product yields expressed on a dry feed basis. As a rule of thumb, the water of pyrolysis is typically 12 wt% of dry feed.

3.3. Heat supply

The high heat transfer rate that is necessary to heat the particles sufficiently quickly imposes a major design requirement on achieving the high heat fluxes required to match the high heating rates and endothermic pyrolysis reactions. Reed et al. (1990) originally suggested that to achieve true fast pyrolysis conditions, heat fluxes of 50 W/cm² would be required, but to achieve this in a commercial process is not practicable or necessary.

Each mode of heat transfer imposes certain limitations on the reactor operation and may increase its complexity. The two dominant modes of heat transfer in fast pyrolysis technologies are conductive and convective. Each one can be maximised or a contribution can be made from both depending on the reactor configuration. The

penalties and interactions are summarised in Table 2 below with some speculations on heat transfer modes.

For ablative pyrolysis in a vortex reactor, a furnace arrangement equivalent to an ethylene cracking furnace has been proposed by the IEA Bioenergy Agreement pyrolysis and liquefaction group (Diebold et al. 1994a and b). Other possibilities to achieve the pyrolysis temperatures and heat transfer rates necessary have included vapour condensation such as sodium, induction heating of the reactor wall and the use of contact electrical heaters. In a circulating fluid bed, the majority of the heat transfer will be from the hot circulating sand, typically at a sand to biomass ratio of 20 (Ensyn, 1998), which therefore requires an efficient sand re-heating system. In a conventional fluid bed the sand requires an external heat source which would typically come from char in an integrated system.

3.4. Feed preparation

The heat transfer rate requirements described above impose particle size limitations on the feed for some reactors. The cost of size reduction in financial and energy terms is clear qualitatively but data is not available to define such a penalty associated with the small particle sizes demanded of fluid bed and circulating fluid bed systems. Reactor performance as for example liquid yields is, therefore, not an adequate criterion by itself.

Drying is usually required to less than 10 wt% water unless a naturally dry material such as straw is available. As moisture is generated in flash pyrolysis, bio-oil always contains at least about 15% water at an assumed product yield of around 60 wt% organics and 11 wt% reaction water. This water cannot be removed by conventional methods such as distillation. The effect of water is complex in that it affects stability, viscosity, pH, corrosiveness, and other liquid properties. Selective condensation may reduce the water content of one or more fractions but at the expense of operating problems and a possible loss of low molecular weight volatile components.

3.5. Temperature of reaction

It is necessary to distinguish between temperature of reaction and reactor temperature. The latter is much higher due to the need for a temperature gradient to effect heat transfer. For fast pyrolysis the lower limit on wood decomposition is approximately 435°C for obtaining acceptable liquid yields of at least 50% with low reaction times.

The effect of temperature is well understood in terms of total product yield with a maximum at typically 500–520°C for most forms of woody biomass. Other crops may have maxima at different temperatures. The effect of temperature is less well understood in terms of product fuel quality. Work by the University of Waterloo

Table 2
Reactor types and heat transfer

Reactor type	Suggested mode of heat transfer	Advantages/disadvantages/features
Ablative	95% Conduction 4% Convection 1% Radiation	Accepts large size feedstocks Very high mechanical char abrasion from biomass Compact design Heat supply problematical Heat transfer gas not required Particulate transport gas not always required
Circulating fluid bed	80% Conduction 19% Convection 1% Radiation	High heat transfer rates High char abrasion from biomass and char erosion leading to high char in product Char/solid heat carrier separation required Solids recycle required; Increased complexity of system Maximum particle sizes up to 6 mm Possible liquids cracking by hot solids Possible catalytic activity from hot char Greater reactor wear possible
Fluid bed	90% Conduction 9% Convection 1% Radiation	High heat transfer rates Heat supply to fluidising gas or to bed directly Limited char abrasion Very good solids mixing Particle size limit < 2 mm in smallest dimension Simple reactor configuration
Entrained flow	4% Conduction 95% Convection 1% Radiation	Low heat transfer rates Particle size limit < 2 mm Limited gas/solid mixing

has demonstrated the effects of ash, DP (degree of polymerisation), heating rate and reactor temperature on chemical yields (Piskorz et al., 1988). As progress is made in defining bio-oil quality better in fuel terms, the secondary gas/vapour phase history may be more important. At prolonged residence times (>1 s), the lignin derived fraction may be further depolymerised to produce a more homogeneous liquids. This is also influenced by the reactor configuration. Work by McKinley (1989) has demonstrated that liquid produced in an ablative pyrolysis reactor has a much lower molecular weight average due to depolymerisation and cracking of the liquids on the metal surface prior to vapourisation.

3.6. Vapour residence time

The effect of vapour residence time on organic liquid yield is relatively well understood although the interaction of temperature and residence time is less understood. Studies by, for example, Diebold and Scahill (1987), Liden et al. (1988) and Gorton and Knight (1984) have attempted to interlink both primary liquids formation and secondary cracking, but one essential component which is neglected is the variation of water yield with temperature and residence time. There is extensive literature on the mechanisms and pathways of fast pyrolysis which has been reviewed (Peacocke 1994). It is believed that at temperatures below 400°C, secondary condensation reactions occur and the average molecular weight of the liquid product decreases. Boroson et al. (1989) have demonstrated that the average molecular weight decreases with the degree of secondary reaction, i.e. increasing residence time and temperature.

