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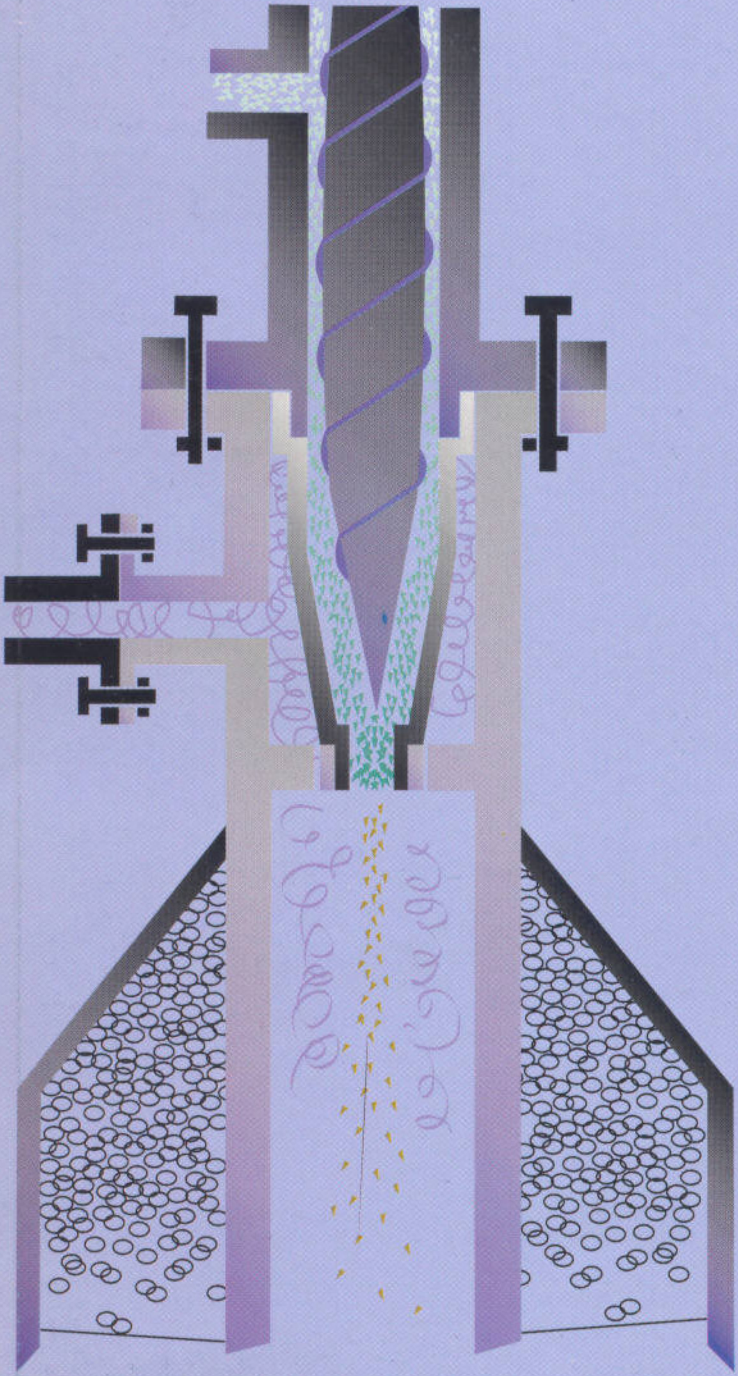

Thermal Biomass conversion and utilisation - Biomass Information System

Agro-Industrial Research Division

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European Commission

Thermal biomass conversion and utilization — Biomass information system

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CONTENTS

EXECUTIVE SUMMARY

A detailed review of the science and technology of fast pyrolysis and related processes has been carried out covering the basic scientific principles of fast pyrolysis for producing liquids; their application to working processes with identification of the main problems; a description of the more commercially and technically advanced of these processes; and opportunities for chemicals recovery and upgrading of vapours and liquids to more valuable chemicals and transport fuels. The contribution that has been made to the development of a Biomass Information System is described and copies of specimen data are included. Finally the conclusions summarise the current status and opportunities for each of the areas described.

CHAPTER 1
INTRODUCTION

1.1 INTRODUCTION

The potential offered by biomass and solid wastes for solving some of the world's energy and environmental problems is widely recognised. The energy in biomass may be realised either by direct use as in combustion to give heat, or by conversion and upgrading into a more valuable and usable fuel such as fuel gas or fuel oil or higher value products for the chemical industry. Liquid products have significant advantages in handling, storage, transport and substitution for conventional fuels and pyrolysis is being rapidly developed for direct production of both crude liquids for direct fuel oil substitution and production of hydrocarbons for more technically demanding applications and transport fuels. There is a further advantage in electricity generation of being able to de-couple fuel production from electricity generation through fuel storage which is not possible in gasification or combustion systems.

Biomass has received considerable attention as a renewable energy resource after the oil crises of the last 20 years. Pyrolysis in particular has been researched and developed for the economic production of fuel products that may be readily integrated into the energy infrastructures of both industrialised and developing countries. More recently, attention has focussed onto much higher value chemicals either as unique specialities or as substitutes for petroleum derived products.

1.2 THERMOCHEMICAL TECHNOLOGIES

There are four thermochemical methods of converting biomass: pyrolysis, gasification, liquefaction and direct combustion. Each gives a different range of products and employs different equipment configurations operating in different modes. These are summarised below in Table 1. 1.

The basis of a fuel or chemical production system is that the feedstock is converted to a useful primary energy product and either used as such, or further converted, upgraded or refined in subsequent processes to give a higher quality and higher value secondary product as shown in Figure 1.1.

When organic materials are heated in the absence of air, they degrade to a gas, a liquid, and a solid as summarised in Figure 1.1. It is possible to influence the proportions of the main products by controlling the main reaction parameters of temperature, rate of heating, and vapour residence time. For example fast or flash pyrolysis is used to maximise either the gas or liquid products, depending on temperature as summarised below:

- Slow pyrolysis at low temperatures of around 400°C and long reaction times (which can range from 15 minutes to days in traditional beehive kilns) maximises charcoal yields at about 30% wt.

Table 1.1 Thermochemical Conversion Technologies and Products

Technology	Primary Product	Typical yield, wt%	Application
Pyrolysis generally	gas	20-90 #	fuel gas
	liquid	5-80	fuel oil
	solid char	5-30	solid fuel or slurry fuel
Flash pyrolysis (low temp.)	liquid mostly	75	fuel oil
Flash pyrolysis (high temp.)	gas mostly	80	fuel gas & chemicals
Slow pyrolysis	solid char mostly	30	solid fuel or slurry fuel
Liquefaction	liquid	35	fuel oil
Gasification	gas	100 #	fuel gas & chemicals
Combustion	heat	-	heating

\# based on carbon conversion

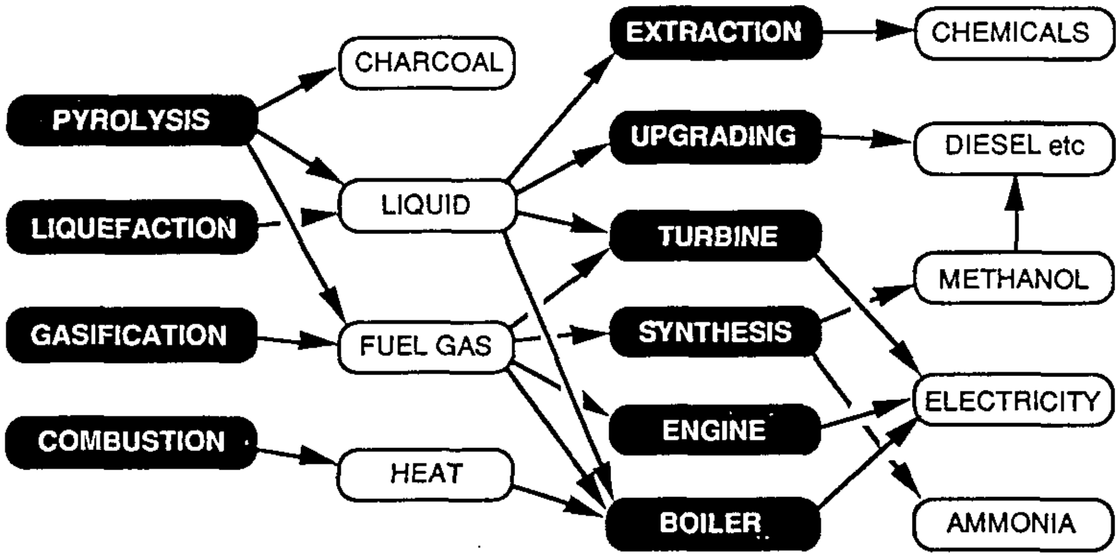

Figure 1 Products from Thermochemical Biomass Processing

- Flash pyrolysis at temperatures of typically 500°C; at very high heating rates and short vapour residence times of typically less than 1 second or 500 ms; maximises liquid yields at up to 85% wt (wet basis) or up to 70% dry basis.
- Similar flash pyrolysis at relatively high temperatures of above 700°C; at very high heating rates and similarly short residence times maximises gas yields at up to 80% wt. with minimum liquid and char production.

- "Conventional" pyrolysis at moderate temperatures of less than about 500°C and low heating rates (with vapour residence times of 0.5 to 5 minutes) gives approximately equal proportions of gas liquid and solid products.

This study is focussed on pyrolysis for the production of liquid fuels by the relatively novel process of fast pyrolysis, as these are currently viewed as a promising process and a promising product both in Europe and North America. The pyrolysis liquids are variously referred to as "bio-oil", "bio crude oil" or even as "oil" although they share few similarities with any oil products.

In order to appreciate the scientific and technical complexities of flash pyrolysis, the development of understanding of reaction mechanisms and pathways is first reviewed which will explain some of the unusual product properties that have been reported and some of the reasons for the way the technology has developed. Modeling of the complex and interactive physical and chemical processes that occur in pyrolysis has also attracted considerable attention and this area is also reviewed to at least partly explain why technology and scale up is still largely empirical. Developments of some of the process technologies that have been promoted and scaled up are subsequently described to show the underlying principles have been applied.

1.3 SUMMARY OF METHOD AND CONTENTS

The project has been carried out through a detailed review of the science and technology of fast pyrolysis and related processes and a contribution to the development of a Biomass Information System. The basic scientific principles of fast pyrolysis for liquids are described and reviewed in Chapter 2 followed by a explanation in Chapter 3 of how these are applied to working processes and the main problems that have been encountered. Chapter 4 summarises the current status of fast pyrolysis and Chapter 5 describes in detail the more commercially and technically advanced of these processes. Opportunities for chemicals recovery and upgrading of vapours and liquids to more valuable chemicals and transport fuels is reviewed in Chapter 6. Chapter 7 summarises the contribution made to the BIS project and includes copies of the data suplied as an annex to that chapter. Finally Chapter 8 provides some conclusions on the current status and opportunities for each of the areas described.

CHAPTER 2
FUNDAMENTALS OF PYROLYSIS

2.1 INTRODUCTION

This chapter describes the underlying mechanisms and pathways of fast pyrolysis for liquids production before showing how these principles have been applied in working processes in subsequent chapters.

2.2 PYROLYSIS MECHANISMS AND PATHWAYS

2.2.1 Introduction

As biomass is heated, its various components become chemically unstable and thermally degrade or vaporise. A number of studies have shown that the main components of most biomass types, i.e. cellulose, hemicellulose and lignin, are chemically active at temperatures as low as 150°C (1). This has recently been indicated by the kinetic parameters determined by Bilbao et al. (2, 3, 4, 5, 6). Wood, is claimed to begin pyrolysis at 250°C (7). A review of the possible reaction pathways and mechanisms which the pyrolysis of wood may follow depending upon the reaction conditions are presented below. It is common to divide the reactions of lignocellulosic materials simplistically into primary and secondary pyrolysis reactions.

The component of wood which has received the most attention is cellulose. Cellulose occurs in most biomass types up to 50 wt % and has a well defined structure which allows its easy purification and separation (1, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19). This has been carried out at two different temperature ranges: up to 300°C and above 300°C. A reaction pathway for the pyrolysis of cellulose has been proposed by Shafizadeh (8, 20), Antal (9) and Kilzer et al. (10) as shown in Figure 2.

It is generally considered that primary pyrolysis of pure cellulose occurs by two competing pathways: one involving dehydration and the formation of char, CO_2 *and water and the second involves fragmentation and depolymerisation resulting in* the formation of tarry products consisting mainly of levoglucosan as shown in Figure 2.1 (8, 9, 10, 11, 12). At temperatures greater than 300°C, fragmentation or transglycosylation predominates which involve the conversion of cellulose into predominantly a liquid product consisting of levoglucosan and other anhydrosugars.

Two hypotheses have been proposed for the formation of levoglucosan: one by Tang (13) and Golova (14) that the glycosidic bonds are broken homolytically and that depolymerisation proceeds by a free radical mechanism. The second assumes a heterolytic transglycosylation reaction with depolymerisation proceeding by a carbonium ion intermediate (8, 9, 10, 11,15,16). The chemistry of the reactions has been reviewed in the literature (9,18).

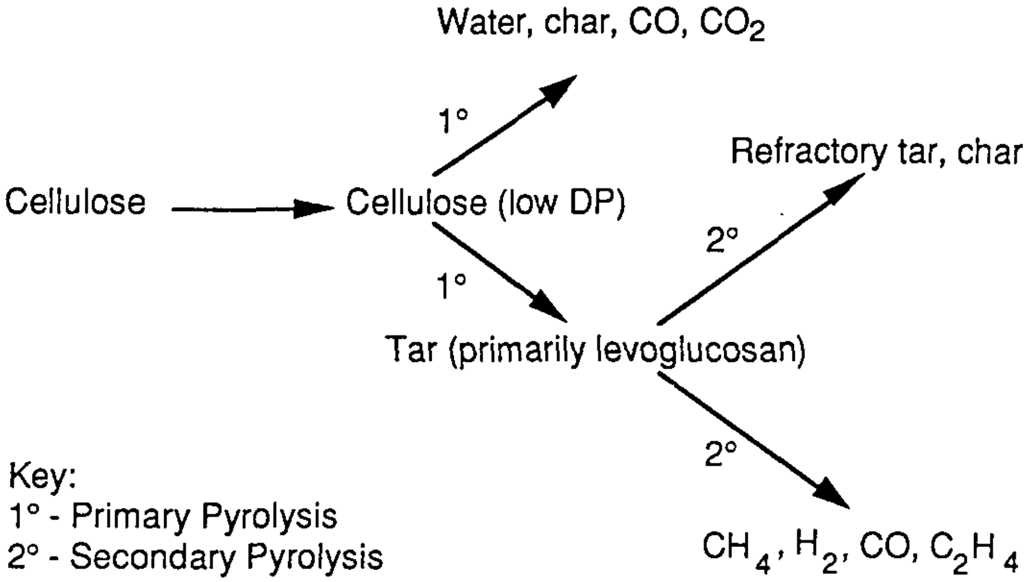

Figure 2.1 **Pure Cellulose Pyrolysis Pathways 1965-1983** (8, 9, 10, 20)

Scott et al. (17) more recently have proposed the Waterloo model for the pyrolysis of cellulose taking into account two major competing pathways for the primary decomposition of cellulose by fast pyrolysis Each pathway is capable of minor rearrangement reactions to account for the variety of different products produced, due to the dependency on the cellulose morphology, degree of polymerisation, presence of alkali cations and the process parameters such as temperature, heating rate and pressure. These potential reaction pathways are shown in Figure 2.2 (17). A typical analysis of liquids obtained from the flash pyrolysis of cellulose is given in Table 2.1.

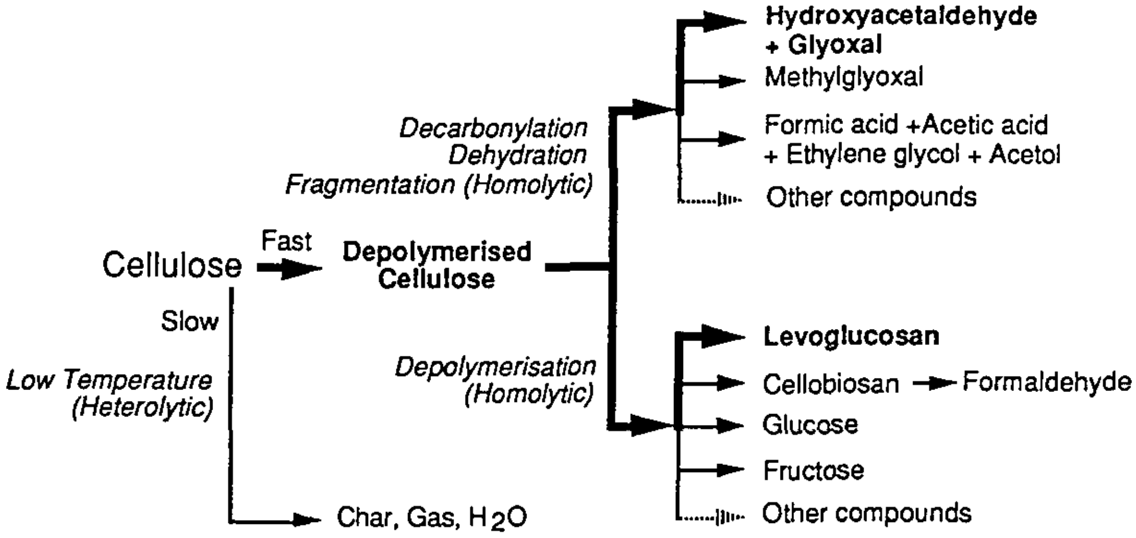

Figure 2.2 **University of Waterloo Reaction Pathways 1988 (17)**

Table 2.1 **Composition of Waterloo Flash Pyrolysis Liquids obtained From Cellulose (21).**

Cellulose source	Commercial SS-144	Treated SS-144°	Avicel
Temperature, °C	500	502	500
Product yields (% based on moisture free feed)			
Organic liquid*	72.5	83.5	87.1
Char	5.4	1.3	2.5
Water	10.8	6.1	3.1
Gas	7.8	3.9	8.9
Hydroxyacetaldehyde	15.3	6.2	8.6
Levoglucosan	7.0	31.8	26.9
Cellobiosan	4.0	11.5	10.1
Glucose	1.0	1.8	2.1
Fructose (?)	2.0	3.0	4.7
Glyoxal	3.5	5.5	6.5
Methylglyoxal	0.8	1.3	0.23
Formic acid	5.5	1.9	3.8
Acetic acid	4.9	0.1	1.4
Ethylene glycol	1.7	0.02	0.56
Formaldehyde	1.2	0.94	0.72
Acetol	2.2	0.12	0.04
Anhydroglucofuranose	N/A	5.5	
Oligosaccharides	N/A	5.3	
Ash	0.062		<0.01

* moisture free liquid

° pretreated with 5 mass % H_2SO_4 at 90°C for 5.5 hours

2.2.2 Hemicellulose Pyrolysis

Other work has been carried out on the pyrolysis of hemicellulose but this has received less attention due to its lower abundance, variety of constituents, high reactivity and rapid degradation at low temperatures (150-350°C). It is believed that the intermediate levoglucosan is replaced by a furan derivative (16, 19). This may be due its lack of crystallinity (22). Soltes and Elder (23) suggest a two step degradation process where the first step is depolymerisation to water soluble fragments subsequently followed by decomposition to volatile components.

2.2.3 Lignin Pyrolysis

The complex structure of lignin has led to a lack of understanding of the pyrolysis of this component. Lignin is the most thermally stable component but its structure varies according to its source and the method of isolation. To date therefore, most detailed work in lignin pyrolysis has been obtained from model compounds. Minor decomposition begins at 250°C but most significant lignin pyrolysis occurs at higher temperatures (13,18, 22). High molecular weight compounds such as coniferyl alcohol and sinaptyl alcohol are formed during the initial stage of pyrolysis by the formation of double bonds in the alkyl side chain of the lignin structure.

Low temperature pyrolysis of lignin (< 600°C) has been carried out by a large number of researchers (16,18, 19, 24, 25, 26, 27, 28, 29, 30). Detailed work using Kraft lignin has also been carried out by Jegers and Klein (31, 32) who identified and quantified 33 products (12 gases, water, methanol, and 19 aromatic compounds such as phenol, cresol and guaiacol) at a range of temperatures from 300 to 500°C. Iatridis and Gavalas (33) studied the pyrolysis of kraft lignin at 400-700°C using a captive sample reactor, obtaining a total volatiles yield of 60 wt%. Nunn et al. (34) have also carried out work in this area obtaining a maximum of 53 wt% liquid at 625°C, again in a captive sample reactor.

High temperature pyrolysis of lignin (> 600°C) leads to complex cracking, dehydrogenation, condensation, polymerisation and cyclisation reactions resulting in the formation of products such as CO, CH_4, other gaseous hydrocarbon, acetic acids, hydroxyacetaldehyde and methanol. Polyaromatics, benzene, phenylphenols, benzofurans and naphthalenes are formed by other secondary reactions (9, 16, 18, 19, 25, 34, 35).

Other work has been carried out with model compounds and mathematical models to obtain reaction mechanisms and reaction kinetics for lignin pyrolysis. Klein and Virk have proposed a reaction mechanism derived from the pyrolysis of the model compound phenethylphenyl ether (18, 32, 33).

Mathematical modelling of lignin pyrolysis has been attempted using the Monte Carlo technique (36, 37). The overall simulation is comprised of two Monte Carlo simulations: one comprising the lignin structure and the second the degradation of its oligomers. The simulation contained model compound reaction pathways and kinetics in a Markov-chain based simulation of the reaction of lignin polymers which subsequently produced yields of various hydrocarbons and oxygenated compounds. Other mathematical models have been developed by Solomon (25, 38) to predict the molecular weight distribution of the tars and Anvi (24, 39) who predicted the rate of evolution of lignin pyrolysis gases.

2.2.4 Whole wood Pyrolysis

The pyrolysis of the three main components of most biomass types have been reviewed above. It could therefore be expected that the pyrolysis of wood would exhibit similar characteristics to the pyrolysis of its components. From TGA DTA and DSC work, it has been concluded that the mechanism of wood pyrolysis is a linear combination of these three components (1, 9, 13, 15, 18, 20, 40, 41, 42, 43, 44, 45, 46). The focus of this section is fast/flash pyrolysis of wood which has been accounted for in three major proposed reaction schemes.

1. Fast Pyrolysis of Biomass Workshop, October 1980

The first comprehensive reaction scheme to account for the fast/flash pyrolysis of wood was proposed by Diebold (47). The reaction scheme was the general consensus of pyrolysis specialists attending a workshop on the Fast Pyrolysis of

Biomass, at the Solar Energy Research Institute (now National Renewable Energy Laboratory, NREL), in October 1980. This is depicted in Figure 2.3.

This was the first model to take into account the influence of heating rate, temperature and pressure with regards to biomass pyrolysis. The focus of the model is the formation of hydrocarbons, CO, CO_2, H_2 and H_2O as the interest at the time was in the production of olefins.

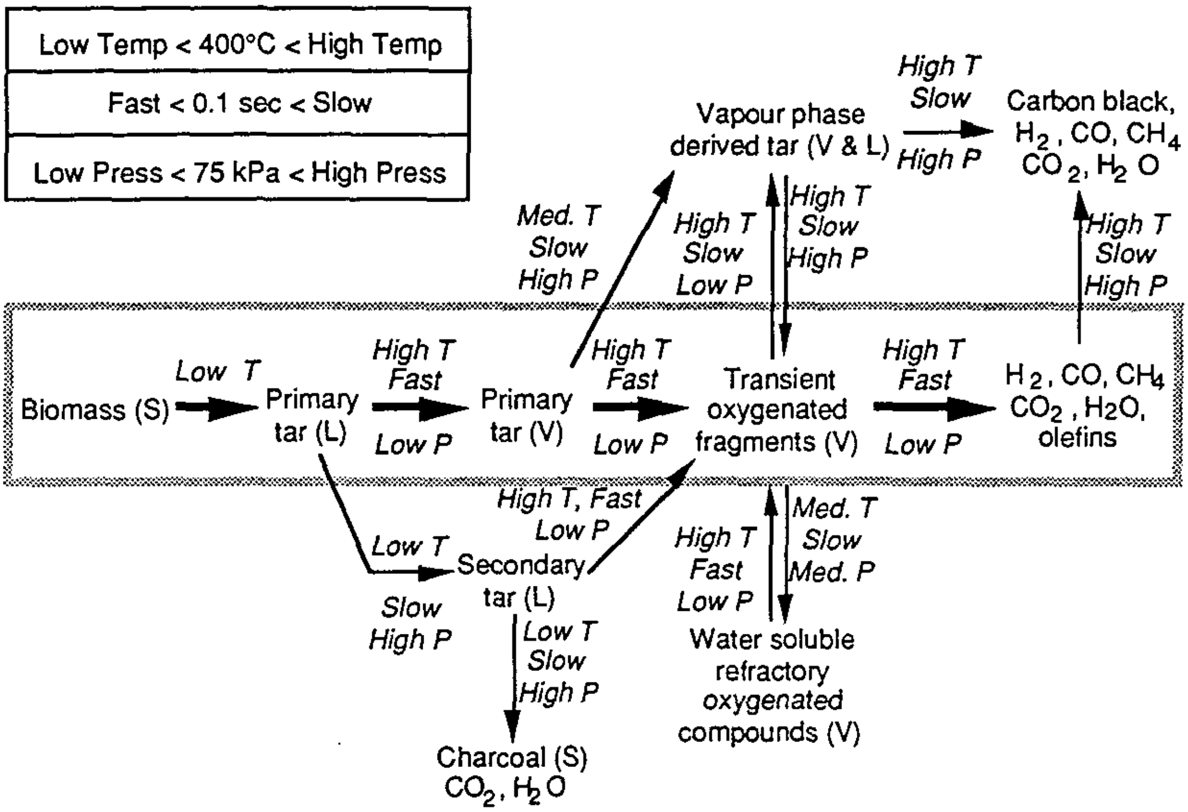

Figure 2.3 Fast Pyrolysis of Biomass Proposal 1980 (47)

2. *Diebold Proposed Modified Reaction Scheme*

Diebold then proposed a more simple reaction scheme in that the biomass initially decomposed to a viscous primary precursor with an elemental structure similar to wood (48). This is shown in Figure 2.4.

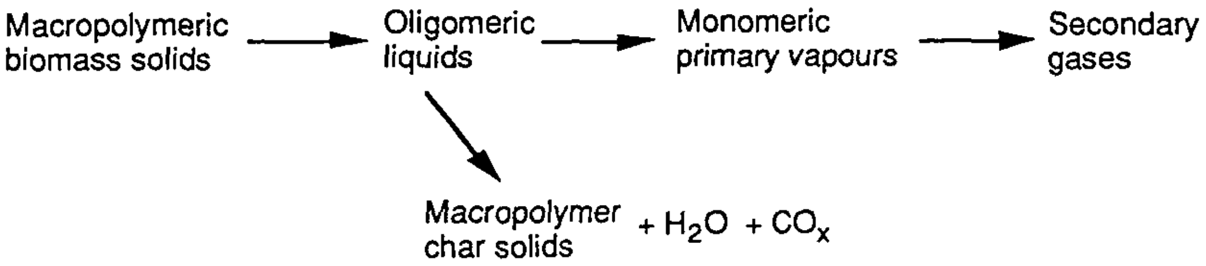

Figure 2.4 Diebold Modified Reaction Scheme 1985 (48)

3. Evans and Milne Proposed Modified Reaction Scheme, 1987

More recently a reaction scheme has been proposed by Evans and Milne as shown in Figure 2.5 (16). Similar to the Copper Mountain reaction scheme, the influence of "pyrolysis severity" is considered as the increase in temperature, heating rate and vapour residence time. Under high pressure conditions, the direct formation of a liquid product is due to the wood deforming to a "plastic" state. This has been confirmed by Diebold (49) and Lédé et al. (50, 51, 52) who have shown that under condition where ablation occurs, the wood may exhibit the properties of a "molten plastic state". At low pressure, however, it is not clear whether a liquid phase exists, after the primary decomposition of the biomass.

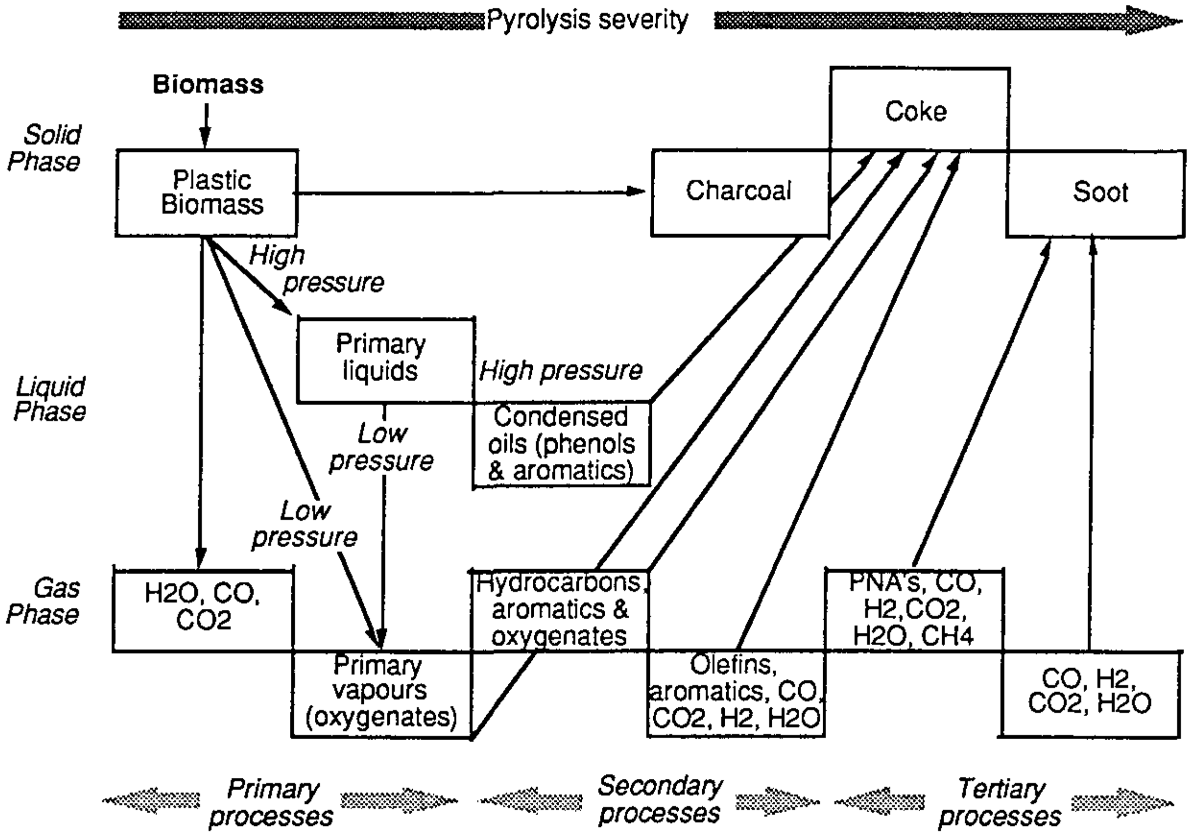

Figure 2.5 Reaction Pathways 1987 (16)

It can be seen that the initial models for the pyrolysis of the main components of wood have developed through to an overall reaction scheme as proposed by Diebold, and Evans and Milne. Evans and Milne do, however, consider a discrete tertiary reaction stage. The process of pyrolysis is complex, but a recent theory is that primary vapours are first produced, the characteristics of which are most influenced by heating rate. These primary vapours then further degrade to secondary tars and gases, the proportions and characteristics of which are a function of temperature and time (53). Yields of liquids from pyrolysis can thus be influenced by the rate of reaction, with fast or flash pyrolysis at lower temperatures of typically 450-650°C giving the highest liquid yields.

2.3 MATHEMATICAL MODELLING OF PYROLYSIS

2.3.1 Introduction

Mathematical modelling may be defined as the art of obtaining a solution, given specified input data, that is representative of the response of the process to a corresponding set of inputs (54). The development of a mathematical model can be mechanistic (theoretical) using physico-chemical principles, empirical based on experimental data, statistical or judgmental as in an expert system or a combination of the above.

2.3.2 Pyrolysis Modelling Objectives

Mathematical modelling is utilised in pyrolysis to account for the effects of the interaction of the parameters on the end products. The objectives of a mathematical pyrolysis model should include:

1. the development of a diagnostic tool in order to evaluate the importance of the various process parameters such as particle size, heat of pyrolysis (reaction) and thermal properties of the feedstock and products;
2. the prediction of the effects of process parameters, i.e. heating rate, reactor temperature, particle size, moisture content, on the product yields and characteristics in order to aid optimisation of the pyrolysis process;
3. the development and establishment of better reactor design techniques in order to specify reactor type and size.

There are four types of pyrolysis model: empirical, kinetic, analytical and stagewise. All models basically derive energy and mass balances across a particle of biomass as shown in Figure 2.6.

where:

T_E:	environment temperature	T_S:	surface temperature
T_C:	char temperature	T_W:	biomass temperature

The pyrolysis of a single particle represented above is not however applicable to conditions where particle ablation is significant or the primary method used to achieve pyrolysis. A typical example is that of Diebold's vortex reactor where the particle is in contact with a heated surface under conditions of high applied pressure and high relative motion where conductive heat transfer is the dominant mode (48).

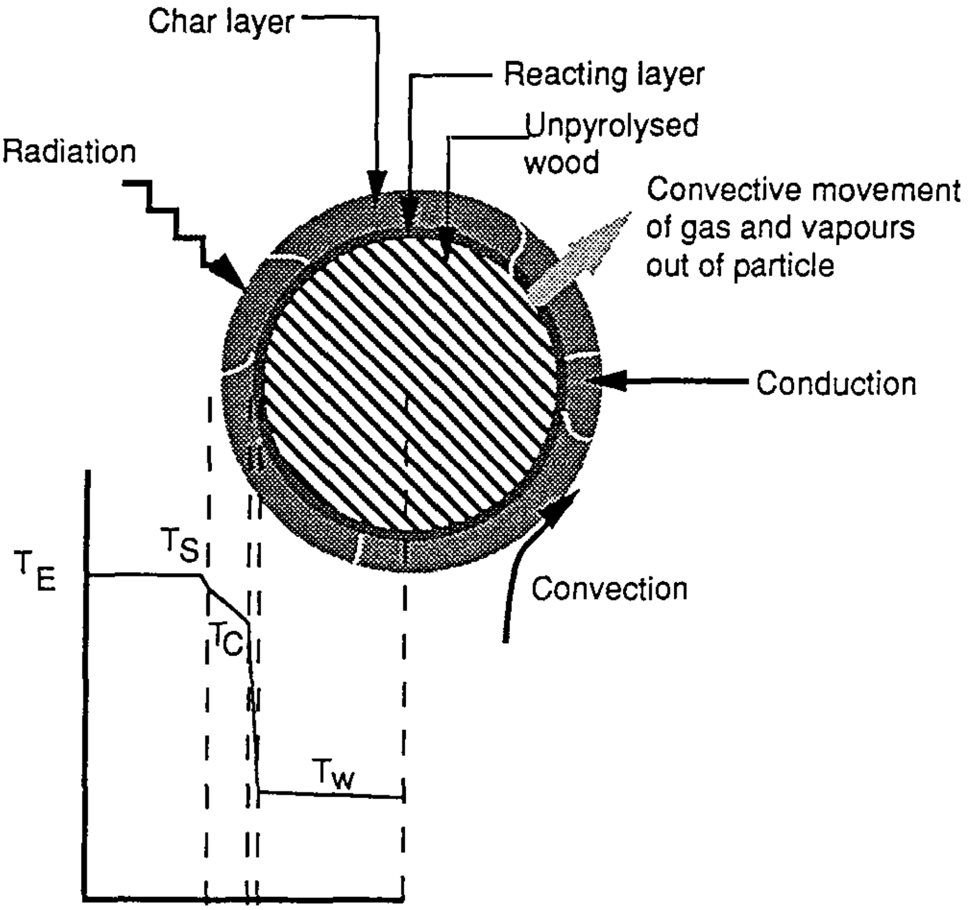

Figure 2.6 **Pyrolysis Behaviour for a Single Spherical Particle**

2.3.3 Empirical Modelling

This is the simplest modelling approach in that the model is based on the overall mass balance as shown in equation M.1.

biomass ---> a char + b liquid + g gas M.1

Such model provides a simple stoichiometry specific to the reactor conditions used and are therefore highly specific and of limited use. functional or empirical relationships between yield and the process parameters may be derived but requires a substantial amount of experimental data.

2.3.4 Kinetic Modelling

Kinetic models are usually derived from particles with the hope that the Arrhenius type equations derived will represent the intrinsic reaction rates of pyrolysis. With small particles mass transport effects will be minimal and may therefore be neglected.

The complexity of the pyrolysis process implies that there are numerous homogeneous and heterogeneous reactions occurring either simultaneously and/or consecutively depending on the reactor conditions. Kinetic modelling is therefore an attempt to represent the overall kinetics as individual reaction pathways are very difficult to determine.

2.3.4.1 Global Kinetic Models

The kinetics of wood degradation and its respective components have been and still are obtained by measuring the rate of weight loss of the sample as a function of time and temperature. The most common technique for this investigation is thermogravimetric analysis (TGA). TGA involves continuous weighing and recording of data obtained from a sample, heated at either constant temperature or a fixed heating rate, enclosed in a furnace (e.g. 1, 2, 3, 4, 5, 6, 9, 13, 15, 18, 20, 40, 41, 42, 43, 44, 45, 46, 55]. These experiments are normally carried out under vacuum or in a nitrogen atmosphere at both low temperatures and heating rates. Some workers have used steam as the gaseous environment in their experimental system [45, 46, 56]. As there is no provision for the collection of volatile pyrolysis products, the TGA data are normally used to derive overall kinetic expressions.

The global thermal degradation process can be described by a simplistic reaction scheme as shown in equation M.2.

$$\text{biomass} \longrightarrow \text{char} + \text{volatiles} \qquad \text{M.2}$$

and the rate of the above reaction is then described in the form of a first order Arrhenius type rate law as shown in equation M.3.

$$\frac{dW}{dt} = -A \exp\left(\frac{-E}{RT}\right)(W - W_f) \qquad \text{M.3}$$

where: W: residual weight fraction,

W_f: final weight,

A: pre-exponential (frequency) factor,

E: activation energy,

R: Universal gas constant.

T: reactor temperature

If the sample is heated at a constant rate M, then

$$\frac{dW}{dt} = -\frac{A}{M} \exp\left(-\frac{E}{RT}\right)(W - W_f) \qquad \text{M.4}$$

where: $M = \frac{dT}{dt}$

Sometimes the weight term is replaced by a density term. It is assumed here that no shrinkage occurs during char formation. Table 2.2 shows some selected kinetic parameters for overall reaction rate expressions.

The Arrhenius kinetic parameters, the activation energy (E) and the pre-exponential (frequency) factor (A) are derived by obtaining best fit curves through the experimental data and solving the Arrhenius rate law, using a least squares method. A comparison of the different kinetic parameter estimation methods is made by Vovelle et al. which highlights the variability in the values obtained (57). Most of these values have been obtained from weight loss data.

Kinetic parameters estimated by the researchers given in Table 2.2 show a wide variability in the values, even with similar feedstocks. Some of the variability in the parameters may be accounted for by the neglect of temperature variation of the sample during heat up and the use of the steady state temperature as the overall reaction temperature. Some of the kinetic modelling has also be performed with large biomass samples where the effects of mass and heat transfer cannot be neglected. This is evidenced by Salazar who gives different value for the pre-exponential factor and the activation energy for two differing cylinders of eucalyptus (68). Other researchers have used two or more consecutive steps of zero and first order reactions to describe the pyrolytic degradation of the biomass (13, 58, 59, 60, 61, 62, 63, 64).

Bilbao et al. have taken into account the influence of heating rate on the kinetic parameters and have therefore studied a range of heating rates from 1.25 C°/min to 80C°/min and the effects on the reaction order (2, 3, 4, 5, 6). Other discrepancies arise from too simplistic modelling and the presence of impurities or ash which may influence the decomposition kinetics. Varhegyi et al. have investigated the effect of NaCl, $FeSO_4$ and $ZnCl_2$ on the pyrolysis of Avicel cellulose under different conditions with four different modelling approaches (55). To predict the product distribution, stepwise models should be applied.

2.3.4.2 Stepwise Models

This modelling approach allows for the formation of intermediate components and their subsequent conversion to final products, as shown in equation M.5.

$$\text{biomass} \dashrightarrow \text{product component } j \qquad \text{M.5}$$

where the rate of formation of component j with a yield Vj at a given time t is given by equation M.6:

$$\frac{dV_j}{dt} = k_{oj} \exp\left(-\frac{E_j}{RT}\right)\left(V_j^{*} - V\right) \qquad \text{M.6}$$

Table 2.2 Experimental Kinetic Parameters for Overall Reaction Rate Expressions

Data source	Sample Range (°C)	Temperature Energy (kJ/mol)	Activation Factor (s^{-1})	Frequency
Akita & Kase (65)	a Cellulose	250-330	224.0	1.0 x 10^{17}
	Modified cellulose	250-330	134.0	1.7 x 10^{10}
Bilbao et al.(2-6)	cellulose	230-300	54.3	5 x 10^{17}
			53.8	1.6 x 10^{17}
	xylan	< 280	10.2	9.8
	lignin	< 325	17.8	2.6 x 10^{3}
	Pinaster pine	290-325	16.4	6 x 10^{2}
		> 325	52.9	1.7 x 10^{16}
	barley straw	240-270	12.5	42
		>270°C	25.7	8.2 x 10^{6}
Broido (66)	cellulose	226-328	221.6	1.7 x 10^{15}
Brown and Tang (67)	Ponderosa	-	149.9	
Chatterjee (68)	Cotton	-	227.3	138.1
Kanuary (69)	a cellulose	100-700	79.5	1.7 x 10^{5}
Lewellen et al. (70)	Cellulose	-	139.8	6.8 x 10^{9}
Maa (71)	Birch wood	400-1200	31.4	0.10 cm/s
	Douglas fir	400-1200	14.7	0.03 cm/s
Simmons & Lee (72)	cellulose	-	36	1.6 x 10^{10}
Stamm (73)	Douglas fir sawdust	110-220	104.7	2.4 x 10^{5}
	a Cellulose	110-220	108.8	6.0 x 10^{5}
	Hemicellulose	110-220	111.8	7.1 x 10^{6}
	Lignin	110-220	96.3	1.1 x 10^{4}
	Coniferous wood	95-250	123.5	6.2 x 10^{7}
Thumer & Mann (74)	oak sawdust	300-400	106.5	2.5 x 10^{6}
Tran & Rai (43)	Douglas fir bark	100-850	101.7+142.7X*	2.1 x 10^{8}
	Catalysed bark **	100-850	102.6+86.2X*	2.3 x 10^{8}
Salazar et al.(75)	eucalyptus regnans	450-600		
	lc hemicellulose		54	165.9
	cellulose		166	1.1 x 10^{12}
	sc hemicellulose		83.6	1.5 x10^{4}
	cellulose		417.6	2.4 x 10^{33}
Samolada et al. (76)	fir wood	400-500	56.5 v	136
			94.5 g	2.4 x 10^{4}
Varhegyi et al. (55)	Avicel cellulose	-	205 #,	1.26 x 10^{15}
		–	222 §	6.3 x 10^{16}
		-	234 ∞	4 x 10^{17}

** bark with 15% K_2CO_3
# 10C°/min heating rate
§ 80C°/min heating rate
∞ preheated, then 10C°/min heating rate

* X denotes fractional conversion
g total gases
v total volatiles
lc large cylinder
sc small cylinder

where:

V_j^* ultimate attainable yield of product j, i.e, the yield at high temperature and long residence times (77).

The constants k_{oj}, E_i and V_j^* cannot be predicted beforehand and must be estimated from experimental data, a problem that increases as the number of reactions postulated increases. The model provides a simple scheme that can be used to predict product yields, This method has been used by Krieger et al. (77).

Some models have taken into account the competitive nature of some of the pyrolysis reactions which have been postulated to account for the variations in product yield. This is done by Bradbury et al. (44) for cellulose as shown in Figure 2.7.

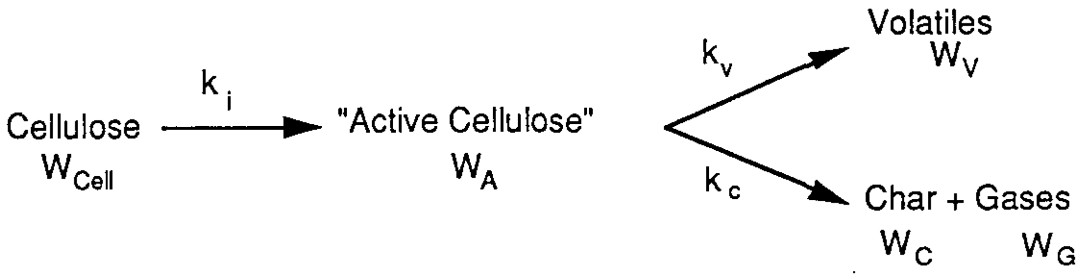

Figure 2.7 Proposed Pyrolysis Model for Pure Cellulose (44)

$$\left(\frac{dW_{cell}}{dt}\right) = ki\,[W_{cell}] \qquad k_i = 1.7 \times 10^{21} \exp\left\{\frac{-58000}{RT}\right\} \text{ min}^{-1}$$

$$\left(\frac{dW_A}{dt}\right) = k_i\,[W_{cell}] - (k_v + k_c)\,[W_A] \qquad k_v = 1.7 \times 10^{16} \exp\left\{\frac{-47000}{RT}\right\} \text{ min}^{-1}$$

$$\left(\frac{dW_C}{dt}\right) = 0.35\,k_C\,[W_A] \qquad k_C = 1.7 \times 10^{11} \exp\left\{\frac{-36000}{RT}\right\} \text{ min}^{-1}$$

Bradbury et al. (45) used this approach for their kinetic model as shown above. This model was based on the pyrolysis of pure cellulose. Theoretical and experimental results for weight loss agreed to within ± 5%. As a consequence this model has been used to account for char yields in the models of large particle pyrolysis (77, 78, 79, 80).

