Future Biofuels for Australia

Issues and opportunities for conversion of second generation lignocellulosics
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RIRDC Publication No 08/117

June 2008

RIRDC Publication No 08/117
RIRDC Project No PRJ-002829
Second generation biofuels are a rapidly expanding area of research, development and commercialisation. Unlike first generation biofuels that are limited by agronomic characteristics of annual crops and production on arable land, second generation biofuels have the potential to replace a significant proportion of our transport fuel requirements as they can be sourced from a wide selection of plant and woody materials. There are many technologies that can be applied to second generation biofuel production and this is reflected in the broad spectrum of research efforts being undertaken worldwide.

This report provides an outline of the current state-of-the-art conversion of lignocellulosic (the major natural polymer components of plants and wood) materials to second generation biofuels. Rural industries, local, state and federal governments, policy makers, first generation biofuels producers, investment bodies, communities and the general public can all benefit from this information. Concise yet thorough summaries of lignocellulosics to biofuels are difficult to come by and the information presented in this report has been gleaned from a wide variety of sources. It is the aim of this report to provide an overview of the second generation biofuels field in an Australian context and to describe the barriers to wider adoption of these biofuels. It builds on RIRDC reports published in 2007 that covered many aspects of current biofuel production and demonstrated the need for new sources of biomass to satisfy a larger scale of biofuel production.

Lignocellulose is usually pretreated prior to processing to fuels and a range of options are available for this. Two major platforms exist for conversion of lignocellulose to fuel: 1) Enzymatic – where natural polymers of sugars found in cellulose and hemicellulose are broken down into individual units and then processed to fuels by fermentation with organisms such as yeast, and 2) Thermochemical – where lignocellulose is heated to moderate or high temperatures to break down the structure of the polymers to smaller chemical mixtures which are subsequently converted into fuels by catalysts or micro-organisms. The technologies involved in the two platforms are described in the report and the approximate costs for commercial scale plants have been summarised from the literature. The report also summarises the major commercial and research programs in second generation fuels production internationally and in Australia. Finally, the report lists Australian research and development gaps that, once overcome, should assist in bringing the industry forward.

This report was financially supported by RIRDC’s Bioenergy, Biofuels and Energy Program and CSIRO’s Energy Transformed Flagship. It is an addition to RIRDC’s diverse range of over 1800 research publications and forms part of our Bioenergy, Biofuels and Energy R&D program, that aims to meet Australia’s research and development needs for the development of sustainable and profitable bioenergy and bioproducts industries and to develop an energy cross-sectoral R&D plan.

Most of our publications are available for viewing, downloading or purchasing online through our website www.rirdc.gov.au.

Peter O’Brien
Managing Director
Rural Industries Research and Development Corporation
Acknowledgments

The authors would like to thank Dr Deborah O’Connell, Dr Tom Beer, Mr Ross Fellowes, Mr Cameron Begley and Dr Roslyn Prinsley for their valuable input and draft revisions. We would also like to thank the CSIRO Energy Transformed Flagship for funding and support.

Abbreviations

AFEX  Ammonia Fibre Explosion
DME  Dimethyl ether
ETBE  Ethyl-tert-butyl ether
FT  Fischer-Tropsch
GM  Genetic modification (or genetically modified)
LHV  Lower Heating Value
LNG  Liquefied Natural Gas
LPG  Liquid Petroleum Gas
MTOE  Million Tonnes of Oil Equivalents
MTBE  Methyl-tert-butyl ether
MTHF  Methyltetrahydrofuran
RON  Research Octane Number
SSF  Simultaneous Saccharification and Fermentation
 t  tonne
TAME  tert-amylmethyl ether
tpd  tonnes per day
tpy  tonnes per year
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What the report is about
This report describes the production of second generation biofuels that are obtained from lignocellulose (a collective term for lignin, cellulose and hemicellulose – components of plants and wood) with a particular focus on conversion processes. Cellulose and hemicellulose are polymers of sugars and are among the most abundant natural polymers on earth. Therefore, they have the potential to supply a considerable proportion of low cost transport fuels if cost effective conversion processes are available. The processing steps required for the conversion of lignocellulose plant material into fuels and potential fuels, and their techno-economic barriers are described in detail in this report. After harvest, lignocellulose usually undergoes pretreatment, at least size reduction, and up to complete solvolysis, before it is further processed. Two major processing platforms exist:

1) Enzymatic conversion of lignocellulose where enzymes are added to pretreated plant material to depolymerise it to individual sugars which can be fermented to fuels, and

2) Thermochemical, where the lignocellulose is heated to moderate or high temperatures and result in mixtures of chemicals which can be further transformed by catalysts or microorganisms, to fuels. The techno-economic aspects of the conversion technologies at commercial scale are also considered.

Some fundamental issues arising from the use of lignocellulose such as its potential role in greenhouse gas mitigation and sustainable harvesting are raised but not dealt with in detail here. The various transport fuels that can be obtained from these processes are briefly described.

The Australian and considerable international efforts in research, development and commercialisation of second generation biofuels production technologies have been summarised and a listing of the research and development needed to assist the establishment of a second generation industry in Australia is also given.

Who is the report targeted at?
The report is intended to inform government policy makers, rural industries, local, state and federal governments, research funding bodies and researchers, first generation biofuels producers, transport fuel experts, investment bodies, communities and the general public.

Background
This report builds on previous RIRDC studies in the area of biofuels, bioproducts and bioenergy (O’Connell et al. 2007a, Batten and O’Connell 2007, Haritos 2007, O’Connell et al. 2007b) but specifically investigates the conversion of second generation lignocellulosic materials to produce known or future transport fuels.

Second generation biofuels utilise non-food plant materials, such as sugar cane bagasse, native grasses, native perennials, forestry waste, farm forestry, wheat straw, newsprint and cotton trash, which could be specifically harvested or diverted from entering landfill, and converted into alternative fuels such as alcohols, ethers, synthetic diesel, hydrogen or biogas. It is possible to convert a wide range of lignocellulosic materials into biofuels and there is increasing global effort being devoted to achieving this end in an economically viable fashion.

Aims/objectives
The advantages of having a lignocellulosic biofuels industry are that the source materials are relatively cheap, domestically available, may not divert resources from food markets, and they can be used to add value to existing rural industry processes. Additionally, they provide unique opportunities for new agricultural industries to be developed, particularly in less productive agricultural lands where woody shrubs and perennial grasses can grow with few inputs and may compete less for land and water needed for food crops. However, there are many questions remaining and technological hurdles to overcome before conversion of lignocellulose conversion to transport biofuels can be conducted cost effectively and sustainably as was highlighted in O’Connell et al. (2007a).

This report aims to inform the development of a second generation biofuels industry in Australia. Information from a wide variety of sources has been summarised and consolidated to give a broad, current overview of what second generation biofuels are, the feedstocks from which they may be produced and the conversion processes employed to do so. References are provided in each section to direct the reader to more detailed information relating to a particular subject. An objective of the report is to stimulate policy makers and industry to examine more closely the opportunities in second generation biofuels that are unique to Australia. It is also an objective of the report to give prominence to second generation biofuels for Australians.
Conversion processes can be divided into two broad categories – thermochemical and enzymatic, although different combinations of the two technologies can be used to produce particular fuels. Most conversion processes involve some manner of pretreatment step which facilitates the actual chemical conversion to a biofuel. Most processes are also feedstock-dependent, meaning they need to be modified to provide a consistent conversion rate if the feedstock changes. Most processes claim to be competitive with oil at around US$40 - 60 per barrel.

There are several different types of liquid and gaseous fuels that can be produced from lignocellulosic sources, each with advantages and disadvantages relating to certain characteristics including their utility, cost/ease of production, public image, energy content, compatibility with existing processes and infrastructure, and yield per tonne of feedstock. There are significant efforts in the USA and Europe towards the development and commercialisation of second generation biofuels industries. There is considerable support being provided by the US Department of Energy in the USA. In general, Europe is more focussed upon thermochemical conversion methods, whereas the USA has focussed more upon enzymatic conversion processes. There is no clear “best practice” or “best fuel” at this point in time, although most effort is currently being put towards the production of ethanol. Globally, there is a growing need for cost effective, plentiful and low CO₂ emission transport fuels industry and second generation biofuels could supply a portion of the global need.

Implications for stakeholders:
The implications for industry are encouraging. Internationally, there is significant funding being provided for fundamental and developmental research into second generation biofuels and also pilot and commercial scale plant development. There are many unexplored areas where innovative thinking could provide breakthrough conversion technologies to lower the cost of lignocellulose conversion. Australia has a technologically-driven, modern agricultural sector that could benefit from development of new regional industries based around non-food biofuel crops.

Communities, particularly rural ones, have an opportunity to explore the options for growing energy crops on underutilised land. Community benefits could also be gained from the creation of jobs from new industries.

Policy makers could use the information provided in this report to make informed decisions on biofuels policies to provide the highest benefit to Australia’s communities and industries in the immediate and long-term future.

It is recommended that this report be used as an introduction to the technologies used to convert lignocellulose to transport fuels and the techno-economic barriers around each. The report is also a source of information on commercial activities and research groups working within the second generation biofuels area.

A number of research and development gaps have been identified where Australia could benefit from increased effort. The areas are (broadly):

- Biomass availability and potential new crops – a full assessment of available volumes and sustainable production rates, along with environmental and societal impacts
- Improvement in biomass crops – an assessment of what can realistically be achieved through genetic modification of crops for enhanced production of lignocellulose and use of less productive land, and the benefits/risks and regulatory requirements of such an undertaking
- Pretreatment and processing technologies – the development of efficient, cost effective, low energy conversion processes tailored to Australian biomass and conditions
- New transport fuels – assessments of the feasibility of adoption of new transport fuel(s) produced from lignocelluloses with a focus on Australian infrastructure and conditions
- Life cycle assessment/ techno-economic modelling – the development of models to predict fuel costs, greenhouse gas emissions and the impact of lignocellulosic biofuels production on local economies
- Integrated biorefineries – identify product streams that can be developed in parallel to add value to second generation biofuels production systems.
1. Introduction

There are two major issues regarding transport fuels facing most countries in the world, including Australia, and they are the price (and remaining reserves) of crude oil that provide most transport fuels, and the significant contribution to total greenhouse emissions and climate change from the transport sector. Petrochemical fuels are a finite resource and are subject to broad pricing swings that are highly unpredictable and have a significant impact on the economy with oil reaching US$130 per barrel in May, 2008.

The greenhouse gas (GHG) mitigation provided by a biofuels industry in Australia could have significant beneficial social and economic impacts. The transport sector is not the major contributor to total greenhouse gas emissions in Australia (Figure 1), however carbon dioxide emissions from transport are increasing and have risen 30% since 1990 (Australian Greenhouse Office 2007).

With the rapidly increasing worldwide demand for fuel and energy, it has been universally recognised that alternative, sustainable sources of transport fuels will be needed to ensure the security and longevity of supply. There has been recent activity around the development of the Australian biofuels industry to partially offset our reliance upon the petrochemical sources and reduce our carbon dioxide emissions. Although in their industrial infancy, these biobased solutions have had some modest early successes and have been drawn from renewable first generation sources such as molasses and wheat starch, tallow, waste cooking oil and palm oil. Rising prices for agricultural commodities such as grains and oilseeds have had a major impact on the cost of bioethanol and biodiesel production. Internationally there has been increasing discussion around the potential impact of biofuels on food prices and their availability (O’Connell et al. 2007a), and their role in greenhouse gas mitigation (Energy Information Administration 2007, Australian Greenhouse Office 2007, Department of Climate Change 2007).

O’Connell et al. (2007a, 2007b) examined the capacity of first generation feedstocks to supply biofuels for Australian domestic transport requirements. In a scenario where all the Australian domestic crop of sugar, molasses, wheat and coarse grains was converted into ethanol using first generation technologies, and all biodiesel inputs were used to make biodiesel we would still not replace all of Australia’s transport fuel requirements by a long margin for diesel. A mandate of 10% ethanol in all Australian petroleum sourced from first generation feedstocks would probably lead to a requirement to import grain in drought years. From the modelling conducted, O’Connell et al. (2007a, 2007b) concluded that biofuels based on first generation feedstocks, while performing a very necessary first step on the transition pathway to renewable fuels, will supply less than 10% of Australia’s transport needs.

A potential solution to the high first generation feedstock price and limited supply is the development of second generation biofuels that utilise non-food plant materials, such as sugar cane bagasse, native grasses, native perennials, forestry waste, farm forestry, wheat straw, newsprint and cotton trash, which could be specifically harvested or diverted from entering landfill. The major component of these materials is lignocellulose - a complex store of the most widely available biological polymers on earth: cellulose, hemicellulose and lignin which can be converted into alternative fuels such as alcohols, ethers, synthetic diesel, hydrogen or biogas. It is possible to convert a wide range of lignocellulosic materials into biofuels and there is increasing global effort being devoted to achieving this end in an economically viable fashion.

The primary advantage of having a lignocellulosic biofuels industry are that the source materials are relatively cheap, domestically available, may not divert resources from food
markets, and they can be used to add value to existing rural industry processes. Additionally, they provide unique opportunities for new agricultural industries to be developed, particularly in less productive agricultural lands where woody shrubs and perennial grasses can grow with few inputs and may compete less for land and water needed for food crops. According to Geoscience Australia (2005), Australia has 498,974 km$^2$ of arable land (6.55% of total land area) and is well-suited to the production of large quantities of lignocellulosic biomass, especially from drought tolerant plants. However, there are many questions remaining and technological hurdles to overcome before conversion of lignocellulose conversion to transport biofuels can be conducted cost effectively and sustainably.
2. Scope

This report builds on previous RIRDC studies in the area of biofuels, bioproducts and bioenergy (O’Connell et al. 2007a, Batten and O’Connell 2007, Haritos 2007, O’Connell et al. 2007b) but specifically investigates the conversion of second generation lignocellulosic materials to existing or future transport fuels. In addition, the report summarises the current worldwide position in lignocellulose-to-biofuel conversion and highlights the potential technical and economic barriers to market entry.

The major pathways and the steps involved in the conversion of biomass to transport fuels are summarised in Figure 2. In the first step, sufficient sustainably harvested lignocellulosic biomass is transported to the plant for processing. These aspects are not covered in any depth in this report other than to raise the deficiencies in our knowledge regarding biomass sources in Australia (Chapter 3.1) and to describe some recent international information on agronomic inputs for dedicated biomass crops, total energy yields and greenhouse gas emissions (Chapter 3.2 - 3) and the biofuel versus biorefinery debate.

The main body of the report includes the components and structure of lignocellulose which are described in Chapter 5. Lignocellulosics generally undergo size reduction and other pretreatment prior to processing and the major technologies in use or at an advanced research stage are discussed in Chapter 6. Pretreatments are usually specific for a particular process – the two main process methods are thermochemical and enzymatic which are covered in detail in Chapter 7. New developments in lignocellulosic conversion are covered briefly in Chapter 8, and techno-economic comparisons of the different pretreatment and conversion technologies are described in Chapter 9. There are a range of fuels produced from lignocellulose and these are explained earlier in Chapter 4 to aid in the understanding of the outcome of different processes in later chapters.