For chemicals, it is considered necessary to “freeze” the process at the appropriate time-temperature point in the envelope to maximise yield. In one case this has led to a commercial reactor design where vapour residence times down to 30 ms are claimed (Enersearch, 1992). Fuels have less specific process requirements and most work has focused on maximising liquid yield rather than product quality. The window for fuel production requires more R and D to better understand the processes and match the product quality requirement to process parameters. There is no definition of product quality in terms of physical or chemical properties or composition, and this area will need to be addressed as more applications are tested and alternative supplies of bio-fuel-oil become available.

3.7. Secondary vapour cracking

Long vapour residence times and high temperatures (>500°C) cause secondary cracking of primary products reducing yields of specific products and organic liquids. Lower temperatures (<400°C) lead to condensation

reactions and the subsequent formation of lower molecular weight liquids which can also react.

3.8. Liquids collection

This has long been a major difficulty for researchers. The pyrolysis vapours have similar properties to cigarette smoke and capture by almost all collection devices is very inefficient. The product vapours are not true vapours but rather a mist or fume and are typically present in an inert gas at relatively low concentrations which increases cooling and condensation problems. They can be characterised as a combination of true vapours, micron sized droplets and polar molecules bonded with water vapour molecules. This contributes to the collection problem as the aerosols need to be impinged onto a surface to permit collection, even after cooling to below the dew point temperature.

Electrostatic precipitators are effective and are now used by many researchers but can create problems from the polar nature of the product and arcing of the liquids as they flow, causing the electrostatic precipitator to short out. Larger scale processing usually employs some type of quenching or contact with cooled liquid product which is effective. Careful design is needed to avoid blockage from differential condensation of heavy ends. The rate of cooling appears to be important. Slow cooling leads to preferential collection of the lignin derived components which is a viscous liquid which can lead to blockage of heat exchange equipment and liquid fractionation. Very rapid cooling of the product has been suggested to be effective as occurs typically in a direct contact quench. Transfer lines from the reactor through the cyclone(s) to the liquid collection system should be maintained at >400°C to minimise liquid deposition and collection.

At present, there are no recognised design methods and most work has been empirical and specific to the characteristics of the feedstock being processed. Commercial liquids recovery processes are usually proprietary and may be specific to individual feedstocks, reactor configurations and products.

3.9. Char separation

Some char is inevitably carried over from cyclones and collects in the liquid. Subsequent separation has proved difficult. Some success has been achieved with hot gas filtration in a ceramic cloth bag house filter (Diebold et al., 1993) and also candle filters for short run durations. Liquid filtration has also proved difficult as the liquid can have a gel-like consistency, apparently due to some interaction of the lignin-derived fraction with the char.

This aspect of char reduction and/or removal will be increasingly important as more demanding applications are introduced which require lower char tolerances in terms of particle size and total quantity. Possible solutions

include changing process conditions to reduce the nature of the pyrolytic lignin, increasing the degree of depolymerisation of the lignin-derived fraction of the liquid, changing the feedstock to one with a lower lignin content, or adding chemicals to the liquid for example to improve handling properties or reduce char–lignin interactions.

It must not be forgotten that an alternative solution is to modify the application to accept a high char content bio-fuel-oil.

3.10. Ash separation

The alkali metals from biomass ash are present in the char in relatively high concentrations and cannot be readily separated except by hot gas filtration which is undergoing development as reported variously in these proceedings.

4. Product characteristics

4.1. Product quality

The elemental and chemical composition of pyrolysis oils is very much dependent on the pyrolysis conditions under which they are produced. Maximum yields are obtained at temperatures in the range 450–550°C and residence times of 0.5–5 s depending on the particular process; these being typical conditions of fast pyrolysis. In this case the oil is highly oxygenated, indeed being not very different in composition from the feedstock (see Table 3).

Table 3
Typical elemental and water content of fast pyrolysis bio-oils

Component	Wt%
Water	20–30
Carbon	44–47
Hydrogen	6–7
Oxygen	46–48
Nitrogen	0–0.2

Typical characteristics of fast pyrolysis liquid are given in Table 4. They can vary considerably according to the feed material and its characteristics, the pyrolysis process parameters and the liquid collection parameters of which temperature of liquid collection system and method of collection are particularly important.

The high oxygen content is indicative of the presence of many highly polar groups leading to high viscosities and boiling points as well as relatively poor chemical stability. As the table shows a significant fraction of the oxygen is present as water. Indeed the description of pyrolysis liquids as “oils” is somewhat misleading as they have low lubricity (Oasmaa, 1997). On account of their high oxygen content and hydrophilic character it is not surprising that fast pyrolysis oils are mostly insoluble in hydrocarbon solvents.

