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Production of high grade fuels and chemicals from catalytic pyrolysis of biomass

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Abstract

The potential offered by biomass and solid wastes for solving some of the world's energy problems is widely recognised. The energy in biomass may be realised either by direct use as in combustion, or by upgrading into a more valuable and usable fuel such as fuel gas, fuel oil, transport fuel or higher value products for the chemical industry. This paper is concerned with conversion and upgrading by pyrolysis and briefly describes the technologies of fast pyrolysis with particular reference to the use of catalysts in chemicals production and the use of catalytic processes in upgrading the primary pyrolysis products to higher quality and higher value fuels and chemicals. There are natural catalysts in biomass which substantially influence the production of high yielding chemicals. Removal or reinforcement of these catalysts has a dramatic effect on product yield and composition. The pyrolysis vapours can be catalytically cracked over zeolites to give aromatics and other hydrocarbon products which can be further converted into gasoline and diesel and the condensed liquid can be hydrotreated to a naphtha like product also for upgrading into transport fuels. There is, however, considerable uncertainty over the ability of the upgrading technology to be scaled up to commercial feasibility most notably in terms of catalyst performance and life. Considerably more research and development is needed to develop and prove suitable catalyst systems. There is also considerable uncertainty over the cost of upgrading in terms of capital costs, operating costs and performance and some preliminary estimates are included.

Keywords: Biomass energy; Waste energy

1. Pyrolysis

When organic materials are heated in the absence of air, they degrade to a gas, a liquid and a solid. 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 can maximise either the gas or liquid products [1,2]: fast pyrolysis at temperatures of typically 500°C; at very high heating rates and short vapour residence times of typically less than 1 s; maximises liquid yields at up to 85 wt.-% (wet basis) or up to 70% dry basis and this is the focus of this paper. Many fast pyrolysis processes have been developed to pilot, demonstration and commercial scale [2].

1.1. Fast pyrolysis liquid (bio-oil)

The crude pyrolysis liquid product is currently attracting the most interest because of its high energy density compared to raw biomass, easy transportability, ease of use and de-coupling of

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Table 1
Typical wood derived pyrolysis oil characteristics

Physical property		Typical value
Moisture content		20%
pH		2.5
Specific gravity		1.20
Elemental analysis (moisture free)	C	56.4%
	H	6.2%
	N	0.2%
	S	< 0.01%
	O (by difference)	37.2%
	Ash	0.1%
HHV (moisture free basis)		22.5 MJ/kg
HHV as produced		18 MJ/kg
Viscosity (ca. 40°C)		50 cp
Kinematic viscosity	ca. 25°C	233 cSt
	ca. 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%

conversion and utilisation processes [3]. The liquid approximates to biomass in elemental composition (see Table 1) and is composed of a very complex mixture of oxygenated hydrocarbons. 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 variously referred to as 'oil' or 'bio-oil' or 'bio-crude-oil' or 'bio-fuel-oil'. Typical properties and analyses of this liquid have been reported from analytical programmes sponsored, for example, by Energy Mines and Resources Canada [4] and the US Department of Energy [5] and the IEA Bioenergy Agreement [6], as well as by technology developers [7]. Typical characteristics are summarised in Table 1. 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, particle size and ash content may have a major effect as summarised in Table 2.

1.2. Applications of bio-oil

Possible applications for the crude liquids are summarised in Fig. 1. The liquid has been successfully burned in a boiler (e.g. [9]) and furnace (e.g. [10]) and other combustion tests have been carried out (e.g. [11,12]). Limited tests have also been carried out in dual or pilot fuelled engines [13]. Problems have been reported with char levels which can block filters and atomisers and problems have also been hypothesised with the alkaline nature of the ash in turbine applications, high viscosity in pumping, water with possible phase separation, and corrosion from the low pH. A comprehensive set of papers on the characteristics of fast pyrolysis oils is contained in the proceedings of a workshop held in September 1994 [14]. It is for all these various concerns and reported problems that research

Table 2
Characteristics of bio-oil and methods for modification [8]