We have reviewed the status of research, development and commercialisation of lignocellulose-derived biofuels both internationally and in Australia (Chapter 10.1-10.2) and then summarised research and development gaps for Australia (Chapter 11).
3. Issues in biofuels production from lignocellulose

3.1 Sufficient feedstocks supply

An overarching issue in second generation biofuels is the availability of sufficient centrally-located biomass to maintain a viable, sustainable biofuels industry. Audits of available biomass by type, location and yield, and modelling of production, harvesting and delivery of biomass have been conducted in some countries to gain better understanding of feedstock costs and likely volumes.

In the USA, biomass stocks available for use in first and second generation biofuels production to meet targets of 30% or more of current petroleum use in that country by 2030 have been assessed in the ‘Billion ton study’ (Perlack et al. 2005). Two main sources were identified that could satisfy the 1 billion dry ton biomass needed to fulfil the biofuel quota: agriculture and forestry, and this is apparently could be achieved without affecting food, feed and export demands. However, there were some important assumptions embedded in the assessment such as the expectation that corn and grains production would increase by 50% over the time period to 2030, all crop land would be managed by no-till methods, and 55 million acres of cropland would be dedicated to biofuels production but that environmentally sensitive areas would be excluded. Further analysis with a greater number of scenarios is planned for the US situation (Graham 2007).

There is some information available for Australia but it has not been specifically collected for assessing the material available for a second generation biofuel industry. In recognition of this need, a comprehensive audit is being conducted by CSIRO of available Australian biomass, sustainability of its harvest and the potential benefits and impacts of new biomass sources (Chapter 10.2).

3.2 Agronomic inputs and land use changes

It has been generally considered that agricultural inputs such as fertilizer, energy for farm machinery, pesticides and water required to produce first generation biofuel crops are higher than those required for second generation biofuel feedstocks. Until recently there has been little data to support this opinion but specific studies for dedicated biofuel crops are now emerging.

- Low-input high diversity mixtures of grassland perennials for production of biofuels could have many positives in comparison to corn or soybean. Tilman et al. (2006) found mixed grasslands produced 238% more bioenergy from cellulosics than mono-cultured crops (e.g. corn) after 10 years and required less inputs. Tilman et al. (2006) concluded that these mixed grasslands can be grown productively on degraded lands and therefore would not require further land clearing nor compete with viable farming land to make a substantial impact. Extrapolating
to the global position, they estimate that 5 x 10^8 ha of degraded land could produce 90 GJ ha\(^{-1}\) per annum, satisfying 13% of global petroleum requirements, 19% of electricity consumption and eliminate 15% of global CO\(_2\) emissions.

- The inputs required to produce switchgrass crops have been reported by Schmer et al. (2008). All inputs such as fertilizer, diesel fuel, herbicides and seed were documented by farmers taking part in the five year trial and found to be lower than previously thought. Switchgrass averaged 5.2 - 11.1 dry t ha\(^{-1}\) under the conditions. Energy gained from the ethanol produced exceeded the non-renewable energy inputs to switchgrass production and conversion by 540%.

Invasive biofuel crops and renewed land clearing for the planting of dedicated biofuel crops are two further impacts that could result from a rapid expansion of second generation biofuels.

- Several groups (e.g. Raghu et al. 2006) have warned that the attributes selected in a biomass crop such as fast growth, low herbicide requirement, few pests and diseases, are shared with many invasive species.

- Searchinger et al. (2008) used a global agricultural model to quantify the effects of land use changes and found that new land clearing causes the greenhouse gas emissions to increase by 50% for switchgrass ethanol. In a similar vein, Fargione et al. (2008) have concluded that first generation biofuels produced through the conversion of rainforest, peatlands, savannahs and grasslands result in CO\(_2\) releases to the atmosphere in the range of 17 – 420 times the reductions achieved by using biofuels.

### 3.3 Total energy of biofuel production and greenhouse gas emissions

Life cycle assessments conducted for biofuels have considered their source, production and use. However, contradictory findings from the studies have caused controversy and confusion and attracted a lot of publicity. Some studies have shown biofuel production requires low levels of fossil energy and results in positive effects on greenhouse gas emissions, and a smaller number of studies have found that production of biofuels requires more energy than is yielded by the fuel and that their production has negative effects in terms of greenhouse gases.

These life cycle studies have been primarily conducted on first generation biofuels, mainly corn. The apparently contradictory outcomes stem from:

- The use of different system boundaries and assumptions in the assessments
- Use of different measures such as total energy (including solar energy) versus total fossil energy
- In some cases the inclusion of outdated agricultural inputs data

- Ignoring the co-firing of lignin as a major source of energy for lignocellulose conversion and allocating low value to corn by-products.
- Making assumptions that all fossil fuel inputs are the same based on energy content only (as discussed in Wang (2005), Farrell et al. (2006), Dale (2007))

A summary of the outcomes of the major life cycle studies conducted on lignocellulosic biofuels and some of the boundary aspects, assumptions and conclusions are given in Table 1 and compared with a review of first generation energy production and greenhouse gas emissions. The importance of key assumptions such as heat and electrical energy source and credit for byproducts (for first generation biofuels) are evident in the study outcomes. However, as shown in several studies to date, substantial reduction in greenhouse gas emissions and petrol use can be achieved with fuels produced from lignocelluloses.

### 3.4 Biofuels versus biorefineries

In an analogy of a petroleum refinery, a lignocellulose biorefinery could produce a large volume of low cost biofuel but support the overall process through additional production of bioenergy and higher-value bioproducts. The biorefinery concept is argued to be even more important for lignocellulosic sources than petroleum because of the likely scale of the lignocellulosic plants (Wright and Brown 2007a and 2007b). There will be limitations to the distance that low density biomass can be economically transported to a processing plant, therefore, valuable co-products could support biofuels production on a relatively small scale.

In current biofuel production, all remaining solids including cell mass, lignin, unchanged celluloses leftover from an enzymatic process are first dried to ~14 % moisture content then fired to produce electricity either \(via\) a boiler (small scale) or gasifier (larger scales). Lignocellulosic materials contain mainly cellulose, hemicellulose and lignin but also small amounts of protein, inorganic compounds, oils and extractives (plant secondary chemicals). Fermentation conversion technologies can also produce large amounts of yeast lees that could be further fermented to biogas and fertilizer. Char, fuel oils, chemical intermediates such as furfural and bioenergy are potential byproducts of the thermochemical conversion of lignocellulose. Carbohydrates not directed to biofuels production could be taken into a production stream making alcohols, carboxylic acids and esters as intermediates for the chemical industry (Ragauskas et al. 2006). Similarly, sugars from biomass can be used for fermentation to monomers for biobased plastics such as polyactic acid (Natureworks LLC.) or polyhydroxyalkanoates (PHAs).

Despite the potential of biorefineries to deliver valuable products that could assist in the viability of biofuels, there are only a few lignocellulosic fuel companies that are actively pursuing the refinery model at this stage.
### Table 1. Comparison of key assumptions, parameter boundaries used in life cycle assessments of selected biofuels

<table>
<thead>
<tr>
<th>Study</th>
<th>Fuel(s)</th>
<th>Conversion method</th>
<th>Model Boundary</th>
<th>Key assumptions</th>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn Farrell et al. (2006)</td>
<td>Ethanol</td>
<td>Fermentation</td>
<td>Reviewed 6 published studies and reanalysed</td>
<td>Applied consistent boundary to 6 studies, added co-product credit, accounted for different energy types.</td>
<td>Net energy calculations sensitive to assumptions about co-product (e.g. protein, oil) utilisation. Best estimate is ethanol replaces petroleum use by 95%, reduces GHG moderately ~13%.</td>
</tr>
<tr>
<td>Corn stover Sheehan et al. 2004</td>
<td>Ethanol</td>
<td>Fermentation</td>
<td>Production of stover including soil carbon dynamics, soil erosion, agronomics of stover, transport, conversion, Iowa USA growing conditions</td>
<td>All farming by no-till Continuous corn farming Extended farming into future based on current technology</td>
<td>8 billion L ethanol per annum, price competitive with starch-derived ethanol. Soil organic carbon drops slightly but remains stable for 90 years. 95% drop in petroleum use for E85 blend. E85 102% lower fossil energy use than petrol vehicle. E85 113% lower GHG.</td>
</tr>
<tr>
<td>Corn, switchgrass, wood Pimentel and Patzek (2005) (see also Patzek (2004))</td>
<td>Ethanol</td>
<td>Fermentation</td>
<td>Wider than other studies e.g. includes fossil energy requirements of farm workers, Corn data from 50 USA states</td>
<td>All energy for ethanol production supplied by fossil fuels No energy requirement for ethanol distribution included No benefit from co-products in primary analysis</td>
<td>Total energy output of ethanol from all biomass sources investigated was lower than the fossil fuel inputs for production. Corn ethanol required 29 %, grass ethanol 50 % and wood ethanol 57 % more fossil energy than the energy that ethanol produced. Primary energy input cost is corn, steam and electricity to effect the conversion of biomass to ethanol. Steam is the major input.</td>
</tr>
<tr>
<td>Switchgrass Wu et al. (2006)</td>
<td>Ethanol, Syndiesel (FTD), dimethyl ether (DME), electricity</td>
<td>Fermentation, Thermochemical / Fischer Tropsch</td>
<td>Biomass farming, transportation, fuel production, transport, distribution, storage, use</td>
<td>2015-2030 timeline Integrated heat &amp; power cogeneration Protein credit for ethanol Exported electricity in thermochemical</td>
<td>Reduce petroleum use (66 - 93 %) on per distance basis in E85 ethanol petrol blends or pure. 82 – 87 % reduction in greenhouse gas emissions compared with unblended fuel. Reductions in most atmospheric pollutants</td>
</tr>
</tbody>
</table>
4. Biofuels obtained from lignocellulosics

Lignocellulosic conversion processes deliver a range of fuels that can be burned in spark or compression ignition, combustion engines. Fuels like ethanol are currently listed under the Fuel Quality Standards Act (2000) for engine fuels (as an E10 blend) but alternative fuels arising from thermochemical and biological conversion processes will be new to the Act. Some properties of the different fuels are introduced below.

Table 2. Properties of selected transport fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Density (g cm(^{-3}))</th>
<th>Btu per US gal (LHV)(^{\dagger})</th>
<th>kJ per L (LHV)(^{\dagger})</th>
<th>RON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrol</td>
<td>0.745</td>
<td>116,090</td>
<td>32,360</td>
<td>90-95</td>
</tr>
<tr>
<td>No. 2 Diesel</td>
<td>0.83</td>
<td>128,450</td>
<td>35,806</td>
<td>n/a</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>0.88</td>
<td>119,550</td>
<td>33,325</td>
<td>n/a</td>
</tr>
<tr>
<td>Liquified natural gas</td>
<td>0.525</td>
<td>74,720</td>
<td>20,828</td>
<td>112</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.791</td>
<td>57,250</td>
<td>15,958</td>
<td>110</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.791</td>
<td>76,330</td>
<td>21,277</td>
<td>130</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.8098</td>
<td>105,000</td>
<td>29,269</td>
<td>96</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0708</td>
<td>30,100</td>
<td>8,390</td>
<td>106</td>
</tr>
<tr>
<td>DME (Dimethyl ether)</td>
<td>0.665</td>
<td>70,980</td>
<td>19,786</td>
<td>n/a</td>
</tr>
<tr>
<td>MTBE (Methyl tert-buty1 ether)</td>
<td>0.746</td>
<td>93,500</td>
<td>26,063</td>
<td>118</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Density (g cm(^{-3}))</th>
<th>Btu per US gal (LHV)(^{\dagger})</th>
<th>kJ per L (LHV)(^{\dagger})</th>
<th>RON</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAME (tart-amyl methyl ether)</td>
<td>0.77</td>
<td>100,600</td>
<td>28,042</td>
<td>109</td>
</tr>
<tr>
<td>ETBE (Ethyl tert-butyl ether)</td>
<td>0.745</td>
<td>96,900</td>
<td>27,011</td>
<td>118</td>
</tr>
<tr>
<td>Synefu1 (synthetic petrol)</td>
<td>0.75</td>
<td>126,608</td>
<td>35,292</td>
<td>n/a</td>
</tr>
</tbody>
</table>


* RON Research Octane Number is a measure of the resistance of a fuel to auto-ignition and affects the anti-knock properties of a fuel.

# LHV Lower heating value

4.1 Ethanol

Ethanol is a linear alcohol of molecular formula C\(_2\)H\(_5\)OH and a liquid at room temperature. It performs as an oxygenate in petrol blends and reduces the effects of photochemical smog. Its energy content is about two-thirds that of petrol (Table 2). However, ethanol has a higher research octane number (RON) than petrol (130 versus 91) meaning it increases the RON of fuel when added in a blend.
60% of the Australian fleet can operate without alteration on E10 (10% ethanol in petrol) blends but require modification to become a “flex-fuel” vehicle to operate on fuel with greater than 10% ethanol (such as E85). A disadvantage of ethanol is its hygroscopic nature which causes it to draw moisture into petrol/ethanol blends, potentially leading to higher corrosion rates.

There has been some recent debate (Jacobson 2007) as to whether E85 actually reduces the levels of airborne carcinogens and other chemicals emitted, with benzene and 1,3-butadiene being reduced but methane, formaldehyde and acetaldehyde all being increased compared to petrol.

4.2 Butanol

Butanol is a higher chain alcohol having the molecular formula C₄H₉OH and exists in three forms - n-butanol (linear), iso-butanol and tert-butanol. The first two forms are liquid at room temperatures but tert-butanol melts at ~25°C. Butanol has a higher energy density than ethanol (but lower RON) and evaporates more slowly (Table 2). According to information distributed by BP, butanol has the added advantage of being less prone to separation from petrol in the presence of water than ethanol, and can improve the blending of ethanol with petrol, being compatible with both fuels. Butanol is miscible with petrol in all proportions and can be blended to 85% with minor or no modification required to a spark ignition engine. Existing petroleum infrastructure such as pipelines, blending facilities, tanks and retail station pumps can be used to transport and process butanol.

Production of butanol from biological sources is very limited at this stage, and it is currently obtained from petroleum sources, although enzymatic routes exist (see Chapter 7.3.6). Butanol is more toxic to the production organisms than ethanol and is hence more expensive to produce, however considerable effort is being made to overcome these technical hurdles.

4.3 Methanol

Methanol is the shortest chain alcohol. It has the molecular formula CH₃OH and is a liquid at room temperature. Methanol has been used widely as a fuel in the past and is one of 10 fuels planned to satisfy European requirements in the future (Directive 2003/30/EC of the European Parliament and of the Council 2003). The energy density of methanol is around half that of petrol and can improve the blending of ethanol with petrol. Like butanol, ethers are apparently highly compatible with the petrol distribution system.

Oxidations were first introduced into petrol in the USA in the 1970s to increase the octane rating of petrol due to the phasing out of tetraethyl lead addition to petrol was being phased out and to assist in the reduction of photochemical smog. Unfortunately, MTBE does not easily biodegrade, is water soluble and became increasingly detectable in ground waters due to spills or leaking tanks. MTBE has a repugnant smell that is detectable at low levels. This caused a policy revision in the United States and by late 2005 most states had banned MTBE use. Currently MTBE is completely petrochemically derived and ETBE is partially petrochemically derived.