Liquid yields decrease at high temperatures and/or long residence times. The liquid also becomes increasingly deoxygenated and at very high temperatures even polynuclear aromatic hydrocarbons may form. Fig. 3 shows a widely accepted simplified model of the principal pyrolysis pathways. A medium heating value gas is the predominant product at high temperatures and high heating rates. The medium (450–550°C) temperature

Table 4
Fast pyrolysis liquid characteristics — typical data

Moisture content	25%
pH	2.5
Specific gravity	1.20
Elemental analysis (moisture free basis)	
C	56.4%
H	6.2%
N	0.2%
S	<0.01%
Ash	0.1%
O (by difference)	37.1%
Higher heating value, HHV (moisture free basis)	22.5 MJ/kg
Higher heating value, HHV as produced (depends on moisture)	17.0 MJ/kg
Viscosity (at 40°C)	30–200 cp.
Pour point	–23°C

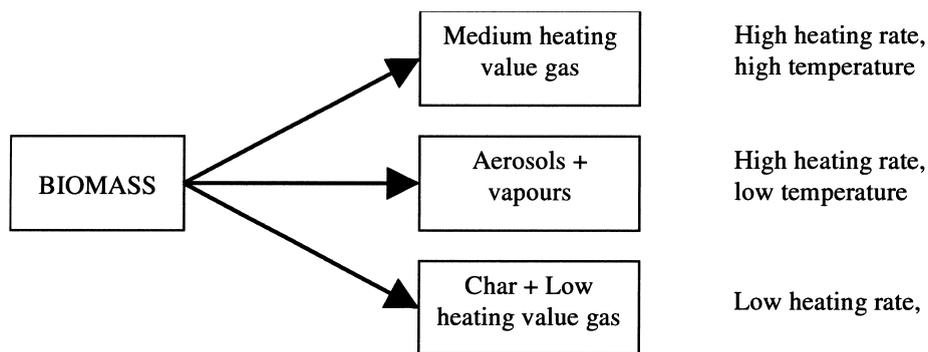


Fig. 3. Biomass pyrolysis pathways.

regime but with high heating rates is characteristic of fast pyrolysis and gives mainly condensable vapours and aerosols. Low temperature, slow pyrolysis gives mostly char. The yields and chemical character of the liquid product in the various pyrolysis regimes is summarised qualitatively in Fig. 4.

Anaerobic biomass degradation over geologic time scales is thought to produce mainly peat, lignite and coal. This is entirely consistent with the model presented here as such processes are characterised by low temperatures and very long “residence times”; conditions which minimise liquid and maximise solid products. On the other hand petroleum is thought to be derived mostly from marine organisms. Therefore there is expected to be very little relationship between petroleum and pyrolysis oils, especially those from fast pyrolysis. Hydrothermal processes for the conversion of ligno-cellulosic biomass to liquids of low oxygen content are

known, for example the PERC (Joyner et al., 1993) and the HTU (Goudriaan and Peferoen, 1990) processes. There is probably a closer relationship of those processes to petroleum and bitumen generation. By contrast, under fast pyrolysis conditions secondary reactions are minimised, many functional groups are preserved and only small changes in the overall oxygen content occur. Indeed, it is possible to identify most individual chemical components as originating from either the lignin or cellulosic components of the biomass feedstock.

The complex interaction of pyrolysis time and temperature on liquid product quality has not been explored, at least partly because the characteristics of pyrolysis oil for different applications have not been defined and there is no “standard” pyrolysis liquid. It is this definition of oil quality that is a major uncertainty and requires to be defined by potential users and may differ by application. While there are set standards and