Koufopanos et al. (41, 42) and Nunn et al. (76) proposed that the biomass pyrolysis rate could be related to the individual pyrolysis rate of the biomass components i.e.

biomass = a (*cellulose*) + b (*hemicellulose*) + c (*lignin*)

where:

- bracketed terms ( ) represent the fractions of the biomass components not transformed into gases or volatiles
- a, b, c are the weight fractions of the corresponding biomass components in the virgin biomass.

The reaction scheme of the individual components then followed a similar reaction scheme as shown in Figure 8. In both cases, theoretical and experimental results for the weight loss agreed to within ± 10%. However, for the model of Koufopanos et al. (41, 42) there was no indication that it could be used to predict product yields. Nunn et al. (76) found that, in general, the calculated values fitted laboratory data within ± 7% for temperatures up to about 950-1000°C. Similar approaches have been adopted by Simmons (65), Salazar (68), Samolada (69) and Varhegyi (55).

2.3.4.3 Secondary pyrolysis kinetics

Secondary pyrolysis kinetics has been studied by number of researchers to account for the conversion of primary liquids to secondary products such as char, tar and gases. Antal (45, 46) *proposed the conversion of primary vapours to either* gases or tars by a temperature based competitive reaction scheme (Figure 2.8).

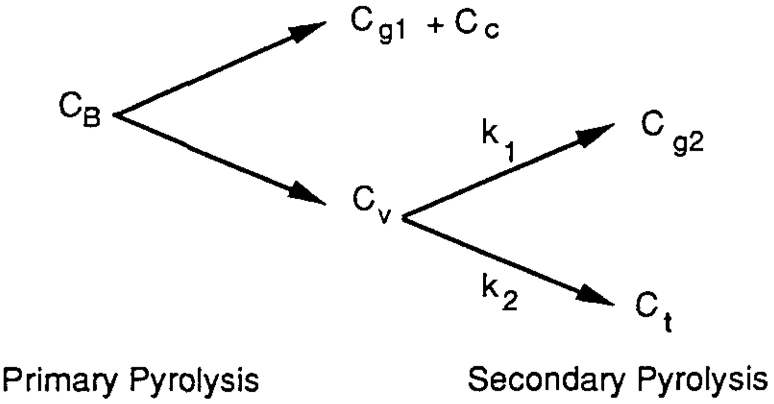

Figure 2.8 Antal's Proposed Reaction Scheme (45, 46)

The first reaction produced more permanent gases by cracking the reactive volatile matter to smaller, less reactive species. The second reaction produced refractory condensable materials, which may be tar or some combination of water-soluble organic compounds.

where:

C_B the mass fraction of carbon in biomass

C_V the mass fraction of carbon composing the reactive volatile matter (carbon in volatile matter/carbon in sample pyrolysate)

C_{g1},C_{g2} the mass fraction of carbon composing the permanent gases

C_t the mass fraction of carbon composing the refractory condensable materials, including the tars.

Recently kinetic models for the secondary decomposition of primary pyrolysis tars have been proposed by Liden (80), Diebold (56) and Knight et al. (81). Lidén (80) and Diebold (56) using different reactor configurations, proposed similar kinetic models. The reaction scheme used is shown in Figure 2.9.

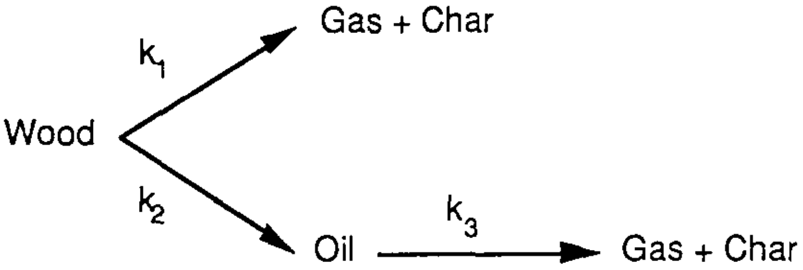

Figure 2.9 Reaction Scheme Used by Liden (80), and Diebold (55)

The kinetic expression used for the estimation of the yield of liquid products and the values of the kinetic parameters used for each model are listed below:

$$x = x_o\left(\frac{1\text{-}\exp(\text{-}k_3)}{k_3\ q}\right)$$

where

k_3: the reaction rate constant for the oil decomposition step [s-1]

q: the mean residence time for the oil decomposition [s]

x_o: the theoretical 'ultimate' oil yield

with: $k_3 = 4.28 \times 10^6 \exp\left(\frac{-107500}{RT}\right)$ s-1; $x_o = 0.703$

and; $k_3 = 1.55 \times 10^5 \exp\left(\frac{-87634}{RT}\right)$ s-1; $x_o = 0.78$ or 0.76

for Lidén and Diebold respectively.

The reaction scheme used by Knight et al. (81) is shown below in Figure 2.10 with the following reaction rate expression :

$$x = \left\{\frac{k_1 b_5}{(k_2\text{-}k_1)[\exp\ (\text{-}k_2 t)]}\right\}$$

with

$$k_1 = 1.483 \times 10^6 \exp\left(\frac{-21380}{RT}\right) \text{ s-1 } k_2 = 23.12 \exp\left(\frac{-7060}{RT}\right) \text{ s-1}, \quad b_5 = 0.811$$

where,

k_1: reaction rate constant for the first order production of oil

k_2: reaction rate constant for the first order decomposition of oil

b_5: maximum fractional conversion of wood to oil

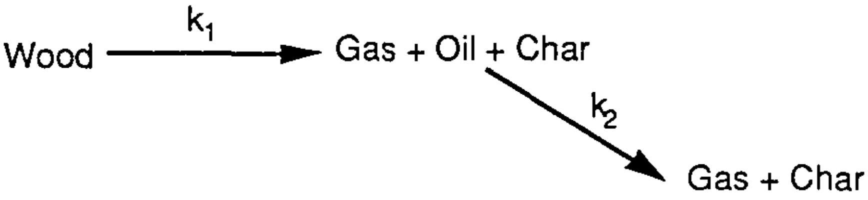

Figure 2.10 The Reaction Scheme of Knight et al. (81)

Vasalos et al. (82) and Scott et al. (83) tested the above models using their own experimental data. Vasalos et al. (82) found that using Lidén's parameters, they obtained a better fit of the liquid yields of -20% for the particle size range 300-425 mm, while Diebold's parameters gave a better fit of ± 10% for the particle size *range 500-600 mm. Knight's et al. model did not predict satisfactorily liquid yields* for either particle size range. They concluded that the variations between the predicted values and the experimental results could be attributed to the exclusion of the water yield in the reaction mechanism, the residence times used, and the *type and size of biomass tested.*

Scott and Piskorz (83) found when testing the models of both Lidén and Diebold, that the predicted liquid yields agreed with achieved yields within ± 10% for the *temperature range 500-700°C with residence times of up to 1 second.* Low predictions of liquid yields at the highest temperature were attributed to the assumed water yield, the constant x_0 parameter or the total yield being normalised to 100%.

2.3.4.4 Summary

As pyrolysis is a very complex process and the different intermediates formed are *difficult to collect and identify, various approaches have been used to develop* kinetic models. Most predict weight loss rather than product yield and distribution. The kinetic parameters vary from one model to another because they are very sensitive to experimental conditions. One research group found that even a *decrease of 1 kCal/mol (from 31.8 to 30.8) in the activation energy of tars caused* the predicted value of the liquid yield to increase by approximately 16 % (84).

Stagewise models have been discussed earlier with regards to pyrolysis pathways and mechanisms.

2.4 ANALYTICAL MODELS FOR LARGE PARTICLES

For small particles the kinetics are sufficient to predict the reaction rate. However, for large particles, both the physical and the chemical changes are essential for obtaining a global pyrolysis rate. To formulation an analytical pyrolysis model, the known parameters that can influence the pyrolysis process must be considered. These affect the energy and mass flows into and out of a pyrolysing particle given by the following methods:

- heat transfer from the reactor environment to the particle surface by convection, and/or radiation and and/or conduction;
- heat transfer from the outer surface of the particle into the interior of the particle by conduction and in a few situations to a lesser degree by convection;
- convective heat transfer between the volatile reaction products leaving the reaction zone and the solid matrix ;
- primary pyrolysis leads to conversion of the biomass to gas, char and a primary liquid product;
- secondary and tertiary pyrolysis leads to conversion of the primary product to a gas, char and a secondary liquid product which then forms primary and secondary products;
- changes in physical properties, enthalpy and heats of reaction of the biomass
- changes in the enthalpy of the pyrolysis products;
- diffusion of volatiles out of the solid and away from the particle surface. Pressure gradients may also occur due to vapour formation in larger particles.

Process Parameters that can influence pyrolysis are given below in Table 2.3 with effects.

These processes are all temperature dependent and, since temperature changes with time and space, they will also be time and spatially dependent. Furthermore, they will also be dependent on the physical structure of the particle along with its properties such as density, thermal properties, size and the orientation of the particle with respect to grain.

2.5 SINGLE PARTICLE MODELS

A variety of pyrolysis models have been derived therefore to account for the pyrolysis of particles, taking into account the process parameters noted in Table

2.3. Some of these models are summarised in Table 2.4 with their predictions and their shortcomings. A more detailed version which includes the formulation and assumptions has been complied by Bridge (85). Each model has its own particular feature or characteristic. These are detailed in Table 2.5.

Table 2.3 Process Parameters that Influence Pyrolysis with Their Effects

Parameter	Effect
Anisotropic nature	heat capacity, permeability, rate of heat transfer, diffusion
Moisture content	temperature profile, weight/density change, product yields and distribution, amount of water released initially during the drying stage, rate of heat transfer
Reactor temperature	temperature profile, weight/density change, product yields and distribution, competing reactions, properties such as thermal conductivity and heat capacity, heat of reaction
Particle size	temperature profile, weight/density change, product yields and distribution, release rate of products, rate of heat transfer, reaction time
Heat flux	rate of heat transfer, temperature profile, reaction profile
Vapour residence time	product yield and distribution

Table 2.4 Summary of Single Particle Pyrolysis Models

Authors	Predictions	Shortcomings
Bamford et al. (84)	• Predicts temperature and weight loss profiles • Predicts volatiles evolution rate	• Cannot be used to predict product yields or composition • No sensitivity analyses were carried out • No convection term • Assumed constant physical properties
Panton and Rittmann (86)	• Predicts temperature and reaction rate profiles • Predicts gas generation rate • Suggests that heat of reaction and activation energy are important parameters for gas generation • Suggests that competing reactions are sensitive to the heat flux	• Cannot be used to predict product yields or composition • No convection term • Breaks down at higher heating flux when investigating the effect of heating rate on the competing reactions
Kanuary et al. (87)	• Shows that convection term is needed in heat balance equation • Suggests that the burning rate depends on particle size	• Can only be used to investigate the importance of convective heat transfer
Kung (88, 89)	• Predicts temperature and density profiles • Predicts volatiles release rate • Suggests that both thermal conductivity and specific heat of char, heat of reaction and particle size are important parameters in wood pyrolysis	• Cannot be used to predict product yields or composition
Maa and Bailie (64, 90)	• Predicts under what conditions heat transfer or chemical reaction is rate controlling • Predicts reaction rate and temperature profiles • Predicts reaction times • Derived simple expressions to estimate reaction time by using either effective thermal conductivity (large particles) or effective activation energy (small particle)	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate
Fan et al. (91, 92, 93)	• Introduces a new parameter, Lewis No., the ratio of thermal diffusivity to mass diffusivity • Predicts concentration and temperature profiles • Suggests that the higher the Lewis No., the greater the conversion of the solid and the smaller the temperature gradient within particle • Suggests that heat of reaction affects pyrolysis rate	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate

Table 2.4 continued

Kansa et al. (94)	• Predicts mass loss, pressure and temperature profiles • Suggests that heat of reaction, both the thermal conductivity and specific heat of char and the permeability constant are important parameters in wood pyrolysis	• Cannot be used to predict product yields or composition • Does not predict volatiles release rate
van Ginneken et al. (95)	• Predicts product distribution • Temperature and particle size influences product distribution	• Does not predict temperature profiles • Assumed constant physical properties
Desrosiers et al.(96)	• Predicts temperature profile • Predicts reaction time • Suggests that the values of pyrolysis temperature, char thermal conductivity and heat of reaction significantly affect wood pyrolysis	• Cannot be used to predict product yields or composition • Does not predict volatiles release rate • Assumed constant physical properties
Capart et al. (75, 97)	• Predicts reaction rate and time • Predicts both internal and surface temperature and mass loss	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate
Phillips et al. (98)	• Predicts mass loss profiles • Predicts surface and internal temperature profiles • Predicts char yields	• Does not predict volatiles yields • Does not predict volatiles release rate • Assumed constant physical properties • For large particles, kinetics and heat transfer are not coupled
Saastamoinen (99)	• Predicts temperature, mass loss and density histories • Predicts moisture distribution • Predicts moisture and volatiles release rate • Predicts generation of steam and volatiles	• Neglect of mass transfer resistance which may play a role in pyrolysis
Lédé et al. (50, 51, 100)	• Predicts under what conditions heat transfer or chemical reaction is rate controlling • Introduces a thermal Thiele Modulus (ratio of heat penetration time to reaction time) • Predicts temperature profile • Predicts reaction time	• Cannot be used to predict product yields or composition • Does not predict volatiles evolution rate • Thermal properties are assumed to remain constant

Table 2.4 continued

Pyle and Zaror (101, 102)	• Introduced two pyrolysis numbers, Py (ratio: reaction time to heat penetration time) and Py' (Biot No x Py) • Evaluated the importance of external and internal heat transfer • Derived four simple models • Predicts conversion and temperature profiles • Predicts conversion times • Particle size affects conversion • Carried out sensitivity study	• Cannot be used to predict product yields or • Does not predicts volatiles release rate • No convection term
Stiles (103)	• Predicts char yields • Predicts cracking activation energies	• Cannot be used to predict volatiles yields or composition • Does not predicts volatiles evolution rate • No convection term • Predicts that smaller particles produce more char than larger ones which is unreasonable
Kothari and Antal (78,79)	• Predicts temperature histories • Predicts weight loss • Calculates reaction times • Derived simple expressions to calculate heat up time and devolatilisation time • Pyrolysis is complete at 500°C	• Cannot be used to predict product yields or composition • Does not predict volatiles release rate
Chan et al (77, 104, 105)	• Predicts product yields and composition • Predicts volatiles release rate • Predicts temperature profile • Predicts effects of moisture • Carried out sensitivity studies	• Neglect of mass transfer resistance which may play a role in pyrolysis
Krieger-Brockett et al. (106)	• Predicts product yields and composition • Predicts volatiles release rate • Predicts temperature profile • Predicts effects of moisture • Carried out sensitivity studies	• Neglect of mass transfer resistance which may play a role in pyrolysis
Samolada et al. (69)	• Predicts volatiles and gas yields • Simple model gives good agreement with experimental work	• assumed lignin pyrolysis dominant step
Alves et al. (107, 108)	• Predicts high temperature drying profiles at >150°C • applicable to wet particles up to the free-water continuity point (~0.45)	• Neglects water vapour diffusion, bound water diffusion and internal pressure gradients • Dimensions in longitudinal and transverse directions must be similar

Table 2.4 continued

Di Blasi et al. (109, 110, 111)	• Simple kinetic scheme used • internal flow convection effects on thermal degradation analysed on dependence of wood and char properties • effects of grain orientation included • variation of transport phenomena, reacting medium properties and primary and secondary reactions included	• structural changes not accounted for during pyrolysis • char permeability assumed constant • long reaction times
Hastaoglu et al. (112)	• Predicts optimal conditions for product yields • Predicts temperature profiles and optimum heating rates • hollow fibrous structure of wood considered in model primary and secondary reactions included	• specific to flash pyrolysis
Wichman and Meleaan (113)	• predicts variable density • predicts product yields • accounts for yield variability with step changes in temperature with time • applied to thick and thin particles • based upon slow heating with a final char yield of 0.35 • predicts temperature profile in sample	• applicable to cellulosics only • not applicable to flash pyrolysis, i.e model does not cover initial weight loss period • transport mechanisms ignored • assumed constant test temperature

Table 2.5 Features of the Models

Models with no Convection Term	Bamford et al. (84), Panton et al. (86), Wichman and Meleaan (113), Alves et al. (107,108).
Models with Convection Term	Kanuary and Blackshear (87), Pyle and Zaror (101,102), Di Blasi (109,111), Hastaoglu et al. (112), Kung (88,89).
Shrinking Core Model	Maa and Bailie (64,90)
Moving Boundary Models	Desrosiers and Lin (93), Saastamoinen (99),
Models including Mass Transfer Effects	Fan et al. (91-93), Kansa et al. (94) Di Blasi (109,111), Kothari and Antal (78,79), Stiles (103), Villermaux et al. (50,51,100),
Uncoupled Heat and Kinetic Approach	Philips et al. (98),
Models which predict product Yields	Capart et al. (75,97), van Ginneken (95), Wichman and Meleaan (113), Di Blasi et al. (109,110,111).

2.6 RESULTS OF PYROLYSIS MODELLING

The various aspects of pyrolysis mechanism, reaction pathways and pyrolysis modelling have been summarised in the previous section. The main benefits of the studies carried out over the past 25 years have been:

1 optimisation of the process parameters to allow the prediction of yields and specification for the production of chemical intermediates.

2 kinetic data has been obtained which aids in the prediction of reaction times and ultimate yields.

3 reaction pathways allow the fast/flash pyrolysis process parameters to be specified for the production of speciality chemicals in significant yields.

4 reactor design and specification is now much simpler due the more data on relevant physical properties becoming available, allowing better design methods.

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CHAPTER 3
PYROLYSIS TECHNOLOGY PRINCIPLES

3.1 INTRODUCTION

This chapter shows how the underlying scientific principles and requirements can be applied to the design and operation of pyrolysis processes. Included are the key product liquid characteristics that result from practical application of pyrolysis.

3.2 PYROLYSIS CONCEPTS

It has already been explained that 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 to before collection which includes the influence of the reactor configuration. 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.

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. Fast pyrolysis processes have been developed for production of food flavours (to replace traditional slow pyrolysis processes which had much lower yields) and speciality chemicals which utilise very short vapour residence times of typically 100-300 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.

Liquids for use as fuels can be produced with longer vapour residence times [up to ~6 s] and over a wider temperature range although yields might be affected in two ways: secondary gas 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 [64 wt% organics and 16 wt% water] at 500-520°C with vapour residence times not more than 1 second. 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 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 (1). This is discussed further below.

3.3 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.

3.3.1 Reactor configuration

A variety of reactor configurations have been investigated as listed in Table 3.1. 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.

Table 3.1 Pyrolysis Reactors, Heating Methods and Heating Rates

Reactor type	Method of Heating	Organisation
Ablative cone	Wall and sand heating	U.Twente
Ablative mill	Wall (disc) heating	CSM
Ablative plate	Wall heating	U.Aston, U.Nancy
Ablative vortex	Wall heating	NREL, Interchem
Auger kiln	Wall heating	U.Tubingen, WTC
Circulating fluid bed	In-bed gasification of char to heat sand	CRES
Cyclone or vortex	Wall heating	See *Ablative vortex*
Entrained flow	Combustion products	Egemin, GTRI
	Hot sand	U.Western Ontario ¶
Fixed bed	Combustion products	Bio-Alternative
	Partial gasification	*Alten §*
Fluid bed	Heated recycle gas	INETI, Union Fenosa, U.Waterloo, Worthing
	Hot inert gas	CPERI, NREL, U.Aston, U.Leeds, U.Sassari,
	Partial gasification	Alten §
	Fire tubes	MTCI ¶
Horizontal bed	Fire tubes	Pyrosol*
Multiple hearth	Hearth heating	U.Laval
Rotary kiln	Wall heating	Deutsche Babcock*, KWU*, PKA*, Stenau*
Stirred bed	Partial gasification	Alten §
Transported bed with *solids recirculation*	Hot sand and gas	Ensyn

NOTES
* Used for solid waste processing, not liquids production
¶ Used for gas production
§ Operational mode unclear

3.3.2 Heat transfer

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

1. to the reactor heat transfer medium (solid in ablative reactor, gas and solid in fluid and transport bed reactors, gas in entrained flow reactors),
2. 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 Egemin process), and solid-solid heat transfer with mostly conductive heat transfer. 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 and transport reactors 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). 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 from the low thermal conductivity of biomass giving low heating rates through larger particles which leads to increased char formation. 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 it's 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 (2). Union Fenosa are using particle sizes of smallest dimension 2 mm in their 200 kg/h fluid bed to achieve total liquid yields of around 55% wt. on dry feed with a 15% water content (3). Ensyn claim that particle sizes of up to 5-6 mm in their reactor will still give total liquid yields of up to 75% wt. on feed with 10% moisture which is equivalent to 83% wt. on dry feed basis. Based on the original vortactor work at the University of Western Ontario, it seems likely that attrition of particles at the base of the Ensyn RTP reactor would be a feature of their system to remove char from the particle surface with some degree of solid-solid heat transfer. Egemin found with their entrained reactor that particle sizes of 6 mm caused a large proportion to be expelled from the reactor substantially unreacted due to poor heat transfer and no char removal from ablation. This resulted in total liquids yields of less than 40% wt on dry feed (4), while GTRI claimed yields of over 60% total liquids with an up flowing entrained flow reactor using feed sizes up to 6 mm (5).

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 11 wt% of dry feed.

3.3.3 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. originally suggested that to achieve true fast pyrolysis conditions, heat fluxes of 50 W/cm^2 would be required but to achieve this in a commercial process is not practicable or necessary (6).

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 3.2 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 (7, 8). 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 which therefore requires an efficient sand re-heating system. In a conventional fluid bed the sand requires an external heat source.

A commercial system would be expected to utilise the by-product char and gas for the process heat requirements as an integrated system as proposed for the NREL wood to gasoline process evaluated by the IEA (7, 8).

Table 3.2 Reactor Types and Heat Transfer

Reactor type	Suggested mode of heat transfer	Advantages/disadvantages/features
Ablative	95% Conduction 4% Convection 1% Radiation	Accepts large feedstocks; Good mechanical char abrasion; Solids decoupled from gas products; 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	Limited char abrasion; High heat transfer rates; Char/solid heat carrier separation required; Simultaneous char combustion to heat solids; 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; Reactor wear can occur.
Fluid bed	90% Conduction 9% Convection 1% Radiation	High heat transfer rates; 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.

3.3.4 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.

3.3.5 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 has demonstrated the effects of ash, DP, heating rate and reactor temperature on chemical yields (9). 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 done by McKinley (1) 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 vaporisation.

3.3.6 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 Diebold et al., Liden et al and Knight et al. 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. 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. have demonstrated that the average molecular weight decreases with the degree of secondary reaction, i.e. increasing residence time and temperature (10).

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 90 ms are claimed.

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&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.

3.3.7 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.

3.3.8 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 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 and reactor configurations/.

3.3.9 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 (11) 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.

3.3.10 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.

3.4 PRODUCT CHARACTERISTICS

3.4.1 Product quality

The complex interaction of time and temperature on liquid product quality has not been explored, at least partly because the characteristics of pyrolysis oil for different applications has 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 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.

3.4.2 Unusual characteristics

Bio-fuel-oil has a number of special features and characteristics which require consideration in any application including production, storage, transport, upgrading and utilisation. These are summarised in Table 3.3 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.

3.5 PYROLYSIS PROCESSES

A brief overview of the current position on fast pyrolysis processes for liquids is given below to show the extent of activities while more details are provided in Chapter 4. A recent review of processes that are advanced technically and/or commercially available has been published (12).

3.5.1 North America

Fast pyrolysis of biomass for liquids began in North America around 1980 and has seen significant RD&D effort since then with one successful commercial organisation offering plants with a performance guarantee and several demonstration and pilot scale processes.

Table 3.3 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.
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 > 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.

3.5.1.1 Ensyn

Ensyn's RTP technology evolved from the research on fast pyrolysis carried out at the University of Western Ontario. They are still the only commercial organisation selling fast pyrolysis plants with a performance guarantee. There are three operational plants: a 25 dry te/d unit at Red Arrow in Wisconsin and an 80 kg/h unit and 10 kg/h R&D unit in Ottawa. Six plants are currently at a design or construction stage: 60, 25, 25, 15, 7.2 and 1 dry te/d which includes the 15 t/d unit for ENEL in Italy for delivery in 1995. Further plants for fuel production are in advanced negotiation in the USA. Ongoing development work includes hot vapour filtration to reduce ash and char, liquid filtration to reduce char, supply of oil for engine and turbine testing in Canada and Europe, combustion testing, upgrading and product characterisation.

3.5.1.2 NREL

NREL have been developing their 36 kg/h vortex ablative pyrolyser since 1980. Designs for scale up have been produced and support has been provided to Interchem for the reactor in their 31 te/d demonstration plant (see below). A second R&D unit has now been constructed and a small fluid bed fast pyrolysis unit has also been commissioned. Zeolite upgrading of the pyrolysis vapours to aromatics has been accomplished at the fundamental level on the MBMS system, on a slip-stream of the vortex reactor and on the full reactor output. Novel multi-functional zeolite catalysts have been produced and tested. A circulating fluid bed zeolite cracker with regenerator is under construction. Only limited results have been published on any of this work including recent work by Czernik et al. (13) on vapour phase thermal treatment to lower the oxygen content of the liquid.

3.5.1.3 Interchem

The 31 te/d demonstration plant was moved from Mountain View Missouri to Kansas City and the reaction system completely redesigned with the support and assistance of NREL (14). The construction of the new reactor was completed in late summer 1993 and work has now stopped on the project. Future plans are unclear.

3.5.1.4 BBC

A 10-25 kg/h unit was constructed to investigate the reactor parameters of surface temperature and gas/vapour product residence time and particle size. Although the unit was built to pyrolyse tyres, it is capable of using wood, MSW and other similar materials as a feedstock. Limited details of the continuous ablation reactor are available (15). Particles up to 6 mm have been used with liquid recovery in a two stage direct liquid quench of the product vapours with recycled liquids after char removal in a high temperature cyclone. Liquids are collected in a sump tank and are returned to quench the hot vapours via a water cooled heat exchanger. Liquid yields of 54% have been obtained from tyres at 470-540°C at 0.88 s residence time and 1.3 mm size particles (16). A 35-50 t/d plant has been built in Nova Scotia where it is operating successfully with combustion of the raw product gas and no liquids collection.

3.5.1.5 University of Waterloo

This program was initiated in 1979 with the main objective of establishing conditions for maximising liquid yields from biomass, particularly from forest materials. The University of Waterloo can be credited with the foundation of modern fast pyrolysis and their research is probably the most extensively published and publicised in this area. Two fluid bed reactors are used of 100 g/h and 3 kg/h. The results from these units were used to design a 200 kg/h unit for Union Electrica Fenosa in Spain as described below. Temperatures of 400-700°C have been examined with a wide range of feedstocks, pretreatment methods, various inert and reactive gases and some work on in-bed catalysts. The fluid beds were designed in a blow-through mode to entrain the char from the bed while retaining the sand hence there is no need for sand circulation or replacement. The highest yields of total liquid product are around 70 wt% on dry feed and are typically obtained at temperatures around 500°C.

3.5.1.6 Worthing Industries

A 200 kg/h fluid bed reactor derived from the University of Waterloo work was originally constructed in 1986 by Encon for wood and peat pyrolysis. The unit was constructed on the back of a trailer for transportation to test sites for demonstration. This is now used for processing old telegraph poles . These have their outer skin of treated wood removed and which is then pyrolysed in a 50 kg/h fluid bed pyrolyser for recovery of chemicals including creosote and PCP as well as bio-oil. Up to 30,000 poles per year are processed. The skimmed poles are re-treated and recycled (17).

3.5.1.7 Other activities

More fundamental studies are being carried out in several laboratories including the University of Hawaii (18) and the University of Montana (19).

3.5.2 Europe

In Europe the situation is more varied but less developed with only one substantial pilot plant. Most interest has been stimulated by the EC JOULE and AIR programmes over the last 8 years.

3.5.2.1 CPERI (Greece)

A small fluid bed reactor has been operating for several years to provide pyrolysis liquids (20) from which phenols and related chemicals are recovered for production of oxygenates such as methyl aryl ethers for use as gasoline additives (21).

3.5.2.2 The Centre for Renewable Energy Sources (CRES) and the Agricultural University of Athens (Greece)

A circulating fluid bed fast pyrolysis system has been designed, built and commissioned. Fast pyrolysis is carried out in the riser of a CFB using reheated sand and hot combustion products from burning char in a bubbling fluid bed at the base of the riser (22).

3.5.2.3 Egemin (Belgium)

This 200 kg/h capacity entrained downflow system was commissioned in 1991 and operated at up to around 50 kg/h giving liquid yields around 45% wt. (4). It was closed down permanently in 1992 due to unpromising results from the unit and lack of further support from the EC. It is unlikely to be restarted.

3.5.2.4 ENEL (Italy)

A contract has been signed to purchase a 650 kg/h Ensyn RTP-III plant (transported bed reactor) employing recycle gas (23). This will be commissioned around September 1995. The bio-oil product will be tested in a variety of applications including firing in a power station boiler, upgrading by hydrotreating and firing both an engine and turbine.

3.5.2.5 INETI (Portugal)

A 100 mm diameter fluid bed has been operated for fast pyrolysis at feed rates of 0.18 to 0.6 kg/h. The maximum total liquid yield at 500°C from pine was 51% which increased to 55% at 600°C. The liquid had characteristics similar to those from other fast pyrolysis systems. Tests have also been carried out on a 300 mm square fluid bed (24). Work is continuing on co-pyrolysis of biomass with plastics (25).

3.5.2.6 Union Electrica Fenosa (Spain)

Union Fenosa have successfully scaled up the Waterloo fluid bed process to 160 kg/h and this has been operating successfully since September 1993 producing around 400 kg/month (26). Total liquid yields of 55% wt on dry feed at 15% water are being achieved which continues to increase as the liquids recovery section is improved (3). Concepts have been announced for units up to 2 t/h (26)

3.5.2.7 University of Aston (UK)

An ablative plate pyrolyser has been successful designed, built and operated at capacities up to 3 kg/h giving liquid yields up to 80% wt on dry feed (27). This will be further developed to establish design and performance prediction models as well as producing liquids for testing and chemicals recovery. A small conventional fluid bed has also been commissioned. Work on chemicals extraction and production has recently started including studies on catalytic pyrolysis.

3.5.2.8 University of Leeds (UK)

Fixed and fluid bed pyrolysis has been carried out on biomass and wastes with catalytic upgrading of the products in the fluid bed work including co-processing with methanol. The fluid bed pyrolysis reactor is externally heated and nitrogen is used as a carrier gas (28). The maximum yield of liquid was 58.8 wt%, obtained at 720°C. Detailed analysis of the liquids by SEC, FTIR have been performed. A dual fluid bed has been used to pyrolyse biomass in an externally heated 75 mm diameter bed, 1 m high with nitrogen as the fluidising gas. Part of the reactor freeboard was packed with ZSM-5 catalyst and a secondary fluid bed has also been used for zeolite upgrading. Liquids were collected before and after pyrolysis for comparison.

3.5.2.9 University of Sassari (Italy)

Work has been recently carried out on fast pyrolysis of Euphorbia in a 6 g/h externally heated fluid bed microreactor. A maximum total liquid yield of 44 wt% was obtained at 500°C (29).

3.5.2.10 University of Twente (Netherlands)

An ablative pyrolysis reactor was developed based on particles sliding over a heated rotating cone mixed with heated sand. Total liquid yields of up to 50 wt% were obtained at capacity of 7 kg/h (30). Work is continuing on development of the system to recycle the sand and char in associated fluid beds and a standpipe to provide a continuous system (31). A 50 kg/h unit has been sold to the University of Beijing in China and is due for commissioning early in 1995 (31).

3.5.2.11 Other

TGA studies are being carried out at the University of Zaragoza, Spain (32) and the Hungarian Academy of Sciences (18); free fall or drop tube experiments at RIT, Sweden (33); modelling studies at the University of Naples, Italy (34); bio-oil analysis studies at the University of Corsica, France (35) and UCL, Belgium (36); wire mesh pyrolysis at Imperial College, London, UK (37); waste wood fast pyrolysis at the Institute of Wood Chemistry, Hamburg, Germany; and waste pyrolysis at low temperature at the University of Cardiff, UK (38).

3.6 PYROLYSIS LIQUID CHARACTERISTICS

3.6.1 General properties

The crude pyrolysis liquid is dark brown and with low viscosity which approximates to biomass in elemental composition, and 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 (39, 40, 41124, 125, 126) and dissolved alkali metals from ash (124) may also be present .

The complexity arises from the degradation of lignin, cellulose, hemicellulose and any other organics in the feed material, giving a broad spectrum of phenolic and many other classes of compounds that result from uncontrolled degradation as described above. The liquid from fast or flash pyrolysis has significantly different physical and chemical properties compared to the liquid from slow pyrolysis processes which is more like a tar.

The primary liquid product is readily combustible and can be used directly, for example in boilers and kilns, or it may be subjected to further chemical processing to give a higher quality fuel or chemical product. The characteristics of the liquid and descriptions of the technologies for upgrading are summarised in Table 3.4 below.

Changes occur in storage due to moisture content changes which affects viscosity, oxygen absorption or reaction, polymerisation and other innate chemical inter-reactions. The effect manifests as changes, usually increases, in viscosity, and the extent and rate of change depends on the mode of production, particularly residence or contact time, feedstock, and conditions of storage. These effects have not yet been fully evaluated, but are being investigated.

Table 3.4 A - Wood Derived Pyrolysis Oils from Ensyn, Canada (127)

Physical property		Typical value		Probable range
Moisture content		20	%	12-25
pH 2.5			2.1-3.3	
Specific gravity		1.21		1.11-1.25
Elemental analysis (moisture free)				
	C	56.4	%	51-58
	H	6.2	%	5.1-7.1
	N	0.2	%	0.16-0.35
	S	<0.01	%	0.00-0.03
	Ash	0.1	%	0.03-0.30
HHV (moisture free basis)		23	MJ/kg	22.1-24.3
HHV as produced		19.3	MJ/kg	
Viscosity (@ 40°C)		51	cp	40-59
Kinematic Viscosity	@ 25°C	233	cSt	
	@ 40°C	134	cSt	
ASTM Vacuum Distillation	160 °C	10	%	
	193 °C	20	%	
	219 °C	40	%	
	Distillate	50	%	
Pour point		-23	°C	
Solubility	Hexane insoluble	99	%	
	Toluene insoluble	84	%	
	Acetone/acetic acid insoluble	0.14	%	

B - Typical Data for Comparison of Liquid Characteristics

	Ensyn (127) Flash pyrolysis	Waterloo (84) Flash pyrolysis	Alten (125) Slow pyrolysis
Moisture content	16%	18%	14.6%
pH 2.5	2.4	2.0	
Specific gravity	1.21	1.19	1.195
Elemental analysis (moisture free)			
C	56.4%	54.7%	61.9%
H	6.2%	6.4%	6.0%
N	0.2%	-	1.05%
S	<0.01%	-	0.03%
Ash	0.1%	-	1.5%
O (by difference)	37.1%	38.9%	29.5%
C/H ratio	9.1	8.5	10.3
HHV (moisture free basis)	23 MJ/kg		26.3 MJ/kg
HHV as produced	19.3 MJ/kg	16.3 MJ/kg	-
Viscosity (@ 40°C)	51 cp	40 cp	300 cp
Pour point	-23 °C	-	27 °C

3.6.2 Particulates

Particulate levels may be high from char and ash carry-over. Separation of solids and liquids is poorly understood with reliance placed on primary separation in the vapour phase downstream of the reactor before condensation. Efficient separation inevitably causes some condensation or precipitation and careful design is essential. Solid separation in the liquid phase is not believed to have been studied, but is very likely to be troublesome. However, it is clear that a fairly high level of charcoal can be assimilated in the liquid product, for example Alten reported up to 15% (126) although some lumpiness was evident in the bio-oil. Both char particle size and proportions will influence the liquid product quality. This is why research into char-oil mixtures could prove valuable.

3.6.3 Oxygen content

The oxygen content of the pyrolysis liquid is very high, at up to 40% wt. When produced from dry or low moisture content feeds it typically has a heating value a little below that of the biomass feed in the range 16 - 20 MJ/kg depending on moisture content (around 22-23 MJ/kg on a dry basis). The oxygen content arises from the wide range of oxygenated compounds including phenols and polyphenols, which are one of the chemical products that can be recovered as a valuable fraction (119).

3.6.4 Water

Water is variously claimed to be completely miscible at up to 30% or 55% by weight of total liquid, above which an aqueous layer separates. Any water that does separate must be carefully managed as it will be heavily contaminated with dissolved organics and require extensive treatment before disposal. Utilisation and consideration of oil on a "wet" basis, therefore, seems to be more sensible. An alternative approach is to condense the liquids at a temperature above the dew point of water i.e. above about 110°C. This has been used successfully by Bio-Alternative in their continuous carbonisation unit (128) but produces a very dirty gas which has to be burned or incinerated immediately. Roy has also used this approach to preferentially separate fractions from his vacuum multiple hearth pyrolyser (129), and early work at Waterloo also employed hot and cold water condensers (18). Indirect cooling has the disadvantage of increasing the residence of the vapour at temperatures where further reaction can still occur, thus impairing the product quality and yield. As processes increase in scale, this effect would become more pronounced. The current approach is for rapid quenching of the total product stream for maximum recovery of the liquid fraction

Water content is important as it has several effects: it reduces the heating value, affects the pH, reduces the viscosity, influences both chemical and physical stability, reduces potential pollution problems from waste water disposal and could affect subsequent upgrading processes (130). The interactions are poorly understood. The water is difficult to measure and remove, since evaporation or distillation at normal temperatures of around 100°C can cause significant and potentially deleterious physical and chemical changes in the liquid. Lower temperature drying is not successful due to the nature of the relationship between water and the organic component in which the water seems to be chemically combined, analogous to water of hydration.

A key feature of flash pyrolysis processes for liquids is that no discrete aqueous phase is produced as all the water of reaction and feed water is incorporated or dissolved in the product bio-oil. This water is thus incinerated when the oil is combusted, and there are no environmental or pollution implications.

From slow pyrolysis processes, however, water is produced in significant quantities of typically between 20 and 40% wt on the feed, depending on feed moisture content. If a liquid product is collected from slow or conventional pyrolysis units, then the maximum water load of the liquid product is around 20 % wt. Above this level a discrete aqueous phase separates. This water phase is highly contaminated with dissolved and suspended organics, with a COD of typically 150000 (125, 126). This therefore represents a major problem of disposal or utilisation. In the selection of the primary pyrolysis products this waste water must be considered. If biological treatment is not appropriate or too expensive, part of the heat of combustion of the products will be required for incineration of this heavily contaminated water fraction. A potentially more attractive alternative route than incineration is oil condensation above the dew point of water, i.e. about 110-120°C. The water then stays in the vapour phase and can be burned with the product gas (128). The pyrolysis gas should primarily be used for this purpose but this may not be enough in cases where the primary feedstock has a high water content and the gas is required for feed drying. Since slow and conventional pyrolysis is now only considered for charcoal production or for disposal of difficult wastes, this waste water problem is not significant in the context of bio-energy.

3.6.5 Stability

Polymerisation or deterioration of the liquid can be caused by temperatures above around 100°C which adversely affect physical properties such as viscosity, phase separation, and deposition of a bitumen-like substance. Heating the liquid to reduce viscosity for pumping or atomisation needs to be considered carefully and thoroughly tested, although in-line steam heating to 90°C has been used successfully in combustion trials (42). Exposure to air also causes deterioration, but at a slower rate than temperature increase. Maintenance in a sealed enclosure has been claimed to cause substantial pressure increases, so some minimal venting is necessary to avoid pressure build-up, but minimise exposure to oxygen. Pyrolysis liquid has been stored in this way in a useable form for up to two years without problems. Liquids produced from refuse/MSW appear to be much more unstable (119, 131, 132).

The low pH arises from the organic acid content (e.g. acetic and formic acids), and is therefore corrosive. Mild steel is not suitable for handling or storage. Polypropylene piping has been used to overcome this problem.

3.6.6 Other characteristics

Health hazards associated with pyrolysis liquids are also poorly understood. It has been claimed that these are no worse than coal tar or crude oil (133).

3.7 APPLICATIONS

3.7.1 Introduction

A summary of the opportunities for using pyrolysis liquids is included as Figure 1. Within Europe the most promising application is seen as 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 systems. There are believed to be substantial longer term opportunities for chemicals from either catalytic pyrolysis or extraction and recovery of chemicals from the liquid products which would enhance the overall economics of conversion.

This liquid product may be readily burned (3) and has been employed for this purpose (13), provided the viscosity is not too high (Huffman Interlaken). Preheating to reduce viscosity is not usually favourable due to thermal degradation of the bio-oil, although short term exposure to temperatures up to 90°C have not had any adverse effects. The water content can be considered an advantage both for the combustion process and because it reduces the viscosity of the liquid. Therefore the oil can be considered an outlet or disposal route for the pyrolysis water. Phase separation is only likely to occur at water concentrations greater than *50% in the case of flash pyrolysis oils which is unlikely to arise. Some precautions* may be needed in handling, storage and combustion due to the water and high oxygen content as described above.

Pyrolysis liquids are immiscible with any form of hydrocarbon liquid, and cannot, therefore, be expected to be assimilated into a conventional fuel marketing infrastructure without some conversion or upgrading to give a product that is compatible with conventional fuels. One alternative is to feed to crude pyrolysis liquid into a refinery for upgrading in orthodox refinery operations, utilising the hydrogen availability and blending opportunities (23). The basic problem with this approach is that bio-oil is immiscible with crude oil and creates handling problems. The alternative is to create a discrete pyrolysis liquids storage, distribution and utilisation system, that is managed by experts who understand the special problems of this fuel.

3.7.2 Combustion

Liquid products are easier to handle and transport in combustion applications and this is important in 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. Problems have been reported in handling the fuel with high viscosity and *suspended char causing atomisation difficulties and incomplete combustion with* some fuels. With recognition of the problems, solutions are unlikely to prove onerous.

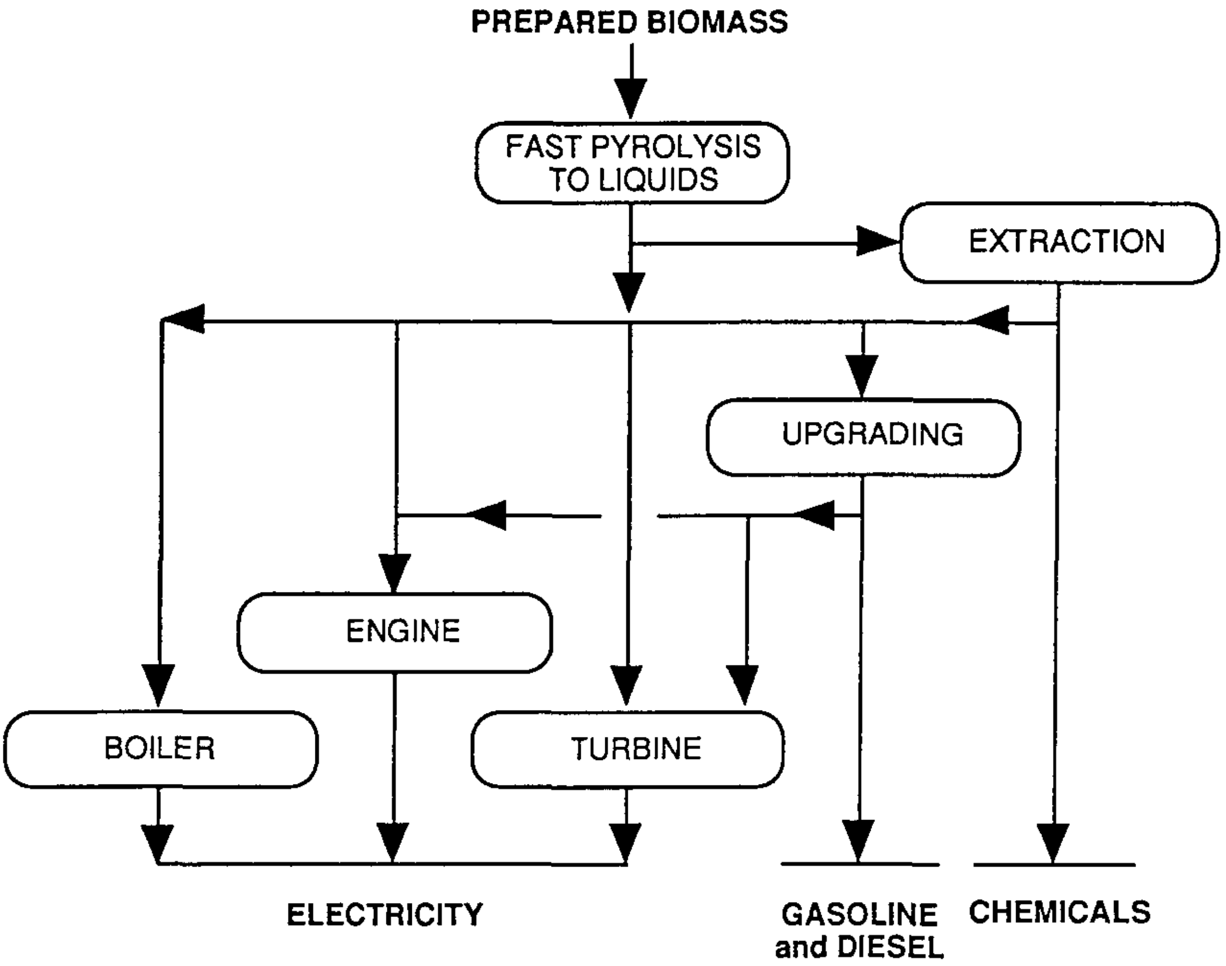

Figure 3.1 Application of Pyrolysis Liquids

3.7.2 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 which is illustrated later.

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 (43). 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. Gas turbine applications are also considered to be feasible although no work has been carried out in the last 10 years nor on fast pyrolysis liquids. However, a new project has recently been implemented to investigate this and this is more likely to be viable for larger scale applications (44).