Characteristic	Effect	Solution
Suspended char	Erosion; Equipment blockage, High CO emissions	Filter vapour; Filter liquid; Modify char; Modify application
Alkali metals	Deposition of solids in combustion; Damage to turbines	Hot vapour filtration Process oil; Modify application; Pretreat feedstock to remove ash
Low pH	Corrosion of vessels and pipework	Careful materials selection;
Incompatibility	Destruction of seals and gaskets	Careful materials selection
Temperature sensitivity	Decomposition on hot surfaces; Adhesion of droplets on surfaces below 400°C	Recognition of problem and appropriate cooling facilities; Avoid hot surfaces > 500°C
High viscosity	High pressure drops can give higher cost equipment, leakage or rupture	Careful low temperature heating, and/or addition of water, and/or addition of co-solvents.
Water content	Complex effect on viscosity, heating value, density, stability, pH, etc.	Recognise problem; Optimise for application
In-homogeneity	Layering or partial separation of phases;	Modify or change process; Change feedstock to low lignin;
	Filtration problems	Additives; Control water content

has continued on upgrading the crude liquids to products that more closely resemble conventional fuels which can be utilised in analogous ways and analogous applications.

2. 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. These chemicals are recovered by physical and/or chemical processing from the crude liquid 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 natural catalysts, it is not practicable to differentiate between

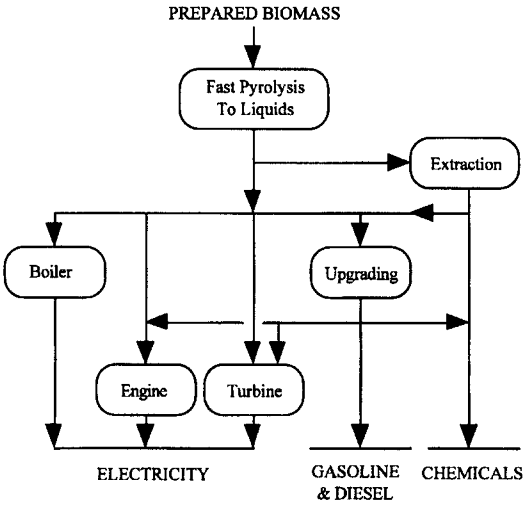

Fig. 1. Applications of fast pyrolysis oil.

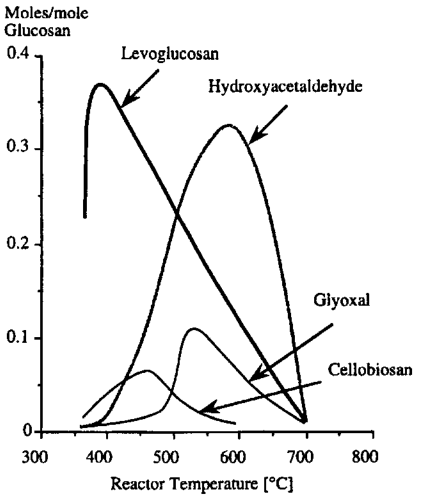

Fig. 2. Yields of levoglucosan and hydroxyacetaldehyde from cellulose.

catalytic and non-catalytic pyrolysis. Catalytic conversion of the primary vapours and whole product oil is discussed separately below. Hydroxyacetaldehyde and levoglucosan are the most significant chemicals that can be derived in high yields from biomass through enhancement or removal respectively of the alkali metal catalysts that are innate to most forms of biomass. The most comprehensive data is available for levoglucosan and hydroxyacetaldehyde and yield data from cellulose feedstock material is shown as Fig. 2. A review of recent developments in thermal and thermo-catalytic biomass conversion has been published [15] and the opportunities for chemicals production reviewed [16]. Table 3 lists the chemicals that have been recovered or derived [17]. There

Table 3
Chemicals recovered from biomass pyrolysis liquids (based on wood unless otherwise stated)

Chemical	Maximum yield	Achieved yield	Purity
Acetol			
Adhesives			
Alkanes and alkenes			
Anhydrosugars			
Anisole			
Aromatics	42–55%	15%	
Aryl ethers			
Calcium acetate			
Carboxylic acids			
Cresols			
Fatty acids			
Food flavourings			
Glyoxal	11% on cellulose		
Hydroxyacetaldehyde	33% on cellulose 18% on wood		
Levoglucosan	37% on cellulose 22% on wood	70% of maximum	95%
Olefins			
Gasoline	45% on wood	23%	
Phenols			
Polyphenols			
Reformulated gasoline		22–27%	

is little information on yields and recovery efficiencies as most products have only been investigated in laboratories.