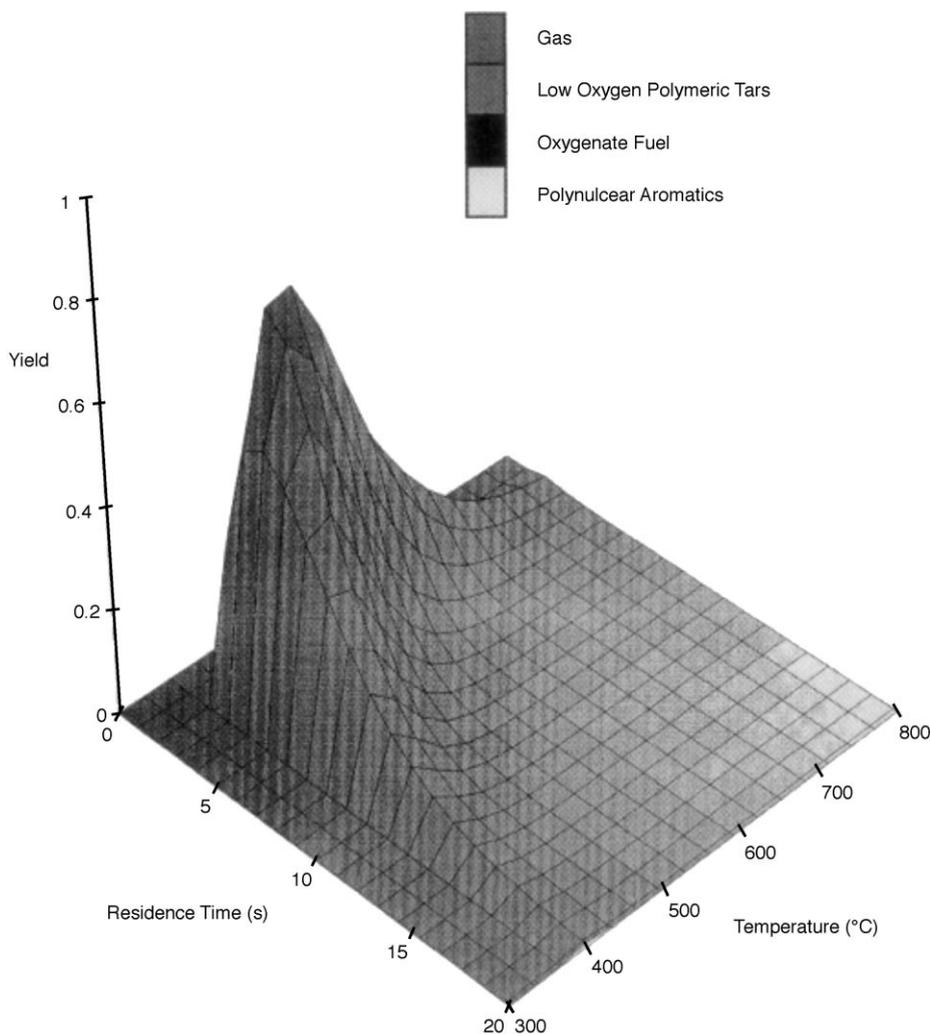


Fig. 4. Qualitative illustration of the yields and character of pyrolysis oils as a function of pyrolysis conditions.

methods of measurement for conventional fuels, analogous standards and methods have not yet been defined for biomass pyrolysis liquids. Density, viscosity, surface tension and heating value are known to be typical key properties for combustion applications in boilers, furnaces and engines; but other characteristics such as char level and particle size and ash content may have a major effect.

4.2. Unusual characteristics of bio-oil

The special features and characteristics of bio-oil require consideration in any application including pro-

duction, storage, transport, upgrading and utilisation. These are summarised in Table 5 below. The conclusion is that some problems are soluble and some are more intractable but none are insoluble. Recognition of problems and awareness of potential difficulties is a major contribution to dealing with any of the above difficulties.

5. Applications

A summary of the opportunities is shown in Fig. 5. Within Europe the most promising application is seen as

Table 5
Characteristics of bio-oil and methods for modification

Characteristic	Effect	Solution
Suspended char	Erosion Equipment blockage Combustion problems from slower rates of combustion “Sparklers” can occur in combustion leading to potential deposits and high CO emissions	Hot vapour filtration Liquid filtration Modification of the char for example by size reduction so that its effect is reduced Modification of the application
Alkali metals	Deposition of solids in combustion applications including boilers, engines and turbines In turbines the damage potential is considerable particularly in high performance machines with, for example, coated blades	Hot vapour filtration Processing or upgrading of oil Modification of application Pretreat feedstock to remove ash
Low pH	Corrosion of vessels and pipework	Careful materials selection Stainless steel and some olefin polymers are acceptable
Incompatibility with polymers	Swelling or destruction of sealing rings and gaskets	Careful materials selection
High temperature sensitivity	Liquid decomposition on hot surfaces leading to decomposition and blockage Adhesion of droplets on surfaces below 400°C	Recognition of problem and appropriate cooling facilities Avoidance of contact with hot surfaces above 500°C
High viscosity	High pressure drops in pipelines leading to higher cost equipment and/or possibilities of leakage or even pipe rupture	Careful low temperature heating, and/or addition of water, and/or addition of co-solvents such as methanol or ethanol
Water content	Complex effect on viscosity, heating value, density, stability, pH, homogeneity etc.	Recognition of problem Optimisation with respect to application
In-homogeneity	Layering or partial separation of phases Filtration problems	Modify or change process Modify pyrolysis parameters Change feedstock to low lignin Additives Control water content

electricity production due to the anticipated ability to use raw bio-oil as produced in an engine or turbine without the need for extensive upgrading as well as the ability to de-couple fuel production from electricity generation with storage and/or transport of the liquid fuel which is not possible for gasifier products and IGCC (Integrated Gasifier Combined Cycle) systems. The much higher added value of chemicals is, however, increasingly seem as the most interesting short term commercial opportunity.

5.1. Combustion

Liquid products are easier to handle and transport than solids and gases and this is important in combustion applications and retrofitting existing equipment. Existing oil fired burners cannot be fuelled directly with solid biomass without major reconstruction of the unit, which may not be attractive in uncertain fuel markets, however bio-oils are likely to require only relatively minor modifications of the equipment or even none in some cases. The problems that have been predicted in handling the fuel with high viscosity and suspended char have not been found to as severe or serious as first thought and many organisations are proceeding with successful developments.

5.2. Power generation with liquids

A key advantage of production of liquids is that fuel production can be de-coupled from power generation. Peak power provision is thus possible with a much smaller pyrolysis plant, or liquids can be readily transported to a central power plant using engines or turbine. There are additional benefits from potentially higher plant availability from the intermediate fuel storage. The economics of power generation suggest that a niche of up to 10 MWe is available for exploitation.