3.7.3 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. The opportunities are described in Chapter 5

An integrated approach to chemicals and fuels production offers interesting possibilities for shorter term economic implementation. Chemicals that have been reported as recovered include polyphenols for resins with formaldehyde, calcium and/or magnesium acetate for biodegradable de-icers, levoglucosan, hydroxyacetaldehyde, and a range of flavourings and essences for the food industry. There are substantial problems to be overcome is 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 with a current market size of around US$ 10 million in North America and which could expand to US $ 40 million in 10 years. A similar market opportumity is believed for Europe (45).

3.7.4 Economics and efficiency

A key factor in the continuing development of fast pyrolysis processes to eventual commercial implementation is their economic viability. The current main interest in Europe is for electricity generation from biomass with the driving forces of environmental benefits, CO_2 mitigation, socio-economic benefits from re-deployment of surplus agricultural land, and energy independence. These have led to significant fiscal incentives being offered for renewable electricity in many European countries such as prices of up to 20¢/kWh in Italy and up to 14¢/kWh in the UK.

An indication of the performance and specific capital cost of various thermal conversion to electrical power technologies is summarised in Figures 3.2 and 3.3 below. This clearly shows the potential impact of a successful development of flash pyrolysis and engines on the cost of electricity production at smaller scales of operation (e.g. up to 10 MWe) since capital costs are similar for pyrolysers as gasifiers and the higher efficiencies will thus give lower production costs.

3.8 CONCLUSIONS

Fast pyrolysis is becoming more accepted as an emerging technology with commercial potential 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 still problems to be resolved but it is clear that considerable progress is being made in firstly identifying these problems and then finding and defining solutions. There are some interesting challenges to be faced in modifying the fast pyrolysis technology, in upgrading the liquids and adapting applications to accept the unusual behaviour and characteristics of the liquid product. International co-operation is one of the key routes to facilitate such developments and this needs to be encouraged as bioenergy is increasingly accepted as a potentially significant resource. Further research and development of the fundamental science which provides the tools for the design engineer to achieve the performance improvements is also required for successful exploitation.

Short term opportunities are likely to be in power generation due to the higher added value of electricity and the incentives available in several European countries. Chemicals will considerably enhance the overall economics but are further away in terms of development. It is important to remember that it may be more effective to modify the application to suit the liquid bio-oil than modify the liquid to suit the application.

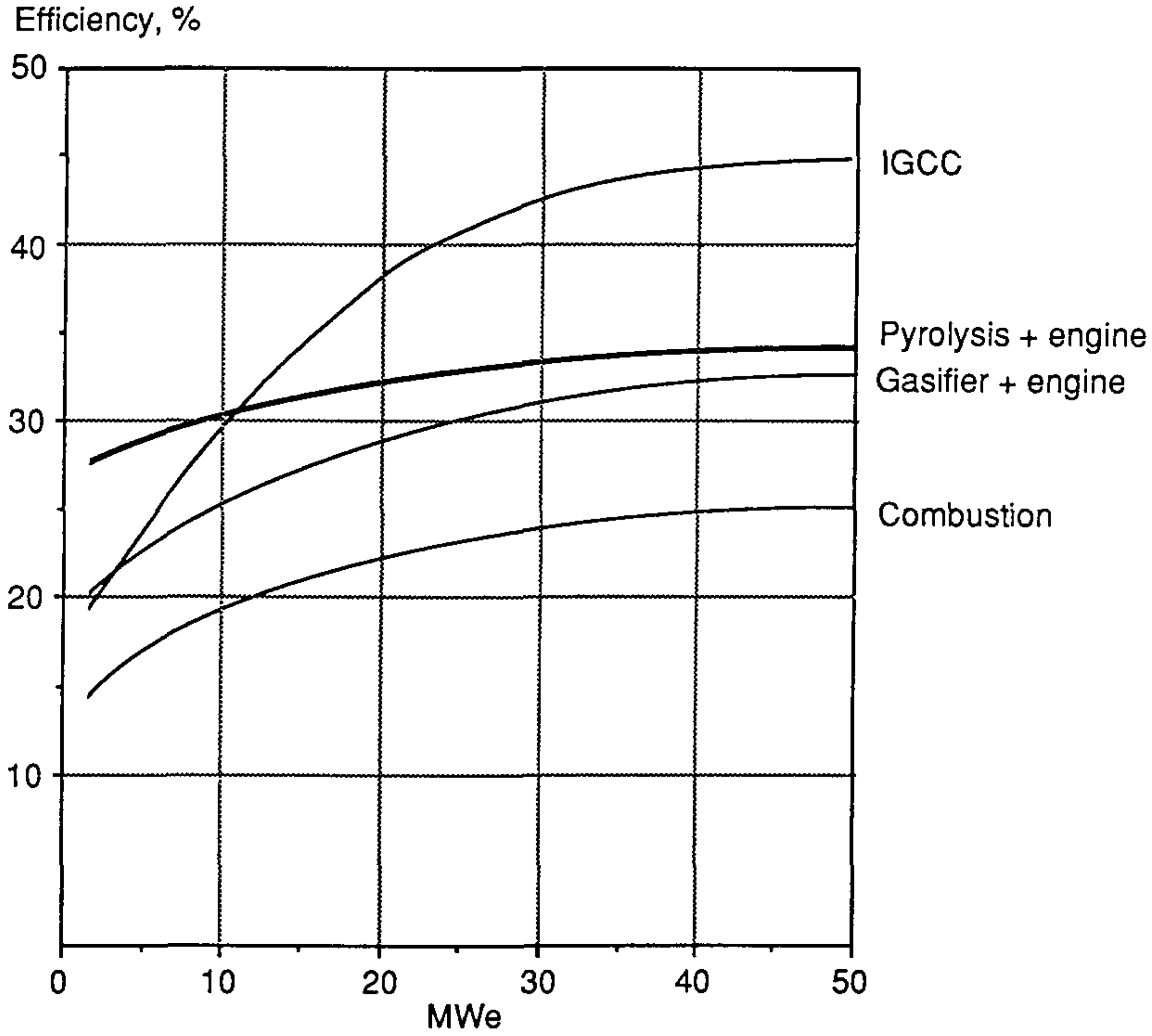

Figure 3.2 **Efficiency vs Size for Power Generation Systems (46)**

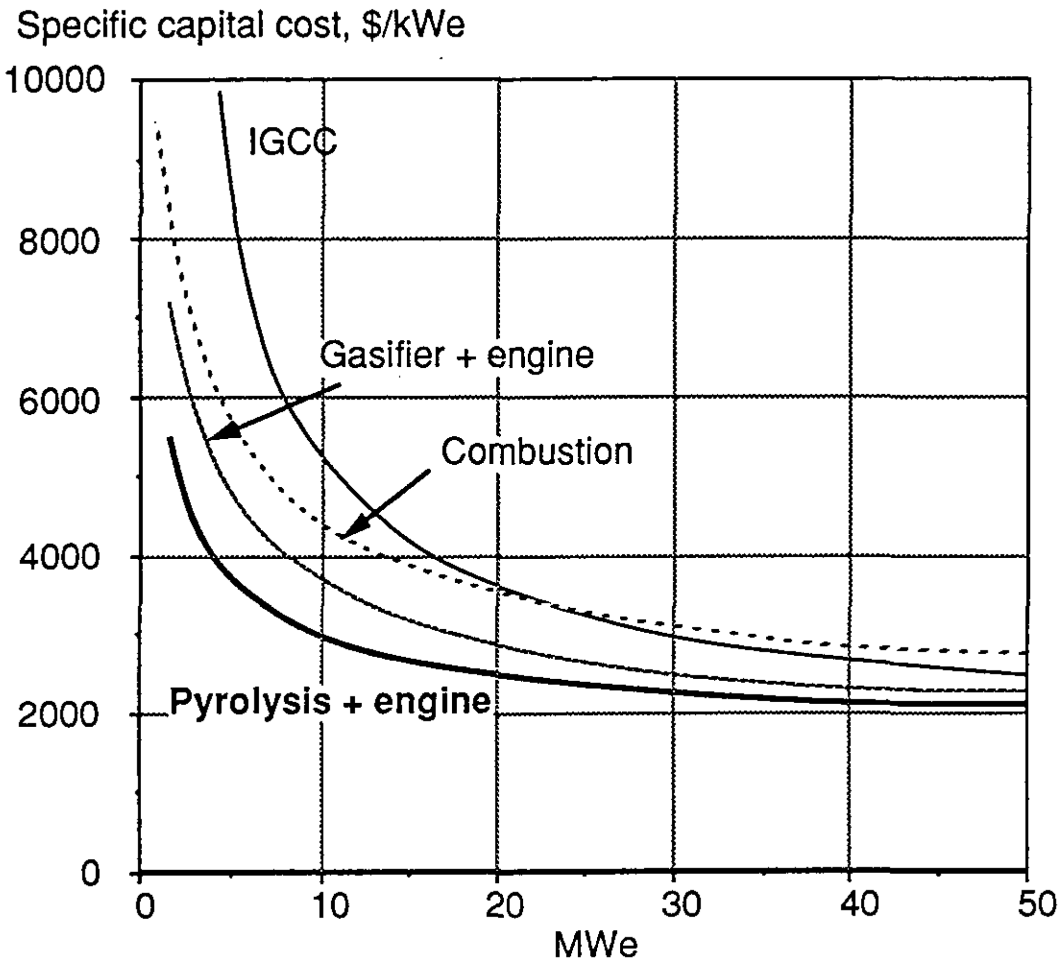

Figure 3.3 Specific Capital Cost for Power Generation Systems (46)

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CHAPTER 4
PYROLYSIS LIQUIDS PRODUCTION TECHNOLOGY

4.1 INTRODUCTION

In the descriptions of pyrolysis pathways and models in Chapter 3, it has been shown how a high yield of fast pyrolysis liquids can be obtained from an optimal combination of very high heating rates; vapour temperatures below about 600°C; very low vapour residence times; and rapid quenching of the resultant vapours. Although the three main products of gas, liquid and solid are formed, both the gas and char are minimised through careful control of temperature and residence time at typically 15-20% weight of the dry feedstock. There is an trade-off between reaction temperature and residence time that has not yet been explored. Higher temperatures with low residence times gives an olefin rich gas which caused much interest in the early developments of flash pyrolysis until it was found that the upper limit on olefin yield was too low to be of commercial interest.

The high temperature required for pyrolysis can be obtained in several ways:

- heating the gas-solid reacting mix through the wall of the reactor;
- heating with a heat transfer medium that may be gas such as preheated recycle gas, or liquid such as molten metal or molten salt;
- heating through exothermic chemical reactions inside the reactor such as partial oxidation;
- heating the particle directly through the wall of the reactor into an ablative pyrolysis.

In all cases the heat transfer mechanism and controlling step is significant in the design of the reactor, the performance of the reactor and its ability to be scaled up (1).

Since high liquid yields result from very high heating rates, low vapour residence times and moderate temperatures, the method of energy transfer has to be very efficient and well controlled. This imposes constraints on the particle size and method of heat transfer. The thermal conductivity of most biomass is relatively low and thus rapid heating of a sufficiently high proportion of the particle to achieve flash pyrolysis conditions and give high liquid yields imposes an upper particle size of 3 to 5 mm. Above this characteristic dimension, the rate of heat penetration into the particle becomes too slow to achieve high heating rates and also results in severe degradation of primary products as they diffuse back through the hotter outer shell of the pyrolysing particle.

This chapter is devoted to the major pyrolysis processes that have been developed from first principles into working processes, and that in some cases have achieved demonstration scale and commercial operation. Direct thermal liquefaction has been reviewed by Elliott et al. (2), and a review of pyrolysis processes for liquid production carried out by Bridgwater and Bridge (1). A survey of commercial and advanced technologies has also recently been published which includes pyrolysis as well as gasification (3).

4.2 CURRENT STATUS

4.2.1 Introduction

Before providing a detailed review of individual processes, the current situation is Europe is described and compared to that in North America.

4.2.2 Europe

Europe has only relatively recently become involved in direct production of liquid fuels from biomass. Up to 1989, a conventional (slow) pyrolysis demonstration plant of 500 kg/h was operated by Alten in Italy for liquid and char production with approximately 25% yield of each (4). The product was derived in relatively low yields from an undefined reaction system. It is likely that the product was at least partially secondary liquids due to the relatively slow reaction, probable high reaction temperature and long vapour residence time. Bio-Alternative in Switzerland operated a fixed bed carbonisation pilot plant fed with wood, waste and MSW for charcoal production with liquids as a low yielding by-product (5). Liquids were recovered in a direct contact scroll cooler with selective condensation of oil at around 120°C which gave low yields of secondary pyrolysis products that were also more tarry.

More recently, a 200 kg/h flash pyrolysis pilot plant based on the University of Waterloo (Canada) process has been constructed in Spain by Union Fenosa which started up in mid 1993 (6). Egemin in Belgium have built and operated a 200 kg/h entrained downflow pilot plant to their own design which started up in July 1991 and operated until late 1992 (7). ENEL are purchasing a 15 t/d Ensyn (Canada) RTPIII pilot plant to produce bio-oils for testing. All these processes and other exploratory studies sponsored by the EEC JOULE (8) and AIR programmes are included in Table 4.1 and described below.

4.2.3 North America

Fast pyrolysis of biomass was "invented" in North America around 1979 with early work being performed by NREL and the University of Waterloo. A number of commercial and demonstration plants for flash pyrolysis are operating in North America at a scale of up to 1000 kg/h. Ensyn (Canada) are marketing commercial flash pyrolysis plants of up to 4 t/h throughput which are offered with a performance guarantee and a number of conditional sales have been concluded (9). Interchem were building a second generation 1360 kg/h demonstration plant in Kansas based on the NREL vortex ablative pyrolysis process (10) but this is now understood to be shelved. There are other smaller scale activities at research and development scale which are listed in Table 4.1 and described later.

4.3 PYROLYSIS REACTORS

Types of pyrolysis reactors and the methods of heating employed are shown in Table 4.2. Configurations are basically similar to those employed in gasification although a wider range of unusual combinations and configurations have been devised. Key features of pyrolysis processes are the method of heating which was described and discussed in Chapter 3.

Table 4.1 Status of Pyrolysis Liquids Production Processes, 1995

Organisation	Country	Technology	Products	kg/h	Status
BBC/Castle Capital	Canada	Ablative	Fuel, Chemicals	2000	Operational
Interchem	USA	Ablative	Fuel, Chemicals	1360	Dormant
Ensyn Engineering	Canada	Transport	Fuel, Chemicals	1050	Operational
U. Fenosa/Waterloo	Spain	Fluid bed	Fuel	160	Operational
Egemin	Belgium	Entrained flow	Fuel	200	Shut down
Ensyn Engineering	Canada	Transport	Fuel, Chemicals	150	Operational
Ensyn Engineering	Canada	Transport	Fuel	80	Construction
GTRI	USA	Entrained flow	Fuel	50	Dormant
Bio-Alternative SA	Switzerland	Fixed bed	Fuel	50	Unknown
Laval University	Canada	Vacuum	Fuel, Chemicals	50	Operational
Schelde	Netherlands	Rotating cone	Fuel	50	Construction
WTC	Canada	Augur kiln	Fuel, Chemicals	42	Operational
NREL	USA	Ablative vortex	Fuel, Chemicals	36	Operational
CRES	Greece	Circulating bed	Fuel	10	Operational
Ensyn Engineering	Canada	Transport	Fuel	10	Construction
Tübingen University	Germany	Augur kiln	Fuel, Chemicals	10	Operational
Twente University	Netherlands	Ablative	Fuel	10	Operational
INETI	Portugal	Fluid bed	Fuel	5	Shut down
Waterloo University	Canada	Fluid bed	Fuel, Chemicals	3	Operational
Aston University	UK	Ablative	Fuel, Chemicals	3	Operational
University of Sassari	Italy	Fluid bed	Fuel	2	Operational
Leeds University	UK	Fluid bed	Fuel, Chemicals	2	Operational
Aston University	UK	Fluid bed	Fuel, Chemicals	1	Operational
CPERI	Greece	Fluid bed	Fuel, Chemicals	< 1	Operational
Colorado School M.	USA	Ablative mill	Fuel	< 1	Dismantled
Inst. of Wood Chemistry	Germany	Fluid bed	Fuel, Chemicals	< 1	Operational

Table 4.2 Pyrolysis Reactors, Heating Methods and Heating Rates

Reactor type	Method of Heating	Organisation
Ablative cone	Wall heating	U. Twente
Ablative mill	Wall (disc) heating	CSM
Ablative plate	Wall heating	U. Aston, U. Nancy
Ablative vortex	Wall heating	NREL, Interchem
Auger kiln	Wall heating	U. Tubingen, WTC
Circulating fluid bed	Partial gasification	CRES
Cyclone or vortex	Wall heating	See *Ablative vortex*
Entrained flow	Combustion products	Egemin, GTRI
Fixed bed	Combustion products	Bio-Alternative
	Partial gasification	Alten §
Fluid bed	Heated recycle gas	CPERI, INETI, NREL, Union Fenosa U. Aston, U. Leeds, U. Sassari, U. Waterloo,
	Partial gasification	Alten §
	Fire tubes	MTCI ¶
Horizontal bed	Fire tubes	Pyrosol*, AEI*, Wastech*
Multiple hearth	Hearth heating	U. Laval
Rotary kiln	Wall heating	Babcock*, KWU*, PKA*, Stenau*
Rotating cone	Wall and recycled sand	Schelde + U. Twente
Stirred bed	Partial gasification	Alten §
Transport	Hot sand	Ensyn

NOTES: * Solid waste processing, not liquids production; ¶ Gas production

The organisations currently involved in fast pyrolysis for production of primary liquids are listed alphabetically in Table 4.3 with an indication of the maximum capacity achieved to date. Each is summarised in the sections below. Figure 4.1 shows how the maximum size of installed plant has grown steadily since pyrolysis was discovered around 1979, and forecasts major plant installations by 2000.

Table 4.3 Organisations Currently Involved with Fast Pyrolysis for Liquids (as at January 1995)

Organisation	Process	Country	Highest capacity dry kg/h feed achieved
BBC	BBC	Canada	2000
Castle Capital	BBC	Canada	2000
CPERI	CPERI	Greece	1
CRES	AUA/CRES	Greece	8
Ensyn	Ensyn	Canada	1050
NREL	NREL	USA	35
Red Arrow	Ensyn	USA	1050
Schelde	U. Twente	Netherlands	10
Stenau	U. Tubingen	Germany	1000
Union Fenosa	U. Waterloo	Spain	160
University of Aston	U. Aston	UK	3
University of Athens, Agricultural	CRES/AUA	Greece	8
University of Laval	U. Laval	Canada	50
University of Leeds	U. Leeds	UK	2
University of Tubingen	U. Tubingen	Germany	10
University of Twente	U. Twente	Netherlands	10
University of Waterloo	U. Waterloo	Canada	3
Wastewater Technology Centre	U. Tubingen	Canada	42
Worthing Industries	Worthing	Canada	200

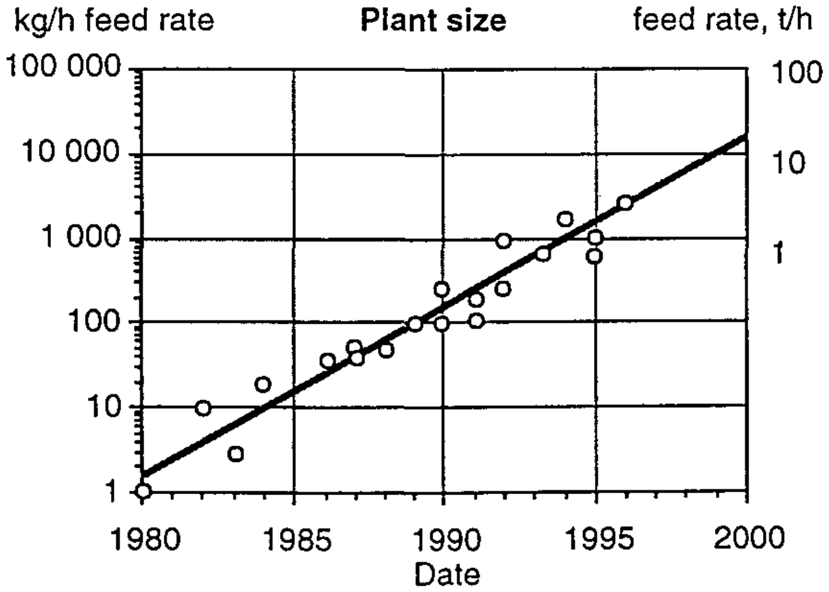

Figure 4.1 Growth in Size of Fast Pyrolysis Plants

4.4 GENERAL PROBLEMS

4.4.1 Feed problems

Fast pyrolysis requires high heating rates. As biomass has a low thermal conductivity, high heating rates throughout the particle either result from small particle sizes or erosion of the char product from around the particle as it pyrolyses as occurs in ablative pyrolysis (see Chapter 2 and 3). The current view of the maximum size feasible for fluid bed or circulating fluid bed or entrained flow reactors for giving high yields of liquids is 6 mm. The exception is ablative pyrolysis which is a surface area controlled process and has no upper size limit as the char layer is constantly eroded or abraded away. This upper particle size limitation for most processes thus carries a cost and energy penalty to grind the feedstock. Some biomass forms exist in a stringy form which cannot be ground in conventional milling equipment. Chopping or slicing mechanisms may work, but extensive testing is needed to evaluate alternative comminution processes. Low bulk density feeds give handling problems and fluidisation problems in bubbling fluid bed reactor systems. Feed that is pretreated such as by acid washing has reduced mechanical strength and gives high fines level which can result in higher solids levels in the product.

As all the feed moisture appears in the product together with all the reaction water, the feed has to be dried to as low a water content as possible. Practically this limit is around 10% moisture. At normal high yields of liquids of 60 to 65 % on a dry liquid basis, the reaction water contributes about 15% moisture to the wet product from a bone dry feed. Each 1% moisture in the feed adds approximately a further 1.25% moisture to the product oil on a wet basis. Drying to much below 10% is generally considered too expensive as well as significantly increasing the fire and safety hazards from handling very dry materials. Forced drying is probably the most expensive pretreatment operation for the feedstock from most primary energy crop sources.

High lignin feeds give higher viscosity products that are also more "sticky" due to the presence of higher levels of partially depolymerised lignin. Optimisation of the time-temperature processing window may improve the product quality and a small sacrifice in yield may be more than compensated for a significant improvement in quality or properties. Resinous feeds give analogous product handling problems from tar products resulting from resin degradation.

All biomass contains some ash, usually appreciable quantities of alkali metals which report to both the char and the liquid. This is compounded by the presence of char in the liquid from incomplete char removal in orthodox cyclones. Although developments are in hand to filter char out in the vapour phase, analogous to hot gas filtration in gasification processes, a proven system is not yet available and preliminary results have suggested that product yields may be adversely affected from the higher vapour residence times.

4.4.2 Processing problems

Heat transfer rates are considered by some researchers to become problematical at large biomass capacities, particularly for ablative pyrolysis which is a surface area controlled process rather than a volumetric process.

Condensation of bio-oil vapours is a known problem. Cooling is not generally difficult but rather the collection of the cooled aerosol. Stable tar aerosols are formed which pass readily through the condensers and require special handling. Direct quenching in hot product oil has been used by Bio-Alternative, and also by Alten in their washing system when cooled separated product water was recycled through a packed tower. NREL and Ensyn also use direct contact with product liquid to aid collection. Electrostatic precipitators are known to work well.

Pretreated feed is claimed to give a "sticky" char product which agglomerates, sometimes in the reactor and sometimes in the downstream equipment causing build up of char-oil cakes resulting in eventual blockage. Another phenomenon is the partially depolymerised lignin which will tend to have a much higher viscosity than cellulose and hemicellulose degradation products. If this is condensed or collected in preference to other constituents due to inadequacies in the design of the liquid cooling and collection system, then blockage may again result. As high temperature char residues encourages product cracking, any char must be removed as it is formed and not allowed to be recycled or remain in contact with the vapours.

Most reactor systems (see Table 4.2) are based on orthodox fluid bed, circulating fluid bed or entrained flow reaction systems and are thus, in principle, able to be designed and operated in conventional ways. It is only the ablative type of reactors that tend to be unique to biomass.

4.4.3 Product problems

The known problems with the liquid product that may require attention are suspended char, high viscosity, alkali metals, and potential inhomogeneity of the oil. The more significant are discussed below while a more comprehensive summary is given in Table 4.4.

4.4.3.1 Char

Direct combustion of the bio-oil is probably the least demanding application and a variety of tests have established that combustion does not present any significant problems. Some problems to date include char particles which cause filtration and pumping problems, atomisation problems and "sparklers" in combustion giving poor burn-out rates and high viscosity which contribute to the handling and pumping problems. More severe problems can be anticipated with atomisation for injection into turbines and engines where precise control of flow rates is essential.

The optimum solution to char suspensions interfering with bio-oil injection and atomisation is to reduce it at source in the vapour phase before condensation. Some success has been achieved with this approach by Ensyn, but only for limited periods of time. There is clearly considerable potential for development in this area.

Char filtration from the liquid bio-oil is known to be difficult due to the nature of the suspension, the high viscosity and the unusual relationship between the char and heavier components of the bio-oil. Dilution with water adversely affects heating value and may cause phase separation. Addition of diluents such as methanol or ethanol reduces viscosity and improves filterability but at a financial and energetic penalty. Heating is not advisable due to the temperature sensitivity of the bio-oil with some changes occurring at around 50°C and significant modification of the oil above 100°C. Pressure filtration is effective for short periods but costly due to the unusual relationship between the char and heavier components of the bio-oil, and may result in unacceptably high bio-oil losses.

Table 4.4 Characteristics of Bio-oil and Methods for Modification (11)

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.
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 > 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.

There are complementary measures that may be taken such as reduction of the injection pressure into the boiler or engine/turbine, thus creating a less arduous environment and greater tolerances for the injector system. This will require careful matching with the atomiser and application characteristics. Also as application size increases, this problem reduces as more bio-oil is required to be injected and nozzles are increased in diameter.

4.4.3.2 High viscosity

This problem can be addressed as above by dilution with a lower viscosity solvent but with the same problems as above. Higher temperatures cannot be used as explained above also. The use of lower injector pressures will increase the problem of high viscosity, thus emphasising the need for system optimisation. This aspect is assigned a substantial part of the budget to allow for purchase of suitable expertise with design and test facilities in order to provide the most cost effective solution of unforeseen problems. As for the char problem, as application size increases, this problem reduces as more bio-oil is required to be injected per cycle.

4.4.3.3 Alkali metals

There is a small but finite amount of alkali metals in bio-oil from the wood ash. Some is in solution as, for example, acetates, while some is bound in with the char. Char removal will, therefore, contribute to reducing the alkali metal problem although there are problems with filtration as described above. It is not clear what will happen to these contaminants in applications. If used in an engine, they may deposit in the engine or be blown out. One possibility is that a suitable lubricant will flush any deposits into the sump where they can be dealt with during routine maintenance or by continuous in-line treatment. Turbines have more exacting requirements but required and achievable tolerances have not been determined.

4.4.3.4 Inhomogeneity of the bio-oil

Flash pyrolysis oils produced at low vapour residence times may suffer from a sort of phase separation when the lignin has not been fully depolymerised resulting in a sludge which can separate out with some char on prolonged storage. This problem becomes particularly acute in filtration of the oil when the pyrolytic lignin forms a sort of gel or jelly which rapidly and completely blocks the filter medium. It is possible that this problem can be mitigated or largely resolved by careful control separation, by homogenisation of the liquid or by the use of suitable additives.

4.4.3.5 Environmental problems

One of the main justifications for the development of bioenergy applications is the positive contribution made to the environment. It is therefore important that the process operates in an environmentally acceptable way and that the environmental risks are minimised. Surprisingly little attention has been paid to any environmental aspect of biomass conversion either in terms of wastes and their management or disposal (12), or as an overall audit of the environmental implication or consequence of constructing such a system (13).

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CHAPTER 5
FAST PYROLYSIS PROCESSES

This chapter contains a description of the significant research, demonstration and commercial processes that are based on fast pyrolysis for production of liquids. The list is alphabetical and is summarised in Table 5.1. Dormant or dismantled or abandoned processes are only included if there is useful information available.

Table 5.1 Activities in Fast Pyrolysis for Liquids Production

Sect	Organisation	Country	Technology	Status
5.1	Alten	Italy	Fluid or stirred bed	Dismantled
5.2	BBC	Canada	Ablative	Operational
5.3	Bio-Alternative SA	Switzerland	Fixed bed	Unknown
	Biomass Technology Group (BTG)	Netherlands		see UNIVERSITY OF TWENTE
	Castle Capital	Canada		see BBC
5.4	Colorado School of Mines	USA	Ablative mill	Dismantled
5.5	CPERI	Greece	Fluid bed	Operational
5.6	CRES	Greece	Circulating bed	Operational
5.7	Egemin	Belgium	Entrained flow	Shut down
	ENEL	Italy		See ENSYN
5.8	Ensyn Engineering	Canada	Transport	Operational
5.9	GTRI	USA	Entrained flow	Dormant
5.10	INETI	Portugal	Fluid bed	Shut down
5.11	Institute of Wood Chemistry	Germany	Fluid bed	Operational
5.12	Interchem	USA	Ablative	Abandoned
5.13	NREL	USA	Ablative vortex	Operational
	Red Arrow	USA		see ENSYN
	Schelde	Netherlands		see UNIVERSITY OF TWENTE
5.14	Stenau	Germany	Rotary kiln	Operational
5.15	Union Fenosa	Spain	Fluid bed	Operational
	University of Athens, Agricultural	Greece		see CRES
5.16	University of Aston	UK	Ablative	Operational
5.17	University of Laval	Canada	Multiple hearth vacuum	Operational
5.18	University of Leeds	UK	Fluid and fixed bed	Operational
5.19	Univ. London Imperial College	UK	Heated grid	Dormant
5.20	University of Tubingen	Germany	Auger kiln	Operational
5.21	University of Twente	Netherlands	Rotating cone	Redesign
5.22	University of Waterloo	Canada	Fluid bed	Operational
5.23	University of Zaragoza	Spain	Fluid bed	Operational
5.24	Wastewater Technology Centre	Canada	Augur kiln	Operational
5.25	Worthing Industries	Canada	Fluid bed	Operational

5.1 ALTEN, ITALY

5.1.1 Introduction

Alten stands for Alternative Energy Technologies which was a consortium of KTI and Italenergie, but is no longer in partnership. The aim of this activity was to develop a small scale pyrolysis process to convert wood and agricultural wastes into marketable fuel products such as fuel oil, charcoal and char-water slurries. It was envisaged that a network of small pyrolysis plants would produce bio-oil to fire a 27MWe power station in Avezzano. The project is important for being the largest plant in Europe and for providing valuable data on process design, optimisation, and qualitative results. Substantial quantities of oil were produced for testing

The pyrolysis plant was in operation from 1985 to 1989, and was, and still is, the largest biomass pyrolysis unit that has been dedicated to bio-oil production in Europe. The design capacity of the plant was 1 t/h dry biomass, but only up to 500 kg/h has been achieved on a continuous basis. The nature of the process was that relatively slow pyrolysis occurred giving a secondary oil that had a low water tolerance and high viscosity. Although the product quality caused problems, the availability of large quantities of pyrolysis liquids for testing and evaluation caused serious attention to be focused on direct liquefaction for the first time in Europe.

5.1.2 Description

Figure 5.1 is a flowsheet of the process (1, 2). Feedstocks tested include wood chips, olive husks, straw and vine trimmings. The feed was screened, rechipped and dried in a rotary drier before entering the fluid bed reactor. The drying fuel was propane, but the product fuel gas would be used in a commercial venture. Air was added to the reactor to give a partial gasification reaction to provide reaction heat. This results in a poor quality, low heating value fuel gas. The reaction temperature and pressure are about 500°C and 1 atm respectively. The char formed is separated from the vapour stream in a hot gas cyclone. The char is cooled in a sequence of water cooled screw conveyors and stored in a silo. The reactor was not well defined - it was specified as a fluid bed, but seemed to behave more like a stirred bed. As the primary objective was the production of oil for testing, little instrumentation was available.

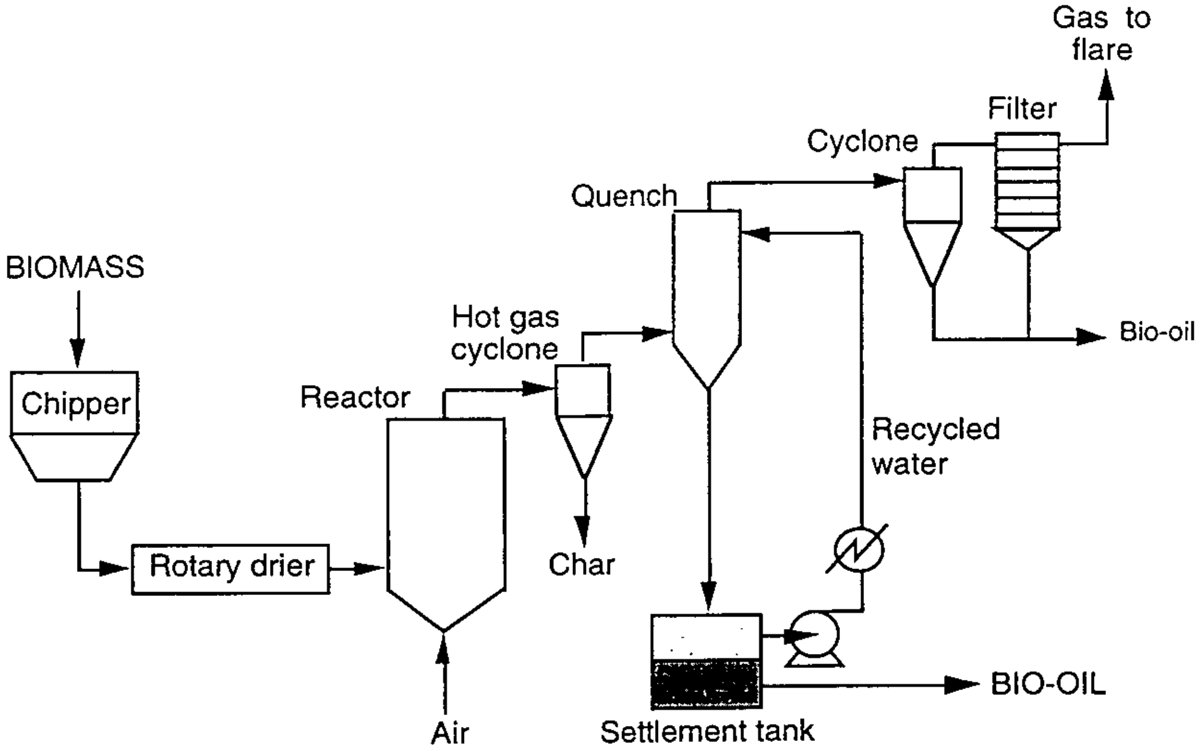

Figure 5.1 **Alten Flow Diagram**

The vapour and gas streams passed through a quench vessel where they were cooled and condensed by direct contact with recycle product water. The mixture of oil and water was separated in a settlement tank before sending the oil to storage and recycling the water through an air cooler. Excess water was removed to maintain a constant height interface in the settlement tank. The resulting water condensate had a very high COD at around 150000 and would require treatment. Further liquid was removed from the product gas in a cyclone and filter, before burning the gas in a flare. The gas from the drier was also sent to the flare to eliminate pollutants. The gas could be used internally as a fuel source for drying the feed or other process heat applications. A typical mass balance and energy output is shown in Table 5.2.

5.1.3 Products

The pyrolysis liquid was black and viscous and contained a significant proportion of charcoal of up to 15% by weight of the oil. This caused a "lumpy" texture in early samples. A typical pyrolysis liquid analysis and a gas analysis is given in Table 5.3. The char was a coarse powder with particle sizes ranging from 40-50 microns to several mm, similar to the size and shape characteristics to the feed.

Table 5.2 Alten Typical Mass Balance

Basis: 100 kg d.a.f. biomass feed

INPUTS	kg	OUTPUTS	kg	HHV, MJ/kg	% Energy
Dry biomass	100.0	Charcoal	20.5	29.7	32
Moisture	2.0	Bio-oil	20.5	26.3	28
Pyrolysis air	39.0	Fuel gas	100.0	4.1	32
		Losses	-		8
TOTAL	141.0	TOTAL	141.0		100

Table 5.3 Alten Typical Product Analyses

LIQUID		GAS		
Elemental Analysis (wet basis)		CO	27.6	% vol.
C (% wt)	61.90	CO_2	21.8	% vol.
H (% wt)	6.00	H_2	4.7	% vol.
N (% wt)	1.05	O_2	0.7	% vol.
S (% wt)	0.03	N_2	38.2	% vol.
O (by difference)	31.02	CH_4	4.7	% vol.
H/C ratio	1.16	C_2H_4	0.4	% vol.
O/C ratio	0.18	C_2H_6	0.3	% vol.
Moisture (% wt)	14.60	Others (by difference)	1.6	% vol.
Ash (% wt)	1.50	Higher Heating Value	5 MJ/Nm3	
Char content (% wt)	9.20			
Viscosity, cp @ 70°C	55	SOLID		
HHV, MJ/kg	26.3	Volatiles	15-20%	
Specific gravity (15/4 °C)	1.195	Higher Heating Value	29.5 MJ/kg	
		Empirical formula	$CH_{0.25}O_{0.07}$	

5.2 BIO-ALTERNATIVE, SWITZERLAND

5.2.1 Introduction

The objective of the process was charcoal production from which a by-product oil was derived by condensation of the vapours in the offgases. A continuous, 50 kg/h demonstration plant process was available in Switzerland and several commercial plants have been sold up to 2 t/h capacity. The oil from one of these units in Spain was successfully utilised in a local hospital boiler. This also supplied oil for testing across Europe at the same time that the Alten plant was operating and served to both encourage interest in direct production of liquid fuels as well as to cause concern about the quality of the oil and the problems in handling and use from high viscosity and water separation. The product was a secondary oil from the long vapour residence times and high formation temperatures and thus had a high viscosity and low water tolerance leading to phase separation in some samples.

5.2.2 Description

A flow diagram of the 100 kg/h pilot plant in Switzerland is shown in Figure 5.2 (2). Biomass such as wood, MSW, bark, sawdust, grape wastes, olive oil wastes and coconut shells, is comminuted and dried to a moisture content of 10 to 15 % before being fed to the top of the reactor from a feed hopper.

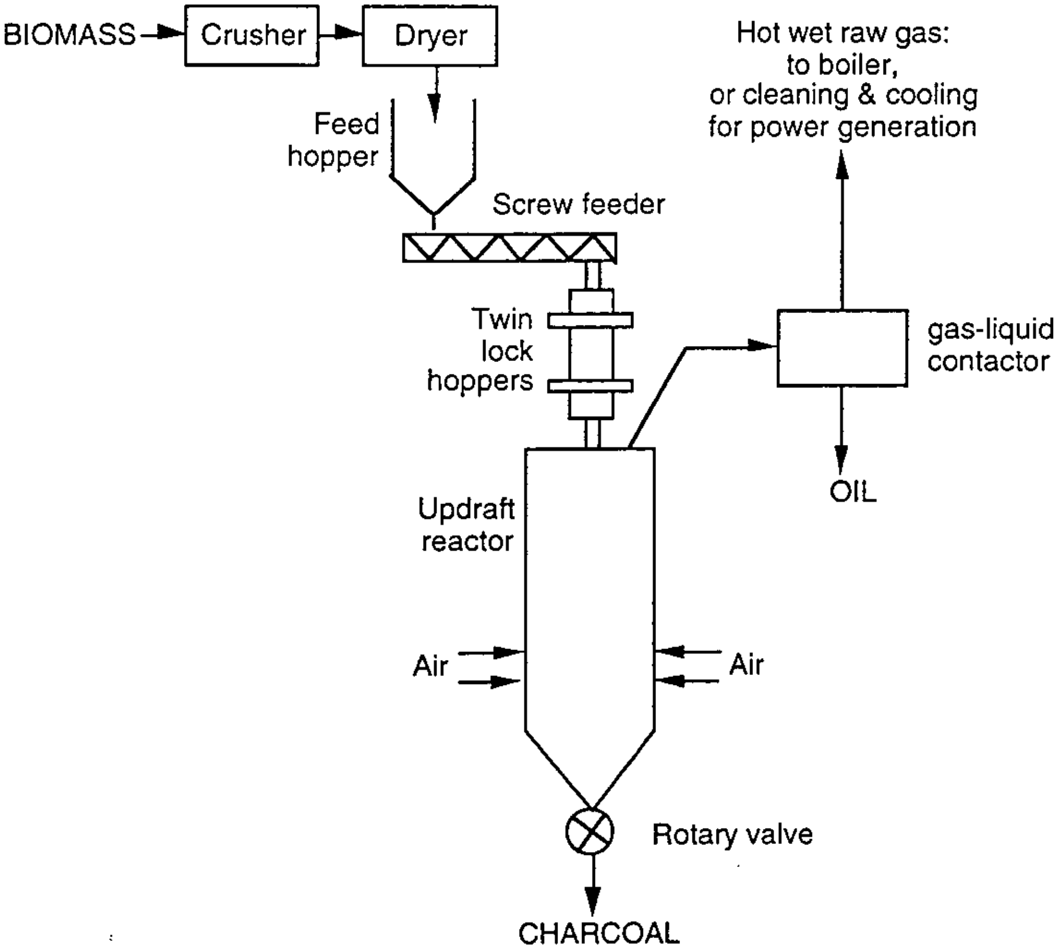

Figure 5.2 Bio-Alternative Pilot Plant Flow Diagram

The pyrolysis pilot unit was effectively a counter-current updraft partial gasifier for charcoal production. It comprised a vertical cylinder about 3 m high and 1 m in diameter. It was fitted with a interlocked twin feed hopper fed by screw feeder. A horizontal stirrer and a vibrator were used to prevent bridging of the feed in the reactor. The heat necessary for the reaction obtained was through internal combustion of part of the feed/char product, regulated by a system of air injection into the reactor through tuyeres.

Product gas left the top of the reactor at 120°C containing tar vapours and moisture. This was contacted with hot pyrolysis oil at 110-120°C which condensed the tar but left most of the water vapour in the gas phase. A sight glass was used to control the liquid level in the contactor and the excess liquid was periodically removed manually. The gas and water vapour were then burned in a boiler. As the oil is condensed at around 110°C, leaving most of the water in the vapour phase for combustion with the fuel gas, this solved the waste-water disposal problem associated with slow pyrolysis processes. Alternatively, the gas could be used for power generation. This requires further cooling by a heat exchanger to remove the water and tars present followed by filtration through a paper cartridge filter to remove tar traces. It was burnt in a 1.6 litre modified Ford engine coupled to a generator. Char was removed through a rotary valve at the base of the reactor and through a water cooled screw for storage in plastic bags or steel containers.

5.2.3 Products

The charcoal yield was typically 30% wt on dry feed which consistent with conventional carbonisation (1). The oil yield was typically 15% wt on feed with no phase separation. It has been successfully fired in a boiler without any problems. Properties of the oil and gas are summarised in Table 5.4.

Table 5.4 BASA Product Analyses [1]

LIQUID	Feedstock - Fir	Feedstock - Beech
Elemental Composition		
Carbon, wt%	58.12	55.10
Hydrogen, wt%	6.55	7.20
Oxygen, wt%	34.81	35.10
Nitrogen, wt%	0.52	2.00
Sulphur, wt%	-	0.6
H/C ratio	1.35	1.56
O/C ratio	0.45	0.47
Water content, wt%	4.5	14.0
Viscosity, cp	250 @60 °C	10 @70 °C
Net Heating Value, MJ/kg	22.2	20.9
Ash, % wt	< 0.05	-
pH	-	2.7
Density at 15°C, g/cm3	-	1.216

GAS	Typical	SOLID	
CO	16.3 % vol.	HHV	30.0 MJ/kg
CO2	13.2 % vol.	Volatiles	12-18 %
H2	7.9 % vol.		
N2	48.4 % vol.		
O and H/C	14.2 % vol.		
HHV	3.8-5.5 MJ/Nm3		

5.3 BBC, CANADA (CASTLE CAPITAL CORP., CANADA)

5.3.1 Introduction

This work was instigated to assess fast pyrolysis as an alternative method for tyres disposal. The primary objective was to demonstrate that short residence times and high heating rates could produce high yields of liquids from rubber. A 10-25 kg/h unit was constructed to investigate the reactor parameters of surface temperature and gas/vapour product residence time and particle size. The system is expected to be capable of using wood as a feedstock.

The process technology has been sold or licensed to Castle Capital who have installed a 1500 - 2000 kg/h plant in Halifax, Nova Scotia, using solid waste as feed. This operates at higher temperatures giving a gas product but can be modified to produce liquids. Little information is available on this plant.

5.3.2 Description

Limited details of the continuous ablation reactor [C.A.R.] are available from patent applications (3, 4). Ablation is achieved by sliding contact of the rubber particles on a hot metal surface. Tests on a 50 kg/h pilot reactor have demonstrated efficient heat and mass transfer and a smaller test unit is presently operating at a throughput of 10 to 25 kg/h. Particles up to 6 mm have been used with liquid recovery in a two stage direct liquid quench of the product vapours with recycled liquids after char removal in a high temperature cyclone. The system is shown in Figure 5.3.