Levoglucosan is a major intermediate in the thermal degradation process [18]. 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 [19–21]. The extraction and recovery of the levoglucosan at high purity has recently been patented [22] and developed by BC Research [23,24]. 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 [25–27]. A range of other chemicals have been extracted or derived from biomass pyrolysis liquid which are reviewed in [17].

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 dimer (hydroxyacetaldehyde), with suppressed levoglucosan production [28]. Similar effects were found with zinc chloride, except that higher yields of furfural were obtained [29], and cobalt chloride additions to almond kernels gave higher yields of 2-furaldehyde [30]. Pyrolysis in molten salts gave significant yields of acetone and hydrocarbon gases [31] and under different conditions, gave high yields of relatively pure hydrogen about 90 vol.-% [32–34]. It was not clear if catalytic effects were 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 [35]. The economic and energetic consequences of melt regeneration have not been evaluated, but may be significant [29].

Hydrogen has been used as a reactive gas in a catalytically modified atmospheric fluid bed flash pyrolysis using nickel to give 70%–75% conversion to a gas containing 85%–90% methane [36,37], and olefins have also been produced in interesting yields [35]. This route has not yet been used to derive liquids although this suggests interesting possibilities with either pressure processing as well as atmospheric pressure catalytic pyrolysis using, for example, modified zeolites which are described below.

In all cases of chemicals recovery, there is insufficient 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. Choice of catalyst and mode of use are, therefore, important.

The recovery of valuable chemicals is seen as a potentially important way of improving the overall economics of fast pyrolysis processes. The residue after recovering these chemicals may then be upgraded and the upgrading process may be made easier if the chemicals contributing to the instability have already been removed or 'neutralised' in the chemical recovery process. The study of integrated systems is important to identify the optimum combinations of chemicals and bio-fuels.

3. Catalytic upgrading

The crude primary liquid product from flash pyrolysis can be used directly in a number of thermal and power generation applications, or can be upgraded to more conventional liquid hydrocarbon fuels. There are currently two basic processes: modified conventional hydrotreating to a naphtha-like product or zeolite cracking to a highly aromatic product. The whole area has been reviewed by Bridgwater [17], recent developments by Elliott et al. [15] and Sharma and Bakshi [38] and future needs identified [39,40].

3.1. Hydrotreating

Hydrotreating can be conceptually characterised as follows:

$$\begin{array}{lll} C_6H_8O_4 + 6H_2 & \rightarrow & 6CH_2 + 4H_2O \\ C_6H_8O_4 + 4.5H_2 & \rightarrow & 6CH_{1.5} + 4H_2O \\ \text{Bio} - \text{oil} & & \text{Hydrocarbons (naphtha equivalent)} \end{array}$$

This is a carbon limited system. A maximum stoichiometric yield of 56–58 wt.-% can thus be achieved on liquid bio-oil corresponding to a maximum energetic yield of about 69%–73% including the significant hydrogen generation requirement which is discussed below.

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 [41,42]. A temperature stepped single upflow continuous fixed bed reaction has been successfully employed for this purpose in both the USA [43,44] and Germany [41,42].

Hydrotreating is based on a modification of well-established refinery practice and involves a family of reactions including hydrogenation, de-oxygenation and reforming. 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. 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 and a variety of related catalysts including Ni, Co, Mo in oxide and sulphide forms on silica and alumina supports have also given good results in work at Battelle Pacific Northwest Laboratory, the University of Louvain and the Institute of Wood Chemistry (see [17] for full citations). There is uncertainty over the catalyst lifetime, although at least one continuous run of 8 days has been completed in a fixed bed reactor configuration but with substantial deterioration in activity [41,42]. The water in the bio-oil may cause this effect by attacking the support, although there are other possibilities such as 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 concern over sulphur stripping from the catalyst which would seriously impair its effectiveness although there is no evidence of this occurring. The water in the feed and product may have an adverse effect on conventional catalysts and they may require modification to improve their water tolerance.