Bio-oil has been successfully fired in a diesel test engine, where it behaves very similar to diesel in terms

of engine parameters and emissions. Over 400 h operation have been achieved (Leech, 1997). A diesel pilot fuel is needed, typically 5% in larger engines, and no significant problems are foreseen in power generation up to 15 MWe per engine. A 2.5 MWe gas turbine has also been successfully tested although for not many hours operation to date (Andrews et al., 1994).

5.3. Chemicals

Several hundred chemical constituents have been identified to date, and increasing attention is being paid to recovery of individual compounds or families of chemicals. The potentially much higher value of speciality chemicals compared to fuels could make recovery of even small concentrations viable. An integrated approach to chemicals and fuels production offers interesting possibilities for shorter term economic implementation (Radlein, 1998).

Chemicals that have been reported as recovered include polyphenols for resins with formaldehyde, calcium and/or magnesium acetate for biodegradable de-icers, fertilisers, levoglucosan, hydroxyacetaldehyde, and a range of flavourings and essences for the food industry. There are substantial problems to be overcome in establishing markets for the less common chemicals and devising low cost and efficient separation and refining techniques. The only currently viable market opportunity is for speciality food flavourings.

6. Fast pyrolysis of contaminated wood

As an example of the application of fast pyrolysis, some work on fluid bed fast pyrolysis of wastewood is included to show how fast pyrolysis can be applied to both derive a useful liquid fuel product and also fix the contaminants in the residual char. This work was carried out at the Institute of Wood Chemistry in Hamburg, Germany.

6.1. Wood waste

Wood waste creates an increasing problem in Germany. It is estimated that 6–8 million tonnes of waste wood arise every year. More restrictive environmental laws will not allow landfill in the near term and therefore the application of new technologies is under investigation. On the other hand, an increasing market for waste wood already exists. Actual prices for different types of waste wood are listed in Table 6.

6.2. Fast pyrolysis results

Fast pyrolysis of waste wood has been studied in a small pilot plant with a capacity of 5 kg/h. A schematic diagram is presented in Fig. 6.

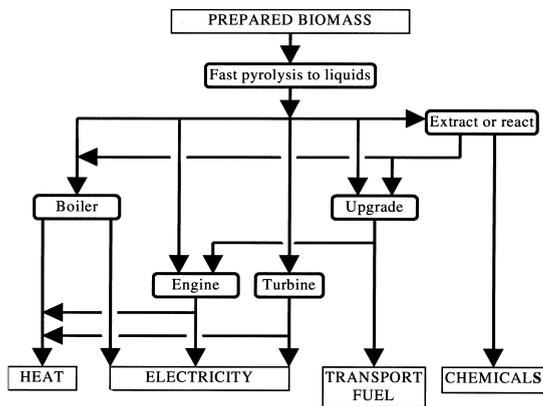


Fig. 5. Applications of pyrolysis liquids.

Typical yields of the main products liquid, gas, and char from untreated wood are depicted in Fig. 7. Oil yields reach almost 70% (wet basis) at 475°C reactor temperature. With increasing temperature the gas yields increase and the char yields decrease correspondingly. Therefore, all subsequent experiments with waste wood were done at a temperature of 475°C. Wood was impregnated with inorganic preservatives containing chromium, copper, and boron salts (CCB). This type of preservative is amongst creosote the most commonly used in Germany. After fast pyrolysis, the metal contents were measured in the oil and char fraction.

The results are presented in Table 7. It is clear that the heavy metals are collected with the char and that the liquid contains only traces of metals. Real samples from a collection site were also pyrolysed and the results are presented in Table 7. The real samples show the same behaviour as those prepared in the laboratory.

Other preservatives which are widely used are complexes of alumina and copper (see Fig. 8). The fast

pyrolysis of wood impregnated with these complexes gave similar results: alumina and copper are predominantly found in the char fraction. The oil contains only traces of these compounds.

6.3. Conclusions

From the results it can be concluded that fast pyrolysis of waste wood seems to be a viable route for disposal of contaminated wood waste. Inorganic contaminants are almost completely recovered in the char fraction. The oil can be used for energy production or as a source for chemical feedstocks. Further investigation with chlorinated compounds are ongoing and results will be presented later.

7. Biodegradability and fertilizers

7.1. Introduction

Issues of bio-oil toxicity to humans are relevant to its handling and distribution. However toxicity to microorganisms in particular is relevant to its biodegradation in the environment. Some results from respirometric biodegradation studies are discussed. They lead to the novel suggestion that bio-oil based fertilisers could play a role in carbon sequestration in soils for the abatement of greenhouse gas emissions.