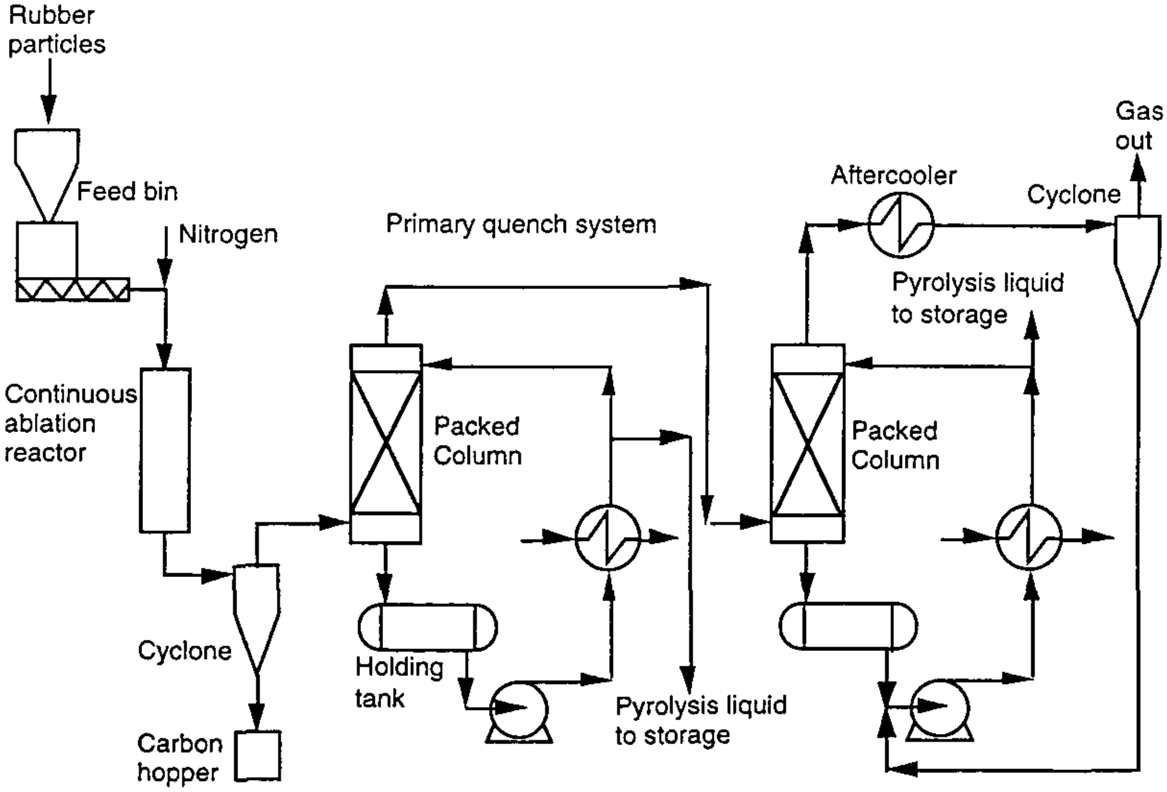

Figure 5.3 Black's Continuous Ablation Reactor System

Tyre rubber is used with a particle size of 1-3 mm. The feeder is mounted on load cells and comprises a pressurised lock hopper with a variable speed discharge screw which feeds the reactor. The reactor has staged external heating for zonal temperature control and catalysts can be added to the reactor.. Vapour product residence time in the reactor is controlled by the addition of nitrogen and are separated from the char and metal in a cyclone before quenching in a baffle plate column. Liquids are then collected in a sump tank and are returned to the column via a water cooled heat exchanger, with a proportion being pumped to storage. The first column is operated at 100°C exit temperature of the vapour/gas products. The second column is similar to the first with a final gas exit temperature of 40°C.

Problems have occurred during sustained periods of operation where the fine carbon black {< 3 µm} gradually made the recycled liquid in the first collection column too viscous to pump after 2 hours. Approximately 30% of the char formed was too fine to be efficiently recovered by the cyclone. A particle size analysis of the product char showed it all to be less than 10 µm. Modification of the system, which has not been detailed, allowed operation to be extended to 3 hours. Black proposes that the problem requires a liquids filtration solution, which may prove difficult in view of the particle size of less than 10 µm.

5.3.3 Products

Liquid yields of 54% have been obtained at 470-540°C at 0.88 s residence time and 1.3 mm size particles. Liquid composition and mass balances are given in Table 5.5 (5).

Table 5.5 Results for the BBC Continuous Ablation Reactor

(wt % of liquid), run Apr. 2b			
Benzene	0.135	Styrene	1.3
Toluene	0.95	Limonene	0.35
Ethylbenzene	0.24	Naphthalene	0.15
Xylenes	1.12	Total aromatics	26

Run Number		Apr. 2b	Apr. 2a	Apr. 1e	Mar 31d
Feed ash content (wt %)		7.1	7.1	7.1	8.8
Reactor Temp. (°C)		450	475	515	535
Residence Time (s)		0.925	0.965	0.881	0.925
Char		52.9	41.2	30.1	37.5
Liquid		39.1	48.1	54.3	50.2
Gas (inert free)		8.0	10.8	15.6	12.3
Gas composition (N_2 free basis)	H_2	0.22	0.00	1.05	0.41
	CO_2	5.25	8.11	4.47	6.65
	CO	0.00	0.00	1.66	1.84
	CH_4	9.96	10.45	16.23	9.97
	C_2H_4	16.26	16.48	20.17	12.79
	C_2H_6	4.60	6.41	5.54	7.71
	C_3H_6	11.49	10.39	11.95	7.88
	C_3H_8	1.63	1.01	0.95	1.79
	1-butene	26.52	22.87	16.87	26.32
	butadiene	15.37	14.07	12.33	14.36
	other C_4's	5.69	7.97	7.21	7.65
	C_5+	3.00	2.24	1.58	2.63

5.4 COLORADO SCHOOL OF MINES, USA

5.4.1 Introduction

The objectives of the work were to produce pyrolysis vapours for catalytic treatment as a parallel study to the ablative pyrolysis work being performed at NREL using the same principle of contacting biomass with a heated surface under conditions of high relative motion and applied pressure. The work was fundamental in assessing the requirements for ablation and preliminary yield data was obtained. The work is significant in establishing some of the basic work on ablative pyrolysis.

5.4.2 Description

Reed and Cowdrey constructed a "heat flux concentrator" initially to investigate ablative pyrolysis comprised of a drill press which forced and rotated wood dowels into a 1.2 cm diameter tapered hole in a heated copper block (6). The vapours produced emerged through 12 holes in the bottom of the block and were condensed and collected in traps and a gas burette. The temperature range used was 500-700°C and total liquid yields of over 50% on an as fed basis were obtained. The forced contact of the wood with the concentrator however caused the holes to be plugged after about 10g of wood was fed.

A "pyrolysis mill" was then constructed as shown in Figure 5.4 (7, 8, 9, 10, 11). This second reactor was designed using the principles of a conventional mill for grain (12). The pyrolysis mill consists of a stationary upper "stone" and a rotating lower "stone" which are both of copper and in contact with heaters. The lower plate is rotated at speeds up to 80 rpm, the pressure being controlled with a spring. The reactor wall is heated to 300-400°C to prevent pyrolysis vapour condensation inside the reactor. Wood particles enter the reactor through the upper plate and the vapours escape through the plate gap and then to a series of four liquid traps. Char and ash accumulate inside the reactor. Reed estimated the average heat flux in the first reactor to be 6.8 W/cm^2 and 5.08 W/cm^2 in the second reactor (13).

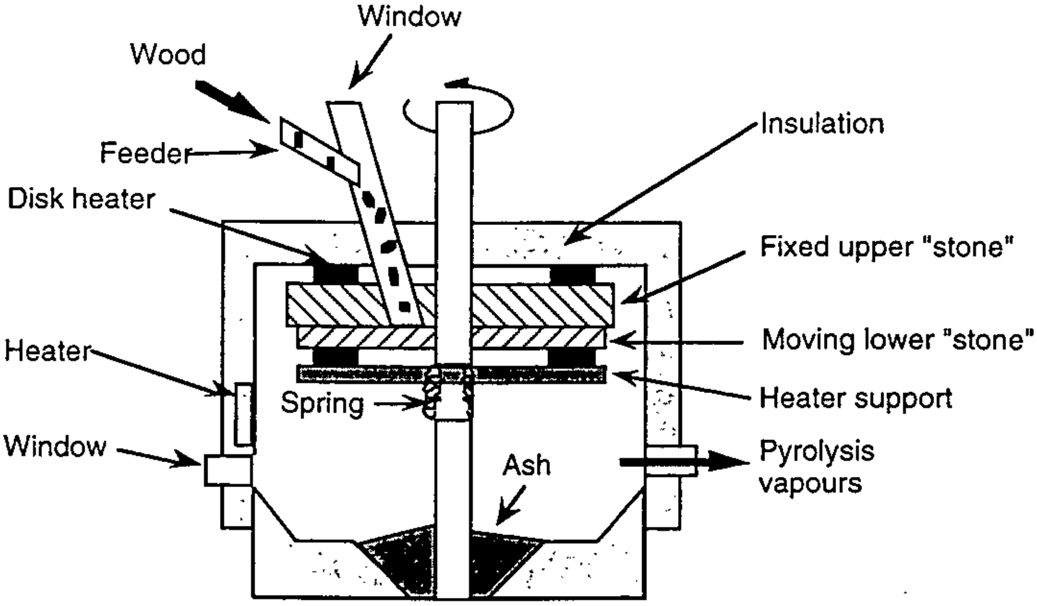

Figure 5.4 **Reed and Cowdrey's Ablative Pyrolysis Mill**

5.4.3 Products

Some results for the contact pyrolysis mill are presented in Table 5.6. Using this reactor system, total liquid yields of up to 54 % of liquid based on dry feed have been achieved. The only feedstock tested was bone dry wood. Feed rates of up to 0.2 kg/h were achieved with run times up to 1.5 hours.

One of the main problems was the escape of the pyrolysis vapours through the plates due to plugging of the holes in the disc. Unreacted feed and char remains in the hot reactor environment where it undergoes more conventional pyrolysis. Scale up of this system could be difficult. No vapour residence time values are quoted. Cowdrey did not take into account the variation of the wood decomposition temperature with heat flux and reactor heated surface temperature as discussed by Lédé in his design study (14). The concept is interesting, but the problem with using disks is that variable particle size causes processing problems due to disk spacing. Small particles will, therefore, not be under applied pressure and will more slowly carbonise on the hot plates. Relative motion between particles and *disk cannot be maintained as the particles tend to stick to one surface and not* move as intended. Ribbed disks did not solve the problem. No further work has been carried out or is planned and the reactor has been dismantled (15).

Table 5.6 Results for the Ablative Pyrolysis Mill

Run Number	105	106	107	109	110	111
Reactor Temp. (°C)	450	550	550	550	550	600
Throughput (g/h)	123.7	62.2	145.4	101.5	52.8	13.0
Char	58.3	31.5	14.1	18.0	16.0	5.5
Liquid	24.1	33.5	48.6	38.5	42.8	54.4
Gas (N_2/Ar free)	9.9	49.9	19.8	18.6	35.1	23.2
Gas composition (N_2/Ar free basis)						
H_2	8.50	1.03	0.00	1.82	0.00	2.95
CO_2	61.09	38.97	50.33	30.53	36.57	30.54
CO	29.29	45.99	40.3	48.92	47.15	44.39
CH_4	1.00	9.13	7.4	12.47	10.58	14.81
C_2H_4	0.00	0.09	0.00	0.12	0.00	3.11
C_2H_6	0.00	1.18	0.00	1.63	1.68	1.88
C_3H_6	0.11	0.95	1.58	1.32	0.41	1.71
C_3H_8	0.02	0.27	0.39	0.33	0.38	0.31
1-butene	0.00	0.20	0.00	0.25	0.32	0.30
C_4H_8	0.00	0.09	0.00	0.12	0.00	0.00

5.5 CPERI, GREECE

CPERI have been investigating the extraction and upgrading of phenolic components in fast pyrolysis liquids for several years. A small fluid bed pyrolyser has been operated to produce liquids (16, 17, 18) from which phenols are extracted then converted into methyl aryl ethers as possible fuel additives (19, 20, 21). The focus of the work has been in chemicals recovery and production and this is discussed in more detail in Chapter 6

5.6 CRES, GREECE

5.6.1 Summary

The Centre for Renewable Energy Sources, CRES, began a project on flash pyrolysis of biomass in spring 1990 as a consequence of the considerable European interest generated in direct production of liquid fuels from the work of Alten and Bio-Alternative. This was one of six activities started at the same time in the EEC JOULE programme (22) - the others were Egemin, INETI, Union Fenosa, University of Aston and University of Twente, all of which are described in this paper.

5.6.2 Description

The process has a nominal capacity of 10 kg dry wood per hour and is based on the principle that the by-product char from flash pyrolysis liquid production has to be used to provide process heat to drive the process. This is derived by burning the char in a conventional bubbling bed to heat sand which is then carried through a recirculating bed with the hot combustion gases to carry out flash pyrolysis in the riser section of the recirculating fluid bed (23). Instead of having two separate reactors as usually practised in steam and pyrolytic gasification processes, these are integrated into one vessel as shown in Figure 5.5. The design is in line with the recommendations of the IEA Bioenergy Agreement liquefaction group of integrating char combustion into the flash pyrolysis reactor.

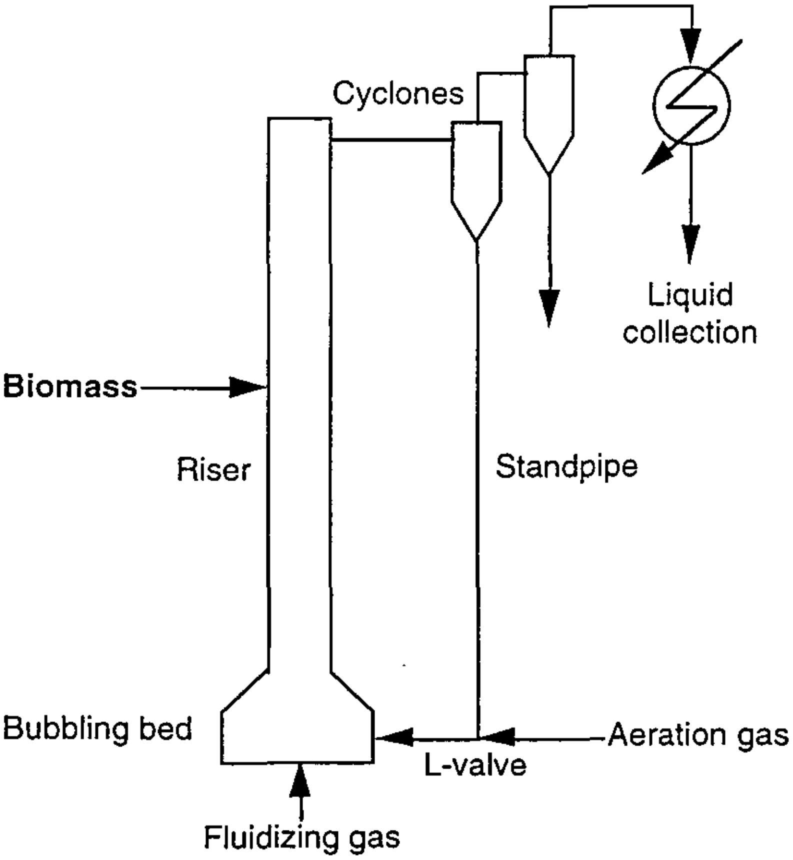

Figure 5.5 **The CRES Circulating Fluid Bed Flash Pyrolysis Reactor**

A cold model has been constructed to understand the hydrodynamics of the system and a hot unit has been built, commissioned and tested. Although some liquids have been produced, no reliable heat or mass balance data is yet available.

5.7 EGEMIN

5.7.1 Summary

The aim of this process was the production of bio-oil by the flash pyrolysis of fine wood particles in a 200 kg/h vertical, down flowing entrained flow pilot plant shown in Figure 5.6 (24, 25). The Egemin plant was commissioned in October, 1991, part funded by the EEC from the Joule programme. The research was finished in 1993 and the project was abandoned due to lack of funding and less promising results. A basic problem of this plant was obtaining a sufficiently high rate of heat transfer in the short residence time needed for high liquid yields. This was one of two entrained flow reactors that have been researched (with GTRI), and abandoned.

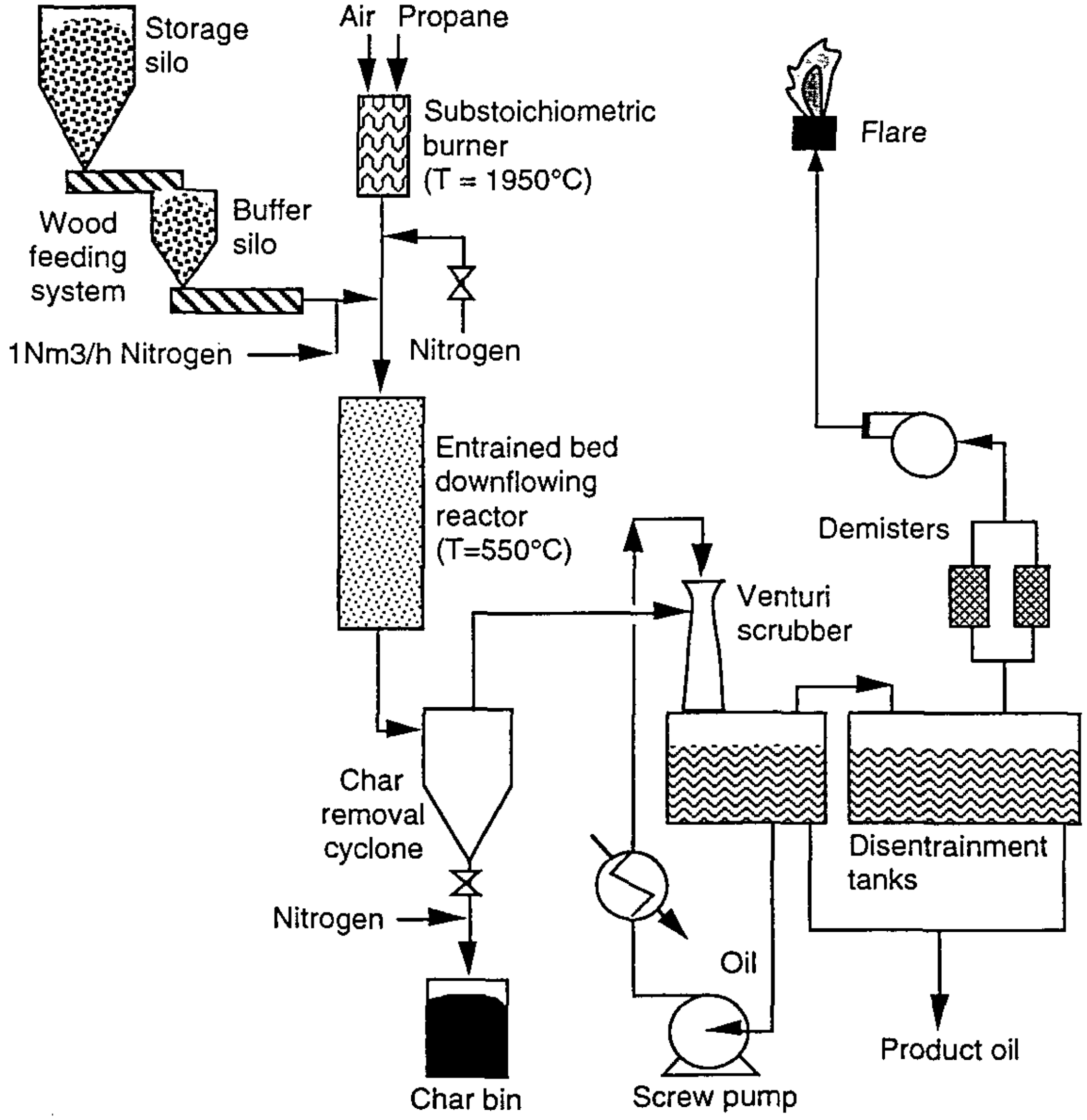

Figure 5.6 **Flow Diagram of Egemin Flash Pyrolysis Process** (3)

5.7.2 Description

The feed was small wood particles of 1 and 5 mm. The reported feed moisture and ash contents are 16% and 0.57% respectively. Wood was transferred from a storage silo to a small buffer hopper before being fed into the reactor using a water cooled screw auger provided with a nitrogen purge. Wood particles were entrained into the down flowing vertical reactor (height 1.2m, diameter 0.4m) in a stream of hot gas at between 700 and 800°C produced by a 90% substoichiometric burner fuelled by propane diluted with nitrogen to limit the temperature. The reactor was designed to give an average particle residence time of 0.6 seconds.

Pyrolysis products left the reactor at approximately 490°C and passed through a cyclone fitted with a nitrogen purge. The liquid products were separated by quenching in a venturi scrubber using product oil as the scrubbing medium. The vapour entry temperature to the venturi scrubber was approximately 400°C and the scrubber liquid exit temperature was 55°C during normal operation. The recycled oil was cooled with a water cooled heat exchanger. Mineral oil was used to start up the scrubbing system. The oil was allowed to accumulate in the disentrainment tank and was drained at the end of a run.

Approximately 75-80% of the oil product was collected by the venturi scrubber system and 20-25% was collected from the fan drain (see below). Gas separated from the liquid products left the venturi scrubber disentrainment tank through fibre mist eliminators using a downstream fan. The oil collected from the fan was highly viscous compared with the oil collected by the venturi scrubber system which may be due to water and volatiles evaporation or physico-chemical changes from the high shear forces. The non-condensable product gas was flared, but still contained up to 5% of the oil produced.

5.7.3 Products

A mass balance is given in Table 5.7. The gas mass flow rate was not measured and was obtained by difference. The bio-oil was collected from three points; the primary collection vessel, the secondary collection vessel and the drain at the fan.

Table 5.7 Mass Balance - Egemin Flash Pyrolysis Process (116)

	Mass flowrate kg/h	Yield %
Input		
Wood (dry)	84.0	-
Outputs		
Oil	33.5	39.9
Gas (by difference)	13.6	29.0
Char	24.4	16.2
Water	12.5	14.9

During the operation, a number of problems have been encountered which has lead to the disappointing yields. The feed was not completely pyrolysed, particularly at high feed rates in excess of 100 kg/h which needs to be compared to the design capacity of 200 kg/h. This is likely to be due to insufficiently rapid heat transfer to the particles in the short residence planned as almost all heat transfer is by convection. Smaller particles would help to reduce this problem. The hot partially pyrolysed wood continued to pyrolyse in the cyclone and char collection pot, potentially contaminating the primary flash products with secondary products. Egemin have suggested a recycle loop for the partially reacted feed which is analogous to the recycle loop in the NREL vortex reactor. Char carry-over from the cyclone collected in the liquid lines and caused blockages in the heat exchanger and pipework. Bio-oil separation from the non condensable gas was poor as suggested by the poor bio-oil yields achieved to date (Table 5.7). This is a common problem with most flash pyrolysis systems and conventional demisters do not appear to be effective.

An elemental analysis of the process products is shown in Table 5.8. The high quantities of hydrogen and oxygen in the char indicate incomplete reaction as discussed above

Table 5.8 Process Products - Elemental Analysis

	C		H		O		Ash		Total		HHV
	wt%	kg/h	wt%	kg/h	wt%	kg/h	wt%	kg/h	wt%	kg/h	MJ/kg
Bio-oil	0.39	13.3	0.08	2.7	0.53	17.4	0	0	1.00	33.4	18.04
Char	0.64	15.6	0.04	1.0	0.22	5.4	0.1	2.4	1.00	24.4	25.19
Gas	0.55	15.1	0.05	1.3	0.41	11.6	0	0	1.00	28.0	20.70
TOTAL		44.0		5.0		34.4		2.4		85.8	

5.8 ENSYN

5.8.1 Introduction

Ensyn's RTP technology evolved from the research on fast pyrolysis carried out at the University of Western Ontario in the early 1980s which had the main objective of employing fast pyrolysis to produce non-equilibrium chemicals such as ethylene and propylene . They are still the only commercial organisation selling fast pyrolysis plants with a performance guarantee. There are three operational plants: a 25 dry te/d unit at Red Arrow in Wisconsin and an 80 kg/h unit and 10 kg/h R&D unit in Ottawa. Six plants are currently at a design or construction stage: 60, 25, 25, 15, 7.2 and 1 dry te/d which includes the 15 t/d unit for ENEL in Italy for delivery in 1995. Further plants for fuel production are in advanced negotiation in the USA. Ongoing development work includes hot vapour filtration to reduce ash and char, liquid filtration to reduce char, supply of oil for engine and turbine testing in Canada and Europe, combustion testing, upgrading and product characterisation.

5.8.2 Description

At least four reactor configurations have been developed referred to as RTP-I, RTP-II, RTP-III and RTP-IV, some of which have variations. Figure 5.7 shows the arrangement of equipment for the RTP II upflow plant (3) and Figure 5.8 (26) shows the arrangement for the RTP-III configuration as proposed for the ENEL Italian plant. The heart of the system is a transport reactor which contacts hot recirculated sand with biomass in an upflowing reactor.

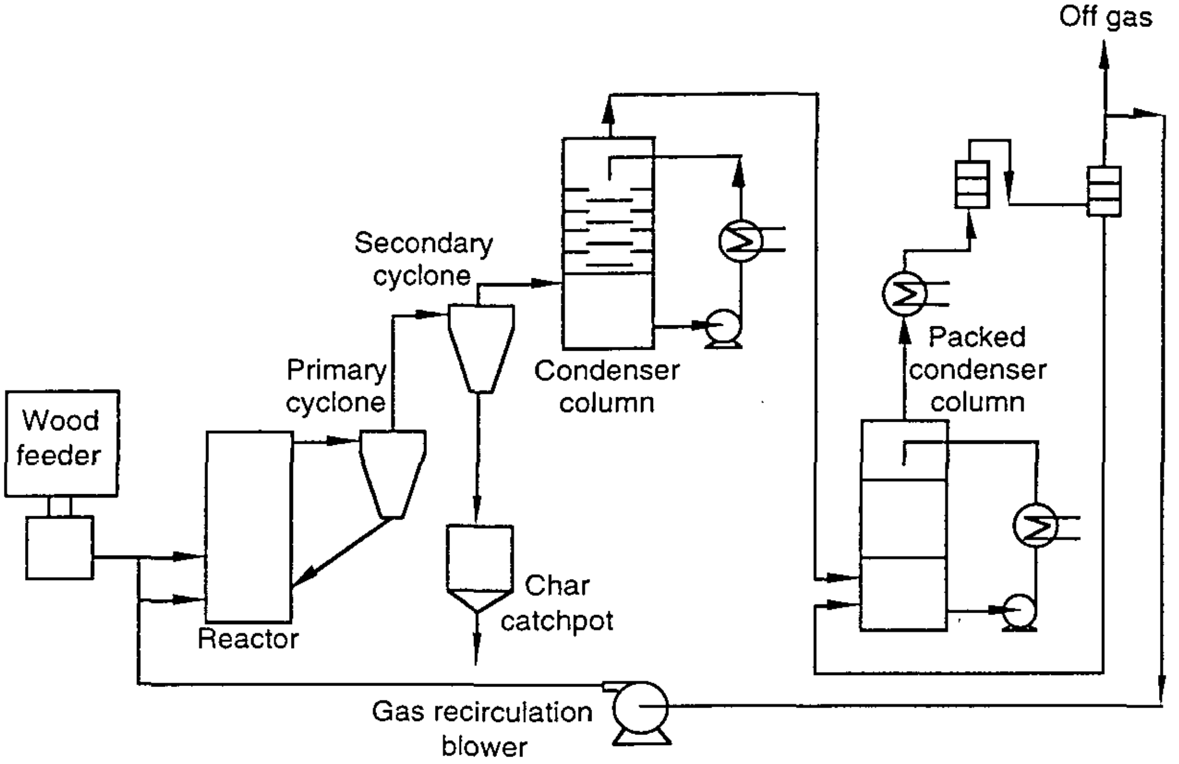

Figure 5.7 **Ensyn RTP II 100 kg/h Commercial Demonstration Plant (Upflow Design)** [27]

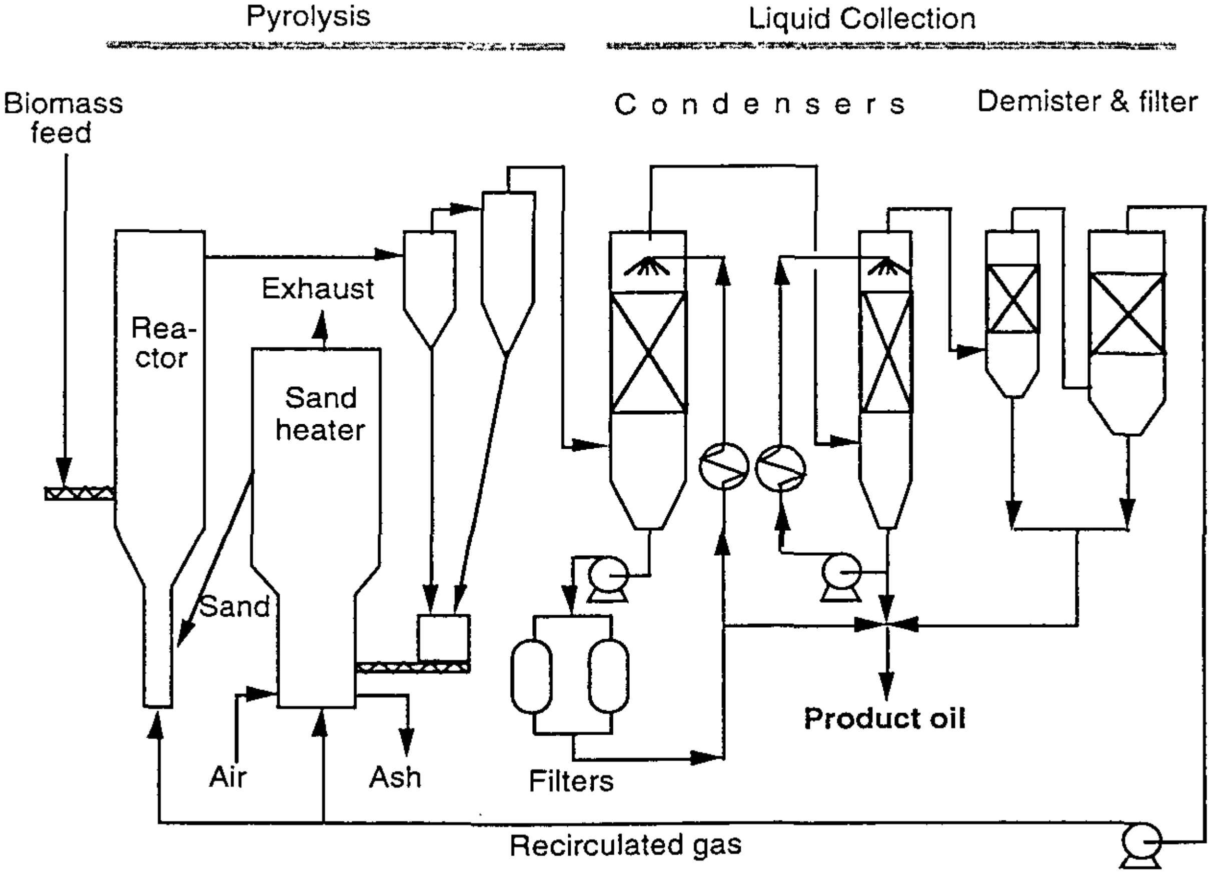

Figure 5.8 **Ensyn RTP III Process Flowsheet** (26)

In all the systems, biomass is comminuted to minus 6 mm and dried to around 10% moisture before feeding to the reactor. The products are passed through two cyclones to separate first sand then char, then the liquid is rapidly quenched and cooled. A condenser and filter cyclone system are used to separate the liquids from the gas. The total residence time for the hot vapours can be controlled down to a hundred milliseconds which "freezes" the thermally unstable liquid intermediates of pyrolysis. These very low residence times are used for chemicals production, while longer residence times are used for liquid fuels in order to more completely crack the lignin. R&D is currently underway to reduce the char and ash levels in the liquid by hot vapour filtration and oil filtration, as shown in Figure 5.8.

A variety of feeds have been processed including wood, lignin, cellulose, sludges, agricultural residues, heavy oils, heavy distillates, asphalt and bitumen, tyre crumb.

5.8.3 Product and yields

From cellulose, the maximum liquid yield from the RTP III reactor system approaches 90% by mass while gas yields are about 10% and char yields are negligible. The overall liquid yield is up to 83% by weight on dry feed basis and has typical characteristics as listed in Table 5.9. Hydroxyacetaldehyde (HA) yields from the RTP III reactor have been reported of up to 12% from wood while from other biomass materials, HA yields of up to 30% can be achieved.

Table 5.9 Wood Derived Pyrolysis Oils from Ensyn (28, 29)

Physical property		Typical value		Range
Moisture content		22	%	14 - 31%
pH		2.5		2.1-3.4
Specific gravity		1.18		1.16-1.22
Elemental analysis (moisture free)				
C		56.4	%	55.3-63.5
H		6.2	%	5.2-7.0
O (by difference)		37.1	%	39.43-28.98
N		0.2	%	0.07-0.39
S		<0.01	%	0.00-0.05
Ash		0.1	%	0.04-0.25
C/H molar ratio		0.76		0.89-0.76
C/O molar ratio		2.02		1.87-2.92
HHV (moisture free basis)		23.1	MJ/kg	22.1-24.3
HHV as produced		17	MJ/kg	15-19
Viscosity (@ 40°C)		45	cp	35 - 55
Kinematic Viscosity	@ 25°C	233	cSt	
	@ 40°C	134	cSt	
ASTM Vacuum Distillation	160 °C	10	%	
	193 °C	20	%	
	219 °C	40	%	
	Distillate	50	%	
Flash point		55	°C	51 - 58
Pour point		-25	°C	
Solubility	Hexane insoluble	99	%	
	Toluene insoluble	84	%	
	Acetone/acetic acid insoluble	0.14	%	

The first commercial application of the Ensyn Technology was at Red Arrow Products in Wisconsin, USA which produce chemicals with the residual oil used as a boiler fuel (30). Two plants are now installed there.

Preliminary combustion tests performed have shown that fast pyrolysis bio-oils could be used in place of heavy fuels oils in industrial boiler applications (30, 31) where bio-oil has been shown to have a similar heat release rate and flame length as Number 6 fuel oil. Special combustion chambers would, therefore, not be required and a fossil fuel fired boiler or furnace could be easily converted to use this oil. Carbon monoxide emissions would be comparable to those from fossil fuel oil combustion, particulate emissions would be greater and NO_X emissions would be lower. SO_2 emissions from bio-oil combustion are less than 2% of those from the combustion of Number 6 oil.

Currently Ensyn is working with a number of companies in Europe to test fire Ensyn oil in an internal combustion engine. Ensyn are also involved in a large project with a gas turbine manufacturer to test fire bio-oil in a gas turbine. However, the oil can contain up to 0.2% by mass of inorganics which is derived from the ash in the feed. This which may present a problem in gas turbine operation and ash removal is being investigated by both hot gas filtration and liquid filtration.

There is an extensive literature relating mostly to the pioneering work on higher temperature fast pyrolysis for gases (e.g. 32, 33, 34, 35) with more recent publications on the commercialisation of the technology and investigations into applications (e.g. 36, 37).

5.9 GTRI

5.9.1 Summary

This project was initiated in 1980 based on early research which showed that higher oil yields could be obtained from a rotating tube furnace with moving particles (typically 28 wt% liquid yield) rather than a stationary reaction bed (typically 17 wt% liquid yield) (38). From this work, an entrained flow bed reactor was designed for the production of pyrolysis oil. This operated successfully until around 1989. Although apparently successful, the process was never scaled up. The only other entrained flow system for fast biomass pyrolysis was built by Egemin (q.v.). GTRI also developed the tech-Air process which similar to that of Bio-Alternative (q.v.) in that the principal product was charcoal with appreciable quantities of secondary oil derived as a by-product. This material was used extensively in early upgrading work.

5.9.2 Description

A process research unit was built and completed in 1983 (39, 40, 41). In 1985, modifications were made so that optimisation of the oil yield could be further investigated, based on experience gained in the operation of the pilot plant and the results of the commissioning runs. The major changes were the replacement of the 8 in. diameter (20.32 cm) reactor tube with a 6 in. (15.24 cm) tube, the addition of a quench vessel and a second demister (42, 43, 44). The nominal operating feed rate was then 56.8 kg/h of dry biomass. Figure 5.9 is a flowsheet of the process.

The feed is dried, hammer-milled to about 1.5 mm and fed from a loss-in-weight feeder into the reactor via a rotary valve. The reactor used is a 6 in. inner diameter vertical tube made of stainless steel. The initial feed point was the refractory lined mixing section, located below the reactor tube. However, by introducing the feed into feed ports higher up the reactor, the effective length of the reactor could be reduced which in turn reduced the residence time. The wood particles are entrained in a stream of hot combustion gas (927°C) obtained by burning propane gas and air stoichiometrically. Gas and wood flow cocurrently upwards through the reactor tube in which pyrolysis takes place; the resulting mixture consists of non-condensable gases, water vapour (moisture plus pyrolytic reaction water), pyrolysis oil vapours and char.

A cyclone separator is used to remove most of the char particles. The exiting gas stream consists of non-condensable gases, water vapour, pyrolysis oil vapours and some char fines. The hot effluent enters a water-sprayed quench vessel where it is rapidly cooled. Following the quench vessel, the mixture enters an air-cooled condenser in which the pyrolysis vapours are condensed with some water vapour. Early problems were reported with accumulation of tarry material in the first stages of the air-cooled condenser.

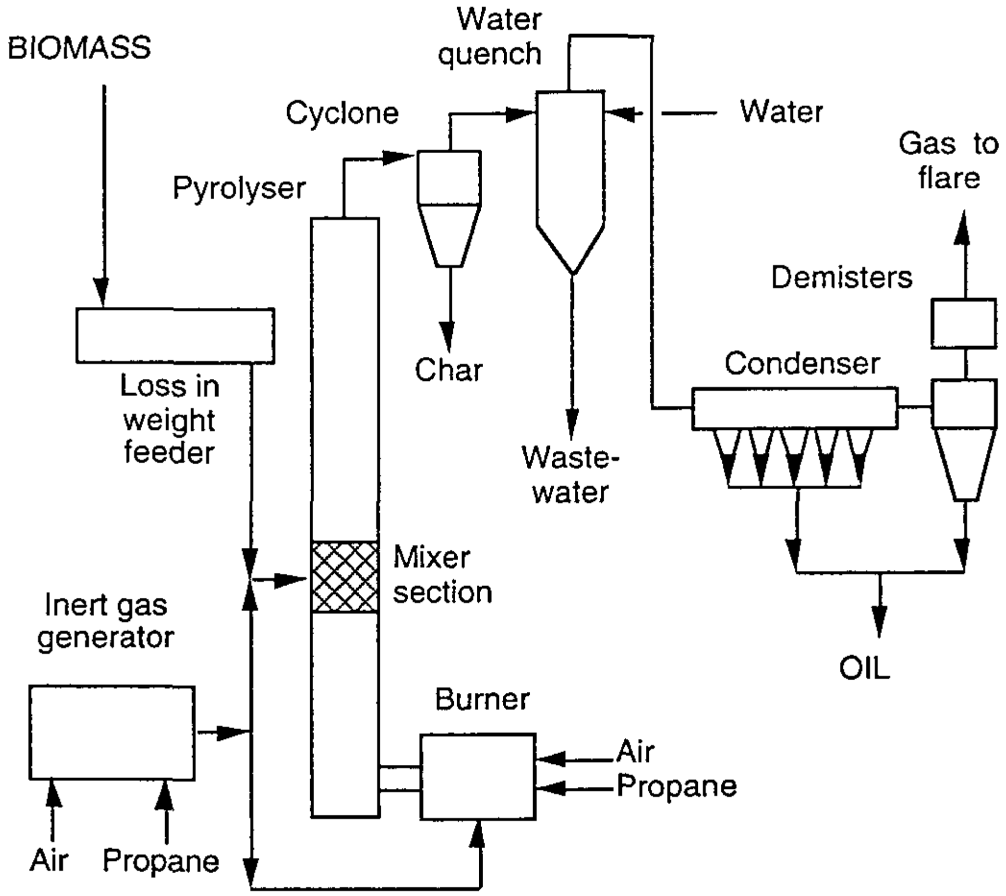

Figure 5.9 **GTRI Pilot Plant Flow Diagram**

The condensed phases are removed via sumps and receivers and the gaseous product is passed through two demisters connected in series. Most of the aerosols present in the gaseous product are removed in the demisters. The remaining effluent, consisting of non-condensable gases, water vapour and remaining aerosols, enters a flare where it is burnt and the combustion products are exhausted to the atmosphere.

In the scaled up process, it was intended that waste water production would be minimised or eliminated by controlled cooling and condensation of oil to retain the water in the vapour phase with subsequent combustion of the water laden by-product gas for process heat. There was, however, no experience of internal gas recycling in the pilot plant.

5.9.3 Product

Table 5.10 shows some of the last results with liquid yields approaching 60% wt on feed (45). Modelling and optimisation studies produced predictive models which indicated that yields of 70 wt% would be achievable with a well designed reactor and system. The oils are highly oxygenated with no phase separation as shown in Table 5.12. They have an initial boiling point range from 70°C to 90°C. They are heat sensitive and will decompose when heated to temperatures greater than 185°C-195°C. The oils are acidic, have an acrid odour and also exhibit corrosive properties with some metals. A typical bio-oil analysis is shown in Table 5.11. The product was upgraded by hydrotreating at Battelle PNL (46) which is discussed in more detail in that chapter. The liquid was also upgraded in the liquid phase over zeolite cracking catalyst - the only known application of this approach to zeolite cracking which is usually carried out on freshly produced vapours. The results have not been published, but extensive coking is understood to have occurred.

Table 5.10 GTRI Product Yields (Modified reactor)

Run No.	2-11/0	2-12/0	3-17	3-18	3-19
Temperature, °C	501	524	499	504	500
Yields (% wt dry ash free feed)					
Oil	48.1	53.8	52.1	60.0	54.9
Char	7.6	8.4	10.0	12.1	21.2
Total gas*	44.3	37.8	37.9	27.9	23.9

* by difference

Table 5.11 Typical Bio-oil Analysis from GTRI (47)

Elemental Analysis (wet basis)	C (% wt)	39.5
	H (% wt)	7.5
	N (% wt)	< 0.1
	S (% wt)	-
	O (% wt)	52.6
H/C ratio		2.28
O/C ratio		1.00
Moisture (% wt)		29.0
Ash (% wt)		0.2
Char content (% wt)		27-31
Viscosity, cp @ 60°C		10
HHV, MJ/kg		24.3
Density, g/cm^3		1.23

5.10 INETI

Fluid bed pyrolysis was investigated by LNETI (now INETI) at two scales of operation using hot gas to effect heat transfer. Initially work was carried out on a 10 cm fluid bed with subsequent research on a 30 cm square fluid bed with top feeding. Several parameters were investigated including pressure, temperature and bed additives or secondary reactants including zeolites, zinc chloride, carbonates and alkali (48). The results were not very satisfactory in that pyrolysis yields were relatively low and the catalysts showed little activity.

5.11 INSTITUTE OF WOOD CHEMISTRY, GERMANY

Work has recently started on small scale fluid bed fast pyrolysis of contaminated waste wood at around 100 g/h in order to devise a better disposal method for such wastes combined with energy recovery. There are no results as yet.

5.12 INTERCHEM INDUSTRIES INC., USA

5.12.1 Summary

Interchem Industries Inc. was founded in 1985. Initial work to scale up an ablative fast pyrolysis process was carried out by Pyrotech Corporation to solve an energy deficit problem at a pulp mill at Samoa, California (49, 50). In 1989 the company entered into a consortium to develop and exploit the commercial potential of the NREL ablative pyrolysis process (see above) to produce a phenol adhesive substitute and an alternative fuel (51).

Although there were some early attempts to demonstrate the principles of pyrolysis in a vortex type reactor, the first significant plant was built in Springfield, Missouri for the conversion of sawmill wastes. Construction of the 32.7 t/d facility for the production of fuel oil and charcoal, referred to as a Petroleum Synthesis Unit, was completed in September 1990 and this was tested until 1992 (52, 53). The plant was redesigned and relocated and a new reactor was built based on the NREL vortex ablative reactor. This second plant was never completed and the project is understood to have been abandoned.

5.12.2 Description

The reactor wall was heated by the combustion of recycled non-condensable pyrolysis gases. The product vapours from the reactor were directly quenched in a 6 tray column, initially using diesel and then product liquids. The collected liquids were split: part was recycled to the quench column and the rest was transferred to a storage tank. The remaining gases and uncondensed vapours were recycled to the reactor furnace where part was combusted for process heat.

The design capacity of 1360 kg/h was not achieved and throughputs of only 90 kg/h were initially achieved at the Missouri site due to the problems noted above. The process had some operational difficulties concerning particle handling, notably particle recycle problems, particle carryover into the product collection system, low particle velocities in the reactor leading to low throughputs and plugging of the plate heat exchanger. (54)

Various modifications were then made to the process including replacement of the plate heat exchanger with a shell and tube exchanger to remove the blockage problems, rebuild the recycle loop in order to retain the particle kinetic energy and improve the process efficiency and placing the reactor exit cyclones in series to improve particle collection efficiency. These modifications and repairs only increased the throughput to 180 kg/h, 13.2 % of the design capacity. The reasons for the low throughput were then surmised to be due to loss of particle velocity upon entering the reactor due to the initial 0.6 m of the reactor tube not being heated, i.e. the particles were experiencing dry friction and consequently lost a significant proportion of their velocity; the recycle gas was not sufficiently reheated in the condenser and the recycle loop was becoming overloaded with unreacted particles.

No quantitative results of the operation of the Springfield first plant have been published. The plant was closed down in late 1992 and decommissioned as the problems could not be solved using the existing equipment. The pretreatment and handling units have been retained as they worked as expected and the heat exchanger on the liquids recirculation system has been improved. Interchem relocated the wood handling equipment to Kansas City and built a second reactor based on the NREL ablative vortex reactor (see above).

A new reactor was designed by NREL based on their work (see above) and was to have being incorporated into the relocated plant in Kansas. The new process is shown in Figure 5.10 (55).This was due for restart in late 1993, but is now understood to have been abandoned.