4.5 Cyclic ethers

Methyltetrahydrofuran (MTHF) is a major product of the Bioline process which converts lignocellulosic biomass using a dilute acid catalysed thermochemical process (Chapter 7.1). MTHF is used as a component of a P-series fuel (a mixture of natural gas ‘pentanes plus’ liquids, ethanol and MTHF – see table 3) designed to be used in flexible fuel vehicles at a RON of around 94 - 98. A P-series fuel has around 10% less energy content than petrol and has lower emissions of most of the problem pollutants from exhaust (Office of Energy Efficiency and Renewable Energy 1999). The mixture can be used alone or mixed in any proportion with petrol. P-series fuels are not being made in substantial quantities at this stage but interest may be renewed with ready supplies of MTHF produced from lignocellulosic sources.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Regular</th>
<th>Volume %</th>
<th>Cold weather</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentanes plus</td>
<td>32.5</td>
<td>27.5</td>
<td>16.0</td>
</tr>
<tr>
<td>MTHF</td>
<td>32.5</td>
<td>17.5</td>
<td>26.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>35.0</td>
<td>55.0</td>
<td>47.0</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.0</td>
<td>0.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>
4.6 Synthetic diesel/Synfuel

Synthetic diesel is equivalent to diesel fuel obtained from crude oil except that it is prepared through thermochemical routes from biomass, coal or gas and proceeds *via* an initial gasification step, followed by Fischer-Tropsch conversion to diesel hydrocarbons. The resulting diesel can be modified, blended and fractionated to meet fuel standards. The product has very low sulfur content which reduces the toxic sulfated particulate matter in engine exhausts which has been an issue with high sulfur diesel.

4.7 Biogas

Biogas is the product of microbial decomposition of organic material in the absence of oxygen (anaerobic process) and is predominately methane (50 – 80 %), CO₂ (20 – 50 %) and small amounts of other gases. Although it is mostly used for bioenergy, biogas can be upgraded to a transport fuel by removing the CO₂ then compressing or liquefying. Once upgraded, biogas has very similar properties to compressed and liquefied natural gas (LNG). LNG has an energy density lower than petrol but with a higher RON (Table 2). The fuel is suitable for use in medium to heavy-duty trucks and buses and is very clean burning.

4.8 Hydrogen

Hydrogen is a gas at room temperature with a high energy density. Although commercial vehicles are not yet available that can use hydrogen and there is limited availability of the fuel the technology is developing and there are demonstration vehicles using hydrogen. One large advantage of hydrogen is the lack of pollutants in tailpipe emissions; the downside is that most of the predictions suggest a 10 to 20 year timeframe for the adoption of hydrogen as a transport fuel.

Hydrogen is not currently widely accepted as a transport fuel due to difficulties with storage and the explosion hazard associated with pressurized flammable gases, although similar hazards are associated with onboard LPG tanks in modern converted cars. In 2005, the US Department of Energy announced a price goal for biohydrogen (independent of the source) of US$2 – 3 per kg (from the current US$8 per kg) by the year 2015 (1 kg hydrogen provides approximately the same amount of energy as 1 gallon (3.79 litres) of petrol).
5. Lignocellulosic feedstocks

5.1 Structure and Properties

Lignocellulose is a complex polymeric material composed of cellulose (40-60%), hemicellulose (20-40%) and lignin (10-25%) (see Table 4 for some common examples). A schematic representation of lignocellulose is shown in Figure 3. Lignin is a biopolymer comprised of phenolic units that give structural integrity to the cell walls of plants. This material is intertwined and covalently bound with hemicellulose (a polymer of 5- and 6-carbon sugars) to form a protective sheath around the cellulose (a polymer of 6 carbon sugars) bundles.

The lignin and hemicellulose structures have evolved over many millions of years to protect plants against attack by microorganisms and insects. Only a few organisms, such as white rot fungus, have the ability to degrade lignin, and these act quite slowly due mainly to the intractable nature of the material. Plants vary in their content of cellulose, hemicellulose and lignin although in general woody material has more lignin.

5.2 Polysaccharide components of lignocellulose

Cellulose is the major polysaccharide of higher plant cell walls and provides much of the strength of wood. It is a linear polymer of glucose units joined via β-1,4-glycoside bonds and arranged in disaccharide units known as cellobiose (Figure 4). A typical cellulose polymer is composed of roughly 10,000 sugars built into long, rigid and insoluble microfibrils. Both the β-1,4-bonds and the crystalline formation of cellulose lead to its resistance to degradation.

Starch, from which wheat and corn ethanol is currently produced, is a branched polymer consisting of sugar chains containing α-1,6-glycosidic linkages that branch to other similar chains through α-1,4-glycosidic linkages. These branches ensure that the structure of starch is highly amorphous and the linkages are easily accessible to fermentation enzymes. Cellulose, on the other hand, is a linear, regular and well-ordered polymer (see Figure 3) that packs tightly to form crystalline structures through a very large number of highly complementary hydrogen bonds which makes it highly resistant to thermal and chemical degradation versus starch which is relatively easy to breakdown.

Hemicellulose is a heterogeneous polymer of saccharides including five-carbon sugars (pentoses: xylose and arabinose), 6-carbon sugars (hexoses: mannose, glucose and galactose) as well as some sugar acids. The main 5-carbon sugar in hemicellulose is known as D-xylose, making it the second most-abundant sugar in the world after glucose. Hemicellulose polymers are found in plant cell walls closely associated with cellulose microfibrils and covalently bound to lignin.

Table 4. Ranges of cellulose, hemicellulose and lignin content in common agricultural lignocellulosic products, wastes and residues (Sun and Cheng 2002)

<table>
<thead>
<tr>
<th>Lignocellulosic materials</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood stems</td>
<td>40-55</td>
<td>24-40</td>
<td>18-25</td>
</tr>
<tr>
<td>Softwood stems</td>
<td>45-50</td>
<td>25-35</td>
<td>25-35</td>
</tr>
<tr>
<td>Nut shells</td>
<td>25-30</td>
<td>25-30</td>
<td>30-40</td>
</tr>
<tr>
<td>Corn cobs</td>
<td>45</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>Grasses</td>
<td>25-45</td>
<td>31-50</td>
<td>10-30</td>
</tr>
<tr>
<td>Office paper</td>
<td>85-99</td>
<td>0</td>
<td>0-15</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>30</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>Leaves</td>
<td>15-20</td>
<td>80-85</td>
<td>0</td>
</tr>
<tr>
<td>Cotton seed hairs</td>
<td>80-95</td>
<td>5-20</td>
<td>0</td>
</tr>
<tr>
<td>Newspaper</td>
<td>40-55</td>
<td>25-40</td>
<td>18-30</td>
</tr>
<tr>
<td>Waste paper from chemical pulps</td>
<td>60-70</td>
<td>10-20</td>
<td>5-10</td>
</tr>
</tbody>
</table>
5.3 Lignin

Lignin is an amorphous, 3-dimensional polymer of phenolic substances which are bound through ether linkages. After cellulose, lignin is the most abundant organic polymer on Earth and stores approximately 30% of the total non-fossilised carbon (Boerjan et al. 2003). A possible lignin fragment is shown in Figure 5 and is made up of phenyl propanoid units in four forms – guaiacyl, p-coumaryl, coniferyl and sinapyl alcohols. Its role in plants is to bind the fibrous cellulose component of lignocellulose and to shield the cellulose from attack by micro-organisms. Hardwoods and softwoods differ in that the latter have lignin composed of guaiacyl units which is rich in coniferyl units whereas hardwoods are rich in coniferyl-sinapyl units where sinapyl dominates.

Lignin can be degraded by selected fungi that employ laccases (polyphenol oxidases), lignin peroxidases and manganese-dependent peroxidases to oxidise the polymer and ultimately mineralise the products. There has been intense research interest around these lignin oxidising enzymes in the past decade, with many new genes identified from (mostly) fungal sources. The intractability and complexity of the lignin substrate and uncertainty as to environmental influences surrounding lignin peroxidase’s mode of action are significant barriers to our full understanding of its mechanisms.

Although it hinders access to the cellulose fibres, lignin itself has the potential to yield interesting and valuable products such as alkyl benzenes which can be utilised in a similar manner to those obtained from petroleum sources.

The fuel applications of lignin have so far been largely limited to direct combustion for heat, or pyrolysis to produce syngas which can then be reformed to make alcohols, methane and hydrocarbons. Currently, nearly all lignin left over from various processes is either discarded or combusted (co-fired) for electricity generation, however some first steps in research have been made towards finding methods for extracting valuable chemicals from lignin (Dumsday et al. 2005, Okuda et al. 2004).
All lignocellulosic biomass undergoes some pretreatment prior to processing into biofuels.

The treatment can be straightforward, for example size reduction, chipping and drying which are usually required for thermochemical processing methods.

The enzymatic conversion process generally requires more extensive pretreatment and ideally one that yields well-exposed and reactive cellulose fibre, returns a high yield of hemicellulose-derived sugars, produces few inhibitors of downstream processes, minimises energy, chemicals, and size and cost of reactor and materials, and produces lignin as a byproduct for either power and steam generation or as a value-added biomaterial (Jørgenson et al. 2007).

The breadth and depth of pretreatment and separation methods for lignocellulosic materials in the patent, scientific and government publications is vast.

We have focussed on the most promising industrially-applicable methods as they relate to the most abundant Australian lignocellulosic feedstocks, and some new developments. Although the pretreatments are addressed separately, below, it should be noted that various combinations of nearly all the following types of pretreatments are used in research and practice to achieve the best yields of fermentable sugars depending on the feedstock.

6.1 Mechanical comminution: milling, chipping and grinding

Comminution is the mechanical means used to reduce the particle size (hence increase the surface area) of biomass prior to further treatment and many different types of equipment and machinery have been developed to achieve this. Certain particle sizes are better for certain biomass types and further treatments, and generally, the smaller the desired particle size, the more energy, time and cost, are required (see Table 5). This must be balanced by the cost advantages of having smaller particles sizes in the downstream processes. Milling or grinding usually results in particle sizes of 0.2 – 2 mm diameter and chipping usually gives particle sizes of 10 – 30 mm diameter.

6.2 Dilute Acid Hydrolysis

Acid hydrolysis conducted using either concentrated or dilute, batch or continuous, with hydrochloric, nitric or sulfuric acids at elevated temperature has been well explored as pretreatment methods for lignocellulosic materials. The economics of several systems have been evaluated with a view to the production of fuel ethanol (Sivers and Zacchi 1995). Several well-developed pilot-sale processes have been established for the production of ethanol from a variety of biomass feedstocks using acid hydrolysis as the pretreatment step.
During acid treatment, hemicellulose and even cellulose at higher acid and temperature conditions are hydrolysed to individual sugars. Dilute acid treatment is conducted using 0.5 - 1.5 % v/v and >160°C which dissolves the hemicellulose and liberates 75 - 90 % of xylose as free sugar. The treatment is effective in allowing access to cellulose of the saccharification enzymes and does not degrade the lignin which can be recovered and burnt to provide energy for the process.

The primary disadvantages of acid hydrolysis are that the reaction vessels need to be acid resistant and large quantities of gypsum are used at the end of the pretreatment prior to fermentation of the soluble sugars to neutralise the solution. Alternatively, ion-exchange is used to recover the acid from the reactor and recycle it for use. During hydrolysis under acidic and high temperature conditions, hemicelluloses can be converted to products such as furfural and hydroxymethylfurfural that are inhibitory to fermentation organisms (at concentrations >1 mg ml⁻¹) used in converting the sugars to ethanol. In general, the more severe the acid treatment at high temperatures, the greater the conversion to inhibitory substances.

### Table 5. Energy required for different types of mechanical comminution for selected agricultural residues (Cadoche and Lopez 1989)

<table>
<thead>
<tr>
<th>Lignocellulosic material</th>
<th>Final size (mm)</th>
<th>Energy consumption (kWh/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Knife mill</td>
<td>Hammer mill</td>
</tr>
<tr>
<td>Hardwood</td>
<td>1.6</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>2.54</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>6.35</td>
<td>25</td>
</tr>
<tr>
<td>Straw</td>
<td>1.6</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>2.54</td>
<td>6.4</td>
</tr>
<tr>
<td>Corn stover</td>
<td>1.6</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>6.35</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>9.5</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Combination of steam explosion with acid catalysis has also been investigated and allows for the recovery of 70 % of xylose sugar. Catalysed steam explosion is used at Iogen's Canadian pilot plant on wheat straw and at Abengoa in Spain and is considered a technology close to implementation at commercial scale.

### 6.4 Steam Explosion

Steam explosion, also known as autohydrolysis, is an increasingly popular pretreatment of raw lignocellulosic biomass to separate the cellulose and lignin. The basic system involves heating biomass in steam under pressure (20 - 50 bar, 210 - 290°C) for a few minutes, and then rapidly releasing the pressure, resulting in the liberation of much of the cellulose fibrous material locked in the biomass. Small amounts of lignin are removed but it is melted and depolymerised and spread back over the surface of the cellulose fibre (Jørgenson et al. 2007). Xylose recoveries are lower than acid treatment, between 45 - 65 %. The ideal residence time, pressure and temperature vary greatly between feedstocks, and other variables, such as pre-wetting the biomass at a particular pH, have been employed to maximise cellulose yields and subsequent enzymatic saccharification and fermentation efficiencies.

Although steam explosion is usually done in batches, continuous processes have been developed. The biomass always undergoes a mechanical comminution step prior to any steam treatment. Steam explosion is very efficient as a pretreatment step for biomass such as hardwoods and agricultural residues but it is less effective for softwoods (Clark and Mackie 1987). However, the overall yield of sugars needs to be increased and costs decreased to make this treatment more attractive in future (Hamelinck et al. 2005).

6.5 Liquid hot water treatment

This relatively new treatment uses compressed hot liquid water at a controlled pH at a pressure above saturation point to hydrolyse hemicellulose. The treatment partially hydrolyses the hemicellulose to soluble oligosaccharides and disrupts the cellulose and lignin structures. Recoveries of xylose (88 - 98%) and exposure to cellulose fibres are high. Maintaining pH > 4 during the treatment by the addition of the yeast lees (‘stillage’) to the biomass minimises the formation of monomeric hemicellulose-derived sugars and therefore the formation of furfural and hydroxymethylfurfural which are toxic to the downstream fermentation process. Recently,
the method has been successfully scaled from laboratory to a throughput of 163 L min⁻¹ with a residence time of 20 min and the authors claimed a recovery of 90 % theoretical yield of sugars and operating cost of US$0.22 per litre ethanol (Mosier et al. 2005). As the process uses no chemicals it is beneficial from both the point of view of disposal and recycling plants.

To date most research has been conducted on corn stover but the performance of the treatment on other lignocellulosic types would be highly beneficial to determine its wider significance for biomass pretreatment.

6.6 Organosolve

The organosolve pretreatment process involves cooking the raw biomass in acidified (usually with hydrochloric or sulfuric acids) aqueous ethanol under various pH, temperature, pressure and time conditions. The solvent-to-wood ratio is usually approximately 7:1 to 10:1. This has been shown to yield a biomass product with less lignin and gives better access to enzymes which is reflected in higher yields of reducing sugars from saccharification steps. It also yields a clean lignin product which is well suited to study as a value-added product. The primary disadvantages of the organosolve technique are that it uses a solvent and acids, though these can be recycled to some extent.

There are numerous studies weighing up the effectiveness of saccharification enzymes on organosolve pretreated lignocelluloses (e.g. Skomarovsky et al. 2006). Many variations of the organosolve process exist, including the use of ethanolic sodium hydroxide solutions (alkali organosolve), and other organic solvent systems such as butanol, methanol and phenol.