There have been several studies of toxicological effects of biomass-derived fast pyrolysis bio-oil but they have been mostly in regard to the potential hazards associated with human contact. For example, Gratson

Table 6

Average disposal costs for wood wastes in Germany

Material	Cost, euros
Untreated wood	47
Fruit boxes	35
Used furniture	86
Mixed woods	85
Painted wood	96
Demolition wood	68
Impregnated wood	237
Windows with glass	146

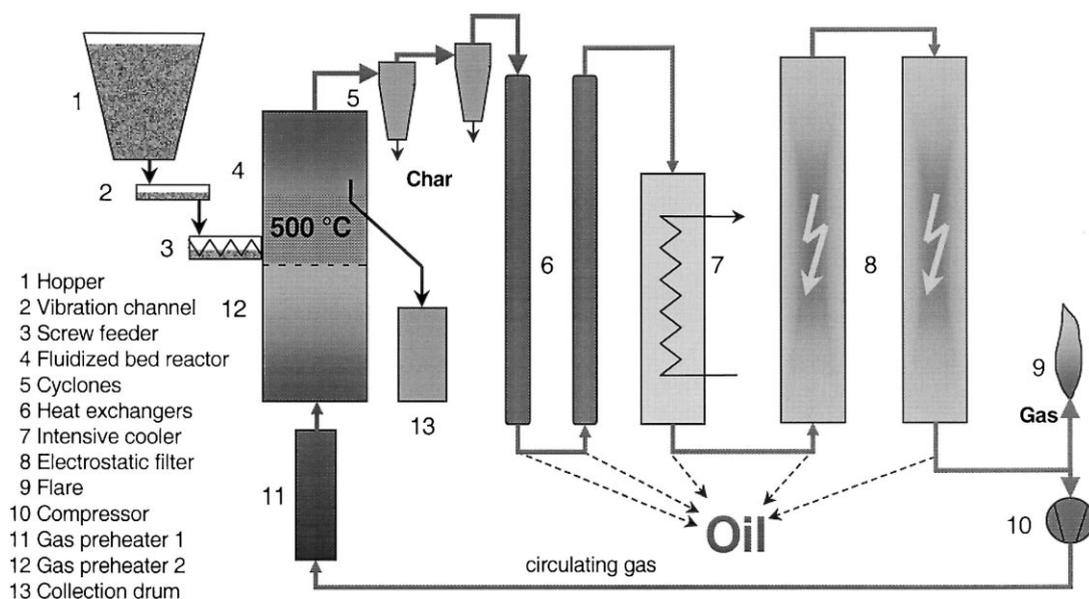


Fig. 6. Schematic diagram of pilot plant for fast pyrolysis of waste wood.

(1994) has discussed dermal toxicity, eye irritation, inhalation toxicity and Ames mutagenicity and a review of bio-oil toxicity has been carried out by Diebold (1999). On the other hand much less is known about its fate in the environment and, in particular, the response of micro-organisms to it. This is important if bio-oil should emerge as a commodity as that would imply the shipment of large quantities with the accompanying hazard of spills. Some of the results from the first respirometric study dealing with this issue are discussed below.

Table 7
Recovery of Cu and Cr from a variety of wood wastes in pilot plant experiments

	Cr (ppm)		Cu (ppm)	
	Char	Oil	Char	Oil
CCB	31561	4	22560	12
CCB + organic preservative	19768	3	8257	16
Cable drums	14103	13	6921	5
Fences	4748	2	1628	7
Railway sleepers	267	2	932	9
Particle boards	527	2	270	9
Window frames	465	2	681	7

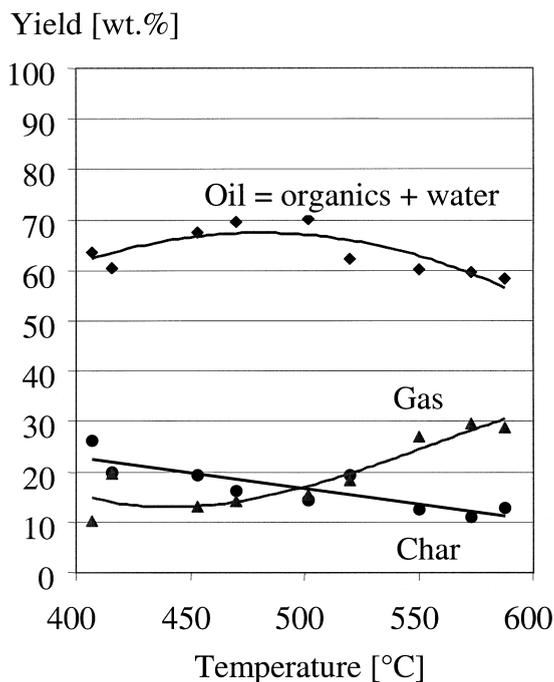


Fig. 7. Typical yields of fast pyrolysis experiments with pilot plant, wt% on dry feed basis.

7.2. Fertilisers

A related aspect to this environmental concern is the proposal that bio-oils can be readily converted to nitrogen slow-release fertilisers by reaction with nitrogen sources like ammonia, urea and proteinaceous materials like manure (Radlein et al., 1997). The favourable results obtained imply that, at least in this modified form, bio-oil is not a hazard to soil micro-organisms. This may prove to be an important observation in the context of another topical environmental issue, namely the mitigation of atmospheric carbon dioxide emissions, since such fertilisers could conceivably have a role to play in the sequestration of carbon in the soil. A preliminary assessment of the potential scope of this proposal will be made.