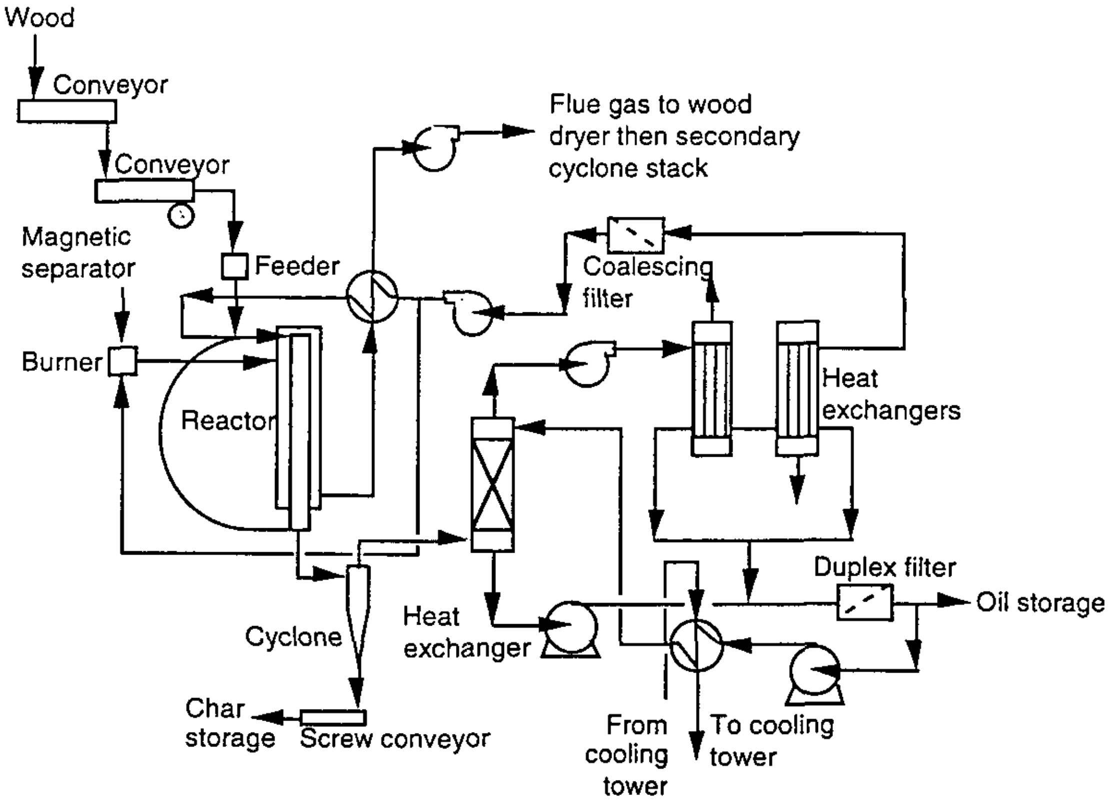

Figure 5.10 **Second Generation Interchem Petroleum Synthesis Process, Kansas, 1993.**

5.13 NATIONAL RENEWABLE ENERGY LABORATORY, USA

5.13.1 Summary

The original aim at the beginning of the 1980s was to convert biomass into non-equilibrium gases in a low pressure process without the addition of a catalyst in an analogous concept as the work at the University of Western Ontario which lead to the formation of Ensyn. This aim was modified in 1984 to produce liquid fuels in high yield, and more recently it has been modified again to consider production of hydrocarbon fuels such as gasoline, aromatics such as benzene, xylene and toluene, and chemical fractions such as polyphenols.

Interchem attempted to adapt the concept of the vortex reactor in their first pilot/demonstration plant at Springfield, MO, USA, (q.v.) but this was not successful. The second attempt was based on an NREL designed ablative vortex reactor and is shown below. While the reactor was built, the completed plant was never operated and the project is understood to have been abandoned.

NREL are continuing to operate their original pilot plant in Golden and has commissioned a second unit. There is more recent work on fluid bed fast pyrolysis (56), on MBMS fast pyrolysis (57) and on close coupled zeolite upgrading (see Chapter 6).

The description below focuses on the ablative vortex reaction system as the major R&D activity in fast pyrolysis.

5.13.2 Description

Initially a smooth walled vortex reactor with a gas recycle loop, made from Inconel 800H in order to withstand temperatures of 1000°C, was used. However, early experimentation demonstrated that severe coke deposits were formed at wall temperatures much above 625°C (58). Since a lower reactor temperature of 625°C was needed, a vortex reactor made from stainless steel was designed, constructed and tested. Very high organic vapour yields resulted from this lower wall temperature operation. The design capacity of the vortex reactor is 50 kg/h biomass but the maximum throughput achieved to date is 36 kg/h (59, 60, 61).

Figure 5.11 shows the current configuration of the reactor system. Biomass, with a particle size of about 5 mm, is metered into the system, where it is entrained and mixed with the recycle stream. The biomass particles, entrained in the carrier gas, enter the vortex reactor tangentially at speeds of over 400 m/s so that the particles are forced to the reactor wall by high centrifugal forces.

The reactor is made from 316 stainless steel with a diameter of 13.4 cm and a length 70 cm. The reactor is heated externally by three electric cylindrical furnaces. To force the particles into tighter helical paths than would naturally occur, a helical rib having a pitch of 25 mm and width and height of 3 mm was machined from the wall of the reactor. An insulated recycle loop is also added tangentially at the exit of the reactor to recycle partially pyrolysed feedstock and any large char particles.

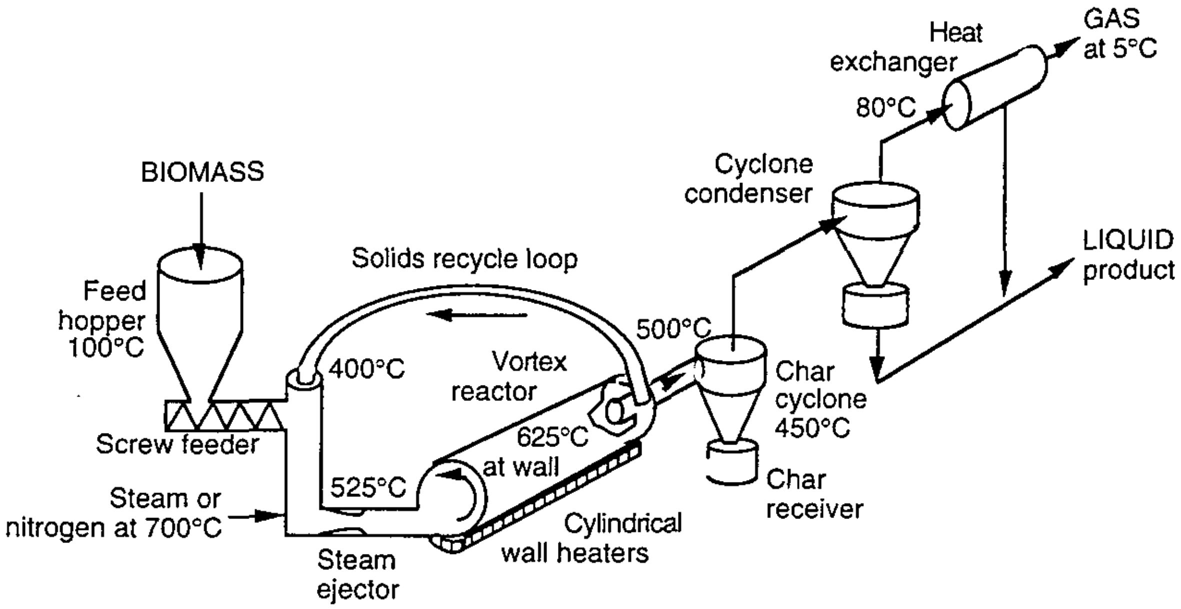

Figure 5.11 NREL Pilot Plant Flow Diagram

The fine char, gases and vapours in the reactor leave through the axial exit which extends part way into the reactor. The reactor has a very high specific capacity and can in principle be easily scaled up. Very high heat transfer rates are achieved between the hot wall and biomass particles centrifuging against the hot reactor wall.

The wall temperature has to be limited to a maximum of about 625°C to ensure production of a liquid film between the wall of the reactor and the particle which then vaporises and leaves the reactor. The product stream then passes through a char cyclone where the char is removed. The diameter is 4 in. (10 cm) and operates at 475-500°C. The vapours pass to the first heat exchanger which is a 38 cm diameter cyclone. The condensed liquids and water are retained in the receiver. The cooled gas stream at about 80°C is then passed to a series of heat exchanger before passing through an orifice meter, and then to flare.

5.13.3 Products

Using this experimental layout, oil yields of 67% wt (including moisture on a wet feed basis) or 55 % (dry oil/ on dry feed basis) have been obtained with 13% wt (on a dry feed basis) char.

The liquid obtained is highly oxygenated, dark brown in colour and acidic with a pH between 2 and 3, presenting corrosion problems. The aqueous and the organic condensates are homogeneous. If nitrogen is used rather than steam as the carrier gas, an organic phase and an aqueous phase are both present at water contents above about 25%. Small samples of the oil have appeared to be stable at room temperatures for a prolonged time but exothermic reactions will occur if the temperature of the oil is raised to 100°C or more. The fresh oil vapours have been found to irritate the eyes and the nose; however, when tested to investigate whether they were carcinogenic with cancer-prone mice, they were found not to promote cancer formation cells. Analytical data is given in Table 5.12.

The phenol fraction has been successfully extracted and polymerised with formaldehyde to form a plywood resin. A consortium of companies including Interchem (q.v.) have attempted to commercially exploited the polyphenol recovery process (62) but it is understood that this has not proved to be economically viable, although the product was technically successful.

While RDF has been successfully pyrolysed, problems arose from deposition of highly viscous condensate (having a melting point of around 80°C) in the first heat exchanger, which required extensive modification of the condenser train (63, 64).

Table 5.12 Elemental Analysis of Pyrolysis Liquids from the NREL Process (65)

Elemental Composition, wt% on feed	Bio-oil A	Bio-oil B
Carbon	48.6	54.4
Hydrogen	7.2	5.7
Oxygen	44.2	39.8
Nitrogen	< 0.1	< 0.1
H/C ratio (atomic)	1.78	1.26
O/C ratio (atomic)	0.68	0.55
Ash	-	0.05
Moisture	-	15
Density, g/cm3 @ 55°C	1.23	-
Viscosity, cp	90 @ 30°C	
Heating value, MJ/kg	22.3 *	20.3

* calculated

The char from wood has a volatile content of 15-45 %, a bulk density between 0.18 to 0.24 g/ml and a higher heating value of 33 MJ/kg. The empirical formula is $CH_{0.53}O_{0.12}$.

5.14 STENAU, GERMANY

The Stenau process is based on the work carried out at the University of Tübingen. There is little information about technical aspects of the process other than a rotary kiln is used to slow pyrolyse refuse/MSW at fairly low temperatures to effect partial liquefaction at a capacity of 1 t/day refuse (66, 67). The performance is summarised in Table 5.13. A flowsheet is given in Figure 5.12 (68). The liquid yield is about 31% weight on dry MSW feed with 71 m^3 off gas per tonne feed, some of which is used for process heat, and a solid residue of 56% wt on feed.

Table 5.13 Summary of the Stenau Process.

Feedstock throughput (d.a.f.)	1	tonne/day
Liquid product yield	0.309	tonne bio-oil/tonne feed
Gas product yield	71	m^3/tonne feed
Solid residue yield	0.56	tonne/tonne feed

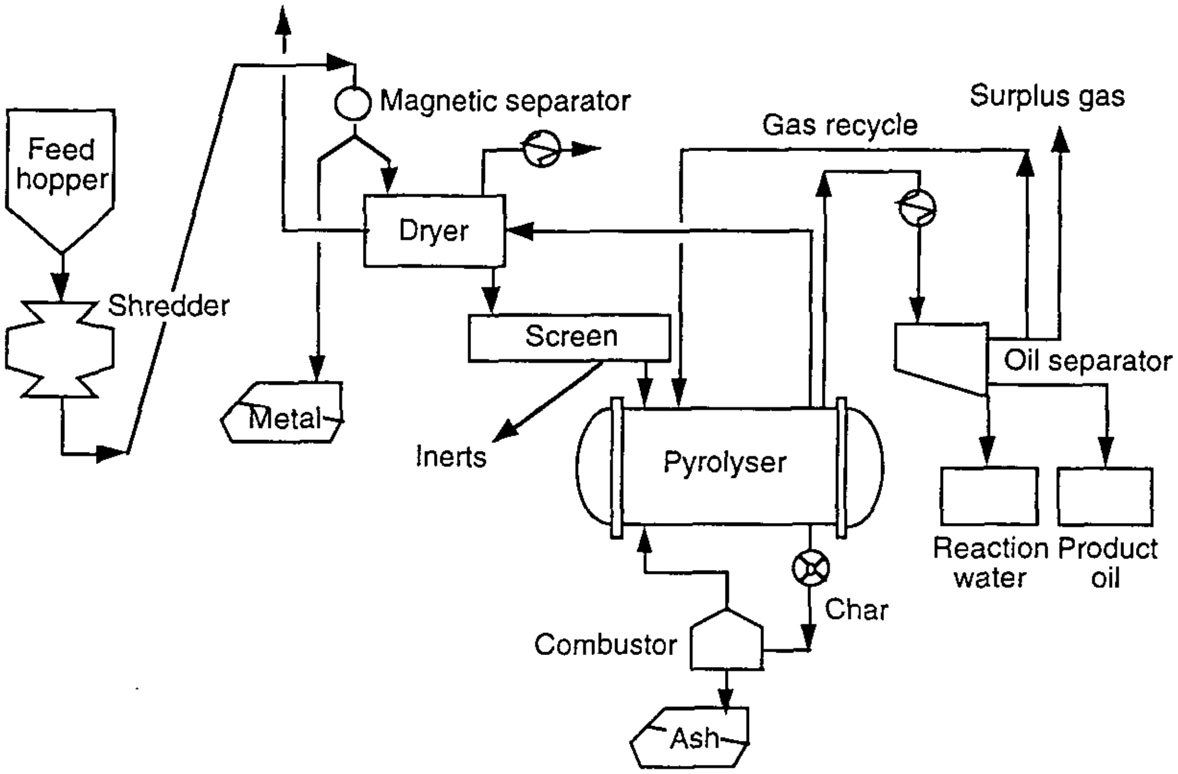

Figure 5.12 Stenau Flowsheet for Pyrolysis of MSW

5.15 UNION FENOSA, SPAIN

5.15.1 Summary

Union Fenosa undertook the construction of a substantial pilot plant in 1989 for the production of pyrolysis liquids for fuels. After a thorough review of available technologies at that time, a license was agreed for the Waterloo Flash Pyrolysis Process (WFPP) developed by the University of Waterloo in Canada (q.v.).

Construction started in 1990 and commissioning started around October 1992. By mid 1993 the unit was operating reasonably satisfactorily at 160 kg/h dry wood throughput, although some problems with liquid collection had to be resolved. Work is continuing on developing the process and considering scale-up.

5.15.2 Description

The flowsheet is shown in Figure 5.13 (6, 69). After storage the eucalyptus feed is ground then dried with propane. A cyclone removes fines prior to venting the combustion products to atmosphere. The dried feed is stored in a closed hopper prior to metering to the fluid bed pyrolyser. The fluidising gas is recycle gas supplemented with nitrogen as required. The gas is heated with a propane fired heat exchanger.

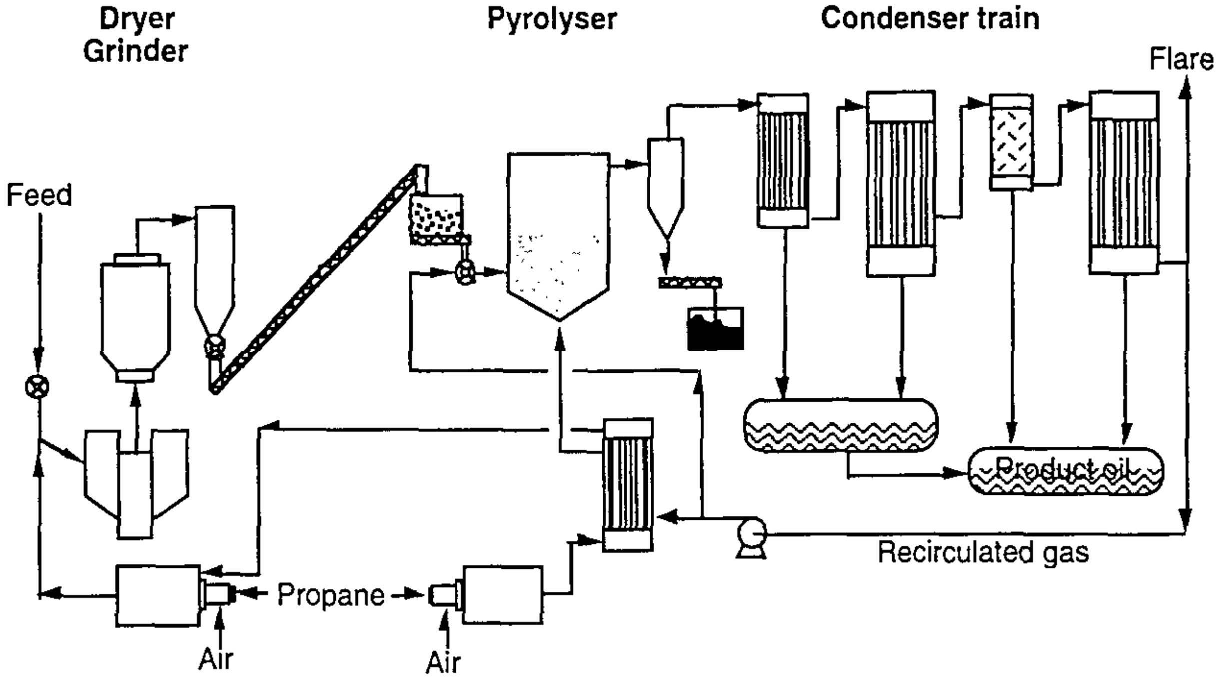

Figure 5.13 **Flowsheet of Union Fenosa Pilot Plant**

The product char is separated in a cyclone and stored in a closed container. The vapours are cooled in two water cooled heat exchangers in series, then passed through a demister and a final cooler to remove as much oil as possible. All liquid product streams are combined.

5.15.3 Products

Detailed mass and energy balances and product analyses are not available at this time, but reported char yields of around 20% wt on dry feed (60) are closer to 15% (71). Oil yields in excess of 55% wt. have been indicated (60) although it seems likely that the oil yield is nearer 65-70% wt. . At the end of the first phase of the work in summer 1993, Fenosa admitted that it had not been possible to produce pyrolysis oil of the right quality. The early operational difficulties in producing a consistent quality oil have now been mostly solved and the plant is producing a consistent relatively viscous liquid with a water content of 15 wt%.

5.16 UNIVERSITY OF ASTON, UK

5.16.1 Summary

The objectives of the work are to develop and operate a novel ablative pyrolysis reactor for the production of liquids in high yields form wood feedstock under a range of operating parameters, primarily reactor temperature and residence time. The process concept has been successfully developed at 3 kg/h and oil yields of up to 80 % wt. on dry feed have been obtained. A scaled up version is being developed.

5.16.2 Description

Figure 5.14 shows the simplified reactor unit used as an example of a laboratory scale R&D unit to study principles and design new concepts (72). Ablative pyrolysis is one of the most extensively researched methods of flash pyrolysis. The underlying principles are applied in this research through pressing the biomass particles onto a heated metal surface using angled blades which also impart horizontal movement of the particles across the hot surface.

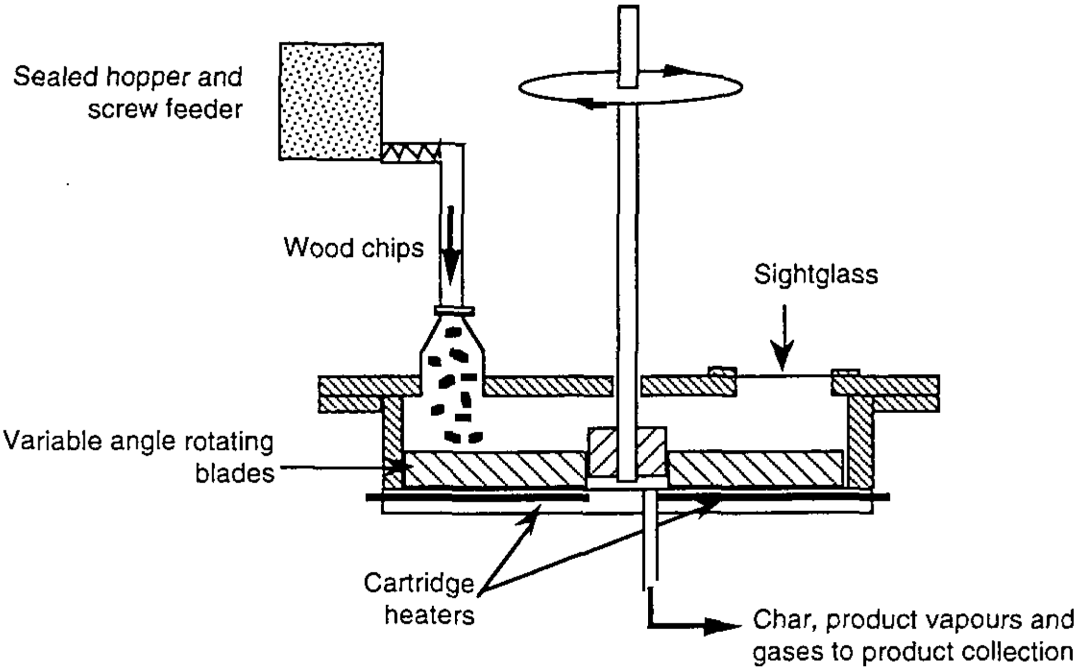

Figure 5.14 **Aston University Ablative Pyrolysis Reactor: Simplified Diagram.**

Dried biomass particles of up to 6.35 mm are fed into the nitrogen purged reactor from a sealed screw feeder. Four asymmetric blades rotating at speed up to 200 rpm generate a mechanical pressure on the particles, pressing the particles onto the heated reactor base, typically heated to 600°C. The mechanical action of the blades causes the particles to pyrolyse (thermally erode) under the conditions of high relative motion to the heated reactor surface. The product vapours and gases are removed from the reactor with the diluting nitrogen under the action of a vacuum pump.

The primary liquids are recovered in an ice cooled condenser arrangement with final stable product vapours in the non-condensable gases being removed by a cotton wool filter. The remaining gas is dried with a molecular sieve before discharge from the vacuum pump to the gas analysers and the fume hoods.

5.16.3 Products

Table 5.14 gives some results from early experiments.

Table 5.14 Results for the Ablative Pyrolysis Reactor - Ablatively Pyrolysed Wood Basis (73)

Run number	CR07	CR11	CR06	CR10
Reactor surface temp. (°C)	550	550	600	602
Gas/vapour temp. (°C)	389	294	415	368
Wood H_2O (wt %, dry basis)	2.44	1.86	9.25	1.99
Residence time (s)	2.83	1.97	6.92	1.71
Ablative char (wt%)	14.3	13.8	14.8	15.7
Organics (wt%)	58.1	55.7	51.8	66.1
H_2O (wt%)	22.7	18.3	28.2	11.5
Total liquids	80.8	74.0	80.0	77.6
Gas (N_2 free, wt%)	9.0	8.2	10.4	6.2
Gas yields (wt%, moisture free feed)				
H_2	0.01	0.06	0.00	0.04
CO_2	3.53	3.80	4.86	1.71
CO	3.65	2.55	3.83	3.38
CH_4	0.33	0.21	0.39	0.20
C_2H_4			0.12	0.07
C_2H_6			0.07	0.06
C_3H_6			0.37	0.00
C_3H_8			0.00	0.03
Closure	101.1	95.8	105.3	99.5

This work is continuing with new heat transfer relationships being derived and further experiments carried out at a range of reactor temperatures and residence times. A scaled up version of the reactor is being developed. There is associated work on catalytic pyrolysis, chemicals recovery from bio-oil and physical property measurement.

5.17 UNIVERSITY OF LAVAL, CANADA

5.17.1 Summary

The objective of this project was to investigate the potential of low pressure pyrolysis of biomass to produce high yields of condensable vapours and selectively condense fractions from different sections of the reactor to examine the potential for fractionation and recovery of chemicals. The reactor is a 30 kg/h multiple hearth furnace operated under vacuum. A range of feedstocks have been tested of which tyre pyrolysis was subsequently successfully scaled up to 250 kg/h. A notable feature of the vacuum type pyrolysis plant was handling whole tyres. Recent work has concentrated on operating the system for waste disposal. A system is believed to have been sold in Switzerland in 1994.

5.17.2 Description

A 30 kg/h vacuum pilot plant multiple hearth reaction system with liquid condensation and collection was designed, constructed and tested (74). Figure 5.15 shows the arrangement of equipment. The optimum temperature range was found to be between 350-400°C and a yield of 60 wt % (on a dry ash free wood basis) of pyrolytic oil was obtained at an average heating rate of 10°C/min and at a total system pressure between 0.3 and 2.3 mm Hg (40-307 Pa). The feedstock used was aspen poplar. There is an extensive literature of which some key references are quoted (75, 76, 77, 78, 79). See also (3) for a more comprehensive overview and extensive referencing.Wood chips with a particle size from 1/4" to 1/2" Tyler mesh (6 mm to 12.7 mm) are fed via a hopper on the top of the reactor, which is hermetically sealed. This is equipped with a variable rate feeding device that feeds the chips into the preheated reactor at a constant feed rate of between 0.8 to 4 kg/h.

The reactor is a multiple hearth furnace 2 m high and 0.7 m diameter, with six hearths. Electric heating elements are used to heat the reactor. The temperatures of the heating plates increase from top to bottom of the reactor. A typical temperature profile is 200°C to 400°C. At steady state conditions, the absolute system pressure of the system is less than 80 mm Hg (10.7 kPa). The organic vapours and gaseous products are removed from the reactor by a mechanical vacuum pump via six outlet manifolds which correspond to the six heating plates. The char falls to the bottom of the reactor where it is collected in a metallic jar on a load cell. The process unit is connected to a central microprocessor which simultaneously gathers data and controls about 75 operating parameters.

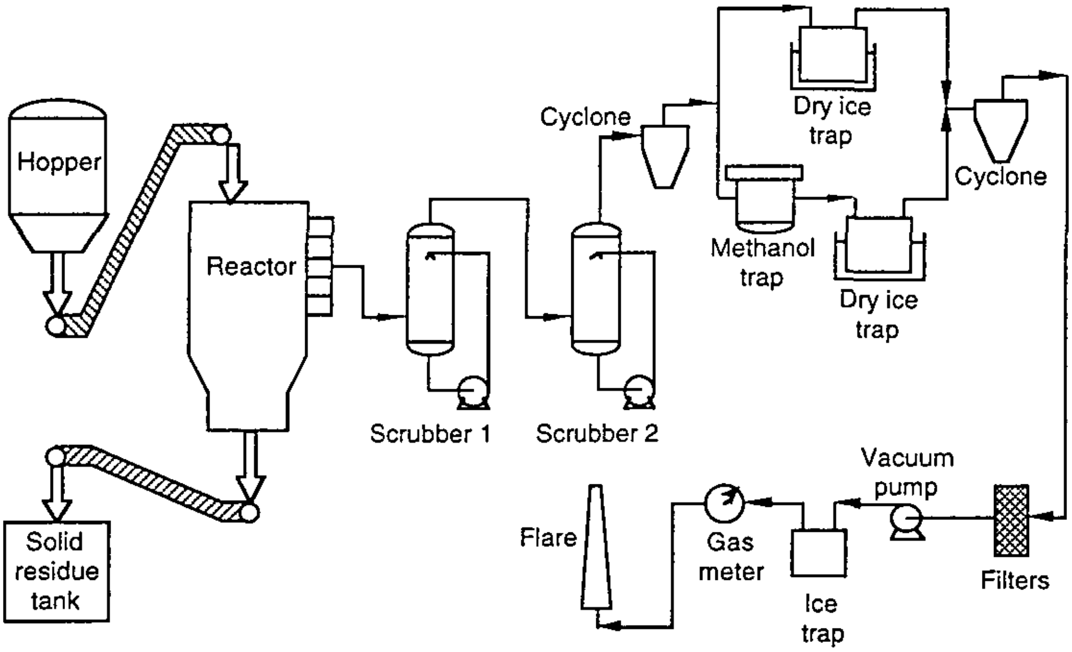

Figure 5.15 **University of Laval Pilot Plant Flow Diagram**

The clean-up system is a series of shell and tube heat exchangers (primary condensing unit) and a train of receivers (secondary condensing unit). Each outlet manifold is connected to a heat exchanger where the vapours are condensed and recovered as organic liquid in individual receivers. Cool to warm tap water is used as the cooling medium on the shell side. The vapours from the heat exchangers are then collected in the secondary condensing unit where the aqueous phase is primarily recovered. The first receiver is immersed in a bath of water-ethylene glycol mixture. The next two are immersed in baths of dry ice-acetone while the final receiver is filled with glass wool at room temperature. The non-condensable gases are pumped into a 500 litre vacuum vessel.

The low pressure removes the primary products quickly and avoids secondary reactions. Fractionation provides some separation of liquids evolved at different temperatures in a continuously operating system, but this has not proved as effective as had been hoped.

Recent testing of this unit at throughputs of 30 kg/h showed that the primary condensing unit composed of six shell and tube heat exchangers were inefficient due to clogging problems. The six individual exchangers were substituted by a single spray type condensing unit, similar to the secondary condensing unit. The new system proved to work very satisfactorily.

A major design consideration is the large volume of equipment due to operation at low pressure and the high cost of maintaining vacuum operation. Scale-up will have to consider the optimum operating pressure and the problems of heat transfer in the multiple hearth furnace.

5.17.3 Products

Some results are shown in Table 5.15. The highest yields of bio-oil are obtained at the lowest pressure and the higher temperature conditions. The optimum temperature range for maximum oil yield from wood was found to be between 425-450°C at the bottom of the reactor.

One potential advantage of using a multiple-hearth reactor configuration is the capacity to fractionate the pyrolysis products by use of multiple outlets at different levels (see Table 5.16). The separation of the aqueous and the oil phases is important at the industrial level because the recovery of chemicals during distillation of large amount of water is less economical.

A typical analysis of the oil is shown in Table 5.17. This oil is highly oxygenated and consists of phenols, sugars and both aliphatic and aromatic hydrocarbons. The gases are mainly CO and CO_2.

Table 5.15 Product Yields For Low Pressure Pyrolysis at Laval University

Temperature, °C	425	363	465	450
Pressure, mm Hg	12	18	80	12
Feedstock, kg	5.98	5.99	3.39	15.43
Yields (% wt wood organic basis)				
Oil	46.4	41.6	39.7	50.9
Water	18.2	14.9	21.6	16.5
Char	24.2	33.0	24.7	21.3
Total Gas	11.2	10.5	14.0	11.3
Gas composition (vol %, dry basis)				
CO	59.2	60.4	60.0	60.7
CO2	33.6	34.9	31.4	31.6
CH4	2.4	0.9	3.3	2.7
H2	0.9	0.1	0.7	-
Others	3.9	3.7	4.6	5.0

Table 5.16 Separation of Water and Pyrolytic Oil During Condensation

Run no	Reactor Pressure (mm Hg)	Temp., °C Hearth VI	Cooling Water	Primary Condensing Unit		Secondary Condensing Unit	
				Oil (%)	Water (%)	Oil (%)	Water (%)
C019	80	465	11-28	52.2	19.2	7.4	21.2
C023	12	450	50-55	32.2	1.5	36.7	29.6
C024	30	450	30-35	39.8	1.6	27.2	31.4
C025	10	450	15-20	47.8	3.4	27.2	21.6

Percentages are based on total condensates

Table 5.17 Elemental Analysis of Bio-oil from Laval University (80, 81)

Elemental Composition, wt%	Carbon	49.9
	Hydrogen	7.0
	Oxygen	43.0
	Nitrogen	-
H/C ratio		1.68
O/C ratio		0.65
Ash		-
Moisture		18.4
Density, g/cm3 @ 55°C		1.23
Viscosity, cp		-
Heating Value, MJ/kg		21.1

5.18 UNIVERSITY OF LEEDS, UK

5.18.1 Summary

Both fixed and fluid bed reactors have been operated for fast pyrolysis and disposal of wastes, with catalytic upgrading of the products in the case of the fluid bed work. The objective has been to carry out screening studies on feedstocks, products and particularly examine the production of noxious products that may mitigate against implementation.

5.18.2 Description

A 200 ml stainless steel fixed bed reactor has been used to pyrolyse tyres. The reactor is externally heated and nitrogen is used as a carrier gas. Heating rates up to 80°C/min and temperatures from 300-720°C (82). More recently, work using polystyrene as the waste has been carried out with secondary thermal cracking of the product vapours at 500, 600 and 700°C (83). Experiments were also carried out with a third catalytic cracker using ZSM-5 catalyst maintained at 400°C which lowered the proportion of styrene oligomers but increased the proportion of PAH.

Work has also been carried out on fixed bed catalytic upgrading of model compounds as a prelude to the pyrolysis of biomass. Model compounds such as furfural, cyclopentanone, anisole, ethylacetate and methanol were upgraded over 10 g ZSM-5 in a fixed bed using nitrogen as a carrier gas and a range of temperatures ranging from 300°C to 500°C, WHSV 4±0.5 (84). The results showed that the EHI [Effective Hydrogen Index] was important in determining the conversion to other products. As the EHI increases for each model compound, the degree of mass conversion also increases. The importance of this is that it was estimated that the products of wood pyrolysis would have a lower degree of mass conversion compared to liquids produced from RDF or rice husks. For biomass liquids with EHI number less than 1, a catalyst at 500°C would produce a liquid with the lowest oxygen content. For biomass liquids with a EHI greater than 1, a catalyst at 400°C would give optimal conversion.

Subsequently, a dual fluid bed was used to pyrolyse biomass. Biomass was pyrolysed in an externally heated 0.075 m diameter bed, 1 m high with nitrogen as the fluidising gas. This is shown in Figure 5.16. Part of the reactor freeboard was packed with ZSM-5 catalyst. Liquids were collected before and after pyrolysis for comparison. Selected results are given below for yield of oxygenated compounds from biomass pyrolysis.

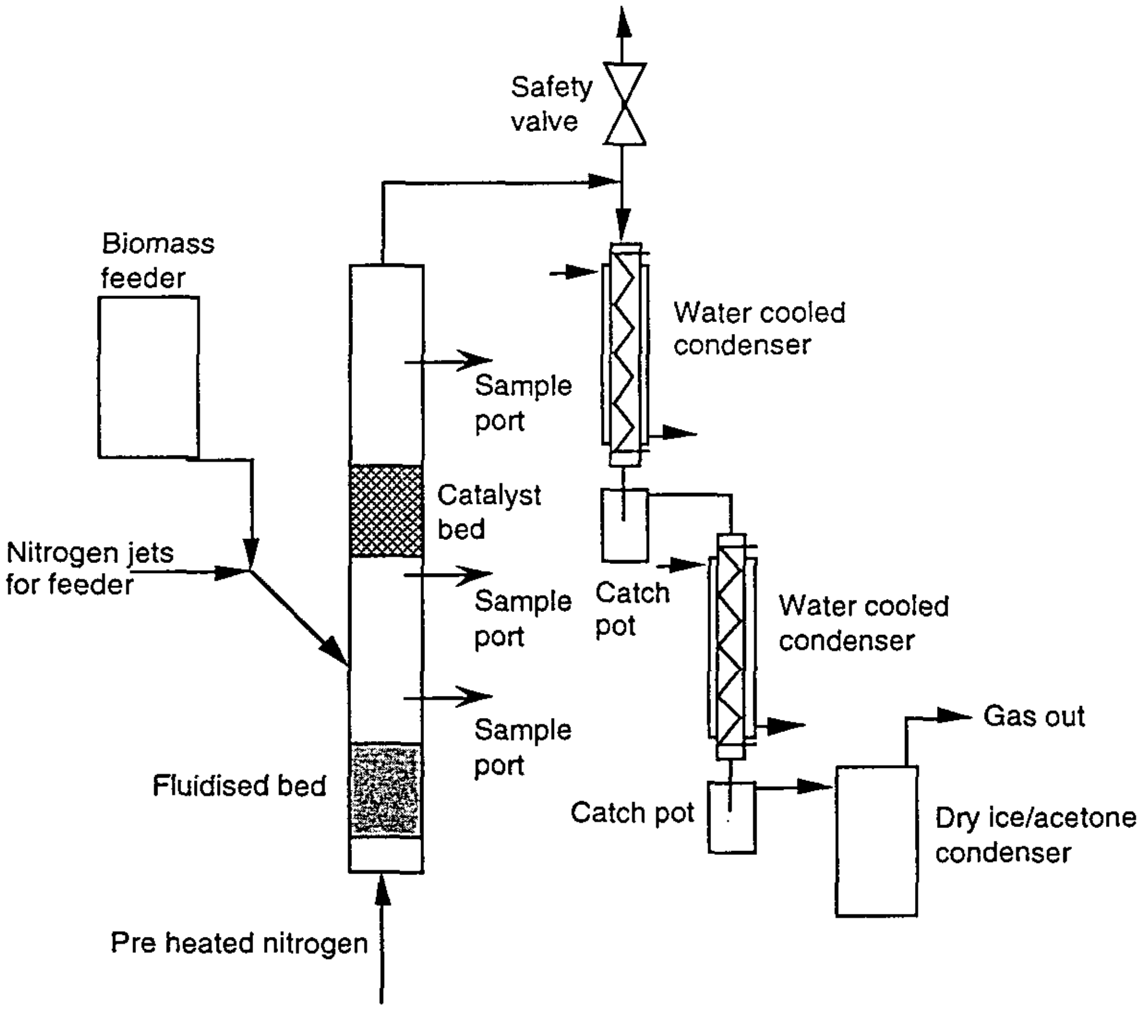

Figure 5.16 **Flowsheet of the University of Leeds Fluid Bed Reactor**

5.18.3 Products

For both reactors, the liquids were recovered and analysed by GC/MS. Analyses for biomass derived liquids are shown in Table 5.18. Quantification of PAH was performed by GC/FID. The recovery of styrene form the polymer was 53.0 wt% ± 1% at cracking temperatures of 500 and 600°C decreasing to 34.0 wt% at 700°C. The effects of metal salts on the pyrolysis of cellulose has been studied in a fixed bed reactor and by TGA (85).

For tyres, the maximum yield of liquid was obtained at 80°C/min and 720°C with a yield of 58.8 wt % liquids, 14.8 wt% gas and 26.4 wt% char. Detailed analysis of the liquids by SEC, FTIR have been performed.

In zeolite cracking, the conversion of oxygenates in the pyrolysis vapours occurs at lower catalyst temperatures to H_2O and to CO_2 and CO at higher catalyst temperatures. Coke formation on the catalyst was typically 11.4-13.1 wt%, although the run times over which this occurred at not quoted.

Table 5.18 Oxygenated compounds from biomass pyrolysis (mg/kg biomass fed)

Name	No catalyst	Catalyst Temperature, °C			
	550	400	450	500	550
Acetic acid methyl ester (T)	5195	0	0	0	0
Acetic acid propyl ester (T)	6800	0	0	0	0
2-cyclopentan-1-one	3825	2630	1430	1005	710
Methylcyclopentanone	745	830	510	350	240
Furanone	3042	0	0	0	0
Methyl furfural	600	435	90	50	40
Phenol	1055	1310	1340	1170	1080
Benzenediol	235	565	220	110	25
2-hydroxy-3-methylcyclopentanone	1840	760	200	110	45
Methylfuranone	470	0	0	0	0
Methylphenol	1785	2360	1885	1605	1590
Methoxyphenol	1935	1070	705	175	170
Dimethoxyphenols	850	2140	2115	1670	1295
Ethoxyphenol	2690	1795	1145	585	275
Methylbenzenediols	1375	1590	1125	915	330
Trimethylphenols	1045	1825	1840	905	550
Methoxypropylphenols	5060	3145	825	500	340
Naphthenols	0	0	315	350	330
Methylnaphthenols	0	0	440	310	280
Dimethylnaphthenols	0	0	240	123	100
Dimethoxypropenylphenols	3421	2230	420	80	70

5.19 UNIVERSITY OF LONDON, IMPERIAL COLLEGE

Exploratory studies on wire mesh fast pyrolysis of biomass has been carried out to derive fundamental kinetic data and compare this approach to that of ablative pyrolysis at the University of Aston (q.v.) (86). The advantage of this approach is that very small quantities of biomass can be processed under very high and controllable heating rates which makes derivation of basic reaction kinetics more reliable. There is little data available.

5.20 UNIVERSITY OF TUBINGEN

5.20.1 Summary

The objective of this research is to convert biomass such as sewage sludge, agricultural wastes and refuse/MSW into fuels or raw materials for the organic chemicals industry as an alternative solution to landfill and incineration of sewage sludge (87, 88). Several batch and continuous laboratory scale plants up to 5 kg/h have been built and tested. The principle is to use low temperatures of less than 350°C and long reaction times of up to an hour to achieve low oxygen content oils and high yield of fine chemicals. The concept has been licensed to several organisations in Europe (Stenau q.v.), North America (Wastewater Technology Centre q.v.) and Australia (Wastewater Technology Centre q.v.) and several plants of up to 2 t/h are planned or operating based on sewage sludge.

5.20.2 Description

Figure 5.17 shows one configuration of the auger reactor system based on dried sewage sludge.

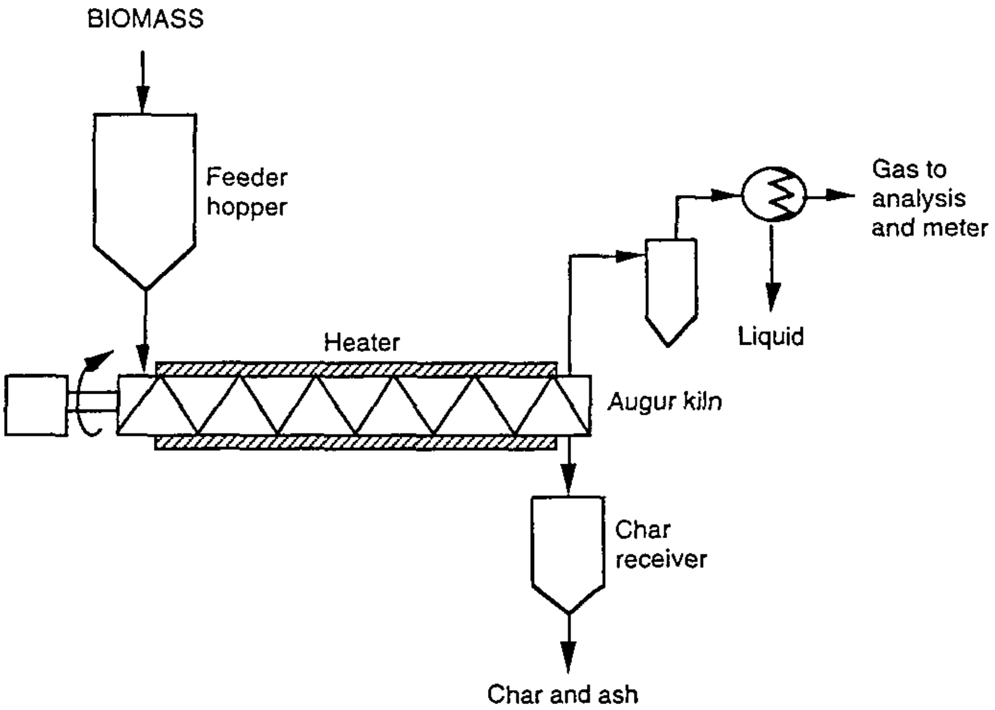

Figure 5.17 **University of Tübingen Pilot Plant Flow Diagram**

At a laboratory scale, both batch and continuous screw reactors have been used. *Sludge dewatered to about 20% wt solids, or other biomass, is heated slowly to* 300-350°C in an oxygen free environment for about 20 minutes, and the liquid product collected in an ice-cooled bath. No additives are needed as the silica, silicates and heavy metals present in the sludge are claimed to act as catalysts. The vapour is condensed and collected. Feedstocks tested include sewage sludge, rape, lupine and Euphorbia.

Four types of equipment have been used on a larger scale for low temperature conversion. There are: a rotary furnace (up to 80 kg/h), a fluidised bed, (up to 400 kg/h), a reactor with a transport belt for MSW conversion (up to 200 kg/h) and a cone screw converter for the conversion of agricultural wastes.

5.20.3 Products

Oil yields ranging from 18-27 wt% (feed basis) and char yields from 50-60 wt % (feed basis) have been achieved. Table 5.19 shows the elemental analysis of the products.

Liquids with very low oxygen content (less than 5% wt oxygen) have been reported from a sewage sludge feed. The low oxygen level and chemical intermediates are claimed to be due to low reaction temperature, natural catalysts in the feed and slow reaction times. The oils contain aliphatic hydrocarbons and fatty acids as the main components (89).

The sewage sludge derived oil has been reported as being used as fuel for a diesel engine.

Table 5.19 Elemental Analysis of Products from University of Tubingen (90)

	Oil	Char	Water vapour	Product water
C	72.62	35.05	0.59	4.33
H	10.75	2.92	11.54	10.53
N	1.27	1.24	0.09	0.35
Cl	0.06	1.08	-	0.06
S	0.24	-	0.15	0.14
O (by difference)	15.06	8.59	87.63	84.59
Others	-	51.12	-	-

5.21 UNIVERSITY OF TWENTE

5.21.1 Summary

This work was instigated under the JOULE programme to develop a new reactor technology for the pyrolysis of biomass by sliding and pressing the particles on a heated surface. Ablative pyrolysis is achieved in a rotating cone where the particles "slide" across a heated metal surface. The process as developed and described has been licensed to BTG and a larger plant of 50 kg/h is being built by Schelde for delivery to China in 1995.

5.21.2 Description

The concept is that biomass particles are fed onto an impeller which is mounted at the base of the heated rotating cone and are then flung on to the heated surface with the final char and ash residue flung out of the top of the cone. The concept is depicted in Figure 5.18.