6.7 Alkaline hydrolysis including lime

The main bases examined in alkaline hydrolysis are lime, sodium hydroxide, sodium carbonate, urea and ammonia. In general, alkaline hydrolysis is more effective at delignification of lignocellulosic sources with lower lignin contents and the remaining cellulose has a higher reactivity and is more susceptible to enzyme attack. The hemicellulose is not hydrolysed in this method but is left as an insoluble polymer. Typical amounts required for lime pretreatment are ~0.1 g per g biomass and at least 5 g water per g biomass is also needed. The treatment can be conducted at temperatures from 25 -130° with higher temperatures giving faster reactions. During lime treatment around one third of the lignin content is removed as well as all of the acetyl groups present on the hemicellulose. Alkaline hydrolysis has been used on substrates such as wheat straw (Bjerre et al. 1996), spruce (Zhao et al. 2007) and corncobs/stover (Karr and Holtzapple 2000). The disadvantages are generally the same as those for acid hydrolysis - neutralisation/recycling and corrosion resistant vessel material are required.

6.8 Ammonia Fibre Explosion (AFEX)

Ammonia fibre explosion is very similar in concept to steam explosion, with the main difference being the ammonia is used instead of superheated steam. Typical loadings are 1 - 2 kg of ammonia per dry kg of biomass. The ammonia is cleaned and recycled in well-developed systems. In contrast to steam explosion, AFEX does not solubilise hemicellulose fractions to any great extent, and has been examined in the pretreatment of a wide range of biomass feedstocks, including alfalfa, wheat straw, wheat chaff, barley straw, corn stover, rice straw, municipal solid waste, newspaper, coastal Bermuda grass, switch grass, aspen chips and bagasse, among others. Lignin is unaffected but cellulose is readily hydrolyzed to glucose with low enzyme loadings (Wyman et al., 2005).

While AFEX has other advantages over steam explosion, such as no need for small particle sizes for efficacy and no production of inhibitors for downstream biological processes (negating the need for washing steps), it is not very effective as a pretreatment for biomass with high lignin content e.g. wood.

6.9 Carbon dioxide explosion

Supercritical carbon dioxide has been examined as an explosion agent in similar processes to the AFEX and steam explosion pretreatments described above (Zheng et al. 1998). Comparisons were made to steam explosion and other gases such as helium and nitrogen were included in the study. Although these specialist explosion areas are not as well explored as the steam and AFEX methods, they hold promise as pretreatments as the process is more cost effective than ammonia and does not form inhibitors of downstream processes as steam explosion does (Hamelinck et al. 2005).

6.10 Ozonolysis

Ozonolysis is a chemical method used to degrade lignin and some hemicellulose. It leaves the cellulose bundles largely untouched. It has the advantage of being performed at room temperature and pressure and leaves no toxic residues in the material produced for downstream processes. The primary disadvantage is that it requires a considerable amount of expensive ozone, which is not recyclable as it reacts with the lignin. It has been used to degrade lignocellulose from wheat straw, bagasse, green hay, peanut, pine, cotton straw and poplar sawdust.

6.11 Oxidative delignification

Oxidative delignification is also sometimes known as “wet oxidation” and involves the pretreatment of the biomass with an oxidizing agent (such as a 2 % aqueous hydrogen peroxide solution). Good efficiencies (ie conversions of cellulose to glucose) and some reduction in operating cost of US$0.22 per litre ethanol (Mosier et al. 2005). As the process uses no chemicals it is beneficial from both the point of view of disposal and recycling plants. To date most research has been conducted on corn stover but the performance of the treatment on other lignocellulosic types would be highly beneficial to determine its wider significance for biomass pretreatment.
1996). As this process is usually used in conjunction with one or more of the abovementioned processes it does not receive a lot of attention as an individual pretreatment step in the literature, however it should be noted that a wet oxidation step is quite often used as a co-pretreatment to enhance saccharification yields by the prior (or possibly concurrent) oxidative degradation of lignin.

6.12 Biological pretreatment

Biological pretreatments of raw biomass are very slow, but have the advantage of employing mild reaction conditions and using very little energy. White rot fungi are the most commonly used organisms for biological pretreatment and a number of studies have been performed looking at the conversion rates and efficiencies of white rot fungi on a range of biomass feedstocks, such as wheat straw and Bermuda grass. As very few organisms are able to degrade lignin, most of the work in this area has focused on assessing the fungal species.

6.13 Solvation methods

The exploration of ionic liquids and other solvent mixtures as pretreatment agents for lignocellulosic materials is increasing, with some recent reports showing excellent cellulose recovery from many different types of biomass (see Zhu 2008, Fort et al. 2006, Dadi et al. 2006). Ionic liquids have the advantage of being easily recovered and reused, being non-volatile and having unique and tunable solvating properties. Swatloski et al. (2002) explored the dissolution of cellulose using ionic liquids and found the most effective forms incorporated anions that were strong hydrogen bond acceptors. Chloride containing ionic liquids performed best among the liquids they investigated and resulted in microscopic changes to the morphology of the cellulose fibres.

Zhang et al. (2007) reported a closed system solvent process involving concentrated phosphoric acid, acetone and water to fractionate lignocellulose into cellulose, hemicellulose and lignin. Cellulose was rendered highly amenable to cellulase breakdown after the treatment. The return of lignin, hemicellulose and acetic acid products in purified form via this treatment is a valuable path for a biorefinery.

6.14 Ultrasonic pretreatment

The use of ultrasound energy as a pretreatment step in the conversion of lignocellulosic biomass to fermentable sugars is not as well explored as most of the other classical pretreatment methods (US 6,333,181, Hromádková 1999). Ultrasound causes an effect known as cavitation in liquids whereby microscopic bubbles are formed and then spontaneously collapse creating an extremely high pressure for a moment in a micro-environment. As yet, this technology has been most widely applied to corn in making first generation biofuels, however it is increasingly being explored as an effective pretreatment method for lignocellulosic materials in the production of biofuels.
7. Conversion processes for lignocellulose

There are two main approaches being pursued for the conversion of lignocellulose to biofuels:

1. Enzymatic degradation of the polysaccharides to sugars which are then fermented to fuel alcohols.
2. Thermochemical treatment of the whole biomass to yield syngas (or bio-oil via pyrolysis) which is then further converted to fuels.

There is also a concentrated acid process which dissolves the polysaccharides in lignocellulose to monomeric sugars, recycles most of the acid and ferments the sugars to alcohols.

This chapter addresses the principal processes used to convert lignocellulosic biomass (usually pretreated) into products that are biofuels or can be further treated to make biofuels, and the main technical factors affecting each process. Some of the more advanced commercial efforts are presented here where relevant to the technology and in the R&D section (Chapter 10.2).

7.1 Pyrolysis

Treatment of biomass at moderately high temperatures in the absence of, or in low levels of oxygen is called pyrolysis, a process whereby organic material is converted to solids (char), oils and gases. The proportions of products formed are highly dependent on the process time, temperature and the feedstock. Thermal degradation of pure cellulose occurs at 240 - 350°C to produce anhydrous cellulose and levoglucosan (Mohan 2006). Hemicellulose degradation occurs at 200 - 260°C and compared with cellulose it produces more volatile material, less char and less tar. Lignin decomposes to phenols at between 280 - 500°C to produce substantial char, water soluble liquids and gases (Mohan et al. 2006).

There are many variants of pyrolysis processes that have been developed to suit specific feedstocks and aimed at specific output streams. As a result, techniques such as fast pyrolysis, fixed bed, fluidised bed, vacuum pyrolysis, flash-vacuum pyrolysis, slow-pyrolysis, free-fall pyrolysis and others have been explored and developed as industrial solutions to some biofuels production steps. Other high temperature techniques such as plasma-arc (ultra-high temperature processing) have also been developed to multi-tonne scales.

One by-product of pyrolysis is charcoal (char). It adds to the economic viability of pyrolysis processes for the production of liquid biofuels as it has application in energy production, water purification, agriculture and many other areas. Char can make very good, stable soil carbon and has been shown to improve soil properties and increase crop yield in some cases. However the benefits depend upon the nature of the feedstock and the nature of the soil. One company involved in the research and development, and commercialisation of pyrolysis char as a by-product of their slow pyrolysis syngas process is Best Energies, Inc, who have a significant char commercialisation effort in Australia.

The primary advantages of pyrolytic techniques are that the only pretreatment required is comminution and/or drying.
as feedstock contamination is not as much of an issue, the technology is well understood and scalable, and it is often well-suited as a continuous process.

7.1.1 Slow pyrolysis

Slow pyrolysis involves the gradual heating of biomass to ~500°C (sometimes up to 800°C) over 5 - 30 minutes. Solid, liquid and gaseous products are generated in the process and their ratios are highly dependant upon the pyrolysis conditions employed and the nature of the feedstock. As an example, slow pyrolysis using steam as a carrier, rather than an inert gas such as nitrogen, can result in a greater fraction of water soluble components and less char (Minkova et al., 2001). This high degree of variability makes it difficult to make a general statement about “typical product distributions” from slow pyrolysis processes.

7.1.2 Fast pyrolysis

Fast pyrolysis is a technique whereby finely ground biomass is heated rapidly (usually in about 1 second) to approximately 500°C in the absence of oxygen, releasing volatiles which are rapidly condensed into a dark, viscous liquid known as bio-oil (Figure 6). The gases that cannot be condensed are usually combusted to provide heat to the pyrolysis process and the charcoal from the process is compressed and sold for a wide variety of applications. Typically, fast pyrolysis of lignocellulosics will result in 60-70 % bio-oil, 15-25 % char and 10-20 % combustible gases (Mohan 2006).

The process is most commonly performed in a fluidised bed reactor, where a heated bed of sand is “fluidised” by pumping an inert gas (commonly nitrogen) up through it at a certain rate. This facilitates rapid and immersive contact between the bed and the biomass when it is introduced into the reactor. A primary advantage of fast pyrolysis is that it can operate on almost any type of biomass feedstock.

The chemical composition of bio-oil varies depending on the feedstock and pyrolysis variables like temperature, heat transfer, residence time but is usually composed of >200 components. As bio-oil is unstable when heated above 100°C it is unsuitable for distillation or fractionation but it can be combusted directly in boilers, gas turbines and diesel generators. Research efforts are underway in Europe, Australia and the United States to develop bio-oil into a transport fuel. Dynamotive have commercialised a proprietary fast pyrolysis process to convert a wide range of forestry and agricultural residues into bio-oil and char. It has just finished construction of a 200 tpd plant in Guelph, Ontario and has another under construction in Missouri USA. Ensyn, also has a proprietary fast pyrolysis technique (“Rapid Thermal Processing”) similar to Dynamotive’s but have also focussed on value-adding to bio-oil components through the production of resins and chemicals.

7.1.2 Catalysed pyrolysis

The use of catalysts during pyrolysis can alter the product distribution of bio-oil marked such as to favour the production of furfural and furans. Furfural is a viscous, clear liquid with a boiling point of 162°C that turns dark brown or black when exposed to the air. It is used as an intermediate to a range of chemicals and solvents, including tetrahydrofuran (THF). Furfural is usually produced from pentoses (5-carbon sugars) previously hydrolysed from pentosans (polysaccharides containing 5-carbon sugars eg hemicellulose). The pentoses are heated (~ 175°C) with sulphuric acid which causes dehydration to give furfural. The use of catalysts in pyrolysis of biomass to obtain biofuels is a largely unexplored area with significant potential for improvement.

The Biofine process (developed by BioMetics Inc.) is a two stage thermochemical dilute mineral acid treatment that transforms lignocellulosic biomass into a mixture of levulinic acid (an intermediate chemical for a range of products), furfural and lignin. The first stage is a high temperature tubular reactor and the second is a mixed reactor. The acid can be recycled and solid char formed from the lignin is fed into a gasifier to make hydrogen. 7.2
7.2 Gasification

7.2.1 General methods
Gasification decomposes biomass by heating to very high temperatures, breaking all molecular bonds in the material while controlling the amount of oxygen present in the mix to produce a synthesis gas (syngas). In contrast to fast pyrolysis, gasification usually occurs at 800°C to 1400°C and at elevated pressures of around 40 bar but similarly to pyrolysis, there is little or no need for pretreatment of lignocellulose other than size reduction and drying to specific moisture content. Syngas is comprised primarily of hydrogen and carbon monoxide and can be produced from almost any biomass feedstock. There is little waste in the process. Most syngas is currently produced by steam reforming of methane at 10 – 20 bar at 850°C over a nickel catalyst. This remains the most competitive process to biomass-derived syngas and provides a cleaner feedstock.

Syngas can then be reformed using a range of technologies that were developed for fossil fuels to give liquid fuels such as methanol, ethanol, dimethyl ether (DME) and synthetic diesel, the latter using the Fischer-Tropsch method.

The primary disadvantages of gasification are that the processes involve relatively large capital and operating costs for commercial plants especially where gasification and Fischer-Tropsch diesel production are combined (IEA Bioenergy 2007). Contaminants from biomass such as ash, alkali metals, tars and chlorine can cause corrosion, clogging of filters, problem emissions and catalyst poisoning. Scrubbing technologies are mostly employed to overcome these difficulties. The level and type of contaminant varies with biomass source, as does moisture content, and the gasification technology used. Temperature gradient issues across large volumes (boundary heating) are also a challenge for scale up of the technology leading to differential heating from the exterior areas to the interior and variable product conversion.

Very little information is publicly available on yields of syngas from biomass. The efficiency of the conversion is around 60 – 70 % and the conversion efficiency then to alcohols or syndiesel is not clear. Overall yields are expected to be in the range 260 – 400 L fuel per dry tonne biomass (IEA Bioenergy 2007). An overview of gasification technologies, including energy efficiencies and conversion rates (with some assumptions) was recently published by Tijmensen et al. (2002).

7.2.2 Fischer-Tropsch diesel from syngas
Fischer-Tropsch synthesis is by far the most well-established and widely used method for building up hydrocarbons from syngas.

\[ n\text{CO} + (2n+1)\text{H}_2 \rightarrow C_n\text{H}_{2n+2} + n\text{H}_2\text{O} \]

The technique is used in conventional coal-to-liquids and gas-to-liquids fossil fuel conversions and attention is now being turned to its application to biomass-to-liquids technologies. There are several types of catalyst (usually iron or cobalt based) and syngas mixtures that have been optimised for various product streams. In general, Fischer-Tropsch is a very efficient conversion process, however the infrastructure and maintenance costs are high. It has to be performed (with currently available catalysts) at a large scale to be economically viable. At 330°C, most of the lighter petroleum products are produced whereas at 180 – 250°C most diesel fractions and waxes are produced.

A German company, Choren Industries, is building the world’s first commercial scale biomass to liquids plant, utilising proprietary gasification process known as Carbo-V®. This is a three-stage gasification process where partially dried biomass of various types undergoes low temperature gasification (400 - 500°C) to produce a gas-containing tar and char. The tar is oxidised at high temperatures using air/oxygen to provide a hot gasification medium and ground char is blown into the hot gasification medium and reacts endothermically to produce a raw syngas. Choren uses conventional Fischer-Tropsch synthesis (see 7.2.5) to build syngas into long hydrocarbon chains which are then separated and scrubbed to remove impurities. The primary final product is SunDiesel® which can be used alone or blended with petroleum fuels.