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

A major disadvantage of hydrotreating is the significant hydrogen requirement of around 700 l/kg pyrolysis oil [39], (31 g mol/kg; 62 g/kg) for full hydrotreating, while Veba suggest 600–1000 l/kg bio-oil [41,42]. This is approximately the stoichiometric requirement, although an excess of 100%–200% is required for processing to maintain a high hydrogen partial pressure. This hydrogen can be generated in a number of ways including recovery and regeneration from the spent gases [45] and supply from refinery hydrogen. A 1000 ton/day biomass processing plant will require about 50 ton/day hydrogen for complete hydrotreating which, if generated from biomass by gasification and CO shifting, would require up to 700 to 800 ton/day additional biomass at a significant economic and efficiency penalty.

3.2. Zeolites

Early zeolite cracking research was carried out on a conventional mono-functional ZSM-5 catalyst, although more recently, specialist catalysts based on modified ZSM-5 have been developed [46]. Details are not published but these are believed likely to be bi-functional or multi-functional zeolites modified by the addition of metals such as nickel. The reaction follows the representative equation below with a maximum stoichiometric yield of 42% on liquid:

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

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. A bi-functional or multi-functional catalyst that can, for example, generate in-situ hydrogen through shifting the carbon monoxide in the product gas might be expected to operate more in a carbon limited environment rather than hydrogen limited, as depicted in the equation below with a maximum stoichiometric yield of 55 wt.-% on liquid:

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

This is a carbon limited reaction with the aromatic product being limited by carbon availability. This second route has not been explicitly attempted although the NREL work on modified zeolites may include this function [46,47]. It is also important to note that actual yields will be lower than these maximum possible. In the case of aromatics and gasoline, yields of 22%–27% have been predicted. 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 [48,49]. 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. An assessment of the resultant technology for production of gasoline has recently been completed by the IEA Bioenergy Agreement [49]. With current technology, the products would comprise 62% gasoline with the rest higher boiling fuel oil (taken as crude aromatics in the mass balances and cost estimates below), while future projections of technology developments suggest that 98% gasoline would be achievable [49].

The processing conditions are atmospheric pressure, temperatures from 350 up to 600°C and hourly space velocities of around 2. 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. The low pressure, processing temperature similar to that preferred for

Table 4
Overall typical mass balances to liquid products

Mass balance		Hydrotreating	Zeolites
Wood, dry ash free basis		100	100
Fast pyrolysis to crude (wet) bio-oil		83	83
Hydrotreating, 98% deoxygenation		30.5	–
Refining to diesel/gasoline		27.5	–
Upgrading to crude aromatics by zeolites (current status)		–	20.5
Refining to gasoline (future projection)		–	24.5
Yield on dry wood feed			
Pyrolysis oil	Overall yield — mass basis	83%	83%
	Overall yield — energy basis	70%	70%
Crude hydrocarbons	Overall yield — mass basis	30.5%	20.5%
	Overall yield — energy basis	ca. 38%	50%
Refined hydrocarbons	Overall yield — mass basis	27.5%	24.5%
	Overall yield — energy basis	ca. 36%	45–55%
including hydrogen			

optimum yields of bio-oil and close coupled process, potentially offer significant processing and economic advantages over hydrotreating. Organisations who have been, or are involved, in zeolite processing have been summarised and reviewed [17].

It must be emphasised that zeolite cracking is less well developed than hydrotreating and there are a much wider range of possibilities to be explored with mono- and multi-functional catalysts. The predictions of performance are based on relatively limited experimental data and the designs and cost estimates later are derived from detailed studies carried by the IEA liquefaction group [49]. The inherent nature of a one-step integrated process for synthesis of hydrocarbons is attractive. In addition, there are no directly analogous refinery processes from which data may be extrapolated.

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. The operations would probably be carried out on a service charge basis.

3.3. Product yield

The yields of the various liquid products from both hydrotreating and zeolite synthesis have been estimated from current data and are summarised in Table 4 for crude pyrolysis liquid, crude and refined hydrotreated bio-oil; and crude and refined aromatics from zeolite cracking [50].

4. Economic analysis

Production costs have been derived for pyrolysis oil, hydrotreated pyrolysis oil (naphtha), refined hydrotreated pyrolysis oil (diesel), crude aromatics from current zeolite cracking and gasoline from future or potential zeolite developments. The data used to construct the cost estimates is summarised in Table 5 with the cost estimates for the five products and a summary of the effect of changing the hydrogen supply strategy and applying learning effects to the capital cost.