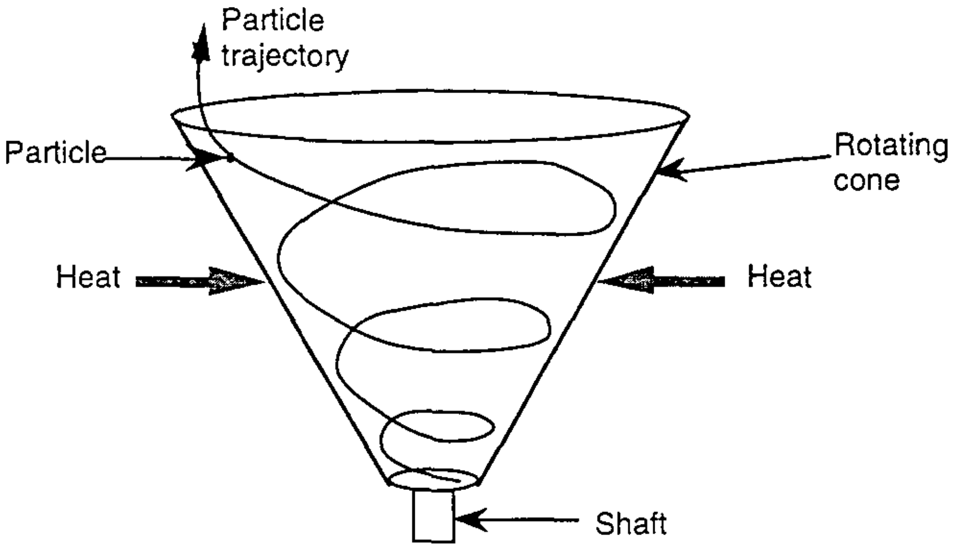

Figure 5.18 **Principle of particle behaviour in the rotating cone**

An initial cold flow experimental cone was built to investigate the dynamic behaviour of nearly spherical mono-sized PVC particles, diameter 140-780µm (91). This work was carried out in a cone of angle 60° [vertical height 0.31 m and cone top width of 0.5 m] and 90°. Rotational speeds up to 1800 rpm were used to determine the influence of gas flow on the residence time and motion of the particles. Particle motion was recorded using an endoscopic camera. Particles greater than 400µm appeared to be unaffected by gas viscous forces and the residence time of the particles is almost independent of the particle diameter. For particles smaller than 200µm, viscous forces become dominant and the residence time of the particles is strongly dependent on the particle diameter. Derived particle residence times were 0.01-0.3 s (92).

A heat transfer rig was then tested with the same cone dimensions to investigate the heat transfer to particles ablatively "sliding" on the cone surface (93, 94). Measurement of particle temperature as it travels along the wall of the cone has bee achieved by fluoroptic methods. The experimental reactor is depicted in Figure 5.19. Initial experiments showed that the fine biomass particles [-250 µm] adhered to the cone surface, thereby reducing the reactor throughput quickly.

Rice husks with a high ash content [~20 wt%] have flowed successfully through the reactor zone with no surface adhesion. Modifications have been carried out to the cone to add sand to promote the flow of solids in September 1992 (95). Initial experiments were carried out mainly with a cone temperature of 600°C and a cone rotational speed of 900 rpm.

The reactor interior has been modified as shown in shown in Figure 5.20 to reduce the operational volume from 0.25 m^3 to 0.003 m^3, otherwise the gas/vapour residence time would be around 80 s giving significant vapour cracking (96). To remove the problem of particle adhesion to the reactor wall, sand is added in a mass ratio of 10 or 20:1 sand to biomass fed. Preheated sand is used on a once through basis. The reactor is to be modified to permit internal sand recycle. The reactor outside the cone quickly becomes filled with sand and char, restricting experimental runs to 10 minutes. The liquids are collected in a series condenser system.

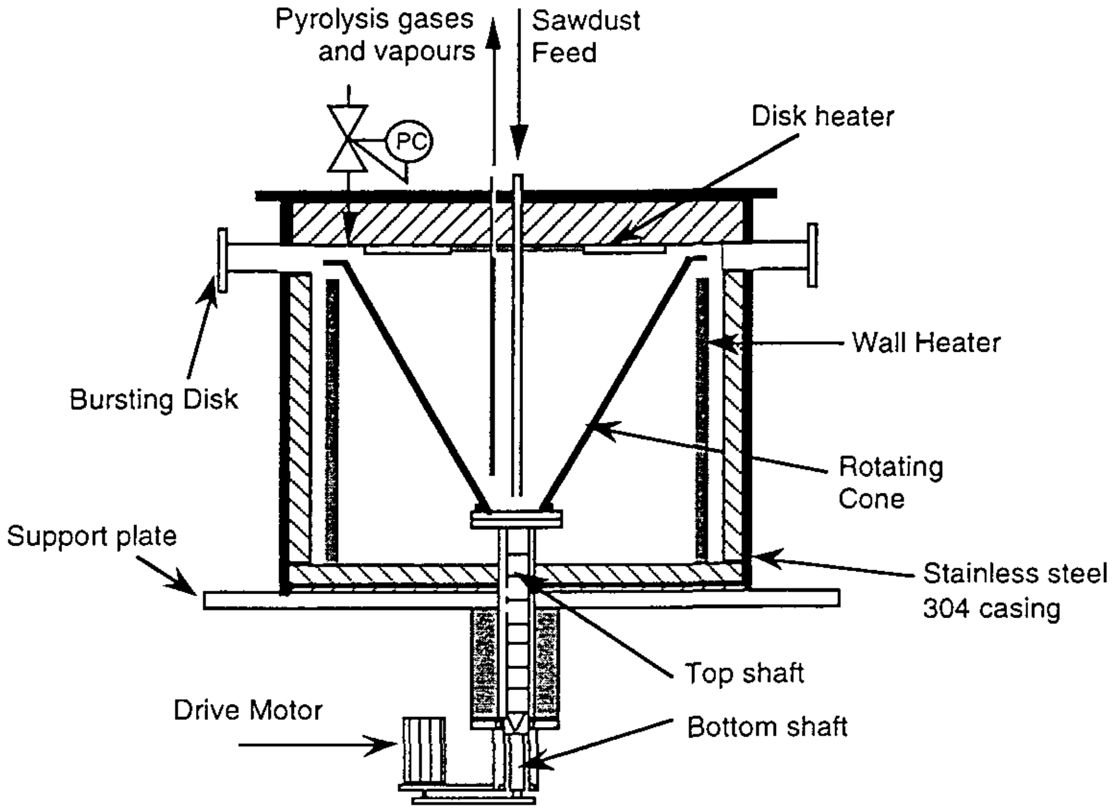

Figure 5.19 Rotating Cone Flash Pyrolysis Reactor: Initial Configuration

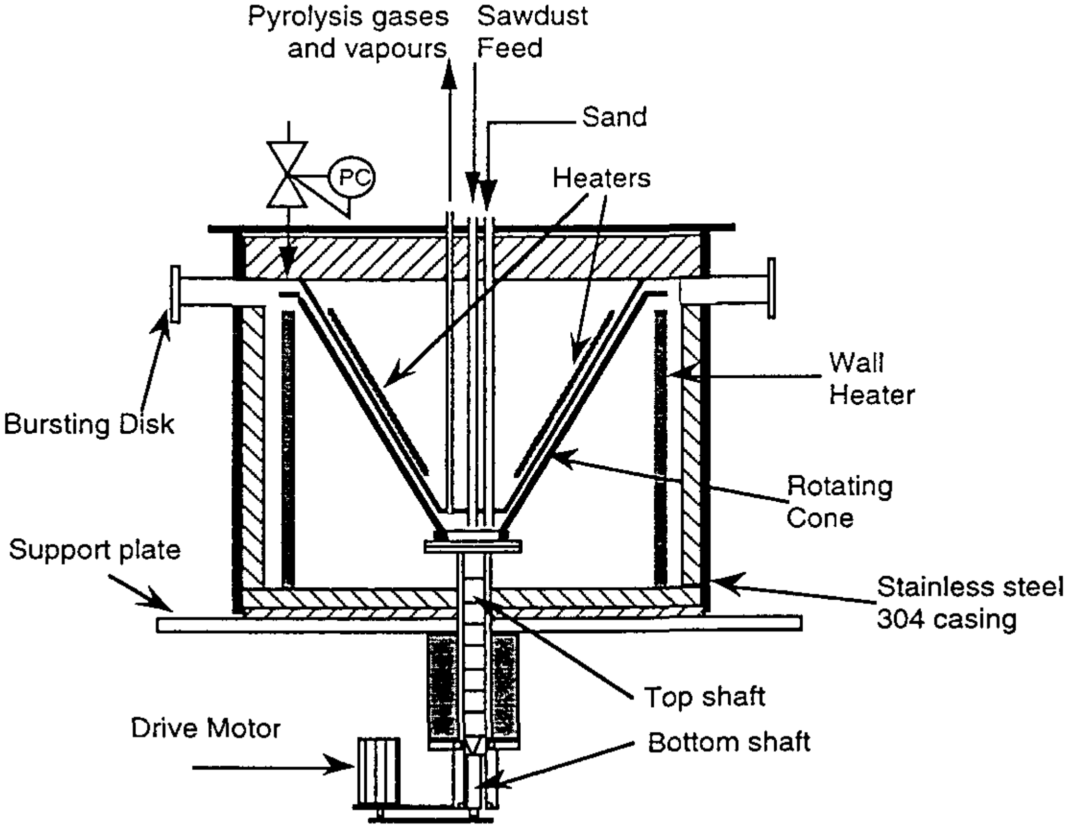

Figure 5.20 University of Twente Modified Reactor

The reactor is to be modified so that the sand is removed from the reactor with the char, the char combusted and the hot sand re-fed to the reactor, i.e. an internal sand recycle. A cold model has been constructed at the beginning of 1995 and this will subsequently be tested as a hot system.

5.21.3 Products

Isothermal reactor operation leads to significant cracking of the product vapours. Typical yields at 1 s residence time and a heated surface temperature of 600°C are: 50 wt% liquids, 30 wt% gases and 15 wt% char. Reactor throughputs are claimed to be 7.2 kg/h of biomass.

5.22 UNIVERSITY OF WATERLOO

5.22.1 Summary

This program was initiated in the early 1980's with the main objective of establishing conditions for maximising liquid yields from biomass, particularly from forest materials. The University of Waterloo can be credited with the foundation of modern fast or flash pyrolysis. Their research is probably the most extensively published and publicised in this area.

Initially, a bench scale continuous flash pyrolysis unit using a fluidised bed at atmospheric pressure was employed. The reactor conditions used were feed rates of up to 50 g/h with a particle size range between 140 and 60 mesh (between 105 µm and 250 µm) in a nitrogen atmosphere over a temperature range of 400-650°C. Results indicated that at an apparent vapour residence time of 0.5 second, organic liquid yields of 60-70% (moisture free) could be obtained from hardwoods such as aspen poplar and maple while yields of 40-60% could be obtained from agricultural wastes such as wheat, straw, corn stover and bagasse. Using the results obtained from the bench scale unit, a larger process unit of 3 kg/h was designed, constructed and tested. This has been extensively studied and a 200 kg/h pilot plant based on results from this unit is being constructed in Spain.

There is an extensive literature available of which some key or recent references are included (97, 98, 99, 100, 101, 102).

5.22.2 Description

A flow diagram of the 3 kg/h process unit at Waterloo is shown in Figure 5.21. The wood is air dried (to 7% moisture), hammer milled and screened to a particle size of -595 µm (-30 mesh). The wood is then conveyed from a hopper by a variable speed twin screw feeder into a cavity where it is conveyed into the reactor by recycled product gas. The feed injection point is within the bed itself. The reactor bed material is sand and the fluidising agent is recycled product gas (a CO-CO_2-CH_4 mixture) which is preheated in the inlet line by controlled electric heaters. In addition, the reactor is wrapped with heating coils allowing extra heat to be added either to the bed of sand or to the freeboard space. The feed hopper and feeder are mounted on a hinged platform resting on a load cell, and hopper weight loss is continuously recorded.

The fluid bed was designed to entrain the char and blow it from the bed while retaining the sand. This is done by careful selection of sand size, biomass particle size, bed velocity and reactor configuration. This is called the "blow-through" mode of operation since there is a negligible amount of char present in the sand and hence there is no need for sand circulation or replacement.

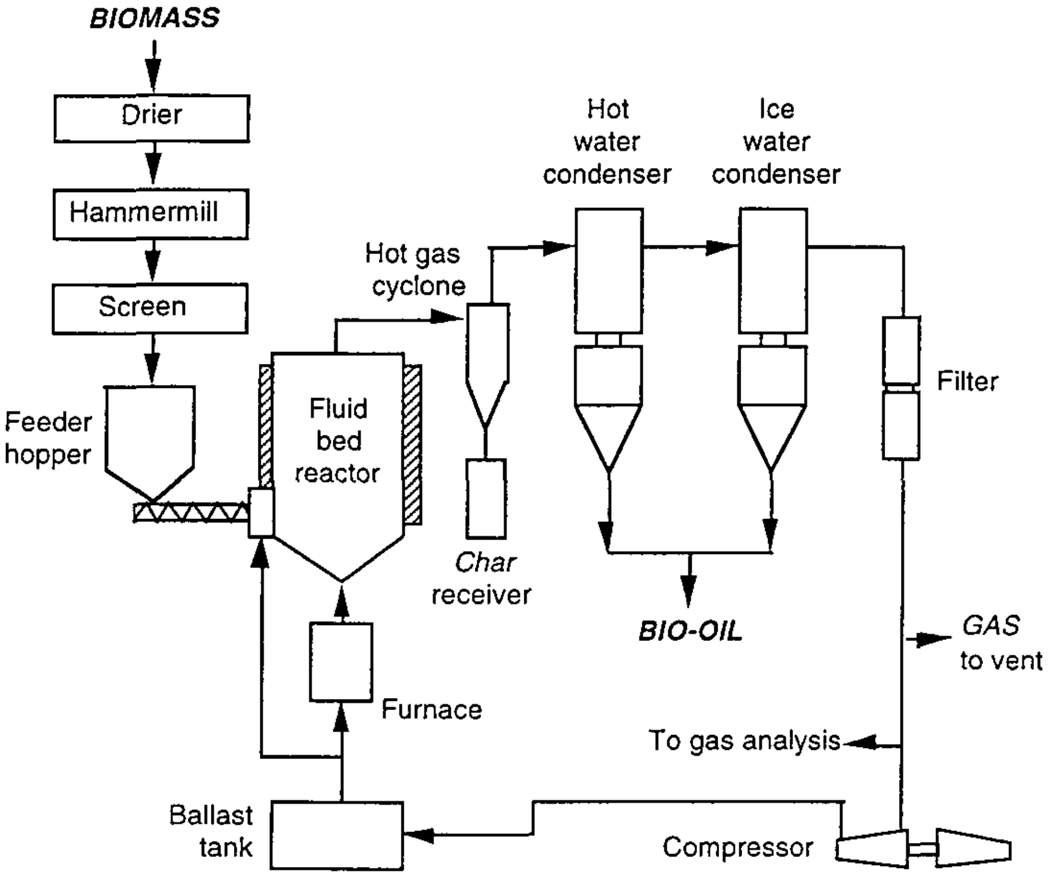

Figure 5.21 **University of Waterloo Pilot Plant Flow Diagram**

The reaction temperature (from 425°C to 625°C) is controlled by a thermocouple within the fluid bed which regulates the inlet gas heating coils. The reactor pressure of about 1.25 bars (125 kPa) absolute is monitored by differential and absolute bellows type gauges. Throughputs from 1.5 kg/h to 3 kg/h have been used.

The reaction products pass through a cyclone where char is removed. The vapours and the gaseous product pass through two condensers in series. These condensers are vertical and have pyrolysis gas inside the tubes; each condenser has a clean-out plug at the top and a condensate collection pot at the bottom. The first condenser is held at about 60°C while the second one uses chilled water at around 0°C as the cooling medium. Tarry products are collected in the condensers. The effluent gases then pass through a filter to remove tar mist and then to a recycle compressor. A proportion of this gas stream is taken from the compressor discharge and used to fluidise the reactor bed and convey feed into the reactor, while the excess is vented through a gas analyser and gas meter as product gas. The product gas is analysed for CO and CO_2 in an on-line infra-red gas analyser-recorder. Samples of the product gas are also taken periodically and analysed by gas chromatography.

5.22.3 Products

High yields of liquid product were obtained at temperatures around 500 °C which is believed to be due to minimum secondary decomposition reactions occurring at such low temperatures (see Table 5.20). The liquid product is highly oxygenated with no phase separation. It has a low viscosity and contains 10 to 20 wt% water depending on the moisture content of the feedstock and the reaction temperature employed. It is dark in colour with an acrid smell. The liquid is quite stable at room temperature over a twelve month period. Some properties of the liquid product are outlined in Table 5.21.

The gas produced has a higher heating value of about 14.4 MJ/Nm^3. This value increases at higher reaction temperatures as the CH_4 content increases and the CO_2 content decreases.

Table 5.20 Reported Pyrolysis Yields from Different Woods at Optimal Conditions

	Brockville Poplar	White Spruce	Red Maple
Temperature, °C	504	500	508
Moisture content, wt %	5.20	7.00	5.90
Particle top size, mm	1000	1000	590
Apparent residence time, sec	0.47	0.65	0.47
Feed rate, kg/h	2.10	1.91	1.98
Yields, wt % (dry wood basis)			
Water (reaction product)	9.70	11.60	9.80
Char	16.50	12.20	13.75
Organic liquids (dry)	62.90	66.50	67.90
Gas composition (wt % dry wood basis):			
CO	4.71	3.82	4.12
CO_2	5.89	3.37	4.89
H_2	0.02	0.02	0.01
CH_4	0.44	0.38	0.36
C_2H_4	0.19	0.17	0.16
Others	0.25	0.04	0.26
Total Gas	11.50	7.80	9.80

Table 5.21 Properties of Pyrolytic Liquids

	Brockville Poplar	White Spruce	Red Maple
Elemental analysis:			
C	54.70	54.00	54.70
H	6.90	6.80	6.40
O (by difference)	38.40	39.20	38.90
H/C ratio	1.51	1.55	1.40
O/C ratio	0.53	0.54	0.53
Water content (wet)	18.70	22.40	18.00
pH	2.40	2.10	2.40
Density, g/cm^3	1.20	1.22	1.19
Higher Heating Value, MJ/kg	23.20	22.70	22.40

5.23 UNIVERSITY OF ZARAGOZA

The University of Zaragoza have recently acquired at least one small fluid bed fast pyrolysis unit of around 2 kg/h. This will be used to screen indigenous feedstocks. No results are yet available.

5.24 WASTEWATER TECHNOLOGY

5.24.1 Summary

The objective of this process (Oil From Sludge, OFS) is the pyrolysis of raw or digested sewage sludge to produce synthetic oil, gas and char (103., 104). Two liquid fractions are produced; a light fraction and a heavy fraction. The process is based on a continuous laboratory scale plant (5 kg/day) for the conversion of sewage sludge to synthetic oil and a solid fuel developed at Tubingen University, Germany for which the Wastewater Technology Centre (WTC) have a license to use the patented technology in combination with the WTC process (104, 105).

Bench scale research work commenced in 1982 (106) leading to the first 1 tonne/day pilot scale plant in 1986 (106). Bench scale results were confirmed and various parameters such as operating temperature, pressure and solid and gas retention times were optimised (106). A second 1 tonne/day pilot plant was built by Campbell Environmental Ltd. (CEL) of Perth, Australia in 1988 (106). Two one tonne/day pilot scale plants have been constructed (Canada and Australia) while a commercial scale plant consisting of three 24 tonne/day process trains is planned for Highland Creek, Toronto, Canada in 1993 (105). Several plans to commercialise the process in Canada have been announced but no plants have yet been built (107).

5.24.2 Description

Sewage sludge consists of a mixture of organic materials and inorganics. The sludge (either raw or digested) needs to be dried from approximately 35% solids to approximately 90 to 95% solids to minimise the production of water which has to be burnt (105). Dried sewage sludge is fed from a live bottomed feed hopper mounted on load cells to the pyrolysis reactor by a variable speed (plug ended to seal the reactor system) screw feeder. If the process is not used continuously, this plug may partially pyrolyse and forming a solid mass which could block the feeding system.

The pilot reactor has an internal diameter of 254mm and is constructed from stainless steel. The reactor operates at a pressure of approximately 2.5 cm water and is heated by hot gases (at 700-800°C) produced by the combustion of propane in an external burner which pass through a jacket surrounding the reactor. Heat is directed to the first third of the reactor by a single inlet pipe and to the second two thirds of the reactor by two inlet pipes. The flow of hot gases to the reactor and hence the heating rate is controlled by baffles. The best oil yields are obtained using a reactor temperature of 450°C and a solids retention time of 20 minutes. The solids retention time in the reactor can be controlled by varying both the sludge feed rate and the reactor operating conditions. It is aimed to quickly heat the feedstock to 450°C in the first third of the reactor and to maintain this temperature along the whole length of the reactor. Waste flue gases from the reactor exit the reactor heating jacket through two flues and are discharged to atmosphere.

Sewage sludge moves through the stainless steel reactor on two conveyors. A screw conveyor moves feed through the first third of the reactor and a series of paddles move the feed through the final two thirds of the reactor. In the first stage of the reactor, the sludge is heated in the absence of oxygen (105). Approximately 50% of the sludge is vaporised in the first stage. In the second stage of the reactor, the pyrolysis gases are contacted with the residual char in either a counter-current or co-current mode to catalyse vapour phase reactions to convert lipids and proteins to hydrocarbons (105, 108).

The char product leaves the end of the reactor through a chute and enters a water cooled plug end screw. The screw conveyor transfers the char into an ash collection skip which is purged with nitrogen to avoid fires.

The vapour phase products enter a condenser which extracts a heavy oil fraction from the product vapours. The condenser is cooled using electrically heated air enabling a small temperature gradient to be maintained permitting control of the heavy oil yield and quality. Vapours leaving the first condenser enter a water scrubber (spray tower) which extracts further oils. The removed oils and water are separated using a disc centrifuge and the water is cooled and recycled back to the spray tower. Following a run, the dirty water is recycled to the water processing plant on site. The non-condensable gases from the system leaving the water scrubber are flared. A flow sheet is given in Figure 5.22.

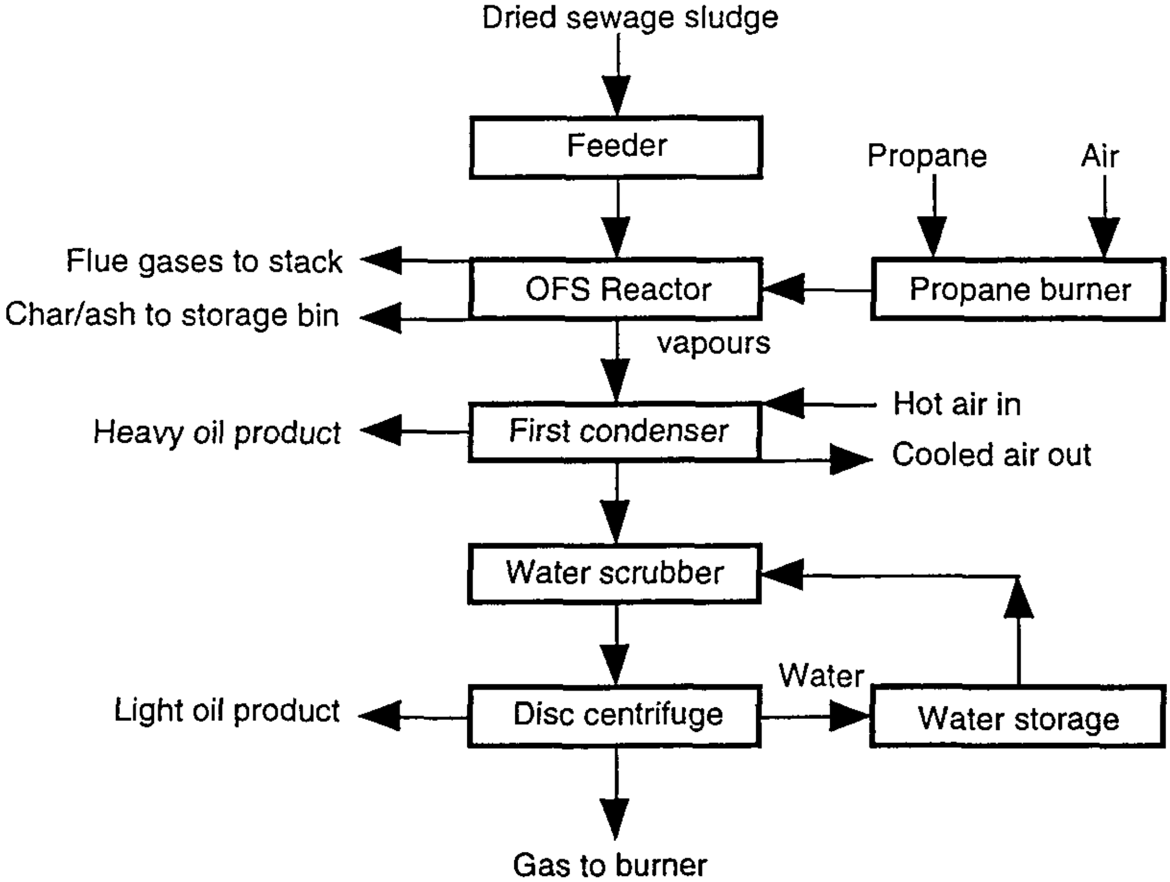

Figure 5.22 Flowsheet of 1 tonne/day Oil From Sludge Pilot Plant

5.24.3 Products

The total yield of oil from the pyrolysis of digested sewage sludge is shown in Figure 5.23. The yield of oil from raw sewage sludge is reported to be 27% of the feed input (basis not reported) while the oil yield from digested sludge is reported to be 11.5% of the mass feed input (105). The exit temperature of the product oil from the system is not reported but it is reported to be cool (105).

The pilot scale oil from sludge process produces two oil products; a light oil fraction and an heavy oil fraction. Both oil products are reported to have very low oxygen contents. The heavy oil product is removed from the first condenser following the reactor. This oil is thick and viscous and flows very slowly at 15°C. The water content of the heavy oil is approximately 1% by mass. The light oil product is removed from the disc centrifuge. The light oil has a caramel colour, has a low viscosity and contains approximately 5% water by mass. The heavy oil does not distil while the light oil is entirely volatile. The as-received (including water) higher heating value of the light and heavy oils is between 35 and 40 MJ/kg. The heavy oil product accounts for approximately 80% of the liquid yield while the light oil product accounts for the remainder. Oil char separation is reported to be efficient - char levels in the heavy oil are not measurable.

The heavy oil product has been found to be suitable as an anti-stripping compound in asphalt as the properties which make the oil a poor quality fuel make it a good anti stripping compound. The use of the product oil in asphalt production would also prevent CO_2 emissions from the use of the product oils. Pilot scale experiments are now, therefore, being optimised towards specific high value non-fuel products. Canmet are currently investigating possible end uses for the products from the oil from sludge process. Liquid composition data for the heavy and light oil fractions is not currently available. The composition data shown in Table 5.22 shows the composition of a single liquid oil product produced by the oil from sludge system before the two separate oil stages were installed. Some heavy metals are carried over from the sludge to the oil although the majority of the heavy metals remain with the char (108).

Table 5.22 Summary of Liquid Characteristics (105, 106)

Composition, % weight		
Carbon	76	
Hydrogen	11	
Oxygen	6.5	
Sulphur	0.5	
Nitrogen	4	
C/H molar ratio	0.58	
C/O molar ratio	15.59	
Output rate	5.68	kg/h
Exit temperature from system	not reported	°C
Heating value from digested sludge*	41	MJ/kg *
Heating value from raw sludge*	31	MJ/kg *
Char content	<1	wt %
Ash content	<0.5	wt %
Heavy metals content	not reported	mg/kg
Other characteristics	-	

* *Heating value basis not reported*

Estimated mass and energy balances for a 180 tonne/day pyrolysis plant are shown in Figure 5.23. The process thermal efficiency (ratio of oil chemical energy to the chemical energy of the dry sludge) calculated using the figures shown in Figure 5.23 is 52.2%. Although the yield of oil varies with the type of sludge processed, the effect of reaction temperature on oil yield is the same for all sludges (108). Peak oil yield is obtained at a reaction temperature between 425 and 450°C. Accurate reactor temperature control is, therefore, required (108). Above 450°C, conditions favour the production of product gas. The data indicate that the heating value of oil produced from digested sludge is higher than the heating value of oil produced from raw sludge (105).

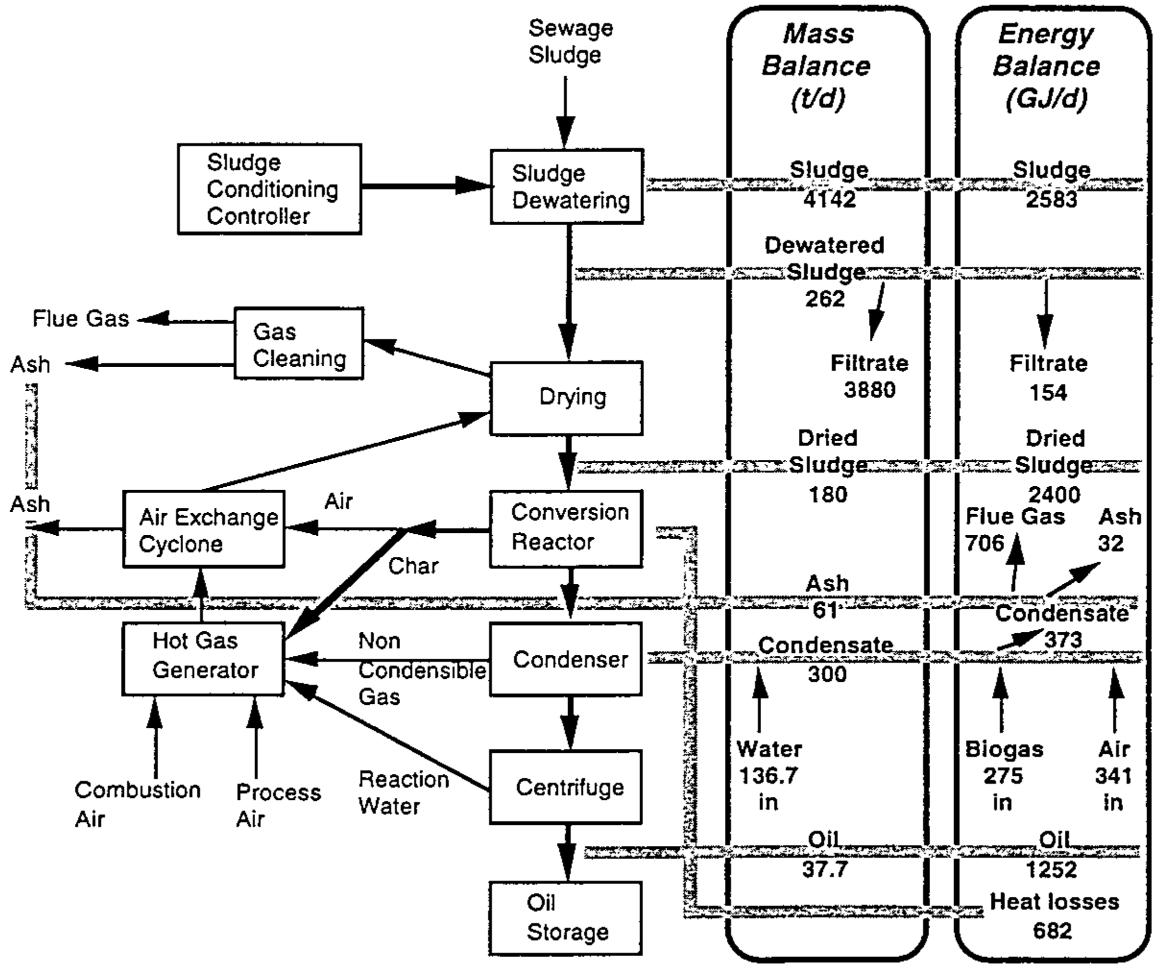

Figure 5.23 Oil from Sludge Plant Mass and Energy Balances (105)

5.25 WORTHING INDUSTRIES INC.

A 200 kg/h fluid bed reactor derived from the University of Waterloo work was originally constructed in 1986 by Encon for wood and peat pyrolysis. The unit was constructed as a self contained plant on the back of a trailer for transportation to test sites for demonstration. This is now used for processing old telegraph poles. These have their outer skin of treated wood removed and which is then pyrolysed in a 50 kg/h fluid bed pyrolyser for recovery of chemicals including creosote and PCP as well as bio-oil. Up to 30,000 poles per year are processed. The skimmed poles are re-treated and recycled (109). No information is available on performance or costs.

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CHAPTER 6
CATALYTIC UPGRADING TECHNOLOGIES FOR PYROLYSIS VAPOURS AND LIQUIDS

6.1 INTRODUCTION

In all thermochemical conversion processes, catalysts are being increasingly used to enhance favourable reactions and inhibit unfavourable reactions. In addition, catalytic processes are both available and are being developed to upgrade the primary products of thermal conversion to higher quality and higher value fuels and chemicals as summarised in Table 6.1 for a range of thermally processed products. This study focuses on fast pyrolysis processes and liquid products as a means to increase the value of resultant products at minimal cost. While reference is made to many of the research activities involving the use of catalysts in biomass conversion (see, for example, 1), attention is focused on particular problems requiring short term solution to enable the benefits of these technologies to be realised.

Table 6.1 Catalytic Processes for Secondary Products

Secondary product	Source	Catalytic process	Status
Oxygenated Fuels			
Methanol	Gasification	Synthesis	Commercial from syngas
Fuel alcohol	Gasification	Synthesis	Development
Hydrocarbon Fuels			
Gasoline	Pyrolysis	Hydrotreating	Research
	Pyrolysis	Zeolites	Research
	Liquefaction	Hydrotreating	Research
	Gasification	MTG #	Commercial from reformed natural gas
Diesel	Pyrolysis	Hydrotreating	Research
	Pyrolysis	Zeolite + MOGD #	Research
	Liquefaction	Hydrotreating	Research
	Gasification	MOGD #	Research
Fuel oil	Pyrolysis	Stabilisation	Conceptual
	Liquefaction	Stabilisation	Conceptual
Chemicals			
Ammonia	Gasification	Synthesis	Commercial
Specialities	Pyrolysis	Extraction / Conversion	Development
	Liquefaction	Extraction / Conversion	Research

Notes # MTG : Methanol To Gasoline process (Mobil)
MOGD : Methanol To Olefins, Gasoline and Diesel (Mobil)

6.2 FAST PYROLYSIS LIQUID PRODUCTS

6.2.1 Introduction

Many flash pyrolysis processes have been developed to pilot, demonstration and commercial scale based solely on thermal conversion without any extrinsic catalytic activity, to give a crude fuel product (2, 3). Concerns over utilisation and assimilation into a fuel market infrastructure have caused attention to be paid to in-situ or close coupled catalytic upgrading.

The liquid product is currently attracting the most interest in Europe and North America because of its high energy density, easy transportability, ease of use and de-coupling of conversion and utilisation processes (4). The liquid approximates to biomass in elemental composition, and is composed of a very complex mixture of oxygenated hydrocarbons. The complexity arises from the degradation of lignin, cellulose and hemicellulose, resulting in a broad spectrum of oxygenated compounds from uncontrolled and interactive degradation. Its composition is determined intrinsically by the temperature, rate of reaction, vapour residence time, and temperature-time cooling and quenching process which controls the extent of secondary reactions, and extrinsically by the feed composition. The liquid is often referred to as "oil" or "bio-oil" or "bio-crude-oil" and can be upgraded to liquid hydrocarbon fuels, as indicated in Table 2 above.

Typical properties of flash pyrolysis oil have been reported from analytical programmes sponsored, for example, by the EC JOULE and AIR programmes (5), Energy Mines and Resources Canada (6), the United States Department of Energy (7) and the International Energy Agency Bioenergy Agreement (8), as well as extensively by technology developers. The key feature from a fuel utilisation viewpoint is the high oxygen content which ranges from 30 to 55% wt. depending on the feed, the feed water content, the oxygenated product spectrum, product water content and basis of reporting.

It is important to note that there are two types of liquids produced by pyrolysis of biomass:

- Primary liquid from flash pyrolysis processes. This is produced in high yields of up to 85% weight. It has a relatively low viscosity and high water miscibility tolerance of up to 35-50% wt water and can be readily combusted in most applications such as boilers, kilns and dual fuel engines. It is relatively unstable compared to conventional fuel oils being, for example, very temperature sensitive and non-volatile in distillation due to polymerisation reactions (1, 4).
- Secondary oil or tar from conventional or slow pyrolysis processes. This is produced in low yields of up to 20% weight It is very viscous and can only tolerate up to about 20% wt water before phase separation occurs. While it can also be combusted in many applications, the high viscosity and potential for water separation require careful handling.

The characteristics of both slow and flash pyrolysis oils are summarised in Table 6.2. Both products may be upgraded by any of the processes described in this chapter, but the low yields of slow pyrolysis liquid products will give very poor overall yields of upgraded products, thus adversely affecting the economics.

Table 6.2 Detailed Characteristics of Wood Derived Flash Pyrolysis Oils

Physical property		Flash pyrolysis	Slow pyrolysis
Moisture content		20%	14.6%
pH		2.5	2.0
Specific gravity		1.21	1.195
Elemental analysis (moisture free)			
C		56.4%	61.9%
H		6.2%	6.0%
N		0.2%	1.05%
S		<0.01%	0.03%
Ash		0.1%	1.5%
O (by difference)		37.1%	29.5%
C/H ratio		9.1	10.3
HHV (moisture free basis)		23 MJ/kg	26.3 MJ/kg
HHV as produced		19.3 MJ/kg	-
Viscosity (@ 40°C)		51 cp	300 cp
Kinematic viscosity	@ 25°C	233 cSt	
	@ 40°C	134 cSt	
ASTM vacuum distillation	160 °C	10%	
	193 °C	20%	
	219 °C	40%	
	Distillate	50%	
Pour point		-23 °C	27°C
Solubility	hexane insoluble	99%	
	toluene insoluble	84%	
	acetone/acetic acid insoluble	0.14%	

6.2.2 Fast pyrolysis gas and solid by-products

The gas is of low to medium heating value, 5-15 MJ/Nm3, depending on the method of pyrolysis. Even after efficient vapour condensation and liquid collection, it still has a relatively high oil content and either needs to be burned hot such as for drying feedstock, or a tertiary clean-up stage may be needed according to how it is used. Physical gas cleaning is difficult due to the complex physical and chemical characteristics of the organics. If water scrubbing is used, this gives a substantial wastewater disposal problem. The most effective utilisation method for the gas is as the fluidising medium if a fluid bed is used and use in-plant for some of the process energy requirement, although its specific energy content is rather low. The gas from high temperature processes can contain a significant proportion of non-equilibrium products such as olefins. These are of potential interest to the petrochemical industry when high temperature flash pyrolysis is employed (9). The yields of any individual or group of constituents is, however, relatively low. Ethylene yields have not exceeded 15% for example which is considered too low to be of economic interest (10). Catalytic conversion of such intermediates is possible by any established petroleum or petrochemical process, although this is not known to have been investigated.

The solid product from pyrolysis is char with any ash or inerts present in the feed.

Carbonisation is pyrolysis operated at low reaction rates and low temperatures to maximise charcoal production. This is established technology in both industrialised and developing countries. High pressure pyrolysis gives higher solid yields, but low pressure (vacuum) pyrolysis behaves analogously to flash pyrolysis in terms of liquids as the primary products are rapidly removed and do not contribute to char formation. In flash pyrolysis the char can be exported or used in-plant for process energy demands.

6.3 CATALYTIC EFFECTS IN PYROLYSIS

Most biomass contains natural salts that will influence the decomposition products. However, since the salts cannot readily be removed without affecting the organic substrate, any catalytic effects become part of the simple thermal degradation process. Much of the early work on fundamentals such as Shafizadeh (11) recognised the effect but did not take advantage of the phenomena. A particular example is pyrolysis of sewage sludge, initially investigated at the University of Tubingen (12) and later applied to development of a commercial plant to recover oil (13, 14, 15). Bayer claimed that the inorganic constituents of sewage acted as a "natural catalyst" (12) and this work was extended to recovery of fatty acids (16). The University of Waterloo has clearly demonstrated the effects of natural catalysts on chemicals production, and details are given in Table 6.3 and beyond.

6.3.1 Chemicals production

The extraction and recovery of chemicals from biomass pyrolysis liquids is rapidly growing in interest as the natural catalysts in most biomass forms are enhanced or removed to emphasise production of specific chemicals or families of chemicals. In addition, specific chemicals are recovered by physical and/or chemical processing and may be subjected to catalytic processing to improve the product quality or yield or derive higher value chemicals. Since the primary formation of organics is significantly influenced by the presence or absence of natural or added catalysts, it is not practicable to differentiate between catalytic and non-catalytic processes, so all chemical extraction and recovery work is included. Secondary upgrading of the recovered compounds or fractions is also included here, but catalytic conversion of the primary vapours and whole product oil is discussed separately below.

Table 6.3 lists the organisations currently and recently involved in chemicals extraction/recovery and derivation, while Table 6.4 lists the chemicals and where they are being investigated.

6.3.2 Extraction and synthesis

The pyrolysis liquids can be used for production of higher value commodities as chemicals rather than fuels. Most are based on physical extraction processes, of which some are commercial and proprietary (32) and some are under development and subject to patent applications and again data is not available (17, 18, 19, 20, 21, 22, 30, 31).

Table 6.3 Organisations Involved in Chemicals Recovery from Pyrolysis Oils since 1980

Organisation	Chemicals	References
BC Research	Levoglucosan,	17, 18, 19
	Calcium acetate	20, 21
	Hydroxyacetaldehyde, glyoxal	22
China Lake	Olefins, gasoline	23
CPERI (a)	Phenols, ethers, anisole	24, 25, 26, 27, 28
DuPont	Phenols and cresols	29
NREL (b)	Phenols, polyphenols, adhesives	30, 31
	Gasoline, olefins, aromatics, ethers	See Table 5
Red Arrow	Food flavourings	32
Texas A&M University	Oxychemicals	33
University of Alicante	2-furaldehyde	34
University of Hamburg	Oxychemicals	35
University of Laval	Specific phenols and specialities	36, 37, 38, 39
University of Montana	Levoglucosan, furaldehyde	40, 41
University of Toronto	Alkanes and alkenes	42
University of Tubingen	Fatty acids	16
University of Waterloo	Levoglucosan, sugars,	43, 44, 45, 46
	Hydroxyacetaldehyde, acetol, acetic acid	47, 48, 49

Notes a) Centre for Process Engineering Research Institute, University of Thessalonika, Greece

b) National Renewable Energy Laboratory, Golden, CO, USA

Phenols are one of the largest group of chemicals in flash pyrolysis liquids and chemical recovery has focused on these compounds. Polyphenols, for example, are potentially valuable chemicals for substitution in phenol-formaldehyde resins for wood processing such as in plywood manufacture (30, 31, 48). Anisole has been derived from phenol extracted from pyrolysis oil (25), in which both proprietary and in-house manufactured catalysts modified with Mn and Cd were used with up to 72% conversion of phenol.

Levoglucosan is a major intermediate in the thermal degradation process. Yields of up to 20% on a dry feed basis have been reported when the feed is pre-treated by acid washing to reduce the alkali metals which catalyse sugar decomposition (47, 48, 49). The extraction and recovery of the levoglucosan at high purity has recently been patented by BC Research (19). High yields of hydroxyacetaldehyde have similarly been reported by the University of Waterloo, some through additions of simple (unspecified) catalysts to the biomass prior to pyrolysis (47, 48, 49).

Table 6.4 **Chemicals Recovered from Biomass Pyrolysis Liquids**

Chemical	Organisations	References
Acetol	University of Waterloo	47, 48, 49
Adhesives	NREL	30, 31
Alkanes and alkenes	University of Toronto	42
Anhydrosugars	University of Montana	40
	University of Waterloo	43 - 46
Anisole	CPERI	25
Aromatics	NREL	See Table 5
Aryl ethers	CPERI	24, 25, 27, 28
Calcium acetate	BC Research	20, 21
Carboxylic acids	University of Laval	37 - 39
Cresols	DuPont	29
Fatty acids	University of Tubingen	16
Food flavourings	Red Arrow	32
Glyoxal	BC Research	22
Hydroxyacetaldehyde	BC Research,	22
	University of Waterloo	39, 40
Levoglucosan	BC Research,	16 - 18
	University of Waterloo	47, 48
	University of Montana	40
Olefins and gasoline	China Lake	23
	NREL	See Table 5
Oxychemicals	Texas A&M, University of Hamburg	33, 35
Phenols	CPERI	24, 28
	Du DuPont	29
	NREL	30, 31
	University of Laval	36, - 39
Polyphenols	NREL	30, 31
Reformulated gasoline	NREL	See Table 5

6.3.3 Direct production of chemicals

Direct production of speciality chemicals by concurrent catalytic processing with pyrolysis has also attracted some attention. There has been scattered research on the effects of adding various catalysts to biomass prior to pyrolysis. Addition of sodium chloride increased yields of char and of certain chemicals such as glycolaldehyde (hydroxyacetaldehyde), and suppressed levoglucosan production (41). Similar effects were found with zinc chloride, except that higher yields of furfural were obtained (50), and also with cobalt chloride additions to almond kernels which gave higher yields of 2-furaldehyde (29).

Pyrolysis in molten salts gave significant yields of acetone and hydrocarbon gases (51) and under different conditions, gave high yields of relatively pure hydrogen (above 90% vol. with the balance methane) (52, 53, 54). It was postulated that careful temperature control and temperature variation such as ramping or predissolution at low temperature could lead to higher yields of potentially valuable speciality chemicals. It was not clear if there were any catalytic effects present, or if the results were derived from physical absorption of carbon dioxide in the alkaline melt with possible effects on the equilibrium through the shift reaction as demonstrated by Hallen (55). The economic and energetic consequences of melt regeneration have not been evaluated, but are recognised as significant (51).

Hydrogen has been used as a reactive gas in a catalytically modified atmospheric fluid bed flash pyrolysis using nickel process to give 70-75% conversion to a gas containing 85-90% methane (48, 56, 57), and olefins have also been produced in interesting yields (57). Although this is referred to as hydropyrolysis, this term is more usually employed for high pressure systems. This route has not yet been used to derive liquids although there are many interesting possibilities based on pressure processing which may be viable at the lower temperatures that are optimal for liquids production as well as atmospheric pressure catalytic pyrolysis using, for example, modified zeolites which are described below.