Choren has a subsidiary company, Choren Biomass, which concentrates on biomass supply, cultivation systems, transport infrastructure and a range of other factors to maximise their production efficiency and economic viability. As a result, Choren is developing a semi-distributed biofuel production system where they will have a series of standard-sized plants (200,000 tpa biofuel from 1,000,000 tpa dry biomass per plant) placed at strategic locations according to biomass density.
7.2.3 Syngas from bio-oil
There are efforts underway to explore the use of bio-oil as a feedstock for gasification to produce syngas for reforming into synthetic diesel. The liquid nature of bio-oil makes it much more amenable to gasification technologies which are well established and can largely utilise existing infrastructure. Additionally, bio-oil is more readily transported as a biomass feedstock than the low-density raw biomass. This area of research is still in early stages but holds promise. The National Renewable Energy Laboratory in the USA also has a steam gasification route to produce hydrogen from bio-oil using a variety of catalyst systems.

The main barrier to commercialisation of bio-oil-to-syngas as a fuel platform is still price competition with syngas from coal gasification. This is particularly stifling to an Australian bio-oil industry as our coal is very cheap and abundant. Economic viability of bio-oil to liquid fuels in Australia will depend heavily upon the nature of a future carbon credits system. Fortunately, the infrastructure from the coal processing capability in Australia could also be utilised in the transition to biobased syngas production.

7.2.4 Ethanol from syngas via catalysis
Catalysts that have been used for production of alcohols from syngas are not specific to production of ethanol and a mixture of chain lengths from methanol to butanol is usually produced. Additionally, catalyst fouling from biomass contaminants is a problem which is attracting research and development and efficient production of alcohol requires a strict ratio of carbon monoxide to hydrogen. Syntec, a U.S.-based company has developed a catalyst that will convert syngas to ethanol at 300°C and 76 bar.

7.2.5 Methanol from syngas via catalysis
Currently, methanol is produced from a syngas mixture of carbon monoxide and hydrogen under 50 - 100 bar pressure at 250°C over a catalyst developed by ICI in 1966 made from copper, zinc oxide and alumina. The syngas is produced by steam reforming of the methane fraction from natural gas. This process is well-understood and highly optimised. Conoco Phillips and Louisiana State University are developing new catalysts to produce ethanol from syngas in a similar manner.

7.2.6 Micro-organism processing of syngas to ethanol
Gasification of biomass can lead to catalyst poisoning (see 7.2.3) due to low level contaminants in the biological material. Micro-organisms are much more tolerant of these contaminants and so have been evaluated for conversion of syngas to alcohols (Rajagopalan 2002). Gasification results in the production of hot gases that need to be cooled before being exposed to micro-organisms known to convert the carbon monoxide and hydrogen into ethanol, butanol and acetate, butyrate and acetate. While many organisms are known to convert syngas to mixed products (reviewed in Henstra et al. 2007) conversion to ethanol and some acetate has been developed into a commercial process using Clostridium ljungdahlii in continuous stirred tank reactors. Factors that limit the rate of conversion include the gas/liquid transfer of the gases to the organisms due to their low water solubility but these have been partially overcome though the use of high flow rates, increased surface area and pressure, and use of solvents. Also, research is aimed at discovery or engineering of micro-organisms that can tolerate much higher temperatures in order to reduce the heat loss through cooling (Henstra et al. 2007).

Coskata Inc. has developed a process whereby they produce ethanol from syngas using proprietary organisms. The syngas is derived from the high-temperature gasification of various types of carbonaceous biomass and is comprised primarily of carbon monoxide, hydrogen and carbon dioxide. After scrubbing the gas to remove impurities, it is fed into a bioreactor and the micro-organisms consume both carbon monoxide and hydrogen simultaneously and it is claimed that ethanol is the only product. The reactor is a plastic tube filled with millions of filaments upon which the bacteria live, providing high surface area in a small volume. Additionally, Coskata Inc. has departed from the traditional distillation technology for ethanol separation to utilising a membrane separation technique that cuts the power consumption of that step by half. The company claims it can produce ethanol for US$0.26 per litre and achieves yields of 375 L of ethanol per dry ton of biomass.
7.3 Enzymes and biological conversion of lignocellulose

7.3.1 General process
The overall biological process of conversion of lignocellulose to ethanol (or other alcohols) can be summarised as the series:
• pretreatment of lignocellulose
• saccharification
• fermentation
• alcohol recovery

As discussed in Chapter 6 there are multiple pretreatment technologies available however, pilot-scale processes are currently employing catalysed steam explosion or dilute acid pretreatments. During hydrolysis, hemicelluloses are depolymerised and solubilised; lignin and cellulose solids are recovered and the exposed cellulose is subjected to saccharification enzymes (e.g. cellulases) to depolymerise cellulose to glucose. The dissolved monomeric hemicellulose sugars are recovered, excess acids are removed through continuous ion exchange, and all monomeric sugars are fermented using organisms capable of accepting pentose (C5) sugars usually together with hexose (C6) sugars. Some processes include both saccharification and fermentation in a single step. Ethanol is separated from water by distillation and then further dehydrated using either distillation and/or molecular sieves. Lignin which is left over from most of the pretreatment and saccharification processes is usually recovered and burnt in the boiler or power station to produce electricity and steam to cover the plant’s requirements.

The complexity and variety in the polysaccharide structures in lignocellulosic materials has meant nature has come up with equally complex and varied means by which to break them down. Although there are relatively few organisms that can achieve this, there is quite a diverse set of enzymes within that group that utilise different routes to metabolise lignocellulosic materials.

7.3.2 Saccharification
Degradation of cellulose is achieved by cellulases; this is an enzyme mixture that is composed of β-1,4-endoglucanases that attack parts of the cellulose chains and breaks them into smaller oligosaccharides of random size, β-1,4-exoglucanase (cellobiohydrolases) that remove cellobiose from the ends of the oligosaccharide chains, and β-glucosidases that hydrolyse cellobiose to glucose units. The action of the exo- and endoglucanases is synergistic (Sukumaran et al. 2005). There has been an enormous increase in interest in cellulases due to their potential for use in lignocellulosic conversion, and many new genes for cellulases have been identified in the last decade. However, using current technology, the cost of producing ethanol from cellulosic materials via thermochemical or enzymatic routes is still approximately twice the cost of producing it from starch (at 2005 prices). As many aspects of enzymatic cellulose degradation are still to be understood, there is much room for improvement in the efficiency, and hence reduction in the cost of ethanol production.

Whilst research conducted by Genencor International and Novozymes Biotech has shown good progress in reducing the cost of cellulase conversion to sugars by about 20-fold, there is still an estimated 10-fold increase in efficiency required to bring costs down to competitive levels (Schubert 2006; Biomass to Biofuels 2006). The enzyme turnover is still considered too slow and it is uncertain whether the gains made in cellulase performance to date will operate as effectively in large scale fermentation systems.

Specific areas where improvement in cellulase performance is being investigated include increasing the thermal tolerance of the enzymes (most pretreatments involve elevated temperatures and materials need to be cooled prior contact with enzymes), improved enzyme activity, reduced non-specific binding to lignin and consideration of ‘cocktails’ of enzymes combining cellulases, hemicellulases and other accessory enzymes.

The search for new sources of cellulases has led some researchers to investigate wood consuming insects, especially termites. Despite the active research in this field there is still considerable scope for the discovery of novel efficient cellulases and catalytic improvement both through protein engineering and manipulation of the individual components of the enzyme complex.

Hemicelluloses are often grouped with cellulases. The enzymatic breakdown of hemicellulose is a more complex situation than for cellulose. Hemicellulose consists of several different types of sugars and has a highly amorphous structure.
While this structure (like starch) makes the material more easily accessed by enzymes, it also requires a wider variety of enzymes to hydrolyse the many different types of linkages between sugars. Xylans are degraded by β-1,4-xylanases that attack internal xylosidic linkages on the main chain, and β-xylosidases which cleave xylosyl residues from the end of the oligosaccharide. Further detail on the enzymatic degradation pathways of hemicellulose given in Shallom and Shoham (2003) and Polizeli et al. (2005).

7.3.3 Fermentation to ethanol
Fermentation is a well-understood process and is not the rate limiting step in the advancement of lignocellulosics-to-biofuels technology development although efficiencies are desirable in this step as well. Yeasts such as *Saccharomyces* spp. are widely used organisms for the conversion of glucose to alcohol and have a long history of production by humans. Fermentation, often referred to as glycolysis, is the conversion of sugar into ethanol, and is accomplished through a series of transformation steps within organisms. Yeasts and bacteria are known to ferment sugars to alcohols under anaerobic conditions. The exact pathway differs between organisms, providing opportunities to make improvements through metabolic engineering to the fermentation process. Overall, one molecule of glucose is converted into 2 molecules of ethanol and the process releases 2 molecules of carbon dioxide.

Molecules produced or included in upstream processes (such as pretreatment) can inhibit fermentation. Chemicals produced during the acid pretreatment of biomass such as furfural, syringaldehyde, levulinic acid, formic acid, acetic acid, vanillin and others have been identified as inhibitors of yeast fermentation (Cantarella *et al.* 2004, Panagiotou & Olsson 2006). Each lignocellulosic feedstock and the pretreatment strategy used to separate the fractions could have downstream effects on enzyme fermentation steps. The issue of inhibition is less well-explored than other aspects of the whole lignocellulosics to biofuels process and is an area that could provide substantial yield improvements with further investigation.

The fermentation of corn and molasses-derived sugars is exactly the same process as the fermentation of cellulose-derived glucose. Therefore in the case of enzymatic process for lignocellulosics, first generation biofuels production is highly compatible with second generation. The latter process requires biomass pretreatment added to existing fermentation infrastructure.

It is difficult to get independent information on overall yield of ethanol from lignocellulose. Older information states a yield of ethanol from hemicellulose and cellulose of corn stover at 227 L ethanol per dry t stover. However, Iogen Pty Ltd report conversions of 340 L ethanol per dry t wheat straw.

7.3.4 Co-fermentation of hexoses and pentoses to ethanol
Co-fermentation presents an exciting prospect for improving lignocellulosic conversion efficiency and is increasingly being adopted in pilot scale processes. Glucose fermentation using yeasts is relatively a mature technology, however many of the other sugars present in lignocellulosic materials are more challenging to efficiently convert to ethanol. Not having to separate hemicelluloses and celluloses, or their monomeric sugars before fermentation provides real efficiency gains to the overall conversion of lignocellulosics to ethanol. However, hemicellulose being composed of a mixture of pentoses (C5) and hexoses (C6) can cause inhibition problems to hexose fermenting organisms. Pentoses can be fermented in a similar manner to glucose by bacteria. The overall conversion can be summarised by 3 molecules of xylose is fermented to 5 molecules of ethanol and 5 molecules of carbon dioxide.

The recent sequencing (Jeffries *et al.* 2007) of the genome of the world’s most efficient xylose-fermenting fungus has opened new doors for an improvement in ethanol yields from lignocellulosic materials. In particular the xylose fermenting pathway of the bacterium *Zymomonas mobilis* has been brought into pilot scale lignocellulosic conversions. Although the ability does not occur naturally, several organisms such as *Z. mobilis* (Mohagheghi 2002), *S. cerevisiae* (Becker and Boles 2003) and *E. coli* (Dien *et al.* 1998) have now been engineered to ferment both hexoses and pentoses. One of the larger projects from the European NILE effort (see Chapter 10.1) is concentrating on the implementation of a co-fermentation strategy as part of a simultaneous saccharification and fermentation process (see Chapter 7.3.5).
7.3.5 Simultaneous Saccharification and Fermentation (SSF)

Instead of having the cellulose degradation feed taken into a separate fermentation reactor, a setup which incorporates simultaneous saccharification of cellulose and fermentation of glucose has been adopted. It is achieved by using a mixture of cellulases and fermentation micro-organisms in the same reactor. One of main benefits is to relieve the substrate inhibition from glucose production experienced by the cellulose-degrading enzymes as the free sugars are removed from the solution when they taken up by the fermentation organisms and converted to alcohols.

Degrading cellulose and fermenting 5- and 6-carbon sugars simultaneously by a mixed consortium of cellulases and other saccharifying enzymes and fermentation organisms in a single reactor has been tested at pilot scale (Hamelinck et al. 2005). This process has greater efficiency potential than co-fermentation of C5 and C6 sugars alone. A logical step forward from combining free enzymes and micro-organisms is to combine the genes for the expression of desaccharification and fermentation enzymes in the one organism. This method, known as consolidated bioprocessing, can reduce significant capital and energy costs of producing cellulolytic enzymes separately and transportation to the biorefinery.

7.3.6 Fermentation to other products

Bacteria (mainly *Clostridium* species) are able to produce a range of alcohols including butanol and its isomers as a product of anaerobic fermentation. Several issues have held back the process from becoming cost effective and efficient: butanol is one product among acetone and ethanol; butanol accumulation is toxic to the organisms and separation of dilute alcohol mixtures from water is energy intensive. Good progress has been made to minimise these issues recently (Ezeji et al. 2007). DuPont in partnership with BP have invested in the production of biobutanol as part of their Advanced Biofuels Pipeline. Fermentation to butanol is less efficient and more costly than the ethanol process but it is an attractive fuel target (see Chapter 4.2) and is therefore the focus of several research groups and organisations.

7.3.7 Alcohol recovery technologies

Purification of alcohol from aqueous solution of alcohol (~5 wt %) and cell mass is an energy intensive step which contributes negatively to the overall energy equation for biological production of alcohols. The first step in the purification of ethanol is to apply the mixture to a distillation column and concentrate the alcohol to around 37 wt % solution. In the next stage, the aqueous ethanol solution is applied to a rectifying column to bring the concentration to ~95 % ethanol. The final removal of water to provide ethanol sufficiently dehydrated for blending with petrol is accomplished by drying with desiccant, further distillation or membrane separation (Hamelinck et al. 2005).

The vast majority of processes employ distillation to collect the ethanol, however pervaporation – separation using membrane technology – is gaining ground but requires more research and development to improve cost and efficiency (Vane 2005). Virent Energy Systems is using a membrane separation technique that they claim has nearly halved the cost of this step of the process. A Japanese company, Mitsui, has developed a Zeolite-based membrane separation system that they plan to sell to ethanol biofuel operators.

7.4 Anaerobic digestion (Biogas)

Biogas is a mixture of methane and carbon dioxide (50-60 % CH₄, 40 % CO₂, 1 % H₂O, 80-100 ppm NH₃ and 1000-3000 ppm H₂S) which is produced by the breakdown of organic waste in the absence of oxygen. Biogas is generated in landfill waste sites, centralised digesters for cattle and pig manure, waste water treatment plants and industrial waste treatment plants. Anaerobic digestion units can be purchased commercially from a variety of places and many farms use their animal waste streams for co-generation of power. The commercial use of biogas is currently limited to direct combustion for heat and power generation, however there are some research projects looking at its potential for use as a transport fuel. It is worth noting that the total European biogas production increased 13.6 % between 2005 and 2006 to give a total of energy equivalent of 5.38 million tonnes of oil, a very similar figure to that for Europe's biofuel consumption.