Table 5
Bio-oil and hydrotreated bio-oil production costs

Feed rate and costs			
Feedstock cost	40.00 ECU/d.a.f. tonne		
Feed cost	2.11 ECU/GJ		
Wood input	250.00 t/day		
Hydrogen cost	468.00 ECU/t		
Yields			
Fast pyrolysis liquid yield,	83.0% on d.a.f. wood feed		
Hydrotreated liquid (naphtha) yield,	36.8% on bio-oil 30.5% on d.a.f. wood feed		
Refined liquid (diesel) yield,	90.0% on hydrotreated liquid 33.1% on bio-oil 27.5% on d.a.f. wood feed		
Crude aromatics (present case)	20.6% on d.a.f. wood feed		
Gasoline/refined aromatics (future case)	24.7% on d.a.f. wood feed		
Hydrotreated product costs (ECU/GJ)	*Bio-oil*	*H/T oil*	*Diesel*
H2 once through WITH fuel gas credit (base case)	6.41	11.48	12.90
H2 once through NO fuel gas credit	6.41	13.73	15.29
H2 recycle WITH fuel gas credit	6.41	12.30	13.77
H2 recovery-recycle NO fuel gas credit	6.41	12.86	14.37
H2 self sufficiency	6.41	13.57	15.13
Hydrotreating learning effect			
BASE CASE Hydrotreating	6.41	11.48	12.90
50% reduction in fast pyrolysis capital cost	5.04	9.86	11.19
50% reduction in hydrotreating capital cost	6.41	10.21	11.56
50% reduction in all capital costs	5.04	8.60	9.85
10% improvement in yield at each stage	5.83	9.88	10.19
Zeolite cracking product cost		*Crude*	*Gasoline*
Crude aromatics (present case)		12.59	
Gasoline/refined aromatics (potential)			10.18
Zeolite learning effect			
BASE CASE Zeolite cracking		12.59	10.18
50% reduction in all capital costs		9.87	7.94
10% improvement in yield		11.44	9.26
Conventional fuel costs	ECU/GJ		
Crude oil at $20/barrel	3.0		
Medium fuel	3.0–3.5		
Diesel	4.5–5.5		
Gasoline	5.0–6.0		

Five hydrogen utilisation options have been examined for the hydrotreating option as summarised in Table 5: four of these include provision for recovering hydrogen and recycling it to the hydrotreating plant to reduce net hydrogen consumption of which two provide for the offgas to be sold for its fuel gas content. In all cases 100% recovery or conversion is assumed. The fifth case, the hydrogen self sufficiency case, it is assumed that the offgas contains sufficient hydrocarbons to be reformed to satisfy the hydrotreating requirement. The most likely short term option is the Base Case, where an existing refinery is utilised for hydrogen supply. Zeolite cracking is more sensitive to feed

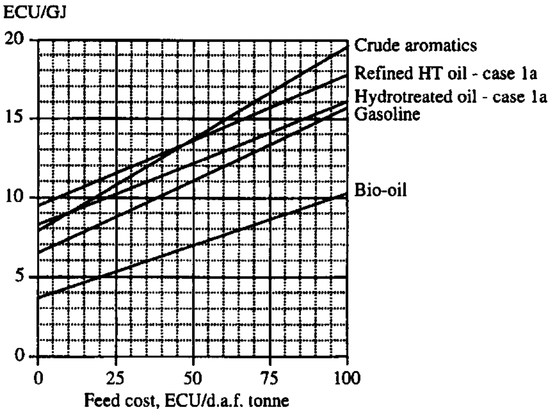

Fig. 3. Variation of product costs with feed cost (using least cost hydrotreating option — base case).

cost due to the lower conversion efficiencies, but this is more than compensated for by the lower capital costs giving more attractive products at lower feed costs as shown in Fig. 3.

5. Conclusions

The use of catalysts to improve either the yield or quality of gas and liquid fuels from biomass pyrolysis 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.

There are considerable opportunities for production of conventional and unconventional fuels for both electricity generation and fuel and chemical synthesis. The R&D requirements 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 for economic optimisation.

The economics of all the products show that none can currently compete at the present cost of purpose grown energy crops, the current state of technology and in the absence of fiscal incentives. However that the gap between these costs and commercial prices is sufficiently close to provide encouragement to continue with R&D.