7.3. Biodegradability and respirometry

Recently Piskorz and Radlein (1998) have reported the results of some respirometric biodegradation studies of bio-oil in both aquatic and soil environments. This is believed to be the first application of this technique to bio-oil. Some of the results from this study and the type of information that can be obtained are illustrated below.

Fig. 9 displays the results from a respirometric test in which various quantities of raw Poplar derived bio-oil (RTI Ltd.) were diluted in 500 ml of water and inoculated with 5 ml of Returned Activated Sludge (RAS) from a local wastewater treatment plant. Nutrient deficiency of the oil was compensated by the addition of KNO_3 and Na_2HPO_4 in amounts proportional to the dissolved organic carbon (DOC) in each sample so as to maintain a C:N:P ratio of 30:5:1. The progress of biodegradation was measured by the uptake of O_2 over a period of time.

The general pattern is a fast initial oxygen uptake followed by a long period of negligible biological activity and a final period of fast oxygen uptake suggesting that bio-oil contains a mixture of both readily and slowly biodegradable substances.

Fig. 10 illustrates the effect on the respirometric behaviour of neutralizing the bio-oil with lime ($\text{Ca}(\text{OH})_2$) to

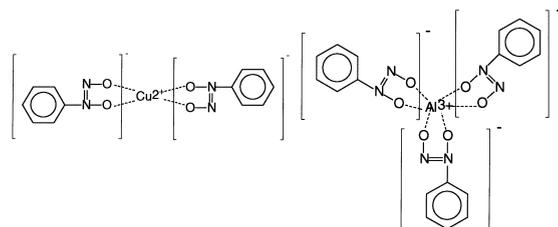


Fig. 8. Copper-HDO and alumina-HDO as an example for wood preservatives.

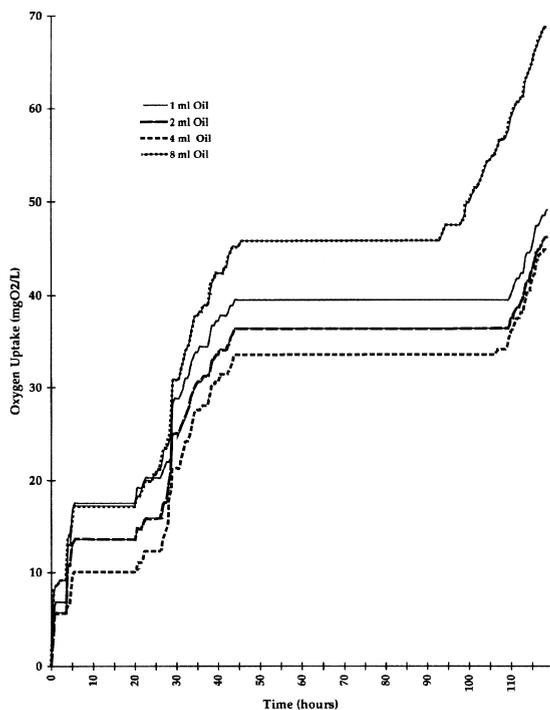


Fig. 9. Respirometric plots of un-neutralized poplar bio-oil and RAS in water (Piskorz and Radlein, 1998).

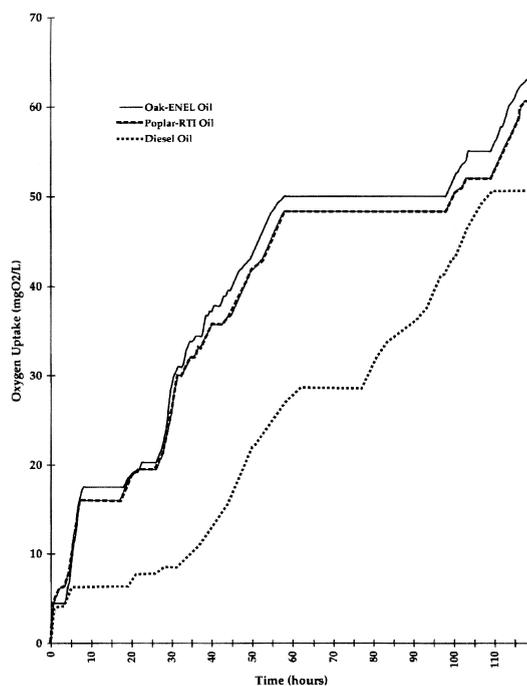


Fig. 11. Respirometric plots of various neutralized bio-oils and diesel with RAS in water (Piskorz and Radlein, 1998).