Biogas can be converted to syngas and reformed in a similar manner as biomass-to-liquids and coal-to-liquids fuels (Chapter 7.2.1). There is not a great deal of research in this area however some progress has been made at the lab scale. Given the early stage of investigations, there is promise for improvements in the conversion of raw biogas into syngas, however most of the work will be in catalyst and process development. A prospective route is the biochemical conversion of the methane fraction into methanol using methanotrophic bacteria that utilise an enzyme known as methane monoxygenase. This technology has not, however, been developed to any great extent.
8. New developments

New research not covered in the previous sections is summarised below. The breadth of research and development being considered beyond the areas covered in the chapters, which mostly relate to technologies in industrial usage or advanced laboratory scale research, is fast changing and likely to be quickly outdated. Some of the areas of greater emphasis are:

- Understanding and modifying cellulose and lignin biosynthesis and deposition in plants
- Woody biomass growth rate, stress tolerance, cell wall composition and wood properties to maximise growth rate and improve conversion of biomass to sugars
- New planting and harvesting methods for biofuel crops (rotation crops, coppicing)
- Genetic engineering of the feedstocks (low lignin breeds, low water demand, high salinity tolerance, accelerated growth)
- Genetic engineering or plant breeding strategies to reduce extractives in wood to reduce toxicity to fermentation organisms and minimise contamination of product streams
- Simultaneous Saccharification and Fermentation (SSF) in one reactor by one organism (consolidated bioprocessing)
- Value-added co-product production (dyes, nutraceuticals, pharmaceuticals, proteins, chemicals, materials, other extractives, ash) as in the Biorefinery concept
- Reducing the energy and chemical usage for biomass pretreatment
- Using molecular modelling in advanced computing to understand the reaction mechanisms underlying enzymatic degradation of lignocellulose
- New catalysts and reactor conditions for thermochemical conversion
- Improvement of yield of hydrocarbons produced by micro-organisms (that consume lignocellulose-derived sugars).

Some specific recent highlights:

In 2007, North Carolina State University and the Taiwan Forestry Research Institute announced success in the genetic modification of Eucalypt trees to contain 18% less lignin and 4.5% more cellulose. This has the two-fold advantage of both making the cellulose more easily obtained through lower lignin content and also increasing the yield of cellulose. Other similar genetic engineering projects have been successful in producing low-lignin strains of sorghum, poplar, willow and perennial grasses. There are, however, many issues to be dealt with before commercial biomass plants based on these technologies can be utilised; in particular, the safety and environmental aspects of deploying genetically engineered trees for biofuel production will need to be addressed.

Lee Lynd and his group in the US are developing the concept of Consolidated Bioprocessing. This involves engineering a biological system in which four distinct steps - cellulase production, cellulose hydrolysis, hexose fermentation, and pentose fermentation – are combined in one organism/process. Professor Lynd’s group is focussing on ethanol as the biofuel target.
9. Techno-economic aspects of lignocellullosic fuel production

Several commercial-scale lignocellulosic to biofuel plants e.g. Iogen's planned enzymatic plant in Saskatchewan, Canada and Choren's thermochemical plant in Germany are in the planning stage and will be coming on-line soon. However, it is still difficult to obtain true capital and operating costs of commercial-scale production of biofuels from lignocellullosics. Therefore techno-economic modelling incorporating many assumptions has been conducted using pilot-scale data to project the costs to commercial scale. Capital costs for lignocellulosic fuels production appear from the modelling to be very high regardless of the process technology adopted.

The techno-economic studies conducted to date that concentrate on capital costs have been summarised below but for full details of the modelling methodologies and assumptions used within, the original material should be consulted.

Wooley et al. (1999) modelled process designs to estimate the cost of ethanol via different technologies, to help direct the US Department of Energy's research and development program and to investigate the impact of research outcomes on the future price of ethanol. Their assessment concluded that a 2000 t per day plant would need a collection radius of around 40 miles for cellulosic feed. Indexed to 1997 figures, capital costs of an enzymatic process plant were estimated at US$234M for an annual production capacity of ~200 ML ethanol.

Eggeman and Elander (2005) concentrated on the biomass pretreatment steps prior to the enzymatic process to compare the different technologies and the consequences for plant design and capital cost, as well as downstream implications for the subsequent enzyme and fermentation steps. They concluded that the five pretreatments considered (dilute acid, hot water, ammonia fibre explosion, ammonia cycle percolation and lime) would require capital-intensive infrastructure of around $25 M except lime which was around $4 M. However, there was very little overall difference between the pretreatment approaches because the lower cost methods were offset by either higher downstream costs or lower sugar recoveries. All pretreatments were significantly better than no pretreatment option due to low ethanol production in that scenario. Direct hot water treatment had estimated pretreatment capital costs one-sixth of the other treatments but due to the diluted nature of the solids arising from pretreatment, increased costs were expected for all subsequent process stages.

In general, for an enzymatic conversion process, approximately half the direct fixed capital cost is accounted for in pretreatment, saccharification, fermentation and ethanol recovery parts of the plant. The steam and power system accounts for one-third, the remainder arises from feed handling, water treatment, storage, other utilities etc. The total fixed capital cost which includes start-up, construction, field expenses in addition to direct fixed capital was estimated at between US$164 – 211 M (Eggeman and Elander, 2005).

Hamelinck et al. (2005) examined the production of lignocellulosic ethanol via the enzyme process using current technology which has an overall process efficiency of ~60% with lignin co-firing and they also included some expectations of future developments, which should bring the overall efficiency to ~68 %. They conclude that the price of ethanol production due to higher lignocellulosic hydrolysis and fermentation efficiency, lower capital costs, increase in scale and cheaper feedstock could be reduced by two-thirds over the next 20 years.

Capital and operating costs of lignocellulosic thermochemical and enzymatic biorefineries have been compared with grain-based production by Wright and Brown (2007). As inputs to the model the authors relied heavily on Hamelinck et al. (2005) for the enzymatic process and some of the thermochemical routes. The capital and operating costs were converted to 2005 figures, normalised for an annual production of 570 million litres of petrol equivalent, and the fuels were normalised on petrol equivalence (as the products ranged from ethanol, methanol, hydrogen and syn-diesel).

According to their analysis, the capital cost of lignocellulosic plants is around 5 to almost 8-fold higher than a starch to ethanol plant (based on technology dating from 2000 – 2005); the capital cost was lowest for hydrogen production and highest for Fischer-Tropsch diesel. Operating costs were cheaper for lignocellulosic hydrogen and similar for methanol, compared with grain ethanol, using input assumptions of US$50 t biomass and corn at US$2.12 bushel. When 2006 price for corn (US$3 bushel) was substituted in the analysis, operating costs for starch ethanol was amongst the highest.

A detailed cost analysis comparing different gasification techniques and Fischer-Tropsch synthesis was published by Tijmensen et al. (2002) that went as far as to demonstrate the optimal plant size and the economies gained across a range of scales. Different hydrocarbon lengths in the products streams were also compared with a view to processing energy versus the energy contained in the product stream.

A consultants report to the IEA (IEA Bioenergy 2007) is the
most comprehensive comparison of the techno-economic aspects of lignocellulosic conversions to transport fuels among current studies. Under consideration was enzymatic, acid hydrolysis-fermentation, gasification with chemical catalysis or by micro-organism. They draw heavily on information supplied to the US DOE in recent applications for financial support for six new pilot lignocellulosic plants. Therefore conclusions from the study are heavily reliant on the accuracy of data submitted by companies. Capital costs for plants producing 47 – 72 ML annually were predicted to range from US$82.5 - $200 M depending on the process used. Concentrated acid hydrolysis and gasification/micro-organisms were found to require the lowest capital costs.

9.2 Summary of conversion technologies

There are two main lignocellulosic conversion technologies competing for prominence in biofuels production: 1) Thermochemical with gasification then conversion to fuels by catalysis/Fischer-Tropsch catalysis and 2) Enzymatic with pretreatment, enzymes and fermentation. The advantages and disadvantages are summarised in the table below.

Neither technology is considered a front runner at this stage with pilot plants currently operating and commercial plants in the planning stage that cover both technology platforms (Chapter 10). Both technologies have limitations in terms of high capital and operating costs, although within each platform new combinations (e.g. gasification with microbiological conversion; liquid hot water pretreatment for enzyme conversion) are emerging that may substantially reduce these costs. Research and development is being directed at both technologies in an effort to reduce infrastructure and operating costs and improve overall efficiencies.

Table 6. Summary of conversion technologies

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<thead>
<tr>
<th></th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>Pyrolysis</td>
<td>Minimal pretreatment; fast, largely established technology/knowledge; continuous; reasonably flexible feedstock requirements (less flexible for gasification to FT)</td>
<td>Large infrastructure; high capital costs, pressurised vessels; energy intensive; further processing required to produce a fuel</td>
</tr>
<tr>
<td>Gasification then Fischer-Tropsch</td>
<td>Sometimes multiple product streams that need separating; expensive catalysts; Large infrastructure; high capital costs; pressurised vessels; energy intensive; biomass contaminants cause poisoning of catalysts</td>
<td></td>
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<tr>
<td>Enzymatic</td>
<td>Mild operating conditions, usually one product stream; fully compatible with first generation ethanol plants</td>
<td>High capital costs; energy intensive; pretreatment can add substantially to overall cost and cause contaminants downstream; longer treatment times; high enzyme requirement; overall efficiency needs improvement; R&amp;D further behind than thermochemical</td>
</tr>
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</table>
10. Status of research, development and commercialisation of lignocellulose-derived biofuels

10.1 International

Biofuels policies have been covered in previous reports (Batten & O’Connell 2007, Beer et al. 2003, O’Connell et al. 2007a) and will not be covered again in detail in this section. Biofuels policies rarely make a distinction between first and second generation biomass sources other than the recognition that in expanding biofuels production to replace a significant proportion of transport fuels will require the conversion of more plentiful, second generation feedstocks.

The U.S. currently produces more than 19 billion litres a year of ethanol, almost exclusively from corn grain, and the industry is growing 30% annually. Recent provisions to the Renewable Fuels Standard described in the US Energy Independence and Security Act (2007) state that of the 36 billion gallons (125 billion litres) of renewable fuel to be produced by 2022, 58% must be obtained from cellulosic ethanol and other advanced biofuels. The USA goal is to reduce the cost of producing cellulosic ethanol from US$0.59 per litre in 2005, to US$0.28 in 2012 and to boost the average yield from 246 litres per ton as it is today, to 340 litres per ton in 2012. The Department of Agriculture and the Department of Energy recently reported the U.S. could yield more than a billion tons of biomass annually for energy needs (Perlack et al. 2005). The 1.3 billion tons of biomass that was forecast contains as much energy as 3.5 billion barrels (560 billion litres) of oil – enough to displace one third of the current demand for transport fuels.

Brazil is the world’s largest ethanol producer. According to Reuters, Brazil’s ethanol consumption was 16.7 billion litres for 2007 with another 3.8 billion litres being exported. Datagro Consultants forecast ethanol demand to rise to 32 billion litres by 2014 supplying around 53% of all fuel used by light vehicles. Grupo Dedini Agro, a Brazilian ethanol producer, claims to be able to produce ethanol from sugar cane bagasse for US$0.27 per litre using a technique known as Fast Acid Hydrolysis in a 100 L per day pilot plant. In August 2006, Spanish energy and construction company, Abengoa, agreed to buy Dedini for US$296 million, making Abengoa the only company to have a presence in the world’s three largest ethanol markets (US, Europe and Brazil). This came a few months after Dedini announced that it planned commercial cellulosic ethanol production from 5 plants in 2012. Abengoa is Europe’s largest bioethanol producer and 5th largest in the U.S., producing 1 billion litres of ethanol from 3 plants in Spain.

In Canada, a non-profit funding body called the Sustainable Development Technology Canada™ has set up two separate funds: The SD’Tech Fund™ (CA$550 million) for the support of projects that address climate change, air quality, clean water, and clean soil, and the NextGen Biofuels Fund™ (CA$500 million) that supports the establishment of first-of-kind large demonstration-scale facilities for the production of next-generation renewable fuels. In mid-2007, the Canadian government announced a four year $200 million capital call program called ecoAgriculture Biofuels Capital Initiative (ecoABC), which was set up specifically for cellulosic ethanol projects, however the funding is limited to projects utilising agricultural feedstocks.

China is the 4th largest ethanol consumer, after Brazil, Europe and the U.S. In June, 2007 an official of the Chinese National Development and Reform Commission announced that China would approve no new projects that produced ethanol from food crops. The country’s four corn-ethanol producers, who currently supply over 1 million tonnes of ethanol each year, will be asked to gradually change over to cellulosic ethanol. China Oil and Food Corporation (COFCO), the country’s largest oil and food importer and exporter, is going to use sweet sorghum in the production of non-food-based ethanol fuel, according to COFCO’s president, with a goal of 5 million tonnes per year in “the near future”. COFCO has entered a co-operative agreement with Novozymes, who is also working with the U.S. on the development of cellulosic ethanol.

In India, the New and Renewable Energy Minister, Vilas Muttemvar, has reported that India’s upcoming (but as yet unrealised) National Biofuels Policy would include a mandate for a 5% renewable component in fuels by 2012 and 10% by 2017. In saying so, he also stated that the policy would have to balance food security and energy security. India has not yet shown a concerted effort in the development of lignocellulosic biofuels technologies or industries.

The European biofuels market is currently dominated by biodiesel. In 2005, over 2.2 million tons of crude oil equivalents (MTOE) in biodiesel was consumed in Europe followed by bioethanol with just over 0.56 MTOE being consumed. Europe has put significant research into decentralised biofuels networks. Factors such as proximity of processing plant to the growth areas, suitability of biomass to the local environment, transport costs and savings from using existing infrastructure and the type of fuel desired are all crucial parameters. The
main European focus is (not exclusively) on thermochemical routes, in contrast to the U.S. who are focussing primarily on enzymatic processes. One major initiative, the NILE (New Improvements for Lignocellulosic Ethanol) project (2005 - 2009) is supported by the European 6th Framework Programme and is a collaborative effort between 21 partner institutions across 11 countries (including Israel) whose goal is to focus on the scientific barriers to the cost-effective production of ethanol from lignocellulosic sources. The total budget for the effort is €12M.

Japan released a report in May 2007 (Tanaka 2007) detailing the potential to supply 10 % of their transport fuels needs by 2030, setting a target of approximately 6 billion litres of renewable fuels. Refiners such as Nippon Oil, Idemitsu Kosan, Cosmo Oil and Showa Shell Sekiyu K.K. will be using ethanol to make ETBE by mixing it with isobutylene and blending it with gasoline stocks. Bioethanol Japan has been producing ethanol from woody urban waste, with plans to expand their current pilot plant capacity to 4 million litres in the near future. This falls well short of the 500 million litres of oil equivalents being aimed for, however Japan plans to import significant amounts of ethanol to achieve this target while concurrently further developing their opportunities in lignocellulosics.

The level of research and commercial effort occurring worldwide around lignocellulosic biofuels is substantial and increasing at a spectacular rate. Table 6 provides a summary of the major industrial efforts occurring around the world. Several of the companies listed already have first generation ethanol plants in operation and are expanding their capability to cellulosic ethanol. Although most are listed as a single entity, the efforts are the result of joint ventures and significant investment by venture capitalists. Other involved parties are usually energy utilities, academic research institutions and government bodies, such as the U.S. Department of Energy. The table does not include co-products being developed nor energy returned to the power grid. Yields and efficiencies have been given where available. Current research in particular is too rapidly evolving to cover in detail here, however Table 6 provides a representative sample of some of the more significant research efforts.