References

[1] A.V. Bridgwater and S.A. Bridge, in A.V. Bridgwater, and G. Grassi (Editors), Biomass pyrolysis liquids upgrading and utilisation, Elsevier, Amsterdam, 1991, pp. 11–92.

[2] A.V. Bridgwater and G.D. Evans, An Assessment of Thermochemical Conversion Systems for Processing Biomass and Refuse, ETSU, Harwell, 1993.

[3] G. Grassi, in A.V. Bridgwater and G. Grassi (Editors), Biomass Pyrolysis Liquids Upgrading and Utilisation, Elsevier, Amsterdam, 1991, pp. 1–10.

[4] J. McKinley, Biomass Liquefaction: Centralised Analysis, Final Report, DSS File No. 232-4-6192, Energy, Mines and Resources Ministry: Ottawa, 1988.

[5] D.C. Elliott, Can. Biomass Liquefaction Res. Group Meet., Report number PNL–SA-10235 (1982) 17.

[6] D.C. Elliott, IEA Co-operative Project D1 Biomass Liquefaction Test Facility Project: Volume 4, Analysis and Upgrading of Biomass Liquefaction Products, Pacific Northwest Lab., Richland, WA, 1988, p. 164.

[7] D.R. Huffman, R.G. Graham and A.V. Bridgwater, Proc. Adv. Thermochem. Biomass Conv., (1994) 1103.

[8] A.V. Bridgwater and G.V.C. Peacocke, Proc. Conf. Bio-oil Product. Util., NREL, (1995).

[9] D.R. Huffman, A.J. Vogiatzis, R.G. Graham and B.A. Freel, 1st Eur. Forum Electric. Prod. Biomass Solid Wastes, (1991).

[10] W.L. van de Kamp and J.P. Smart, Proc. Adv. Thermochem. Biomass Conv., (1994) 1265.

[11] C. Rossi, R. Frandi, O. Bonfitto, S. Jacoboni and L. Pistone, Proc. Adv. Thermochem. Biomass Conv., (1994) 1205.

[12] P. Barbucci, G. Benelli, M. Graziadio, G. Ligasacchi and C. Rossi, 8th CEC Biomass Energy, Ind. Agricult. Environ., (1994).

[13] Y. Solantausta, N.-O. Nylund, M. Westerholm, T. Koljonen and A. Oasmaa, in Proc. Power Prod. Biomass, (1992).

[14] T.A. Milne (Editor), Proc. Symp. Bio-oil Product. Util., NREL, (1995).

[15] D.C. Elliott, A.V. Bridgwater, D. Beckman, J.P. Diebold, B. Gevert and Y. Solantausa, Energy Fuels, 5 (1991) 399.

[16] M.A. Connor and J. Piskorz, Proc. Adv. Thermochem. Biomass Conv., (1994) 1502.

[17] A.V. Bridgwater, Appl. Catal. A, 116(1–2) (1994) 5.

[18] F. Shafizadeh, Proc. 9th Cellulose Conf., (1983) 723.

[19] D.S. Scott, J. Piskorz, D. Radlein and S. Czernik, in G-L. Ferraro, K. Maniatis, A. Buekens and A.V. Bridgwater (Editors), Pyrolysis and Gasification, Elsevier, Amsterdam, 1989, p. 201.

[20] J. Piskorz, D. Radlein and D.S. Scott, Proc. Adv. Thermochem. Biomass Convers., (1994) 1432.

[21] D.S. Scott, J. Piskorz, D. Radlein and S. Czernik, Proc. 7th Can. Bioenergy R&D Sem. Energy Mines Res. Can., (1989) 713.

[22] C.J. Longley, J. Howard and D. Fung, Proc. Adv. Thermochem. Biomass Conv., (1994) 1441.

[23] C.J. Longley, J. Howard and A.E. Morrison, in E. Hogan, J. Robert, G. Grassi and A.V. Bridgwater, Levoglucosan from Pyrolysis Oils: Isolation and Applications, (Biomass Thermal Processing), CPL, 1992, p. 179.

[24] C.J. Longley and D. Fung, Proc. Adv. Thermochem. Biomass Conv., (1994) 1484.

[25] D.S. Scott, J. Piskorz and D. Radlein, Energy Biomass Wastes XVI, (1993) Paper 19.