Integrated catalysis and flash pyrolysis has been carried out on lignins for improved cracking to fuels and chemicals over a temperature range of 500 - 800°C (58).

A review of recent developments in thermal and thermo-catalytic biomass conversion has been published (3) and the opportunities for chemicals production reviewed (59).

In all cases of chemicals recovery, there is little evidence that the higher yields of specific chemicals will be economically viable or that there are markets for the products. Addition of environmentally sensitive materials such as chloride may cause treatment and disposal problems for wastes and by-products. For char production, addition of chloride can only be deleterious and expensive in most applications for the charcoal.

6.4 CATALYTIC UPGRADING OF LIQUIDS

The crude primary liquid product from flash pyrolysis contains very high levels of oxygen which give the product some unusual characteristics including water miscibility and temperature sensitivity as described above. While the oil can be used directly in a number of thermal and power generation applications, this is considered to be unsuitable in some demanding applications such as turbines and engines and substitution for transport fuels, so upgrading to more conventional liquid hydrocarbon fuels has been examined.

There are currently two basic processes: modified conventional hydrotreating to a naphtha-like product can be characterised as CH_2; or zeolite cracking and synthesis to a highly aromatic product which can be characterised as $CH_{1.2}$. Recent developments have been reviewed by Elliott et al. (3), Sharma and Bakshi (60) and Milne and Soltes (61) and future needs identified (62, 63).

6.4.1 Hydrotreating

Hydrotreating aims to remove the oxygen through a family of de-oxygenation reactions which can be conceptually characterised as follows:

$$C_6H_8O_4 + 6H_2 \longrightarrow 6CH_2 + 4H_2O$$

or

$$C_6H_8O_4 + 4.5H_2 \longrightarrow 6CH_{1.5} + 4H_2O$$

Bio-oil Hydrocarbons (naphtha equivalent)

This is a carbon limited system and gives a maximum stoichiometric yield of 58% by weight on liquid bio-oil or a maximum energetic yield of about 50% wt. ignoring the significant hydrogen generation requirement which is discussed below.

A summary of the activities in catalytic hydrotreating of pyrolysis and liquefaction products is given in Table 6.5.

Table 6.5 Organisations Involved in Catalytic Upgrading of Pyrolysis and Liquefaction Oils since 1980 by Hydrotreatment and Related Processes

Battelle Pacific Northwest Laboratory (PNL), USA	64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74
Colorado School of Mines, USA	75
Institute Nationale Recerche Scientifique (INRS), Canada	76
Imperial College, University of London, UK	77
Institute of Wood Chemistry, Germany	78
Lawrence Berkeley Laboratory, CA, USA	79
National Renewable Energy Laboratory, USA	80, 81, 82
Saskatchewan Research Council	83
Technical University of Berlin, Germany	84
Technical University of Compiegne, France	85
Texas A&M University, USA	33, 86, 87, 88, 89, 90
University of Chalmers, Sweden	91, 92, 93, 94
University of Louvain (UCL), Belgium	95, 96, 97, 98, 99, 100, 101, 102, 103, 104
University of Rouen	105
University of Sassari, Italy	106
University of Waterloo, Canada	107
University of Saskatchewan, Canada	108
University of Toronto, Canada	109
Veba Oel, Germany	110, 111, 112
VTT (Technical Research Centre of Finland), Finland	113, 114, 115

The essential processing features for pyrolysis bio-oil hydrotreating are:

- high pressures of 70 to 200 bars to provide a high hydrogen partial pressure,
- a two stage process: an initial stabilisation reactor or reaction zone operating

at about 250-275°C followed by a more conventional hydrotreating process operating at 350-400°C. The initial stabilisation consumes little hydrogen but is essential to avoid polymerisation at the higher temperatures of hydrotreating. Without this initial stabilisation, the pyrolysis liquid rapidly polymerises and cokes the catalyst (110, 112). A temperature stepped single upflow continuous fixed bed reaction has been successfully employed for this purpose in both the USA (61, 69) and Germany (110, 112).

In practice, for pyrolysis liquids, hydrotreating yields of about 35% wt on wet liquids, based on better than 98% de-oxygenation, have been achieved from pyrolysis oils in a continuously operated carbon limited system which is about 70% of the theoretical maximum (62, 63, 116).

Conventional sulphided CoMo hydrotreating catalysts that are utilised commercially for hydro-desulphurisation have been found to be quite effective, although there is much potential for catalyst development both with conventional catalysts and with novel catalysts. Liquefaction oils do not require the initial stabilisation step and may be conventionally processed.

Hydrotreating is based on a modification or extension of well-established refinery practice for hydro-desulphurisation and involves a family of reactions including hydrogenation, de-oxygenation and cracking. The pyrolysis or liquefaction material being processed is made up of a wide range of classes of organic compounds, which all behave differently under different reaction conditions. The hydrotreating process, therefore, has to be "customised" to a particular feed and a specified product. It has been successfully demonstrated at a continuous laboratory scale on pyrolysis products (64, 65), liquefaction products (78, 84), selective extracts from liquid products (82, 107), lignin (75, 80, 81, 82) and black liquor (114, 115). Optimisation is required to establish the best catalyst system for the highly oxygenated liquids and the optimum process parameters.

Conventional sulphided cobalt/molybdenum (Co/MoS) hydrotreating catalysts have proved successful. A variety of related catalysts including Ni, Co, Mo in oxide and sulphide forms on silica and alumina supports have also given quite good results in work at Battelle Pacific Northwest Laboratory, the University of Louvain (UCL) and the Institute of Wood Chemistry (see Table 5 for full citations), although catalyst activity of the oxide forms is significantly lower. However the absence of sulphur and sulphided catalysts may be an advantage to be exploited if longer term tests show that sulphur retention is a problem with the essentially sulphur-free pyrolysis oil feedstock.

There is uncertainty over the catalyst lifetime as few extended runs have been reported. At least one continuous run of 8 days has been completed but with substantial deterioration in activity (110, 112). There is no information on the cause of this loss in activity, although physical examination of the catalyst afterwards suggests that the water in the bio-oil may have attacked the support and drastically reduced the surface area through agglomeration. Other hypotheses include alkali attack, coking, and loss of sulphide from the catalyst. There is also uncertainty over catalyst stability and activity with regard to the sulphur and possible contamination of the product oil. One of the concerns is sulphur stripping from the catalyst which would seriously impair its effectiveness. The water product may have an adverse effect on conventional catalysts, and they may require modification to improve their water tolerance. Other contaminants may also have an adverse effect but this has not yet been explored and long term testing and detailed catalyst examination is necessary if this route is to be further developed.

Other catalytic environments have also been tested including the use of hydrogen donor solvents (89, 90, 97) and less conventional catalyst systems including oxide forms of CoMo and NiMo and modified NiMo which have so far proved to be less active than sulphided catalysts (97). Soltes employed platinum and palladium catalysts in a hydrogen donor solvent, claiming superior results to other catalysts (88).

Basic work has been carried out on model compounds (75, 101) and constituents of wood, notably lignin to devise a more effective method for utilisation of wastes from the pulp and paper industry (75, 80, 81, 101). This has included hydrotreating black liquor (113 - 115). Use of model compounds has some value in establishing pathways and kinetics as well as establishing minimum and optimum reaction parameters, but the pyrolysis liquid is so complex that this approach may be of only limited use in the short term. There will, however, be potential benefits from this approach in developing partial hydrotreating to derive a stable but only partially de-oxygenated product and in the production of chemicals rather than fuels.

Integrated conversion and upgrading has been employed in a number of configurations and processes including a first stage of hydrolysis with hydrotreating (76) and solvolysis followed by hydrotreating (79).

Analysis of products is always an important contribution to improve understanding of the processes involved so that they can be optimised and scaled up. Most of the organisations listed in Table 5 have developed appropriate analytical techniques, and some publications have focused on these analytic methods (87, 95, 98)

One of the useful side-effects of full hydrotreating, i.e. less than 2% wt oxygen in the final product, is that the product water readily separates from the hydrocarbon product and is relatively clean. The water will also tend to strip out the alkali metals present, for example, in wood ash and resolve one of the problems in using biomass derived fuels in turbines.

6.4.2 Partial hydrotreating

For some applications, such as gas turbine fuel, complete de-oxygenation may not be necessary to give a suitable fuel with acceptable chemical and physical properties. This concept of partial hydrotreating has not yet been properly explored. For example, raising the LHSV (liquid hourly space velocity) from around 0.1 to 0.2 or 0.3 will give an oxygen level of around 4 or 15% respectively compared to 0.5% oxygen at 0.1 LHSV (116). The typical oxygen content of a flash pyrolysis oil is about 35-40%. The uncertainty lies in the selectivity of hydrotreating and hydrogenation of different classes of compounds in the crude bio-oil and the properties of the resultant partially upgraded oil. Some exploratory work has, however, been carried out (96) including studies on model compounds (75, 101).

A 15% oxygen content product would have a similar oxygen content as pressure liquefaction products which have very high viscosity and limited water miscibility under ambient conditions. This is, therefore, relatively difficult to use in most conventional applications. A partially hydrotreated pyrolysis oil has not been produced, however, so it's characteristics cannot be defined. If there is a separate water phase, this would be highly contaminated with soluble organics and would require extensive and costly treatment. However, if this approach were successful in producing a stable and directly usable product, the hydrogen consumption could be reduced by 60% and the capital cost reduced by about 30%. In addition, the product may either retain the water in a solubilised form, or a relatively clean water could be separated. The concept of stabilisation by partial hydrotreatment deserves further consideration.

6.4.3 Hydrogen supply

A major disadvantage of hydrotreating is the significant hydrogen requirement of around 700 l/kg pyrolysis oil (62), (31 g moles/kg; 62 g/kg) for full hydrotreating, while Veba suggest 600 - 1000 l/kg bio-oil (110, 112). These should be compared to the theoretical yields of 380 l/kg for CoMo catalysts and 440 l/kg for NiMo catalysts (97). An excess of typically 100% is thus required for processing due to hydrogenation of components such as light aromatics.

The hydrogen can be generated in a number of ways including recovery and/or regeneration from the spent gases. These options are summarised in Table 6.6 which includes approximate relative costs, and depicted in the flowsheet of Figure 2. These alternatives have not been evaluated, but will significantly affect the economics. A 1000 t/d biomass processing plant will require about 50 t/d hydrogen for complete hydrotreating which, if generated from biomass by gasification and CO shifting would require up to 800 t/d additional biomass at a significant economic and efficiency penalty. A potentially attractive route is to utilise the surplus hydrogen which is available at fuel value in many refineries. Product yields and process costs are discussed below.

6.4.4 Zeolites

Early zeolite cracking research on biomass derived pyrolysis liquid was carried out on a conventional mono-functional ZSM-5 catalyst, although more, recently specialist catalysts have been developed by modification of the structure in an unspecified way (117). The reaction follows the representative equation below with a maximum stoichiometric yield of 42% on liquid, or a maximum energetic yield of about 50% wt.:

$$C_6H_8O_4 \longrightarrow 4.6CH_{1.2} + 1.4CO_2 + 1.2H_2O$$

This is a hydrogen limited reaction with the aromatic product being limited by the availability of hydrogen for aromatics and water formation and oxygen is rejected as both CO_2 and H_2O.

Table 6.6 Hydrogen Generation Options

Alternative	Status	Relative ¶ Cap. cost	Relative ¶ Op. cost
Using existing surplus hydrogen from a conventional refinery	Available	Low	Low
Recovering and recycling unused hydrogen	Available	Moderate	Moderate
Reforming and/or shifting product gas "in-situ" with a modified catalyst	Unproven	Low	Low
Reforming/shifting product gas externally, *for hydrogen recovery and recycle*	Unproven (118)	Moderate	Moderate
Gasifying biomass, shifting CO to H2 and recovering hydrogen	Unproven	High	Moderate
Gasifying charcoal, then as for biomass	Unproven	High	High
Converting fossil fuel by steam reforming or partial oxidation with shift and CO2 removal	Available	Moderate	Moderate
Electrolysing water using either solar or conventionally produced electricity	Available	High	High
Purchasing hydrogen in bulk.	Available	Low	Moderate

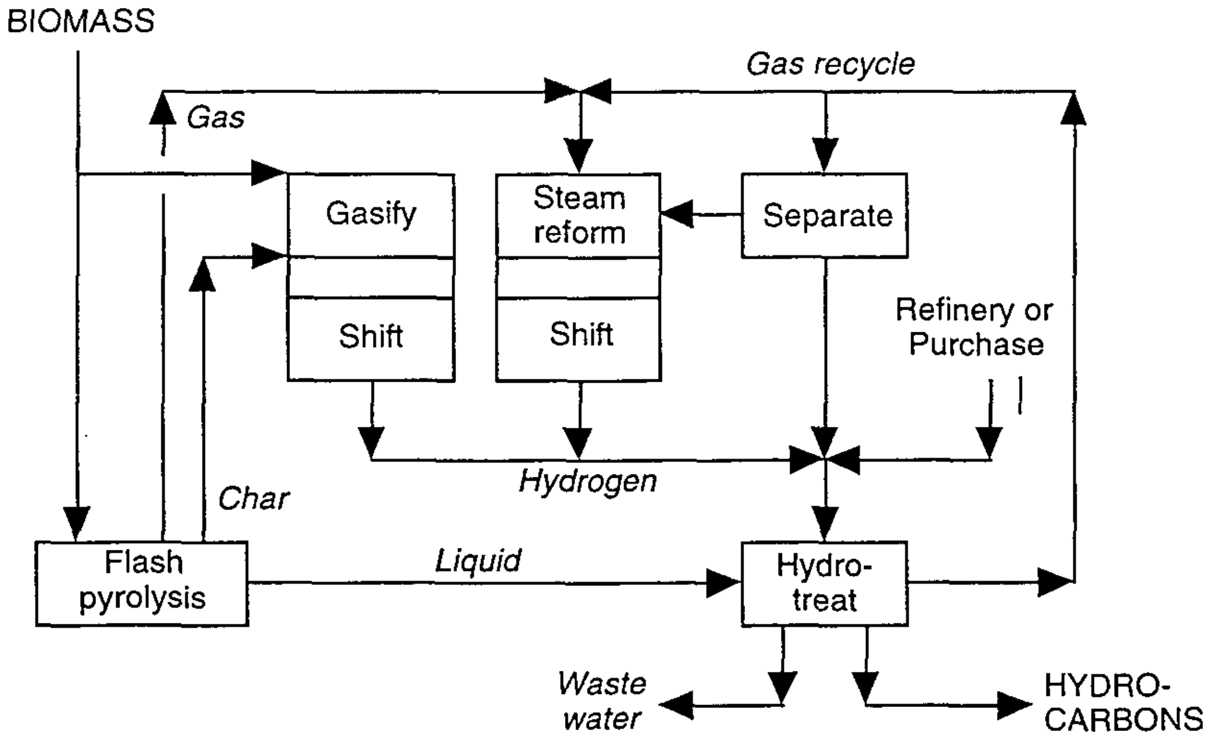

Figure 6.2 Hydrogen generation options

One conjectural way of overcoming the hydrogen deficit is through modification of the catalyst to include a shift component to generate in-situ hydrogen from product gases through the water-gas shift reaction. This might be carried out in a bi-functional or multi-functional catalyst that can operate in a carbon limited environment rather than a hydrogen limited one. This is depicted in the equations below which would give a maximum stoichiometric yield of 55% weight on liquid:

$$3.6CO + 3.6H_2O \longrightarrow 3.6H_2 + 3.6CO_2$$

$$C_6H_8O_4 + 3.6H_2 \longrightarrow 6\,CH_{1.2} + 4H_2O$$

This is now a carbon limited reaction with the aromatic product being limited by carbon availability assuming that there is sufficient CO available in the product gas for production of hydrogen. This second route represents an optimum but has not been attempted.

Thus on this simplistic stoichiometry, there is little difference in yields conceptually in either the upgrading route of hydrotreating or the zeolite cracking one, although aromatics have a higher potential value than naphtha particularly as a chemical feedstock.

Organisations who have been, or are involved, in zeolite processing are listed in Table 6.7.

Table 6.7 Organisations Involved in Zeolite Cracking of Pyrolysis Oils since 1980

Georgia Tech Research Institute (GTRI), USA		119
INRS, Canada		120, 121, 122
Mobil R&D, USA		123, 124
NREL, USA:	Fundamental research	125, 126, 127, 128, 129, 130
	Applied research	118, 131, 132, 133, 134, 135, 136, 137, 138, 139
Occidental, USA		140
University of Cambridge, MA, USA		141
University of Essen, Germany		142
University of Laval, Canada		143, 144, 145
University of Leeds, UK		146
University of Saskatchewan, Canada	pyrolysis oil	60, 147, 148, 149, 150
	tall oil	151, 152, 153
	liquefaction oil	154, 155, 156
University of Toronto, Canada		157
University of Waterloo		158

The processing conditions for zeolite cracking are atmospheric pressure, temperatures from 350°C up to 600°C and hourly space velocities of around 2. Earlier work focused on the lower temperatures, but as catalyst development continued, better results are understood to have been obtained with modified catalysts at higher temperatures with much lower coke formation and longer catalyst life (118). The mechanisms of cracking and reforming are not well understood, but there appears to be a combination of cracking on the catalyst "surface" followed by synthesis of aromatics in the catalyst pores. There are a number of potential advantages over hydrotreating including low pressure (atmospheric) processing; temperatures similar to those preferred for optimum yields of bio-oil; and a close coupled process. These offer significant processing and economic advantages over hydrotreating.

Actual yields of 15% aromatics in a hydrogen limited environment have been achieved, with projections of 23% if the olefinic gas by-products are utilised through alkylation (133). These correspond to 40% and 60% of the theoretical maxima respectively. Most work has been carried out in the vapour phase acting as quickly as possible on the freshly produced primary pyrolysis vapours to take advantage of the special conditions under which they are formed. Some early but limited work has been carried out on liquid phase processing, including Occidental (140), GTRI (119), INRS (122) and Mobil who mixed methanol with the condensed bio-oil before spraying it into a fluid bed (124). Liquefaction oil has also been processed in the liquid phase with aromatics yields of up to 37% when co-processed with water (155).

Related work on specific chemicals and model compounds derived from biomass including sugars and carbohydrates has been carried out by INRS (120), and later extended to pyrolysis oils (121) and liquefaction oils (122). Poor yields of hydrocarbons were obtained with high coke and tar and rapid deactivation of the catalyst. Other work carried out on model compounds includes that of Milne et al. at NREL (125, 126, 128) who have carried out fundamental R&D for about 15 years on both pyrolysis and zeolite cracking (see Table 7), and University of Laval (143).

The most extensively reported work is that by NREL (see Table 7). Milne et al. have carried out screening studies on zeolite catalysts in the NREL molecular beam mass spectrometer which is particularly well suited to this type of work (125, 126, 128, 129). Diebold et al. (131-135) have carried out more applied and larger scale work by close coupling a zeolite cracking unit to the NREL vortex flash pyrolyser. Early work was carried out on a slip stream of pyrolysis vapours from the reactor, while more recently a substantial fixed bed of catalyst was added to process all the pyrolysis product. An assessment of the resultant technology for production of gasoline has recently been completed by the IEA Bioenergy Agreement (159). Optimum catalysts and conditions have yet to be determined, but there is a trade-off between olefins and aromatics and process conditions in which catalyst life and catalyst regeneration are significant factors. Data from various researchers are insufficiently compatible to draw conclusions.

In addition to work on bio-oil or pyrolysis liquids, the process has also been applied to wastes from the wood, pulp and paper industry including tall oil (151 - 153), and biomass derived materials using synthetic clays (160).

An unusual project in the context of this review is the synthesis of zeolite catalysts from rice hulls through thermal processing at the Indian Institute of Technology although specific applications and efficacy of the resultant catalysts are unclear

(161, 162).

Zeolite cracking seems to be less well developed than hydrotreating and there is a much wider range of possibilities to be explored with mono- and multi-functional catalysts. In this respect the screening methods of NREL are particularly valuable. There is not only less information available from specific work carried out, but there are no directly analogous refinery processes from which data may be extrapolated, as well as an enormous variety of catalysts from which to choose. Conversely, the inherent nature of a one-step integrated process for synthesis of hydrocarbons is very attractive and offers much potential for fuels and chemicals.

6.4.5 Further developments in catalysis

These two upgrading routes offer quite different opportunities for development. Hydrotreating is fairly well established and understood in the context of hydrodesulphurisation although the very high oxygen content and relative instability of many constituent chemicals require careful study for catalyst and process optimisation. Partial hydrotreating to stabilise the pyrolysis liquids and render them more suitable for direct firing into a gas turbine for power generation is an interesting concept if pyrolysis liquids cannot be fired directly. This would require significantly less hydrogen and a lower capital cost plant. The extent of hydrotreating required is dependent on the demands of gas turbine fuel characteristics. An inherent problem in the concept of hydrotreating is the progressive de-oxygenation as conditions become more severe, resulting in total hydrogenation of some components and barely adequate de-oxygenation of others, compared to the cracking and seemingly selective synthesis of the zeolite route summarised below. The major problems to be overcome are in catalyst selection and catalyst support in relation to catalyst life and water resistance; and also selectivity in de-oxygenation.

Zeolite catalysts are interesting as they give a higher value transport fuel product (high aromatic content) and also offer the possibility of deriving even higher value chemical intermediates. There is a wider potential through catalyst design and development including possibilities based on multi-functionality, none of which has been investigated. The nature of wood pyrolysis liquids, however, particularly lignin derived components, creates potential problems through coking as well as by-passing of larger less cracked molecules through the catalyst without reaction. Again, the high oxygen content and relative instability of many constituent chemicals require careful study for catalyst and process optimisation. Such problems might be overcome through careful catalyst design and development as being undertaken by NREL (163); through modification of the reactive environment such as addition of steam or operation at different temperatures; or through technology development for example through the adaptation of processes such as fluid catalytic cracking for catalyst regeneration that is widely employed in oil refining. These possibilities currently remain conjectural, although a number of organisations are known to be active as shown in Table 8 including NREL and the University of Saskatchewan.

6.4.6 Product refining and product yield

The hydrocarbons produced from both upgrading processes can, in principle, be used directly for some applications including firing in a turbine or an engine but require conventional refining to produce orthodox transport fuels. This would be carried out in a conventional refinery using established catalytic operations such as reforming, alkylation and hydrotreating (110 - 112, 164).

The yields of the various liquid products from both hydrotreating and zeolite synthesis have been estimated from current data and are summarised in Table 6.8 for crude pyrolysis liquid, three varieties of hydrotreated products - partial, complete and refined; and crude and refined aromatics from zeolites (165).

Table 6.8 Overall Typical Mass Balances to Liquid Products (165)

Mass balance		Hydrotreating	Zeolites
Wet wood		200	200
Biomass feed at 10% moisture		110	110
Flash pyrolysis to crude (wet) bio-oil		83	83
Partial upgrading by hydrotreating, 50% deoxygenation		50	-
Full upgrading by hydrotreating, 98% deoxygenation		30.5	-
Refining to diesel / gasoline		27.4	-
Upgrading to crude aromatics by zeolites		-	23
Refining to gasoline (current - future projection)		-	20.7-25.1
Yield on dry wood feed			
Pyrolysis oil	Overall yield - mass basis	83%	83%
	Overall yield - energy basis	70%	70%
Partially hydrotreated	Overall yield - mass basis	50%	-
(15% oxygen in product)	Overall yield - energy basis	#66%	-
Crude hydrocarbons	Overall yield - mass basis	30%	23%
	Overall yield - energy basis	#64%	53%
Refined hydrocarbons	Overall yield - mass basis	27%	25%
	Overall yield - energy basis	#57%	55%

\# ignoring hydrogen

6.5 TECHNO-ECONOMICS

Techno-economic assessments are important for identifying more promising process routes, and for identifying major areas of uncertainty where further R&D would have a significant impact on technical feasibility and commercial viability. The technical and economic viability of liquid fuels production that include catalytic processing has been investigated by a number of researchers and research groups as summarised in Tables 6.10 and 6.11.

Table 6.10 Techno-economic Assessment Groups

Colorado School Mines, USA	chemicals and liquid fuels	166
IEA Bioenergy Agreement	liquefaction test facility	167
	liquefaction & pyrolysis	117, 168, 169, 170
	gasoline via zeolites	159
Science Applications Inc., USA	liquid fuels	171, 172, 173, 174
SRI, USA	Albany liquefaction plant	175
Statens, Sweden	wood and peat liquefaction	167
University of Aston, UK	liquid fuels: gasification mainly	176, 177, 178
	flash pyrolysis, upgrading	165, 179, 180, 181
VTT, Finland	liquefaction	159, 167 - 170, 182
Zeton, Canada	upgrading	183
	flash pyrolysis	184

Table 6.11 Techno-economic Assessment of Catalytic Biomass Conversion Processes

Topic	Organisation	References
Primary conversion		
Pyrolysis	IEA	117, 168-170
	SAI	171-174 **285-288**
	University of Aston	165, 179 - 181
	Zeton	184
Liquefaction	IEA	117, 167, 168 - 170
	SRI	175
	Statens	167
	VTT	159, 167 - 170, 182
Gasification	University of Aston	4, 176 - 178
Upgrading		
Zeolites	IEA	159
	University of Aston	165, 179 - 181
Hydrotreating	IEA	117, 168 - 170
	SAI	171 - 174
	University of Aston	165, 179 - 181
	Zeton	183
Synthesis	University of Aston	176 - 178
Applications		
Chemicals	BC Research	*15
	Red Arrow	*25

NOTES * Market assessment

Many individual cost estimates and economic evaluations have been carried out which are difficult to compare as the bases are rarely published in sufficient detail for valid comparisons to be made. The IEA Bioenergy Agreement has also been sponsoring process, technical and economic assessments for over 10 years, beginning with the conceptual design of a biomass test liquefaction plant (167) and progressing through direct liquefaction, flash pyrolysis and upgrading (117, 159, 168 - 170) to the current examination of electricity generation systems. Some dedicated computer packages have been developed by Aston University which include process simulations and a common approach to cost estimation to provide a consistent comparison of alternative routes (176 - 181). This enables the user to examine alternative technologies, process conditions, routes, feedstocks and products.

Typical estimates of transport fuel costs from direct liquefaction processes are summarised in Figure 4 (296). In both cases the current pre-tax cost of fossil fuel derived products is shown. The conclusions agree well with those carried out by the IEA Bioenergy Agreement over the last few years (117).

For gasification derived synfuels, Table 13 summarises the ratio of costs of biomass derived liquid fuels to conventionally produced fuels as an example of analysis of results from cost estimates (177).

Table 6.12 Comparison of Fuel Costs to Prices (292)

Basis: Capacity 1000 t/d d.a.f. feed,
Feedstock costed at 50 ECU/dry t (US$40/dry t)

	Product	Feed	Route	Uncertainty	Cost/Price
1	Methanol	straw	gasification	low-moderate	1.17
2	Gasoline	wood	pyrolysis + zeolites	high	1.48
3	Methanol	wood	gasification	low-moderate	1.46
4	Fuel alcohol	wood	gasification	moderate	1.56
5	Methanol	RDF	gasification	moderate	1.58
6	Gasoline	wood	pyrolysis + hydrotreating *	high	1.69
7	Gasoline	wood	liquefaction + hydrotreating *	high	1.81
8	Gasoline	wood	gasification + MTG	low	2.14
9	Diesel	wood	gasification + SMDS	low-moderate	2.15
10	Gasoline	wood	gasification + MOGD	moderate	2.52
11	Diesel	wood	gasification + MOGD	moderate	3.56

* includes consideration of lower quality product

The overall conclusion from all these assessments is that transport fuels cannot currently be produced economically from purpose grown biomass or energy crops without some economic support. For site specific wastes, there are opportunities for fuel gas and liquid fuels for heat and electricity production. The short term prognosis is, however, very hopeful as the more promising products only require modest improvements in process performance or cost to be competitive with fossil fuels (159). Catalyst development is likely to play a key role in meeting these objectives.

6.6 CONCLUSIONS

The use of catalysts to improve either the yield or quality of gas and liquid fuels from thermochemical biomass conversion processes is still in its infancy. While there is extensive fundamental work underway, considerably more research is necessary to explore the wide range of conventional and unconventional catalysts. Of particular potential significance is the integration of catalytic processes into the thermal conversion process to improve efficiency and reduce costs.

For fast pyrolysis processes, there are considerable opportunities for production of conventional and unconventional fuels for both electricity generation and fuel and chemical synthesis. The R&D requirements here are for more fundamental research into catalyst selection and evaluation for higher product specificity and/or higher yields of marketable products, since the products from these processes are much more complex than from gasification. Chemicals are always of greater potential interest due to their higher value compared to fuels. Here also catalysis has a significant role to play, and is more likely to justify more intensive R&D. Integrated fuel and chemicals production is the most likely scenario.

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CHAPTER 7
CONTRIBUTION TO BIS

7.1 INTRODUCTION

One of the main activities in this contract was to support and help develop a biomass information system (BIS) that would establish the basic structure of a comprehensive database of biomass related activities for access and analysis by EC officials and interested researchers. The contract was let to Hendyplan.

7.2 BIOMASS INFORMATION SYSTEM

7.2.1 Introduction

A database was designed that would allow the collation and interpretation of state of the art information in each of the areas covered by the bio-energy R&D activities. Unfortunately each area had such diverse information requirements and availability that fusion was proved impossible and the rest of this section is devoted to describing the thermal conversion contribution.

The database was initially envisaged as taking the form of three separate files linked by a common set of keywords as follows:

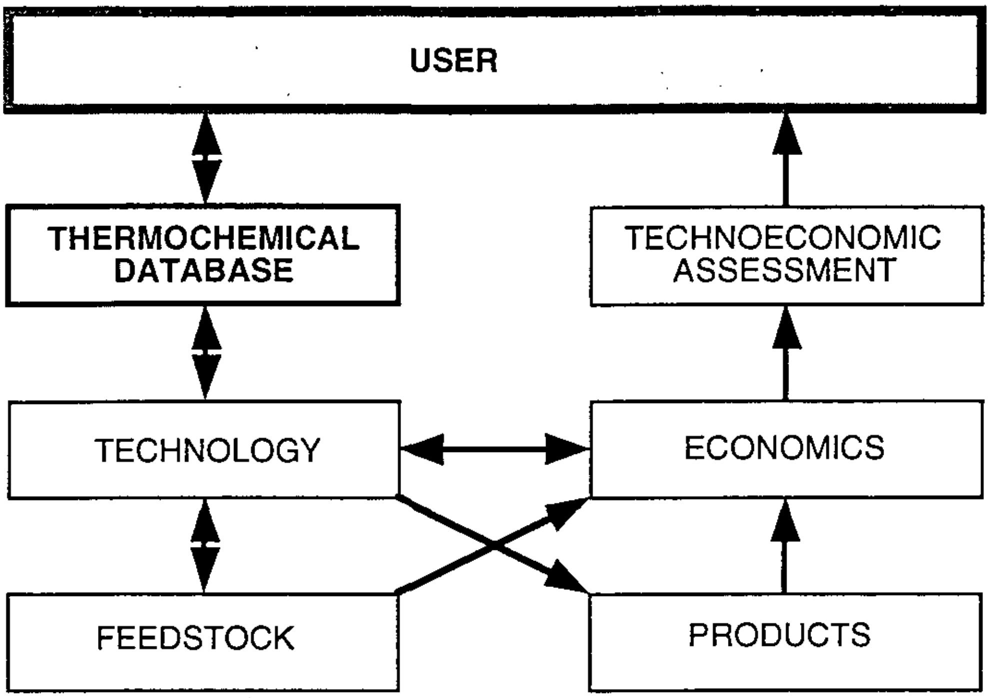
- **Database:** Containing basic contacting information;
- **Technology:** Providing information on the basic technologies and who is involved with their development; and
- **Products:** Providing information on the individual products that may be derived and how they can be used.

A flow diagram of the anticipated and planned interactions is given in Figure 7.1 which is described in more detail below.

Having identified the necessary interactions required for a successful and self-evolving system the database methodology was then simplified to aid a successful outcome to the project and the resultant database was formulated and is summarised in sections 7.2.2 to 7.2.4 below as a preliminary outline of the database worksheet.

Subsequent discussions and requests for the database to include assessments and comparisons of each EC contract included led to the final version shown below in Table 7.1, preceding the 20 sets of specimen data supplied.

Although the final data was sent in January 1994, no further contact has been possible with Hendyplan and requests for reports and working versions of the final database for testing and appraisal have not been fruitful. A critical review of the final database would have provided valuable feedback to Hendyplan and the EC to help formulating future plans for such an activity.



Thermochemical Database:	Masterfile, directory, keywords
Technology:	Description, performance, cost
Feedstock:	Characteristics, costs
Product:	Characteristics, values
Economics:	Calculation of capital costs & product costs
Technoeconomic assessment:	Evaluation of costs and performance

Figure 7.1 Components of projected database and interactions

7.2.2 "DATABASE" section of BIS

The initial proposed composition is summarised below:

Organisation -	Abbreviation, full name
Contact name -	Main person by surname and initials
Address -	Including fields for town/city, post code, country.
Telephone -	
Fax -	
Objective -	Define, maximum 10 words
Technology developed -	Define as keywords from list supplied: Pyrolysis, Gasification, Combustion, Liquefaction, Upgrading, Power generation, Chemicals, Catalysts, Other, to be defined - for cross referencing to **TECHNOLOGIES** and **PRODUCTS**.
Scale of operation -	Feed rate kg/h
Feeds tested -	Define all by name including pseudonyms and alternatives. Can be established to link to a **FEEDSTOCK** file.

Feed characteristics -	Define any special requirements such as maximum particle size or maximum moisture content
Product -	Define major product produced or required - for cross referencing to **TECHNOLOGY** and **PRODUCTS**
Product characteristics -	Define any special or peculiar properties
Year activity started -	Define
Year activity finished -	Define
Industrial collaborators -	Names in full and abbreviations where relevant
Academic collaborators -	Names in full and abbreviations where relevant
Financial sponsors -	Names in full and abbreviations where relevant

7.2.3 "TECHNOLOGY" section of *BIS*

The following technologies were proposed:

- Pyrolysis
- Gasification
- Liquefaction
- Combustion
- Upgrading
- Chemicals production

For each technology the following data should be provided:

Brief description -	maximum 50 words
Keywords -	for cross referencing to **DATABASE** and **PRODUCTS**
Feed requirements -	Can be established to link to a **FEEDSTOCK** file
Typical temperatures	
Typical pressures	
Catalyst requirements	
Minimum viable size	kg/h feed d.a.f. basis
Maximum viable size -	kg/h feed d.a.f. basis
Maximum size built -	kg/h feed d.a.f. basis
List of developers -	for cross referencing to **DATABASE** and **PRODUCTS**
List of researchers -	for cross referencing to **DATABASE** and **PRODUCTS**

7.2.4 "PRODUCTS" section of BIS

There are three types of product - solid, liquid and gas. Each type and a selection of examples is given below. For each individual product, there are three sets of data that can be provided as indicated under 1, 2 and 3 below.

<u>Gas</u>	LHV fuel gas, MHV fuel gas, SNG, hydrogen, ammonia,
<u>Liquid</u>	Naphtha, diesel, gasoline, fuel oil, bio-oil, liquefaction oil, tar, methanol, ethanol, fuel alcohol, MTBE, ETBE, char-water slurry, char-oil slurry,
<u>Solid</u>	Charcoal.

In addition chemicals might be included as a separate category as follows:

Chemicals Methanol, ethanol, ammonia, benzene, toluene, xylene, phenol, hydroxyacetaldehyde, acetic acid, and several hundred other specialities such as hydroxyacetaldehyde, levoglucosan etc.

a Physical and chemical properties

For each product, basic data on physical and chemical properties should be provided. This can range from simple to extensive according to resources available and might include:

- Higher heating value - MJ/kg,
- Lower heating value - MJ/kg,
- Elemental analysis - weight basis - CHONS etc. and minor and trace components,
- Molecular weight,
- Viscosity,
- Density,
- Solubility in water, hydrocarbons, other solvents,
- Flash point,
- Explosive limits,
- Toxicity,
- etc.

b Production methods

The sources by technology can be identified for each product and cross referenced to the **TECHNOLOGY** file.

c Production costs

It would be possible to derive simple relationships that express product cost as a function of plant size and feed cost. This could not be achieved in the current budget and time scale.

7.2.5 Final format of database on thermal processing

The final format of the database contribution on thermal processing was agreed as in Table 7.1 with staff at Hendyplan and the EC project officer at the time and 20 sets of data provided in hard copy and disc copy for incorporation into the master database. Copies of this data is included as an annex to this chapter.

Table 7.1 BIS Thermochemical Database Methodology & Preliminary Worksheet

NO.	PRIMARY FIELD	Secondary field	Tertiary field	CONTENTS
1	ORGANISATION			
		Name		
		Contact person		
		Address		
		Telephone		
		Fax		
2	KEYWORDS			
3	OBJECTIVES			
4	CONVERSION PROCESS TYPE			
5	REACTOR TYPE			
6	PERFORMANCE			
		Efficiency		
		Capital cost		
		Problems		
7	PROCESS			
		Description		
		Objective		
		Conversion efficiency		
		Capital cost		Define scale and money units
		Scalability		
8	FEEDSTOCK			
		Main feedstock used		Name and/or type
			Analysis	CHO, Ash, Moisture
			Characteristics	Size, Size range, Shape,
			Cost	
		Other feedstocks used		Names and/or types
			Analysis	CHO, Ash, Moisture
			Characteristics	Size, Size range, Shape,
			Costs	
9	PRODUCT GAS			
		Yield, wt %		
		Analysis		CO, CO2, H2, CH4, H2O, N2, (defined)
		Quality		Tars, Particulates
		Clean-up		
			Methods	
			Efficiency	
		Main use		

continued.....

Table 7.1 continued

10	**PRODUCT LIQUID**			
		Yield, wt %		
		Analysis		C,H,O,S,N,Cl,H2O,
		Quality		
		Clean-up		
			Methods	
			Efficiency	
		Main use		
		Upgrading		
			Methods	
			Product	
			Efficiency	
			Yield, wt %	
			Analysis	C,H,O,S,N,Cl,H2O,
			Quality	
11	**PRODUCT SOLID**			
		Yield, wt %		
		Analysis		CO, CO2, H2, CH4, H2O, CxHy (defined)
		Quality		Tars, Particulates
		Clean-up		
			Methods	
			Efficiency	
		Main use		
12	**ACHIEVEMENT**			
13	**KEY RESULT**			Typical results
14	**COMPARISON**			With other similar processes. Advantages
15	**REFERENCES**			
		1		Full bibliographic details
		2		Full bibliographic details
		3		Full bibliographic details
16	**SOURCE**			
		Name or originator		
		Publication or source		
		Date		

AVB October 1993

It should be clear from the above description that the project could not cover all these facets. It was therefore recommended that a meeting be held to agree what is both desirable and realistic, and the data base could then be initiated.

A meeting was held which resulted in agreement for each contributor to supply a selection of typical data. The resultant database would then be distributed to each contributor for review and comment. The data was collated and supplied as hard copy (copies attached in the Annex to this chapter) and disc in the requested format.

In spite of repeated requests directly to Hendyplan and representations via the EC a review copy of the final database was never supplied.

7.3 CONCLUSIONS

The Biomass Information System as proposed was an ambitious project that required considerably greater resources and time to be successful. The collation and management of extensive data such as was requested requires skilled and knowledgeable scientists and computer experts as well as solid experience at managing extensive and complex information, crystal clear objectives and a degree of ruthlessness in managing the project. Unfortunately none of the requisite criteria was available. Although the final product has not been seen, it seems likely that it has not met many of its original objectives.

A good database is an invaluable tool for planners and researchers, but it requires an ongoing commitment to first establish it with sufficient resources under experience and sound management, then needs critical review to ensure it meets the objects of the users, and finally needs ongoing support to maintain it and update it as such databases quickly become outdated.

CHAPTER 8
CONCLUSIONS AND RECOMMENDATIONS

Production of primary liquids by fast pyrolysis of biomass has been commercialised at a small scale in Canada and has been actively and extensively developed throughout Europe. Some of the early problems with liquid quality are being successfully addressed and rapid progress is being made in producing a liquid that will satisfy most applications. There are many aspects of the pyrolysis system that require addressing as well as in the development of more innovative, more efficient and more lower cost reactors. Of particular importance is minimisation of solid char and ash in the product through vapour or liquid phase processing and improvements in liquid collection. In addition the quality of the product is important for different applications and work is needed to both measure these properties against application requirements and provide appropriate norms and standards. There is a need for better co-ordination between the research institutions and companies involved in this area to ensure that problems, solutions and developments are fully and sensibly exploited to more quickly bring the technologies to commercial fruition. This will be partly addressed in the new IEA programmes and the PyNE Concerted Action project.

Upgrading of pyrolysis oils to transport fuel and higher quality energy products by hydrotreating is very expensive and unlikely to be viable in the short to medium term, as well as having a number of technical problems relating to catalyst stability that require resolution. Work should however continue to ensure that the science is sufficiently well understood so that the technology can be developed when required. Zeolite upgrading and analogous in-situ or close-coupled catalytic upgrading is less well developed but offers more short term promise, as a separate process is not required, there is no hydrogen requirement and costs would probably be little different from fast pyrolysis. This is an area that deserves more consideration and support. Other innovative possibilities for upgrading should also be encouraged.

Chemicals recovery is potentially important from the novel chemicals that might be recovered the high added value of speciality chemicals and the contribution that these would make to an integrated biomass based conversion system. There is a need for continued evaluation and exploration of products and applications. Development of catalytic pyrolysis systems will add to the interest of this approach.

Annex to Chapter 7

20 Sets Of Specimen Data Supplied to Hendyplan for BIS

BIS Information

	Mnemonic	*STEI01*
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	Fax	+31 1 34 65 43 99
	Keywords	Gasification, Pressure, Oxygen, Reforming, Methanol, Electricity
SUMMARY	*Achievement*	Successful testing of pressurised oxygen blown fluid bed gasifier with secondary partial oxidation for thermal cracking of tars. Stein Industries have abandoned this process and it is understood that the pilot plant has been dismantled.
	Key Results	A 2500t/h pressurised fluidised bed gasification plant was started in 1986 at Clamecy near Auxerre, France. Wood chips (oak and eucalyptus) are the main feedstock and a gas yield of 1.36Nm3/kg feed has been produced. The gas produced is a synthesis gas which can be used as a feedstock production of methanol or as a fuel gas. The cold gas efficiency (the ratio of outlet gas enthalpy to inlet dry wood enthalpy) is 43.6%.
	Comparisons	See IGT, USA.
PROCESS	*Reactor Type*	Pressurized fluidized bed gasifier
	Description	Pressure oxygen fluid bed gasification for methanol or electricity. Gasifier operates at pressures up to 20 bars with oxygen for primary gasification and additional injection in secondary reactor for tar cracking
	Objective	Fuel gas and syngas production
	Capital cost	$59m (excluding working capital), at 150 t/d methanol . A 500t/day plant requires
	Scalability	Good potential, but essential as system is pressurized. 40 t/h claimed feasible
	Reactor problems	Raw material in small particles
FEEDSTOCK	*Main feedstock used*	Eucalyptus chips
	Other Feedstocks	Oak Chips, Eucalyptus chips

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS			LIQUID			CHAR	
CO	19.87	wt %	C		wt %	C		wt %
H_2	26.17	wt %	H		wt %	H		wt %
CO_2	40.38	wt %	O		wt %	O		wt %
CH_4	0.00	wt %	H_2O		wt %	Other		
N_2	13.48	wt %	Char		wt %			
Tar		wt %	Other					
Dust		wt %						
Other	Ar 0.11							
Yield	1.45 Nm3/kg feed			None				
HHV	5.52 MJ/Nm3							
Viscosity								
Density								
Other								
Clean up / Upgrading methods	Wet scrubbing							
Clean up / Upgrading problems	None known							

SECONDARY PRODUCTS

Upgraded or derived products			
Characteristics			
C		wt %	
H		wt %	
O		wt %	
H_2O		wt %	
Other			

PUBLICATION DETAILS

Originator	A V Bridgwater
Date	28 January, 1994
Source	Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

REFERENCES

1 Energy from Biomass IX: IGT Symposium Orlando 1986.

2 Biomass for Energy and Industry, Orléans 1987 #

3 EEC Contractors Meeting Proceedings Florence Nov 1990 #

BIS Information

	Mnemonic	AERI01
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	Keywords	Gasification, CFB, RDF, Electricity, Cerment, Process heat, Direct firing
SUMMARY	Achievement	Successful testing of both fluid beds on RDF pellets.
	Key Results	Gas has been produced with a heating value of 4.5-5.5MJ/Nm3. The RDF pellets have a moisture content of 5-10%, ash content of 15%. Paper forms up to 80% of the pellet. Ash is estimated to have a carbon content of 5%. The gas yield is 2.53 kg/kg feed.The cold gas efficiency (ratio of cold gas enthalpy to enthalpy of feed) is 67.8%. The hot gas efficiency (ratio hot gas enthalpy to feed enthalpy)is 85.8%. The raw gas efficiencyRatio of energy in hot raw product gases including tars to enthalpy feed) is 85.8%.
	Comparisons	See TPS, Sweden; Ahlstrom, Finland; Gotaverken, Sweden; Lurgi, Germany.
PROCESS	Reactor Type	Circulating fluid bed air gasifier (x2)
	Description	Circulating fluid bed air gasification of RDFon TPS design for hot raw gas for cement kiln and/or boiler for steam turbine. Two circulating fluid bed air blown atmospheric pressure gasifiers operating on RDF pellets. Secondary catalytic dolomite cracker.
	Objective	Waste disposal with energy recovery as proces heat and/or electricity via asteam turbine.
	Capital cost	
	Scalability	None foreseen
	Reactor problems	
FEEDSTOCK	Main feedstock used	RDF pellets
	Other Feedstocks	RDF, wood, bagasse pellets

C		wt %	Size	
H		wt %	Size range	
O		wt %	Shape	
Ash		wt %	Cost	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS			LIQUID			CHAR	
CO	7-9	wt %	C		wt %	C		wt %
H2	9-13	wt %	H		wt %	H		wt %
CO2	12-14	wt %	O		wt %	O		wt %
CH4		wt %	H2O		wt %	Other	Ash 450kg/h	
N2	47-52	wt %	Char		wt %			
Tar	25-50g/Nm3	wt %	Other					
Dust		wt %						
Other	CxHy 6-9%, H20 10-14% Other 0.5-1.0%, HCl 0.5-1.5g/Nm3, H2S							
Yield	1.94-3.33 Nm3/kg							
HHV	4.5-5.5 MJ/Nm3							
Viscosity								
Density								
Other								
Clean up / Upgrading methods	Cyclones							
Clean up / Upgrading problems								

SECONDARY PRODUCTS

	GAS	LIQUID	CHAR
Upgraded or derived products			
Characteristics			

C		wt %
H		wt %
O		wt %
H2O		wt %
Other		

PUBLICATION DETAILS

Originator: A V Bridgwater

Date: 28 January, 1994

Source: Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

REFERENCES

1 EEC Contractors Meeting Proceedings Florence Nov 1990 #

2 Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

3

BIS Information

Mnemonic: UAST04

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Keywords: Flash pyrolysis, Ablation, Liquid fuels, Bio-oil, Design, Pyrolysis liquids, Characterisation

SUMMARY

Achievement: Successful design, construction and testing of novel plate ablative flash pyrolyser. Good yields and closures.