<table>
<thead>
<tr>
<th>Company</th>
<th>Origin</th>
<th>Product</th>
<th>Feedstock</th>
<th>Pretreatment</th>
<th>Process</th>
<th>Capacity</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abengoa Inc.</td>
<td>Spain</td>
<td>Ethanol</td>
<td>Woody and herbaceous biomass</td>
<td>Steam explosion</td>
<td>Enzymatic hydrolysis, fermentation then distillation</td>
<td>44 ML/yr planned</td>
<td>172 L/tonne biomass (calc’d from 700 tpd giving 44,000,000 L/yr)</td>
</tr>
<tr>
<td>AE Biofuels</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Corn stover, straw, switchgrass, miscanthus</td>
<td>n/a</td>
<td>Enzymatic hydrolysis of 5- and 6-carbon sugars then fermentation - combined with starch ethanol process (Ambient Temperature Cellulose Starch Hydrolysis - ATCSH)</td>
<td>n/a Pilot plant under construction</td>
<td>489 L/tonne corn (calc’d from 27 gal/bushel - assumed dry)</td>
</tr>
<tr>
<td>ALICO - Bioengineering Resources Inc. (BRI Energy)</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>“Any” carbonaceous waste</td>
<td>n/a</td>
<td>Gasification then fermentation of the syngas</td>
<td>52 ML/yr under construction</td>
<td></td>
</tr>
<tr>
<td>American Energy Enterprises</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Wood waste</td>
<td>Acid pretreatment</td>
<td>Enzymatic hydrolysis then fermentation</td>
<td>91- 204 ML/yr beginning construction</td>
<td>n/a</td>
</tr>
<tr>
<td>American Process Inc.</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Pulp mill waste - hemicellulose</td>
<td>Pulp process</td>
<td>AVAP™ (American Value Added Pulping)</td>
<td>n/a plant under construction</td>
<td>124 L/tonne pulp (calc’d from 500 tonne per day pulp giving 22.6 million L/yr)</td>
</tr>
<tr>
<td>Bioethanol Japan</td>
<td>Japan</td>
<td>Ethanol</td>
<td>mainly woody urban waste and construction materials</td>
<td>n/a</td>
<td>Genetically engineered E.coli fermenting both C5 and C6 sugars (same as Verenium technology, see above)</td>
<td>1.4 ML/yr started and 4 ML/yr planned</td>
<td>n/a</td>
</tr>
<tr>
<td>Company</td>
<td>Origin</td>
<td>Product</td>
<td>Feedstock</td>
<td>Pretreatment</td>
<td>Process</td>
<td>Capacity</td>
<td>Yield</td>
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<tr>
<td>Bluefire Ethanol</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Agricultural residues, wood waste, paper,</td>
<td>Concentrated acid hydrolysis</td>
<td>Fermentation - 5- and 6-carbon sugars</td>
<td>64.4 ML/yr started</td>
<td>318 L/dry tonne</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>green waste</td>
<td>“Arkenol process”</td>
<td></td>
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</tr>
<tr>
<td>China Resource Alcohol</td>
<td>China</td>
<td>Ethanol</td>
<td>n/a</td>
<td>High pressure anhydrous ammonia,</td>
<td>Enzymatic hydrolysis, fermentation then</td>
<td>6.4 ML/yr started</td>
<td>2149 L/dry tonne</td>
</tr>
<tr>
<td>Corporation</td>
<td></td>
<td></td>
<td></td>
<td>steam explosion or alkali hydrolsis</td>
<td>distillation</td>
<td>1,249 ML/yr planned</td>
<td></td>
</tr>
<tr>
<td>Choren</td>
<td>Germany</td>
<td>Syndiesel</td>
<td>Agricultural, forestry, biogenic waste,</td>
<td>Comminution (&lt; 120 mm particle size)</td>
<td>Gasification - Fischer-Tropsch</td>
<td>0.005 ML/yr</td>
<td>20%</td>
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<td></td>
<td></td>
<td></td>
<td>recycling waste</td>
<td></td>
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<tr>
<td>Citrus Energy/ FPL Energy</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Citrus waste</td>
<td>n/a</td>
<td>Enzymatic saccharification followed by</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>搭</td>
<td></td>
<td></td>
<td></td>
<td>fermentation with brewer’s yeast</td>
<td>fermentation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colusa Biomass Energy Corp.</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Rice straw</td>
<td>n/a</td>
<td>“Proprietary technologies”</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coskata/ General Motors</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Carbonaceous biomass</td>
<td>n/a</td>
<td>Gasification to syngas (CO and H2) then</td>
<td>0.15 ML/yr under</td>
<td>7.7:1 energy in:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>microbial conversion to ethanol. Separation</td>
<td>construction,</td>
<td>energy out</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>via pervaporation</td>
<td>commercial scale</td>
<td></td>
</tr>
<tr>
<td>Dedini</td>
<td>Brazil</td>
<td>Ethanol</td>
<td>Sugar cane bagasse</td>
<td>Organic solvent</td>
<td>Rapid acid hydrolysis then membrane</td>
<td>0.005 ML Ethanol</td>
<td>100 L/tonne</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>separation (Siftek)</td>
<td>per day</td>
<td></td>
</tr>
<tr>
<td>Dynamotive</td>
<td>Canada</td>
<td>Bio-oil</td>
<td>Agricultural, forestry, biogenic waste,</td>
<td>&lt; 10 % Moisture, 1-2 mm particle size</td>
<td>Fast pyrolysis</td>
<td>214,000 barrel of</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>recycling waste</td>
<td></td>
<td></td>
<td>oil equivalents/yr</td>
<td>60-75% by wt.</td>
</tr>
<tr>
<td>Enerkem</td>
<td>Canada</td>
<td>Methanol and ethanol</td>
<td>Woody waste, construction materials, other materials of opportunity</td>
<td>&lt; 25 mm particle size and &lt; 20 % water</td>
<td>Gasification to produce syngas, then catalytic reforming.</td>
<td>4 ML/yr started</td>
<td>n/a</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>then 50 ML/yr planned</td>
<td></td>
</tr>
<tr>
<td>Ensyn Group Inc.</td>
<td>U.S.A.</td>
<td>Bio-oil</td>
<td>Woody and herbaceous biomass</td>
<td>n/a</td>
<td>Fast pyrolysis</td>
<td>18.9 ML/yr</td>
<td>75 % by wt</td>
</tr>
<tr>
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<tr>
<td>Elek Etanoteknik</td>
<td>Sweden</td>
<td>Ethanol</td>
<td>Various carbonaceous biomass</td>
<td>n/a</td>
<td>n/a</td>
<td>0.2 ML/yr pilot since 2004</td>
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<tr>
<td>Florida Crystals Corp.</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Sugar cane bagasse, wood chips, other biomass</td>
<td>Acid hydrolysis</td>
<td>Enzymatic fermentation</td>
<td>7.6 ML/yr under</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>construction</td>
<td></td>
</tr>
<tr>
<td>GreatPoint Energy Inc.</td>
<td>U.S.A.</td>
<td>Renewa-blue™ (99.5% methane)</td>
<td>Various biomass</td>
<td>n/a</td>
<td>Gasification (catalytic)</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>(Citi Alternative Investments/Dow Chemical Company)</td>
<td></td>
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</tr>
<tr>
<td>ICM Inc</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Corn fibre, corn stover, switchgrass and</td>
<td>Milling, 1° and 2° liquefaction at</td>
<td>Simultaneous saccharification and fermentation (50-60 hrs), distillation, drying</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>sorghum</td>
<td>221°F 5 mins, 180-190 deg F 1-2 h</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Iogen Corporation</td>
<td>Canada</td>
<td>Ethanol</td>
<td>Corn stalks, leaves, wood fibre, other</td>
<td>Modified steam explosion</td>
<td>Enzymatic</td>
<td>2.5 ML/yr with 75</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>biomass</td>
<td></td>
<td></td>
<td>ML/yr planned</td>
<td>ML/yr planned</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>340 L/Tonne</td>
<td></td>
</tr>
<tr>
<td>“fibre”</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>KL Process Design Group</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Forest thinnings, wood waste</td>
<td>n/a</td>
<td>Enzymatic</td>
<td>5.6 ML/yr with</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>another 3.7 ML/yr planned</td>
<td></td>
</tr>
<tr>
<td>Company</td>
<td>Origin</td>
<td>Product</td>
<td>Feedstock</td>
<td>Pretreatment</td>
<td>Process</td>
<td>Capacity</td>
<td>Yield</td>
</tr>
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</tr>
<tr>
<td>LanzaTech</td>
<td>New Zealand</td>
<td>Ethanol</td>
<td>Carbon monoxide from industrial processes such as steel mills</td>
<td>n/a</td>
<td>Microbial</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Lignol Energy</td>
<td>Canada</td>
<td>Ethanol</td>
<td>Hardwoods and softwoods</td>
<td>&quot;Alcell&quot; biorefining technology</td>
<td>Organosolve 50:50 ethanol: water at 200°C and 27 bar</td>
<td>Enzymatic hydrolysis and fermentation</td>
<td>plant under construction for 100 tonnes per day woodchips</td>
</tr>
<tr>
<td>LS9 Inc.</td>
<td>U.S.A.</td>
<td>Synfuels and Syndiesel</td>
<td>Cane and cellulosic material</td>
<td>n/a</td>
<td>Microbial</td>
<td>Pilot plant planned</td>
<td>n/a</td>
</tr>
<tr>
<td>Masada/TVA</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Municipal Solid Waste, sewage sludge, waste water</td>
<td>Removal of glass, plastic and metal, then drying and shredding</td>
<td>Cellulose chemically broken down into sugars, then fermentation</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Mascoma (ex Celsys Biofuels Inc.)</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Multiple, e.g, corn fibre, distiller grains, switchgrass</td>
<td>n/a</td>
<td>Enzymatic</td>
<td>plant under construction for 19 ML/yr</td>
<td>n/a</td>
</tr>
<tr>
<td>Meridian Biorefining Corp/Gulf Ethanol Corp.</td>
<td>U.S.A.</td>
<td>Ethanol, gasoline, biocrude</td>
<td>Various cellulosic sources</td>
<td>n/a</td>
<td>&quot;Vortex Implosion Disintegrator&quot; high pressure, high velocity, sudden &quot;polarity shifts&quot; - turns biomass to powder in seconds</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Newpage Corp. (ex Stora Enso North America)</td>
<td>U.S.A.</td>
<td>Syndiesel</td>
<td>Paper and woody waste</td>
<td>n/a</td>
<td>Gasification then Fischer-Tropsch conversion to Syndiesel</td>
<td>21.5 ML/yr planned (calc’s based on 370 bbl syndiesel per day)</td>
<td>n/a</td>
</tr>
<tr>
<td>Nova Fuels</td>
<td>U.S.A.</td>
<td>Ethanol, propanol, butanol and pentanol</td>
<td>Various carbonaceous materials</td>
<td>n/a</td>
<td>Gasification then reforming over novel catalysts</td>
<td>6 pilot plants planned</td>
<td>n/a</td>
</tr>
<tr>
<td>Pacific Ethanol</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Wheat straw, wood chips, corn stover</td>
<td>Steam explosion/wet oxidation (BioGasol Process)</td>
<td>Simultaneous saccharification and fermentation (6-carbon sugars), separate fermentation of 5-carbon sugars, Anaerobic digestion of remaining mass to make Biogas</td>
<td>10.2 ML/yr under construction</td>
<td>n/a</td>
</tr>
<tr>
<td>Pearson Technologies/ ClearFuel technology</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Cane trash and bagasse</td>
<td>n/a</td>
<td>Gasification and reforming</td>
<td>120 tons biomass per day</td>
<td>n/a</td>
</tr>
<tr>
<td>Poet (ex Broin)/ DuPont</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Corn grain and stover</td>
<td>n/a</td>
<td>Fermentation - 5- and 6-carbon sugars - Zymomonas mobilis</td>
<td>94.6 ML/yr started</td>
<td>n/a</td>
</tr>
<tr>
<td>Pure Energy Corp./Raven Biofuels International Corp.</td>
<td>U.S.A.</td>
<td>Ethanol, and furfural</td>
<td>Pine, woodchips, corn cobs</td>
<td>Double dilute sulfuric acid to get separate streams of lignin, 5-carbon and 6-carbon sugars</td>
<td>5-carbon sugars to furfural stream, 6-carbon sugars to ethanol stream</td>
<td>18.9 ML/yr under construction (India), 375 ML/yr planned in 4 yrs and 750 ML/yr planned in 5 yrs</td>
<td>n/a</td>
</tr>
<tr>
<td>Purevision Technology Inc.</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Corn stalks, straws, cane bagasse, wood, grasses</td>
<td>High pressure countercurrent fractionation into hemicellulose, cellulose and lignin streams</td>
<td>Fermentation of the 5-carbon sugars</td>
<td>91 kg/day biomass with 3000 kg/day under construction</td>
<td>n/a</td>
</tr>
<tr>
<td>Company</td>
<td>Origin</td>
<td>Product</td>
<td>Feedstock</td>
<td>Pretreatment</td>
<td>Process</td>
<td>Capacity</td>
<td>Yield</td>
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</tr>
<tr>
<td>Range Fuels Inc</td>
<td>U.S.A.</td>
<td>Methanol, Ethanol, other alcohols</td>
<td>Various - over 20 tested - will start with urban wood</td>
<td>n/a</td>
<td>Gasification to produce syngas, then catalytic reforming.</td>
<td>75 ML/yr started then 378.5 ML/yr planned</td>
<td>n/a</td>
</tr>
<tr>
<td>Sicco A/S</td>
<td>Denmark</td>
<td>Ethanol</td>
<td>Wheat straw</td>
<td>n/a</td>
<td>Integrated Biomass Utilisation System (IBUS) - enzymatic saccharification then yeast fermentation</td>
<td>8,600,000 kg biomass/yr pilot demo facility (cal's on 24hr, 365 days operation)</td>
<td>n/a</td>
</tr>
<tr>
<td>SunEthanol/ICM</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Corn stover, switchgrass, sugarcane, woodchips, recycled paper</td>
<td>n/a</td>
<td>Anaerobic microbial process that, in one organism (the Q microbe) converts cellulose and hemicellulose to 6- and 5-carbon sugars and also ferments them to ethanol</td>
<td>small scale pilot planned</td>
<td>n/a</td>
</tr>
<tr>
<td>SunOpta BioProcess Inc.</td>
<td>Canada</td>
<td>Ethanol</td>
<td>n/a</td>
<td>High pressure anhydrous ammonia, steam explosion or alkaline hydrolysis</td>
<td>Enzymatic hydrolysis, fermentation then distillation</td>
<td>None. Now a technology and solutions broker for cellulosic biofuels development. Major deals with Abengoa, Celunol (pre Verenium), China Resources Alcohol Corporation and Greenfield Ethanol</td>
<td>n/a</td>
</tr>
<tr>
<td>Syntec Biofuel Inc.</td>
<td>U.S.A.</td>
<td>Methanol, ethanol, n-propanol and n-butanol</td>
<td>Wood waste, crop residues including sugar cane bagasse and corn stover, organic waste, manure, sewage digestor gas or landfill gas</td>
<td>n/a</td>
<td>Gasification - reforming over novel non-rare-earth catalyst at low pressures - separation of alcohols</td>
<td>n/a</td>
<td>397 L/tonne biomass</td>
</tr>
<tr>
<td>Verenium Corp. (ex Celunol/Diversa)</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Bagasse, dedicated energy crops, woody waste</td>
<td>Comminution and acid hydrolysis of hemicellulose</td>
<td>Cellulose hydrolysis and fermentation/fermentation of pentoses from hemicellulose</td>
<td>200 Tonne biomass per day (pilot) with 5.3 ML/yr ethanol planned</td>
<td>n/a</td>
</tr>
<tr>
<td>Virent Energy Systems/Shell</td>
<td>U.S.A.</td>
<td>Synfuel</td>
<td>Glycerol, cellulose, starches, 5- and 6-carbon sugars</td>
<td>Extraction of the polysaccharide components from biomass</td>
<td>Aqueous phase reforming -</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Woodland Biofuels Inc</td>
<td>Canada</td>
<td>Ethanol, methanol and hydrogen</td>
<td>Various carbonaceous biomass</td>
<td>n/a</td>
<td>Catalysed Pressure Reduction™ technology - a gasification and reforming process</td>
<td>small scale plants sold to forestry, agricultural, municipal solid waste and waste water processing facilities</td>
<td>n/a</td>
</tr>
<tr>
<td>Zeechem</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Carbonaceous biomass</td>
<td>Separation into lignin and carbohydrate fractions</td>
<td>Carbohydrates fermented to give ethylacetate, lignin gasified to give hydrogen, hydrogenolysis of ethylacetate to give two molecules of ethanol</td>
<td>3.7 ML/yr planned/under construction</td>
<td>n/a</td>
</tr>
<tr>
<td>Zymetis Inc</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Various carbonaceous biomass</td>
<td>Ethazyme™ Pre</td>
<td>Unique enzyme mixtures (Ethazyme™ C5 and Ethazyme™ C6)</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>
Table 8. Selected international research and development programs across a range of lignocellulosics to biofuels technologies