[26] J. Piskorz, D.S. Scott, D. Radlein and S. Czernik, in E. Hogan, J. Robert, G. Grassi and A.V. Bridgwater (Editors), Biomass Thermal Processing, CPL, 1992, p. 64.

[27] D.St.A.G. Radlein, J. Piskorz, A. Grinshpun and D.S. Scott, Am. Chem. Soc., Div. Fuel Chem., 32(2) (1987) 29.

[28] M. Essig, T. Lowary, G.N. Richards and J. Schenck, Res. Thermochem. Biomass Conv., (1988) 143.

[29] A.E. Pavlath and K.S. Gregorski, Res. Thermochem. Biomass Conv., (1988) 155.

[30] R. Font et al., in G.-L. Ferraro, K. Maniatis, A. Buekens and A.V. Bridgwater (Editors), Pyrolysis and Gasification, Elsevier, Amsterdam, 1989, p. 230.

[31] P.J. Iredale and B.W. Hatt, in R.P. Overend, T.A. Milne and L.K. Mudge, Fundamentals of Thermochemical Biomass Conversion, Elsevier, Amsterdam, 1985, pp. 143–155.

[32] J.K. Maund and D.M. Earp, Res. Thermochem. Biomass Conv., (1988) 542.

[33] J.K. Maund and D.M. Earp, in G-L. Ferraro, K. Maniatis, A. Buekens and A.V. Bridgwater, Pyrolysis and Gasification, Elsevier, Amsterdam, 1989, pp. 238–245.

[34] J.K. Maund and D.M. Earp, Biomass Energy Ind., 5th EC Conf., (1990) 2663.

[35] R.T. Hallen, L.J. Sealock and R. Cuello, in R.P. Overend, T.A. Milne and L.K. Mudge (Editors), Fundamentals of Thermochemical Biomass Conversion, Elsevier, Amsterdam, 1985, pp. 157–166.

[36] J. Arauzo, D. Radlein, J. Piskorz and D.S. Scott, Proc. Adv. Thermochem. Biomass Conv., (1994) 201.

[37] D.S. Scott, D. Radlein, J. Piskorz and S.L. Mason, Biomass Energy Ind., 5th EC Conf., (1990) 2.600.

[38] R.K. Sharma and N.N. Bakshi, Can. J. Chem. Eng. 69 (1991) 1071.

[39] D.C. Elliott, Res. Thermochem. Biomass Conv., (1988) 1170.

[40] B. Delmon, S. Kaliaguine and E. Laurent, Proc. Adv. Thermochem. Biomass Conv., (1994) 1495.

[41] W. Baldauf, U. Balfans and M. Rupp, Proc. 7th Eur. Conf. Biomass Energy Environ., Agricult. Ind., Paper 14.05, in press.

[42] W. Baldauf, U. Balfans and M. Rupp, Final report of EC Contract JOUB-0055, 1993.

[43] D.C. Elliott and E.G. Baker, in D. Klass, Energy from Biomass and Wastes X, IGT, Chicago, 1987, pp. 765–784.

[44] D.C. Elliott and E.G. Baker, Catalytic Hydrotreating of Biomass Liquefaction Products to Produce Hydrocarbon Fuels, PNL Report 5844, Pacific Northwest Laboratory, 1986.

[45] D. Beckman et al., Techno-economic Assessment of Selected Biomass Liquefaction Processes, Technical Research Centre of Finland (VTT) Report 697, VTT, Espoo Finland, 1990.

[46] B. Rejai, R.J. Evans, T.A. Milne, J.P. Diebold and J. Scahill, Energy Biomass Wastes XV, (1992) 855.

[47] R.L. Bain, J.P. Diebold, R.P. Overend and B. Rejai, Energy Biomass Wastes XVI, (1993) Paper 18.

[48] J.P. Diebold, D. Beckman, A.V. Bridgwater, D.C. Elliott and Y. Solantausta, Proc. Adv. Thermochem. Biomass Conv., (1994) 1325.

[49] J. Diebold, D.C. Elliott, A.V. Bridgwater, Y. Solantausta and D. Beckman, Assessment of liquefaction and pyrolysis systems, 230 pp, VTT Research Note 1573, VTT on behalf of the IEA Bioenergy Agreement, VTT, 1994.

[50] A.V. Bridgwater and M.-L. Cottam, Biomass Energy, Ind. Environ., 6th EC Conf., (1992) 679.