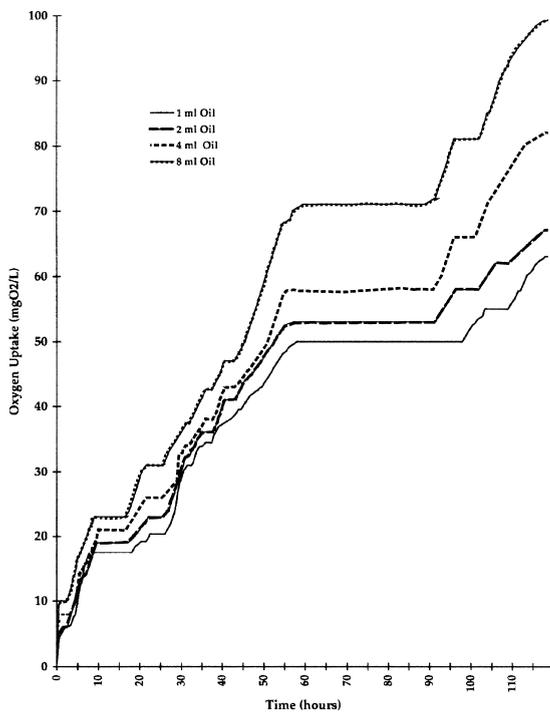


Fig. 10. Respirometric plots of neutralized poplar bio-oil and RAS in water (Piskorz and Radlein, 1998).

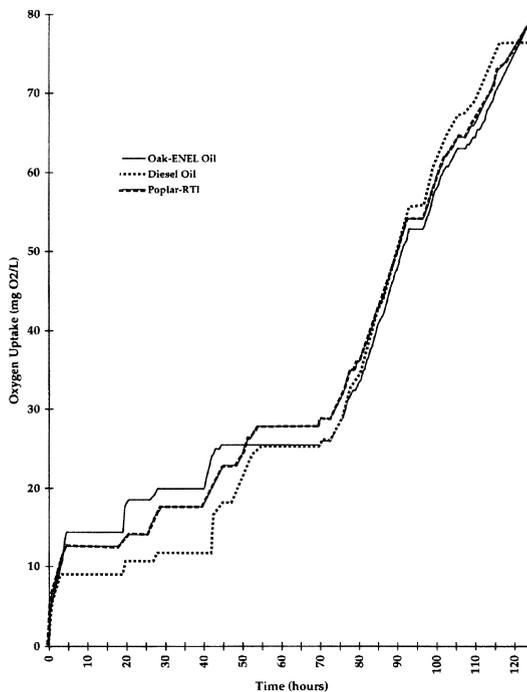


Fig. 12. Respirometric plots of various un-neutralized bio-oils and diesel with RAS in soil (Piskorz and Radlein, 1998).

Table 8
Estimation of bio-kinetic parameters

Sample	Medium	Specific rate of bio-degradation (fraction/day)
<i>Poplar bio-oil (RTI)</i>		
Neutralized	Water	0.18
Raw	Water	0.122
Raw	Soil	0.188
<i>Diesel oil (Shell)</i>		
	Water	0.072
	Soil	0.071

pH \sim 7 with the other parameters remaining the same. A clear enhancement of the biodegradation rates is apparent together with a decrease in the length of the period of inactivity.

Fig. 11 is a comparison of 1 ml of each of two different neutralized bio-oils, RTI poplar derived and ENEL oak derived bio-oils, and a petroleum derived diesel fuel oil. The other parameters of the experiment were the same as before. This demonstrates that the bio-oils have substantially higher degradation rates than a typical hydrocarbon based fuel oil.

As a final illustration Fig. 12 shows the respirometric results when the same samples were tested in soil without either neutralisation, inoculation or nutrient addition in order to simulate natural environmental conditions. In this case 3 ml of each of the oils was added to 10 g of soil representing a substantial loading.

From measurement of the solids contents of the reactors it was possible to estimate specific biodegradation rates using the methodology of Rozich and Gaudy (1992) with the results summarised in Table 8. These show that bio-oil degrades approximately twice as fast as diesel oil.

To summarise, some of the important conclusions of the study were that:

- Respirometry is a suitable technique for assessment of the degradation behaviour of bio-oils in natural environments.
- Pyrolysis bio-oils biodegrade aerobically at a substantially higher rate than hydrocarbon fuels like diesel oil.
- pH neutralisation of bio-oil enhances its biodegradability

7.4. Summary

Bio-oil does not appear to be a significant environmental hazard even in raw form, thereby providing a margin of safety in the event of spills. Biodegradability is enhanced by neutralisation with bases like lime.

Neutralisation of bio-oil with nitrogenous bases like ammonia, urea or animal manure renders the nitrogen into a “slow-release” form useable as a fertiliser. Such materials represent not only a value-added product from bio-oil but can also play a role in carbon sequestration in soils. This is especially so if they are used in the context of “energy plantations”. Furthermore they can play a role in alleviation of the problem of nitrogen run-off which characterises the use of animal manure.

8. Conclusions

Fast pyrolysis is now accepted as a technology for producing high yields of liquid fuels that can be used in many applications as direct substitutes for conventional fuels or as a source of chemicals. There are some interesting challenges to be faced in developing and modifying fast pyrolysis technology, in upgrading the liquids and adapting applications to accept the unusual behaviour and characteristics of the liquid product. Higher added value products than fuels offer the most challenging and interesting opportunities including bulk chemicals such as fertilisers. Pyrolysis also offers potential for waste treatment by fixing contaminants in the char while also producing a clean liquid fuel.

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