Key Results:

- Maximum yield of liquid 78% wt. at residence times of up to 5 seconds.
- Mass balance closure average 96.5%.
- Maximum throughput achieved 2.5 kg/h = 50% design capacity.
- Biggest problem has been liquids collection which has limited runs to a maximum of 40 minutes

Work will be continued under EC Contract AIR-93-0889

Comparisons: Liquid yields comparable to best reported world wide. Product quality difficult to define, but apparently very similar to NREL ablative pyrolysis.

PROCESS

Reactor Type: Flat plate ablative pyrolyser
Description: Ablative pyrolysis for liquid fuel production in a plate pyrolyser
Objective:
Capital cost:
Scalability: Yes without substantial redesign
Reactor problems: None yet

FEEDSTOCK

Main feedstock used: Wood
Other Feedstocks: Wood (IEA poplar)

C		wt %	Size	
H		wt %	Size range	
O		wt %	Shape	
Ash		wt %	Cost	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS		LIQUID		CHAR
CO	wt %	*C*	wt %	*C*	wt %
H2	wt %	*H*	wt %	*H*	wt %
CO2	wt %	*O*	wt %	*O*	wt %
CH4	wt %	*H2O*	wt %	*Other*	
N2	wt %	*Char*	wt %		
Tar	wt %	*Other*			
Dust	wt %				
Other					
Yield					
HHV					
Viscosity					
Density					
Other					
Clean up / Upgrading methods					
Clean up / Upgrading problems					

SECONDARY PRODUCTS

Upgraded or derived products			
Characteristics			
		C	wt %
		H	wt %
		O	wt %
		H2O	wt %
		Other	

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

Source

REFERENCES

1 EEC Contractors Meeting Proceedings Florence Nov 1990 #

2 in: "Advances in Thermochemical Biomass Conversion", A V Bridgwater (ed.), pp 1134 (Blackie 1994)

3

BIS Information

	Mnemonic	BASA01
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	Keywords	Carbonisation, Pyrolysis, Charcoal, Bio-oil
SUMMARY	*Achievement*	The 50 kg/h pilot plant was transported and re-erected in Umbria, Italy in 15 days. The oil yieldswas increased by 5% but the quantity and quality of charcoal is reduced.
	Key Results	The 50 kg/h pilot plant was demonstrated to be transportable. This is not of major interest for a plant of this size would normally be skid mounted. The maximum oil yield was around 15% wt on dry feed. Sweet sorghum bagasse gave a more typical oil yield of 10% wt. Oil yield was increased by 5% by reducing the operating temperature from 550°C to 500°C but the quantity and quality of charcoal was reduced. The maximum char yield reported was 32% wt for swet sorghum bagasse of 13% moisture content which is typical for a carbonisation process. Gas yields were 0.72Nm3/kg sweet sorghum bagasse at 13% moisture. Overall energy balances of 80% are claimed, with the balance being lost. The oil is a secondary oil with high viscosity and apparently low water content although no data is supplied
	Comparisons	A carbonisation unit of average performance. A novelty is the high temperature condensation and recovery of secondary bio-oil with low water content. The oil yield is too low to be of interest as a major product.
PROCESS	*Reactor Type*	Continuous updraft carboniser with air addition
	Description	Pyrolysis for charcoal and liquids
	Objective	Slow pyrolysis of biomass and wastes for primarily production of charcoal and as a subsidiary objective, production of secondary pyrolysis liquid (tar).
	Capital cost	2.88 million SF, at 2 t/h feed, 1986
	Scalability	None up to 10 t/h
	Reactor problems	None known

FEEDSTOCK

Main feedstock used	Wood (oak)
Other Feedstocks	Agricultural waste, forestry waste, wood waste, vine prunings

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	
Moisture		wt %		

BIS Information

PRODUCTS	GAS		LIQUID		CHAR
CO	16.3 wt %	C	58.9 wt %	C	wt %
H_2	7.9 wt %	H	6.9 wt %	H	wt %
CO_2	13.2 wt %	O	33.4 wt %	O	wt %
CH_4	5.6 wt %	H_2O	15% wt %	Other	
N_2	48.4 wt %	Char	wt %		
Tar	wt %	Other	N: 0.5; Carbon 3%		
Dust	wt %				
Other	C_{2+} 1.8%; O_2 6.4%				
Yield	@ 20% of energy input		10% on feed input		25-32%
HHV	6.7 MJ/Nm3		20.9-26.0 MJ/kg		
Viscosity					
Density					
Other					
Clean up / Upgrading methods	Confidential		Selective condensation of oil at 110°C		
Clean up / Upgrading problems					

SECONDARY PRODUCTS

	GAS	LIQUID	CHAR
Upgraded or derived products		Low water product	
Characteristics		High viscosity 250 cp @ 60°C, density 1.21, pH	

C	wt %
H	wt %
O	wt %
H_2O	wt %
Other	

PUBLICATION DETAILS

Originator: A V Bridgwater

Date: 28 January, 1994

Source:

REFERENCES

1 5th European Conference on Biomass for Energy, Industry and the Environment, Lisbon, Portugal. 9-13 October 1989. (Elsevier)

2 Advances in thermochemical biomass conversion, Interlaken, Switzerland, 11-15 May 1992

3 1st European forum on electricity production from biomass and solid wastes by advanced technologies, C.E.E. Firenze, Italy, 27-29 November 1991

BIS Information

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	Keywords	Flash pyrolysis, Transport reactor, Bio-oil, Chemicals, Upflow reactor, Downflow reactor, Circulating fluid bed, Catalysts, Lignin, Hydroxyacetaldehyde, Levoglucosan
SUMMARY	*Achievement*	A 1kg/h downflow reactor has been constructed (RTP I). Two upflow transport reactors (RTP II) have been tested at wood feed rates of 30 & 100kg/h. A 100kg/h unit for the production of chemicals and fuels has been established at Red Arrow. RTP III is a 50kg/h upflow reactor.
	Key Results	The main product is bio-oil to be used as fuels and chemicals. Yields of 0.67 kg/kg feed are achieved. Red Arrow use the process commercially to make aqueous smoke flavourings. Woody biomass is used as a feedstock. It should have less than 10% moisture and a particle size less than 5mm. Acceptable ash contents are not reported. Tyre crumb has been successfully converted but the condensors are designed to work with woody biomass.
	Comparisons	See also NREL and Interchem, USA; Union Fenosa, Spain.`
PROCESS	*Reactor Type*	Transport reactor
	Description	Flash pyrolysis in transported bed fast pyrolysis reactor for liquid fuels and chemicals
	Objective	Fast or flash pyrolysis of various biomass forms for production of pyrolysis oil and chemicals
	Capital cost	Confidential, at 100, 250, 500 t/d,
	Scalability	Very good. Maximum size probably 10t/h in one unit.
	Reactor problems	None known
FEEDSTOCK		
	Main feedstock used	Wood
	Other Feedstocks	Cellulose, wood, lignin

C		wt %	*Size*	- 5mm
H		wt %	*Size range*	0-5mm
O		wt %	*Shape*	Not specified
Ash		wt %	*Cost*	Varies
Moisture	10% after	wt %		

BIS Information

PRODUCTS

	GAS		LIQUID		CHAR
CO	0.1 wt %	*C*	55.3-63.5 wt %	*C*	wt %
H2	16.5 wt %	*H*	5.2-7.0 wt %	*H*	wt %
CO2	9.9 wt %	*O*	39.43-28.98 wt %	*O*	wt %
CH4	3.3 wt %	*H2O*	wt %	*Other*	
N2	wt %	*Char*	wt %		
Tar	wt %	*Other*	N 0.07-0.39 S 0.00-0.05 Ash 0.04-0.25		
Dust	wt %				
Other	C2H4 1.6 Others 1.5				
Yield	0.26 kg/kg feed		0.67 kg/kg feed		0.08 kg/kg feed
HHV			15-19 MJ/kg		
Viscosity			35-53St (40°C)		
Density			1.16-1.22kg/l		
Other			Pour pt. (-25) to (-30)°C Flash pt. 51-58°C		
Clean up / Upgrading methods	Cyclone, scrubber, ESP		Condensors, filters, demisters		
Clean up / Upgrading problems			Char and ash in liquid		

SECONDARY PRODUCTS

Upgraded or derived products			Chemicals, liquid fuels, hydrocarbons,		
Characteristics			Not known		
		C	wt %		
		H	wt %		
		O	wt %		
		H2O	wt %		
		Other			

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

Source Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

REFERENCES

1 Energy from Biomass and Wastes X p593 1986 #

2 Research in Thermochemical Biomass Conversion pp 629, Ed AV Bridgwater & JL Kuester Elsevier Applied Science #

3 7th Canadian Bioenergy R&D Seminar NRC Ottawa. p669-673

BIS Information

	Mnemonic	UIWC01
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	Keywords	Liquefaction, Hydropyrolysis, Catalysts, Upgrading, Hydrotreating, Chemicals, Analysis, Characterisation. Pyrolysis, Bio-oil
SUMMARY	*Achievement*	
	Key Results	
	Comparisons	
PROCESS	*Reactor Type*	Three autoclave system. Continuous reactor
	Description	Catalytic liquefaction and hydropyrolysis for production of synfuels and chemical feedstocks. Flash pyrolysis. Uprading of bio-oil. Analysis and characterisation#
	Objective	Production of high quality liquid s from biomass and wastes
	Capital cost	
	Scalability	Yes with continuous operation
	Reactor problems	Long (60 min) heat up time
FEEDSTOCK	*Main feedstock used*	Wood, lignin
	Other Feedstocks	Softwoods, hardwoods, technical lignins, C4-crops, black liquor

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS			LIQUID			CHAR	
CO		wt %	*C*	79.0	wt %	*C*		wt %
H2		wt %	*H*	9.0	wt %	*H*		wt %
CO2		wt %	*O*	12.0	wt %	*O*		wt %
CH4		wt %	*H2O*	0	wt %	*Other*		
N2		wt %	*Char*		wt %			
Tar		wt %	*Other*					
Dust		wt %						
Other								
Yield				36% wt of feed			0-5%	
HHV				33.61-39.8 MJ/kg				
Viscosity								
Density								
Other								

	GAS	LIQUID	CHAR
Clean up / Upgrading methods		Hydrotreating	
Clean up / Upgrading problems			

SECONDARY PRODUCTS

	GAS	LIQUID	CHAR
Upgraded or derived products		Hydrocarbons	
Characteristics		Density <1, viscosity~ 1DcP (20 ° C)	

C		wt %
H		wt %
O		wt %
H2O		wt %
Other		

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

Source

REFERENCES

1 Biomass for Energy and Industry Orléans May 1987.

2 J. Wood Chem. Tech. 8 (4) pp 523-524 1985

3 Research in Thermochemical Biomass Conversion p 384 #. AV Bridgwater & JL Keuster (eds) Elsevier Applied Sci.

BIS Information

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	Fax	
	Keywords	Bio-oil, Combustion, Pyrolysis liquid, Slow pyrolysis, Atomisation
SUMMARY	*Achievement*	Slow pyrolysis oil from BASA and KTI was successfully fired in a test furnace
	Key Results	
	Comparisons	
PROCESS	*Reactor Type*	Furnace
	Description	Evaluation of secondary bio-oil combustion from slow pyrolysis processes from BASA and Alten in a 1-2 MW furnace
	Objective	Test combustion characteristics of secondary pyrolysis liquid (tar)
	Capital cost	
	Scalability	Not applicable
	Reactor problems	Viscosity; variable water content; water separation; oxygen; char content
FEEDSTOCK		
	Main feedstock used	Bio-oil from BASA and Alten from slow pyrolysis process
	Other Feedstocks	Bio-oil from slow pyrolysis

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS		LIQUID		CHAR
CO	wt %	*C*	20-60% wt %	*C*	wt %
H2	wt %	*H*	5-10% wt %	*H*	wt %
CO2	wt %	*O*	20-50% wt %	*O*	wt %
CH4	wt %	*H2O*	10-40% wt %	*Other*	
N2	wt %	*Char*	wt %		
Tar	wt %	*Other*	% W/W		
Dust	wt %				
Other	Flue gas composition +NOx 250-1200 ppm				
Yield					
HHV			12-26 MJ/kg		
Viscosity					
Density					
Other					
Clean up / Upgrading methods			No upgrading - direct combustion		
Clean up / Upgrading problems			Variable quality, feeding, see gas product after		

SECONDARY PRODUCTS

	GAS		LIQUID		CHAR
Upgraded or derived products					
Characteristics					
		C	wt %		
		H	wt %		
		O	wt %		
		H2O	wt %		
		Other			

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

Source

REFERENCES

1 Proceedings of Energy from Biomass Contractors' Meeting Florence 1990 G Grassi P Moncada and H Zibetta (eds.)

2 EEC Contractors Meeting Proceedings Florence Nov 1990 #

3 6th EEC Conference on Biomass for Energy Industry and the Environment Athens 1991.

BIS Information

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	Fax	+351 1 716 4635
	Keywords	Flash pyrolysis, Fluid bed, Upgrading, Zeolite, Bio-oil, Upgrading
SUMMARY	*Achievement*	Flash pyrolysis achieved but yields below comparable work elsewhere. Scant data in reports.
	Key Results	Flash pyrolysis was achieved at lower yields than comparable work in North America. Zeolites have been tried in-bed but no details are provided and no results given other than a claim that the liquid yield was not impoved.
	Comparisons	Results claimed to be comparable to University of Waterloo (one of the bench marks in this field) but data does not support this in terms of absolute yield nor in terms of optimum temperature.
PROCESS	*Reactor Type*	Batch and continuous fluidised bed pyrolysers, vacuum operation
	Description	Fluid bed flash pyrolysis and zeolite upgrading of forestry wastes. Gasification with steam. Pressure upgrading of pyrolysis liquids
	Objective	Carry out flash pyrolysis and product upgrading with zeolites
	Capital cost	
	Scalability	Not known
	Reactor problems	Feeding, solid loss from bed.
FEEDSTOCK		
	Main feedstock used	Wood
	Other Feedstocks	Pine, helm oak

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS			LIQUID			CHAR	
CO	36	wt %	C	30.5	wt %	C		wt %
H_2	18	wt %	H	8.5	wt %	H		wt %
CO_2	18	wt %	O	54.5	wt %	O		wt %
CH_4	27	wt %	H_2O	25.0	wt %	Other		
N_2		wt %	Char		wt %			
Tar		wt %	Other	N: 0.09				
Dust		wt %						
Other	Analyses at 500°C in wt%. CH_4 includes H/C to C_4H_{10}							

	GAS	LIQUID	CHAR
Yield	55%at500°C, 40%at600°C	Maximum 55% wt total liquids from both feeds at 600°C	5% at 600°C, to 19% at 425°C
HHV		17.9 MJ/kg	
Viscosity		Kin. viscosity 115 mm2/s	
Density		1.250	
Other		pH 2.5	
Clean up / Upgrading methods	Cooler	None	
Clean up / Upgrading problems	None known		

SECONDARY PRODUCTS

	GAS	LIQUID	CHAR
Upgraded or derived products		N/A	
Characteristics			

C		wt %
H		wt %
O		wt %
H_2O		wt %
Other		

PUBLICATION DETAILS

Originator: A V Bridgwater

Date: 28 January, 1994

Source: Interim reports to the EC

REFERENCES

1. INETI interim report to CEC dated2 July 1993
2. 6th EEC Conference on Biomass for Energy Industry and the Environment, 1991
3. EEC Contractors Meeting Proceedings Florence Nov 1990 #

BIS Information

DIRECTORY

Mnemonic	SOFR01
Group	Sofresid/Caliqua
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Keywords	MSW, Gasification, Updraft, Heat, fuel gas

SUMMARY

Achievement	The gasificationof MSW in two 8tonne/hr fixed bed slagging updraft gasifiers for the disposal of MSW. The low value heating gas produced is used to produce electricity and for district heatingSix plants were constructed, only one remains in operation (Créteil, France)
Key Results	A low value heating gas is produced for steam raising for electricity production and for district heating. Yield is not reported. Calculations based on a feedstock throughput of 7 tonne/hr and a mean efficiency of 68% show that the process will yield an electricity output of 1603 kW and a heat output to the network of 10537kW.
Comparisons	See Wellman, UK; Voest-Alpine, Austria; Volund, Denmark

PROCESS

Reactor Type	Updraft slagging fixed bed gasifier
Description	Gasification for the disposal of MSW in slagging updraft gasifiers to produce low heating value gas
Objective	Disposal of MSW with energy recovery for district heating
Capital cost	FF100million, at Andco-Torrax plant at Créteil, 1979-1980
Scalability	Limited to around 5t/h, probably at maximum size.
Reactor problems	Feeding gas clean up (excessive heat exchanger fouling)

FEEDSTOCK

Main feedstock used	MSW
Other Feedstocks	MSW

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS		LIQUID		CHAR
CO	wt %	*C*	wt %	*C*	wt %
H2	wt %	*H*	wt %	*H*	wt %
CO2	wt %	*O*	wt %	*O*	wt %
CH4	wt %	*H2O*	wt %	*Other*	
N2	wt %	*Char*	wt %		
Tar	wt %	*Other*			
Dust	wt %				
Other	Constituents are steam, H2, CO, CO2, N2, CH4, tars , traces of O2, some HCl, NOx, SO2. It is				
Yield	Not known				
HHV					
Viscosity					
Density					
Other					
Clean up / Upgrading methods	Cyclone Electrostatic precipatator				
Clean up / Upgrading problems					

SECONDARY PRODUCTS

	GAS		LIQUID		CHAR
Upgraded or derived products					
Characteristics					
		C	wt %		
		H	wt %		
		O	wt %		
		H2O	wt %		
		Other			

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

Source Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

REFERENCES

1 Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

2

3

BIS Information

Mnemonic	*TPST01*

DIRECTORY

Group	TPS Termiska Processer AB (Studsvik) formely Studsvik Energiteknik AB
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Keywords	Gasification, Circulating fluid bed, Tar cracking, Dolomite, Catalyst, Scrubbing, Engine, Fuel gas, secondary circulating fluid bed

SUMMARY

Achievement	The gasification of woody biomass or municipal solid waste in an atmospheric circulating fluidised bed reactorfor the production of a fuel gas. A secondary reactor cracks any tars in the raw product gas. Two 15MWth units without the secondary crackers have been installed at Chianti, Italy by Aerimpianti SpA
Key Results	A low heating value gas of 4-7MJ/Nm3 is produced to be used for fuelling dual fuel engines, gas turbines or gas burners. Yields are not reported. The Studsvik 2MWth gasifier has total of 2500hrs. The CFB gasifier/CFB cracker have been operated for 1400hrs and the CFB gasifier/CFB cracker/turbo-deisel engine system for 800hrs. The hot gas efficiency is reported to be about 90%. The carbon conversion efficiency is reported to be greater than 95%. Tar conversion efficiencies of 90-95% are reported
Comparisons	See Aerimpianti who have licensed the technology, Italy

PROCESS

Reactor Type	Circulating fast fluid bed
Description	Gasification of woody biomass or MSW in an atmospheric circulating fluidised bed gasifier for the production of fuel gas.
Objective	Heat and power production in short term, liquid fuels in long term.
Capital cost	£30 000 000 (300 000 000SEK), at 52MWth, May 1992
Scalability	Very good
Reactor problems	

FEEDSTOCK

Main feedstock used	Wood
Other Feedstocks	Woody biomass, RDF pellets, RDF

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS	
CO	7-9	wt %
H2	9-13	wt %
CO2	12-14	wt %
CH4		wt %
N2	47-52	wt %
Tar		wt %
Dust		wt %
Other	CxHy 6-9v% H2O 10-14v% Other 0.5-1.0v%	

	LIQUID	
C		wt %
H		wt %
O		wt %
H2O		wt %
Char		wt %
Other		

	CHAR	
C		wt %
H		wt %
O		wt %
Other		

	GAS	LIQUID	CHAR
Yield	not reported		
HHV	4-7 MJ/Nm3		
Viscosity			
Density			
Other			
Clean up / Upgrading methods	Cyclone Fabric filter Water (venturi) scrubber		
Clean up / Upgrading problems			

SECONDARY PRODUCTS

	GAS	LIQUID	CHAR
Upgraded or derived products			
Characteristics			

C		wt %
H		wt %
O		wt %
H2O		wt %
Other		

PUBLICATION DETAILS

Originator: A V Bridgwater

Date: 28 January, 1994

Source: Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

REFERENCES

1 EEC Contractors Meeting Proceedings Florence Nov 1990 #

2 Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

3

BIS Information

	Mnemonic	UTWE01
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	Keywords	Flash pyrolysis, Ablation, Liquids, Bio-oil, Model
SUMMARY	*Achievement*	Process works in that quite good yields of pyrolysis liquids are obtained, but large quantities of sand are required and the equipment has a limited run time of 10 minutes. The mechanism of pyrolysis is unclear.
	Key Results	Oil yield (total liquid) typically 60-65% which is lower than typical flash pyrolysis processes.
	Comparisons	Ablative pyrolysis is the most widely researched flash pyrolysis method with 6 processes - Univ. Aston, NREL, CSM, BCC, Univ Nancy.
PROCESS	*Reactor Type*	Vertical indirectly heated rotating cone
	Description	Rotating cone flash pyrolysis to produce pyrolysis liquids as fuel
	Objective	Flash pyrolysis of biomass for liquids.
	Capital cost	
	Scalability	Uncertain.
	Reactor problems	Solids build up in reactor
FEEDSTOCK		
	Main feedstock used	
	Other Feedstocks	Wood

C		wt %	*Size*	< 200 microns
H		wt %	*Size range*	50-200 microns
O		wt %	*Shape*	Powder
Ash		wt %	*Cost*	Not known
Moisture	< 5%	wt %		

BIS Information

PRODUCTS

	GAS			LIQUID			CHAR	
CO		wt %	*C*		wt %	*C*		wt %
H2		wt %	*H*		wt %	*H*		wt %
CO2		wt %	*O*		wt %	*O*		wt %
CH4		wt %	*H2O*		wt %	*Other*		
N2		wt %	*Char*		wt %			
Tar		wt %	*Other*					
Dust		wt %						
Other								
Yield				Not yet determined				
HHV								
Viscosity								
Density								
Other								
Clean up / Upgrading methods				None				
Clean up / Upgrading problems				None				

SECONDARY PRODUCTS

	GAS	LIQUID	CHAR
Upgraded or derived products			
Characteristics			

C		wt %
H		wt %
O		wt %
H2O		wt %
Other		

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

Source

REFERENCES

1 EEC Contractors Meeting Proceedings Florence Nov 1990 #

2 In "Advances in Thermochemical Biomass Conversion" Ed A V Bridgwater, pp 1122, (Blackie 1994).

3

BIS Information

Mnemonic	FENO02

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Keywords	Flash pyrolysis, Fluid bed, Bio-oil,

SUMMARY

Achievement	Pilot plant was achieving full capacity of 160-170 kg/h in November 1993. Oil quality was not defined at that time but was described as "very good".
Key Results	Successful scaling up of University of Waterloo flash pyrolysis process from 3kg/h to 200kg/h. Good quality bio-oil obtained.
Comparisons	Yields and product quality are qualitatively comparable to University of Waterloo but detailed mass balances and product characterisation was not completed by December 1993.

PROCESS

Reactor Type	Shallow fluid bed.
Description	Flash pyrolysis in a shallow fluid bed to produce liquids. Process designed by and based on University of Waterloo.
Objective	Production of bio-oil.
Capital cost	
Scalability	Claimed possible to 2 t/h.
Reactor problems	Air leaks, measurement techniques, biomass agglomeration

FEEDSTOCK

Main feedstock used	Wood
Other Feedstocks	Eucalyptus wood, bagasse,

C		wt %	*Size*	<10 mm
H		wt %	*Size range*	0 - 10 mm
O		wt %	*Shape*	Small chips and pins
Ash		wt %	*Cost*	Not known
Moisture	< 10%	wt %		

BIS Information

PRODUCTS

	GAS		LIQUID		CHAR
CO	wt %	*C*	wt %	*C*	wt %
H2	wt %	*H*	wt %	*H*	wt %
CO2	wt %	*O*	wt %	*O*	wt %
CH4	wt %	*H2O*	wt %	*Other*	
N2	wt %	*Char*	wt %		
Tar	wt %	*Other*			
Dust	wt %				
Other					
Yield			# 50% wt.		# 10 - 15% wt
HHV			# 20.9 MJ/kg		
Viscosity					
Density					
Other					
Clean up / Upgrading methods					
Clean up / Upgrading problems			# = anticipated		

SECONDARY PRODUCTS

Upgraded or derived products					
Characteristics					
		C	wt %		
		H	wt %		
		O	wt %		
		H2O	wt %		
		Other			

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

Source

REFERENCES

1

2

3

BIS Information

	Mnemonic	VEBA01
DIRECTORY	*Group*	Veba Oel AG
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	Country	Germany
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	Keywords	Upgrading, Hydrotreating, Bio-oil, Catalyst
SUMMARY	*Achievement*	One continuous run of 8 days was achieved but this resulted in total deactivation of catalyst. Economics of hydrotreating are strongly dependant on cost of hydrogen.
	Key Results	Better than 92% de-oxygenation gave a black oil with good water separation. 99.5% deoxygenation gave a water-white hydrocarbon product.
	Comparisons	Battelle PNL work by D C Elliott operated continuously without deterioration. B Delmon from UCL has only done batch work.
PROCESS	*Reactor Type*	Fixed bed upflow/downflow catalytic reactor
	Description	Upgrading pyrolysis oils by hydrotreating and assessment of compatibility with conventional fossil oils
	Objective	De-oxygenation of biomass derived bio-oil from flash pyrolysis.
	Capital cost	
	Scalability	Very good as conventional refinery operation
	Reactor problems	Rapid catalyst deactivation, coking, plugging

FEEDSTOCK

Main feedstock used	Primary bio-oil
Other Feedstocks	Ensyn flash pyrolysis oil

C		wt %	*Size*	N/A
H		wt %	*Size range*	N/A
O		wt %	*Shape*	N/A
Ash		wt %	*Cost*	N/A
Moisture	15 - 25%	wt %		

BIS Information

PRODUCTS

	GAS		LIQUID		CHAR
CO	wt %	*C*	85.9-87.2 wt %	*C*	wt %
H2	wt %	*H*	10.8-13.2 wt %	*H*	wt %
CO2	wt %	*O*	0-3 wt %	*O*	wt %
CH4	wt %	*H2O*	50-55 wt %	*Other*	
N2	wt %	*Char*	wt %		
Tar	wt %	*Other*			
Dust	wt %				
Other					
Yield	15 -19 wt%		Up to 35% wt		
HHV			Up to 42 MJ/kg		
Viscosity					
Density					
Other					
Clean up / Upgrading methods			Hydrotreating		
Clean up / Upgrading problems					

SECONDARY PRODUCTS

	GAS		LIQUID		CHAR
Upgraded or derived products			Various levels of deoxygenation		
Characteristics					
		C	wt %		
		H	wt %		
		O	wt %		
		H2O	wt %		
		Other			

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

Source

REFERENCES

1 EEC Thermochemical contractors meeting Oct 1991

2 1st European Forum on Electricity Production from Biomass and Wastes by Advanced Technologies, Florence 1991

3

BIS Information

	Mnemonic	VOLU01
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	Keywords	Gasification, Updraft, Straw, CHP, Electricity, Heat, Combustion, Pyrolysis, Tar cracking
SUMMARY	*Achievement*	The gasification of straw or wood for the production of a low heating value gas. As of May 1992 approximately 1200hrs operating experience have been gained and 100 tonnes of straw and 40 tonnes of wood chips have been separately gasified.
	Key Results	
	Comparisons	See Wellman, UK; Sofresid, France; Voest Alpine, Austria
PROCESS	*Reactor Type*	Updraft gasifier
	Description	The gasification of straw or wood in a 1-1.3MWth pilot scale updraft gasifier. Now owned by Ansaldo (1993)
	Objective	Production of heat and power from agricultural wastes and energy crops
	Capital cost	
	Scalability	Probably limited to about 5 t/h in one reactor.
	Reactor problems	Solids flow; ratholing

FEEDSTOCK

Main feedstock used	Straw
Other Feedstocks	Straw, wood

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS		LIQUID		CHAR
CO	4.4 wt %	C	wt %	C	wt %
H_2	11.6 wt %	H	wt %	H	wt %
CO_2	14.7 wt %	O	wt %	O	wt %
CH_4	4.0 wt %	H_2O	wt %	Other	
N_2	64.3 wt %	Char	wt %		
Tar	wt %	Other			
Dust	wt %				
Other	Water 170-240g/Nm3 TOC 6.5-10.0g/Nm3				
Yield	1.81-2.55kg/kg daffeed				
HHV	2.6-5.0MJ/Nm3				
Viscosity					
Density					
Other					
Clean up / Upgrading methods	Cyclone				
Clean up / Upgrading problems					

SECONDARY PRODUCTS

Upgraded or derived products			
Characteristics			
C		wt %	
H		wt %	
O		wt %	
H_2O		wt %	
Other			

PUBLICATION DETAILS

Originator: A V Bridgwater

Date: 28 January, 1994

Source: Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

REFERENCES

1 Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

2

3

BIS Information

	Mnemonic	EGEM01
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	Keywords	Flash pyrolysis, Entrained flow, Bio-oil, wood particles, sawdust
SUMMARY	*Achievement*	A pilot plant of 200kg/hr was commissioned in October 1991 for the production of bio-oils by entrained downflow flash pyrolysis funded by the CEC and Egemin. Fuel oil quality is inconsistent and yields are low. The plant is currently not operational, the last tests being conducted in May 1992
	Key Results	A yield of 39.9 wt% of bio-oil has been achieved. The use is not reported. The main feedstock is fine wood particles with moisture and ash contents of 16% and 0.57% respectively. A number of problems have been encountered with the system which it is estimated will take two years at a cost of ECU700 000.
	Comparisons	*See GTRI, USA for similar process.*
PROCESS	*Reactor Type*	Entrained downflow pyrolyser
	Description	Entrained down-flow flash pyrolysis. Abandoned 1993.
	Objective	Production of pyrolysis liquids for energy.
	Capital cost	
	Scalability	Not known. Entrained flow coal gasifiers have been built to a large scale.
	Reactor problems	Incomplete reaction of feed, condensation of tars on cyclone reduces cyclone

FEEDSTOCK

Main feedstock used	Wood
Other Feedstocks	Sawdust

C		wt %	*Size*	< 5 mm
H		wt %	*Size range*	2 - 5 mm
O		wt %	*Shape*	Chips
Ash		wt %	*Cost*	70ECU/t
Moisture	< 10%	wt %		

BIS Information

PRODUCTS

	GAS		LIQUID		CHAR
CO	wt %	C	39% wt %	C	64 wt %
H2	wt %	H	8% wt %	H	4 wt %
CO2	wt %	O	52% wt %	O	22 wt %
CH4	wt %	H2O	18.3% wt %	Other	Ash 10wt%
N2	wt %	Char	wt %		
Tar	wt %	Other	1%		
Dust	wt %				
Other					
Yield	16.2%		39.9% (dry basis)		29% (dry)
HHV			18 MJ/kg		
Viscosity					
Density					
Other					
Clean up / Upgrading methods	Cyclone, venturi scrubber, demisters				
Clean up / Upgrading problems					

SECONDARY PRODUCTS

	GAS		LIQUID		CHAR
Upgraded or derived products					
Characteristics			High oxygen		
		C	wt %		
		H	wt %		
		O	wt %		
		H2O	wt %		
		Other			

PUBLICATION DETAILS

Originator: A V Bridgwater

Date: 28 January, 1994

Source: Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

REFERENCES

1 EEC Contractors Meeeting Proceeding, F Core & Co Nov 1990, 6th EEC Conference on Biomass for Energy etc, Elsevier 1992

2 Maniatis K, Baeyens J, Roggeman G, Peeters M Flash Pyrolysis of Biomass in an Entrained Bed Reactor, GLR EC Conference on Biomass for Energy, Industry and Environment - Abstracts 22-26, April 1991 Greece ppOR 09 02

3 K Maniatis, J Baeyens, M Peeters, G Roggeman The Egemin Flash Pyroysis Process: Commissioning and initial results, proceedings of the conference at Interlaken, May 1992

BIS Information

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	Keywords	Pyrolysis, Fluid bed, Chemicals, Sewage sludge, Paper mill, Pyrolysis oil, Pyrolysis gas, Pilot plant, Heavy metals, Plastic, Rubber, Oil
SUMMARY	*Achievement*	The pyrolysis of plastic/rubber/oil/other organic wastes to liquid hydrocarbons. A commercial demonstration plant was constructed in Ebenhausen, Germany consisting of two 500tonne/yr fluidised beds one of which was never operated. A 600kg/h demonstration scale plant was built in Grimma, Germany.
	Key Results	Waste plastic (the main feedstock) is pyrolysed in a fluidised bed to produce a aromatic hydrocarbon oil at yields of 50wt% for use as a crude chemical. Pyrolysis gases are used as fluidising gases and for process heat. The product yields from the pyrolysis of used syringes were gas 59.3%, gasoline 23.8%, high boiling components11.1%.
	Comparisons	See University of Sherbrooke, Canada; JWP, USA; SEI, USA
PROCESS	*Reactor Type*	Fluidised bed
	Description	Pyrolysis of wastes in a fluidised bed reactor for the production of liquid hydrocarbons.
	Objective	Recovery of chemicals from plastics
	Capital cost	£14.4million, at 20 000t/annum, April 1992
	Scalability	Good. A 1 t/h plant has already been commercialised
	Reactor problems	
FEEDSTOCK		
	Main feedstock used	Plastics
	Other Feedstocks	Waste plastic, waste rubber (tyres), sewage sludge, oil sludge

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS			LIQUID			CHAR	
CO	0.80	wt %	*C*		wt %	*C*		wt %
H2	0	wt %	*H*		wt %	*H*		wt %
CO2	0	wt %	*O*		wt %	*O*		wt %
CH4	31.70	wt %	*H2O*		wt %	*Other*		
N2	0	wt %	*Char*		wt %			
Tar		wt %	*Other*					
Dust		wt %						
Other	C2H6:3.10v% C2H4:23.20 v% C4H8:6.80v% Cyclopentadiene0.7v%							
Yield	40wt%			50wt%			5wt%	
HHV	50MJ/m3							
Viscosity								
Density								
Other								

	GAS	LIQUID	CHAR
Clean up / Upgrading methods	Cyclone, condenser, electrostatic precipitation		
Clean up / Upgrading problems	Particulates adhere to condensor	High levels of organo-chlorides in product.	

SECONDARY PRODUCTS

	GAS	LIQUID	CHAR
Upgraded or derived products			
Characteristics			

C		wt %
H		wt %
O		wt %
H2O		wt %
Other		

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

Source Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

REFERENCES

1 In "Advances in Thermochemical Biomass Conversion" Ed A V Bridgwater, pp 1222, (Blackie 1994).

2 Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

3

BIS Information

	Mnemonic	*AHLS01*
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	Fax	+358 5229 3309
	Keywords	Atmospheric, Gasification, Bark, Peat, Lignite, Coal, Sawdust
SUMMARY	*Achievement*	Six atmospheric gasifiers have been installed between 1982 and 1986 in Finland, Sweden and Portugal. Four were known to be operational as of June 1992. A pilot scale plant is installed in Karhula, Finland chich is currently non-operational.
	Key Results	Low value heating gas (7.5 MJ/Nm3) has been produced. Wood, bark, peat, lignite, and coal have been produced. Ash content and composition depend on the feed.
	Comparisons	See Lurgi, Germany; Gotaverken, Sweden; TPS, Sweden; Aerimpianti, Italy
PROCESS	*Reactor Type*	Circulating fluidised bed gasifier
	Description	Atmospheric circulating fluidised bed gasifiers.
	Objective	Disposal of pulp wastes with energy recovery
	Capital cost	
	Scalability	Very good
	Reactor problems	
FEEDSTOCK		
	Main feedstock used	Pulp wastes
	Other Feedstocks	Wood, bark, peat, lignite, coal, sawdust, paper waste, MSW, heavy oil

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	
Moisture		wt %		

BIS Information

PRODUCTS

	GAS			LIQUID			CHAR	
CO	15-16	wt %	C		wt %	C		wt %
H_2	21-22	wt %	H		wt %	H		wt %
CO_2	10-11	wt %	O		wt %	O		wt %
CH_4	5-6	wt %	H_2O		wt %	Other	Ash (quantity depends upon feed)	
N_2	46-47	wt %	Char		wt %			
Tar		wt %	Other					
Dust		wt %						
Other								
Yield	3.27 kg/kg daf feed 1181 Nm3/h							
HHV	7.5 MJ/Nm3							
Viscosity								
Density								
Other								
Clean up / Upgrading methods	Cyclone, cooler, bag house, hot ceramic filter							
Clean up / Upgrading problems								

SECONDARY PRODUCTS

	GAS	LIQUID	CHAR
Upgraded or derived products			
Characteristics			
C		wt %	
H		wt %	
O		wt %	
H_2O		wt %	
Other			

PUBLICATION DETAILS

Originator	A V Bridgwater
Date	28 January, 1994
Source	Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

REFERENCES

1	Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)
2	
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BIS Information

	Mnemonic	AHLS02
DIRECTORY	*Group*	A Ahlström Corporation
	Leader	R Lundqvist
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	Zip or post code	
	Country	Finland
	Telephone	+358 5229 3314
	Fax	+358 5229 3309
	Keywords	Pressurised, gasification, wood waste, chips
SUMMARY	*Achievement*	Research in cooperation with Sydkraft, a joint venture company, Bioflow Ltd., has been established. Construction of a pressurised fluidised bed gasifier at Värnamo commenced in September 1991. Commissioning began in spring 1993 and the integrated gasifier - gas turbine first ran in spring 1994
	Key Results	None as yet. The purpose is to integrate gasification with combinbed cycle power generation. The proposed process parameters are: Throughput 3000kg/hr Reactor operating pressure 25bar Reactor operating temperature 950-1000°C Wood/waste chips of 50-55% moisture will be used.
	Comparisons	There is no comparable process or plant anywhere.
PROCESS	*Reactor Type*	Circulating fluidised bed
	Description	Pressurised fluidised bed gasifier.
	Objective	IGCC
	Capital cost	
	Scalability	Very good. Large capacity plant needed for economic viability
	Reactor problems	Not yet known
FEEDSTOCK		
	Main feedstock used	Wood
	Other Feedstocks	None as yet

C		wt %	*Size*	10 mm
H		wt %	*Size range*	5-15 mm
O		wt %	*Shape*	Chips
Ash		wt %	*Cost*	Not known
Moisture	< 15%	wt %		

BIS Information

PRODUCTS	GAS		LIQUID		CHAR
CO	wt %	*C*	wt %	*C*	wt %
H2	wt %	*H*	wt %	*H*	wt %
CO2	wt %	*O*	wt %	*O*	wt %
CH4	wt %	*H2O*	wt %	*Other*	Ash
N2	wt %	*Char*	wt %		
Tar	wt %	*Other*			
Dust	wt %				
Other	No data avilable yet				
Yield	Gas for 6MWe +9MWth				
HHV					
Viscosity					
Density					
Other					
Clean up / Upgrading methods	Cyclone				
Clean up / Upgrading problems					

SECONDARY PRODUCTS

Upgraded or derived products

Characteristics

C	wt %
H	wt %
O	wt %
H2O	wt %
Other	

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

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BIS Information

	Mnemonic	LURG01
DIRECTORY	*Group*	Lurgi Energie- und Umweittechnik GmbH
	Leader	Johannes C. Löffler (Manager, Coal and Energy Technology Division, Solid Fuels
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	Country	Germany
	Telephone	+49 69 5808 3468(Löffler)
	Fax	+49 69 5808 2757(Löffler)
	Keywords	Gasification, Fuel gas, RDF, MSW, Electricity, Pressure, Atmospheric
SUMMARY	*Achievement*	The gasification of wood, RDF, and coal for the production of low and medium heating value gas. A commercial circulating fluidised bed gasification plant was installed at Zellstoffwerke Pöls AG (ZPA), an Austrian pulp producer. It is operational as of April 1992.
	Key Results	The main product is low value heating gas .Yields of 3.1 kg/kg feed produced from bark have been reported from the commercial scale plant. The design availability of the Pöls plant is 95%. Currently the plant is operating at 60% capacity.
	Comparisons	See Ahlstrom, Finland; TPS, Sweden; Aerimpianti, Italy; Gotaverken, Sweden.
PROCESS	*Reactor Type*	Circulating fluid bed
	Description	The gasification of wood,RDF or coal for the production of a low or medium heating value fuel in a circulating fluidised bed gasifier
	Objective	Disposal of pulp wastes; production of heat and power from agricultural wastes; IGCC
	Capital cost	£7.5million (Dm21million), at Similar to Pöls plant, ?
	Scalability	Very good
	Reactor problems	None known
FEEDSTOCK		
	Main feedstock used	Biomass, coal
	Other Feedstocks	Bark, wood, RDF, lignite coal, petroleum coke, waste wood, rice husks, straw

C		wt %	*Size*	< 5 mm
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	Not known
Moisture		wt %		

BIS Information

PRODUCTS

	GAS			LIQUID			CHAR	
CO	19.6	wt %	*C*		wt %	*C*		wt %
H2	19.6	wt %	*H*		wt %	*H*		wt %
CO2	13.5	wt %	*O*		wt %	*O*		wt %
CH4		wt %	*H2O*		wt %	*Other*		
N2	42.9	wt %	*Char*		wt %			
Tar		wt %	*Other*	Very few tars produced				
Dust	50g/Nm3	wt %						
Other	C+ 3.8 sulpher very low							
Yield								
HHV	5.8MJ/Nm3							
Viscosity								
Density								
Other								
Clean up / Upgrading methods	Cyclone							
Clean up / Upgrading problems								

SECONDARY PRODUCTS

	GAS		LIQUID		CHAR
Upgraded or derived products					
Characteristics					
		C	wt %		
		H	wt %		
		O	wt %		
		H2O	wt %		
		Other			

PUBLICATION DETAILS

Originator A V Bridgwater

Date 28 January, 1994

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REFERENCES

1 Bridgwater, A V, Evans, G D, "An Assessment of Thermochemical Conversion Systems", Contractors Report for ETSU B/T1/00207/REP, (ETSU-UKDTI 1993)

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LURG01

BIS Information

	Mnemonic	TAMP01
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	Country	Finland
	Telephone	+358 31 241 3555
	Fax	+358 31 241 3599
	Keywords	Pressurised fluidised bed, Gasification, Fuel gas, Gas turbine, Coal, Peat, Wood
SUMMARY	*Achievement*	The gasification of carbonaceous feedstocks in a 1800kg/hr pilot scale pressurised fluidised bed gasifier for the production of low heating value fuel gas. The plant underwent commissioning in March 1992.
	Key Results	The gasification of coal yielded a low heating value gas (4-6MJ/Nm3) at 4.2kg/kg feed for use as a boiler fuel. It was planned to modify the plant to process biomass for the end of 1992. A computer model of the biomass process predicted the cold gas efficiency to be 67.3%. A demonstration scale plant is proposed for Sweden in which the estimated efficiency to electricity is 45% and the estimated efficiency to district heating is 88%.0
	Comparisons	See IGT, USA
PROCESS	*Reactor Type*	Pressurised fluid bed gasifier
	Description	Gasification of carbonaceous feedstock in a pressurised fluidised bed gasifier for the production of a low heating value gas. Process is based in the IGT U-gas process developed for coal and subsequently modified for biomass
	Objective	IGCC
	Capital cost	£120-140 million (demonstration), at Demonstartion of 30t/h, 1992
	Scalability	Good
	Reactor problems	
FEEDSTOCK		
	Main feedstock used	Coal, wood
	Other Feedstocks	Peat (wood after modifications), coal, wood

C		wt %	*Size*	
H		wt %	*Size range*	
O		wt %	*Shape*	
Ash		wt %	*Cost*	Not known
Moisture		wt %		

BIS Information

PRODUCTS

	GAS			LIQUID			CHAR	
CO	11.3	wt %	C		wt %	C		wt %
H2	13.5	wt %	H		wt %	H		wt %
CO2	12.9	wt %	O		wt %	O		wt %
CH4	4.8	wt %	H2O		wt %	Other		
N2	40.2	wt %	Char		wt %			
Tar	not reported	wt %	Other					
Dust	not reported	wt %						
Other	H2O 17.1							
Yield	4.2kg/kg feed							
HHV	4-6 MJ/Nm3							
Viscosity								
Density								
Other								
Clean up / Upgrading methods	Cyclone, hot gas filter, electrostatic precipatator							
Clean up / Upgrading problems	GTblade fouling may occur with alkali metals							

SECONDARY PRODUCTS

Upgraded or derived products			
Characteristics			
C		wt %	
H		wt %	
O		wt %	
H2O		wt %	
Other			

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A. Bridgwater

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It should be stated that this document represents the findings and opinions of the authors and should not be considered as the opinions or recommendations of the Commission services.