<table>
<thead>
<tr>
<th>Company</th>
<th>Country</th>
<th>Fuel</th>
<th>Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Fuels and Energy/AFSE Enzyme</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Testing 10 candidates of “supenzyme” that are expected to reduce cellulosic ethanol production costs by 50%</td>
</tr>
<tr>
<td>Amyris Biotechnologies</td>
<td>U.S.A.</td>
<td>Various fuel additives</td>
<td>Engineering microbes to carry out a range of synthetic chemistry functions, including the production of “next generation biodiesel”</td>
</tr>
<tr>
<td>Aosic Bioenergy</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Exploring a novel biomass pretreatment (the “CFC” process) and develop high temperature/pressure enzymes from marine and terrestrial extremophiles to improve hemicellulosic conversion to ethanol</td>
</tr>
<tr>
<td>Archer Daniels Midland Company/Purdue University</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Studying how to get cellulosic ethanol from parts of the corn kernel not usually used for ethanol</td>
</tr>
<tr>
<td>Biocoup</td>
<td>Europe/International</td>
<td>Synfuel/Syndiesel</td>
<td>17 research laboratories investigating the potential to use existing petroleum infrastructure to upgrade bio-oil to synfuels and syndiesel. Focus on value-added chemical co-products to enhance economics</td>
</tr>
<tr>
<td>BP University of California Berkley/EBI/LBNL</td>
<td>USA</td>
<td>Ethanol</td>
<td>US$500 million investment over 10 years is the largest petroleum company investment in biofuels area.</td>
</tr>
<tr>
<td>Ceres</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Energy crop development - high biomass sorghum, improved switchgrass</td>
</tr>
<tr>
<td>DuPont/BP</td>
<td>International</td>
<td>n-Butanol, 2-butanol, iso-butanol</td>
<td>Development of biocatalysts and commercial processes for the production of butanol isomers. 60 Patents from the partnership so far</td>
</tr>
<tr>
<td>Dyadic International Inc.</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Biotechnology company - gene discovery, enzyme production</td>
</tr>
<tr>
<td>General Motors</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>By 2012 half of the GM fleet will be flex-fuel vehicles</td>
</tr>
<tr>
<td>Gevo (Khosla Ventures/ Virgin Fuels)</td>
<td>U.S.A.</td>
<td>Butanol</td>
<td>Engineering cellulase enzymes through directed evolution and also putting the cellulase enzymes in E. coli strain able to ferment sugars to ethanol.</td>
</tr>
<tr>
<td>Globex Inc.</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Supercritical fluid pretreatment technology developer</td>
</tr>
<tr>
<td>Green Biologics</td>
<td>United Kingdom</td>
<td>Butanol</td>
<td>Thermophilic enzyme saccharification then microbial fermentation</td>
</tr>
<tr>
<td>Hyvolution</td>
<td>Netherlands</td>
<td>Hydrogen</td>
<td>The aim is to develop a blue print for a hydrogen from biomass plant. Biomass is converted to fermentable feedstock which is processed to hydrogen by dark and photofermentation. The hydrogen gas is upgraded to fuel cell specifications. Cost reduction is addressed through system integration</td>
</tr>
<tr>
<td>KiOr</td>
<td>Netherlands</td>
<td>n/a</td>
<td>Biomass Catalytic Cracking (BCC) - A novel method whereby biomass is impregnated with a material, which is then “crystallised” to push apart the lignin sheath’s from the cellulosic fibres.</td>
</tr>
<tr>
<td>National Renewable Energy Laboratories</td>
<td>U.S.A.</td>
<td>Multiple</td>
<td>World’s largest research program dedicated to production of fuels and biobased products from biomass. Very heavily involved in enzymatic processing and pretreatment of lignocellulosic but have programs covering all aspects of alternative fuels.</td>
</tr>
<tr>
<td>Netherlands Biohydrogen Network</td>
<td>Netherlands</td>
<td>Hydrogen</td>
<td>The objective is to increase productivity from hydrolysates of lignocellulosic biomass and potato steam peels to produce hydrogen for fuel cells</td>
</tr>
<tr>
<td>Novozymes</td>
<td>Netherlands</td>
<td>Ethanol</td>
<td>Development of enzymes that can efficiently convert cellulose into fermentable sugars. Recently moved into fermentation capability</td>
</tr>
<tr>
<td>University of Massachusetts</td>
<td>U.S.A.</td>
<td>Synfuel</td>
<td>Developed a solid catalyst that, in water, converts cellulose to synfuel with very little energy input in less than two minutes. Process generates heat and a zero carbon footprint is claimed.</td>
</tr>
<tr>
<td>Xenathol Corporation/Southeast Biofuels</td>
<td>U.S.A.</td>
<td>Ethanol</td>
<td>Process development, yeast engineering, xylose/citrus focus</td>
</tr>
</tbody>
</table>
10.2 Australia

Biofuels have been the subject of several government-sponsored reports and inquiries over the past three years and the recommendations have generally been that we increase our renewable fuels consumption and production capacity.

A Senate Inquiry entitled “Australia’s future oil supply and alternative transport fuels” was conducted in 2007 and involved members from all the major political parties. It is understood that the recent change in government leadership may catalyse the development of an action plan for renewable fuels, however in the absence of a federal renewables policy and no specific timeframe being given for the delivery of one, only the relevant recommendations from the inquiry will be outlined below. The following recommendations are taken from the executive summary:

“The Committee recommends that the Government publish the results of its review of progress made towards meeting the biofuels target of 350ML per year, including which companies are meeting the target.”

“The Committee recommends that the Government examine the adequacy of funding for lignocellulose ethanol research and demonstration facilities in Australia, and increase funding where appropriate.”

“The Committee recommends that the Government commission a research group within the Department of the Treasury to identify options for addressing the financial risks faced by prospective investments in alternative fuel projects that are currently preventing such projects from proceeding. This group should determine how these risks might be best addressed in order to create a favourable investment climate for the timely development of alternative fuel industries, consistent with the principles of sustainability and security of supply.”

The current Australian policies relating to biofuels were summarised by Batten and O’Connell (2007). The following statements were provided in the executive summary:

“Estimates of subsidies to fossil fuel use in Australia range from 2.2 to 10 billion dollars per year.”

“Assistance currently provided to producers includes (a) a production grant of 38.1 cents per litre (c/L), which fully offsets the excise paid on biofuels; (b) a capital grant for new facilities that effectively provides around $1/L in additional assistance over the lifetime of the plant.”

“Assistance to biofuels is scheduled to fall to 12.5c/L for ethanol by July 2015. A banded excise system will impose rates on different fuels, classified into high, medium and low energy groups. This strategy broadly keeps constant the excise payable per kilometre travelled by vehicles using the fuel, with biofuels retaining a 50% discount on this excise”

10.2.1 Research and Development

Transport infrastructure is particularly important for Australia. A handful of studies have been performed that look at the ideal processing plant size and the maximum distance that the biomass can be from the plant for some lignocellulosic-to-biofuel conversion scenarios. The sugar cane situation is particularly well-understood by the industry, however such detailed knowledge appears to be lacking for many of Australia’s other high-quantity biomass resources. Again, this highlights the importance of considering each biomass and biofuel type in isolation and extreme caution should be used when applying metrics garnered from studies performed overseas. There are usually several workable solutions for any particular biofuel and this is borne out by the diversity of conversion processes, engineering designs and biomass choices seen in the burgeoning industries overseas.

Commercial biofuels from lignocelluloses

Commercial progress is being made toward biofuels from lignocelluloses in Australia.

- Renewable Oil Corp (ROC) is working towards its (and Australia’s) first commercial scale pyrolysis plant (200 tpd wood waste) based on similar plants by Dynamiot in Europe. The plant is expected to be fully commissioned and operational by late 2009. The primary product will be bio-oil however the charcoal by-products have markets and there are plans to develop techniques for extracting chemicals (ie industrial resins, food flavourings, others) from the material(s) at various stages of the process.

- The Proserpine Co-operative Sugar Milling Association Ltd was issued a $12 million grant from the Australian government in 2006 to build a 5000 tpd plant near Proserpine. The plant will utilise a proprietary process known as Suprayield® and will use sugar cane bagasse as a feedstock. Civil work commenced in mid-2007. Although furfural is not a fuel, it can be further processed via cracking and reforming to produce fuels.

- Syngenta partnered with the Queensland University of Technology in 2007 to develop technologies around the efficient and cost effective conversion of sugar cane bagasse to biofuels. The Queensland government has provided funding of $4.6 million for the project which will include the delivery of plant-expressed enzymes.

- Enecon Pty Ltd is actively involved in the development of thermochemical (pyrolysis) technologies licensed from CSIRO. Enecon offers project collaborations to parties wishing to develop a particular technology or a particular biomass conversion process. In 2002, they conducted a comprehensive review (Enecon et al. 2002) of the potential for bioenergy and alcohols from Eucalyptus trees planted as part of the Oil Mallee Project. They also reviewed the development stage of technologies that could convert mallee to liquid fuels. While many environmental benefits were identified for large scale oil mallee plantings, and the use of ethanol to replace petroleum the conversion technologies were not sufficiently advanced to compete with petroleum (crude oil then at $22 bbl). The large amount of international research activity and advances were noted in the study along with the expectation that the technology would be cost effective in the future.

- Ethtec (Ethanol Technologies) is a subsidiary of Willmott Forests Ltd and commenced construction in November 2007 of a pilot scale plant to add value to lignocellulosic residues, including pine, bagasse and other forestry residues. The pilot plant is situated at the NSW Sugar Milling Co-Operative Harwood Mill and Refinery in Northern NSW. Apace Research in conjunction with University of Southern Mississippi, the Tennessee Valley
Authority and the University of New South Wales developed, firstly a laboratory scale, then mini-pilot plant scale to demonstrate the technology. The process is based on acid treatment of lignocellulosics to produce optimal depolymerisation to C5 and C6 sugars that are co-fermented to ethanol.

*Australia has active research and development* aimed at supporting a lignocelluloses-to-biofuels industry although the contribution is fairly modest compared with international activity. The major research programs are summarised below.

- **CSIRO’s Energy Transformed Flagship** has a major program focussing mainly but not exclusively on Australian second generation biofuels research that spans four major work areas:
  - **Sustainable Biomass Production**: Assessing the potential for biomass production systems to support a biomass based energy industry.
  - **Thermochemical Production**: To extract the energy contained in the widest possible range of lignocellulosic materials in a valuable liquid product that can serve as a ‘bio-crude’ using < 1 atmosphere pressure.
  - **Transport Biofuels**: To assess the technological and social drivers in transport fuels use.
  - **Enzymatic Conversion of Australian Biomass**: The improvement of the lignocellulose saccharification steps through discovery of novel enzymes and through protein engineering of existing enzymes.

- The Cooperative Research Centre for Sugar Industry Innovation through Biotechnology has several projects in the area of lignocellulosic ethanol as part of a large program in sugarcane biofactories. They are investigating sugar cane as a biofuels and bioenergy crop (value-adding to sugar production), plastid transformation technologies, value-adding to lignin and several programs investigating biorefinery potential of sugarcane for biobased products such as plastics and chemical industry intermediates; biomass pretreatment methods using salivation.

- The Australian National University in conjunction with the CSIRO’s Energy Transformed Flagship is conducting research in to solar powered biomass gasification technology. They can produce a biofuel from which 30% of its energy content is solar in origin.

- The Sugar Research Institute has projects underway investigating the production of biofuels from sugar cane bagasse. Technologies being investigated include both gasification and fermentation, in addition to looking at novel solvents and capital costs reduction.

- Professor Peter Rogers at University of New South Wales has been active in developing microorganisms that could ferment both 5- and 6-carbon sugars to ethanol simultaneously and is working with Australian company, Ethtec, to produce ethanol at pilot scale.

- **Associate Professor Trevor Stevenson of the Royal Melbourne Institute of Technology (RMIT)** is investigating the expression of cellulose-degrading enzymes in wheat and barley that could be activated after harvesting to assist in the pre-digestion process *in planta*.

- **Thermochemical processing of agroforestry biomass to fuels and bioproducts** has been investigated at laboratory scale in Australia at the University of Melbourne (Butt 2006). A two-stage fast pyrolysis technique has been described that produces furfural (which can be processed to fuels and bioproducts), phenols and cellulose, and separately Eucalyptus oil. The conditions of temperature and oxygen concentration were optimised for each product stream.

- **The Green Chemistry Department at Monash University** is looking at ionic liquids as a medium for the separation of lignocellulosic materials into cellulose, hemicellulose and lignin.

- Microbiogen, based in Sydney, are developing strains of *Saccharomyces cerevisiae* through natural selection (non-GM technology) that can ferment both 5- and 6-carbon sugars to ethanol.
11. Research and development gaps for Australia

In the previous section, Australia’s current research and development activities in lignocellulosic conversion to biofuels were described as modest compared with other developed countries. Here we have built on the framework for research and development that has already been described for biofuels in a recent RIRDC publication (O’Connell et al. 2007b) to outline areas where Australia could benefit from increased research and development in lignocellulosic biofuels while recognising that some of this research is underway as described in the previous chapter.

Table 9 Broad research and development areas in need of increased effort and support for a viable Australian second generation biofuels industry

<table>
<thead>
<tr>
<th>R&amp;D area</th>
<th>Examples of coverage</th>
</tr>
</thead>
</table>
| Lignocellulosic biomass availability and sustainability of harvesting    | - What biomass and how much is available, could it be harvested sustainably, where is it located?  
- What waste streams are available?  
- Which new crops for where?  
- For new biomass crops, what is their potential for weediness and other biodiversity impacts?  
- What won’t we be doing with the land if we use it for biofuel crops? How much can we grow?  
- Water usage impacts.  
- What are the benefits, particularly for the use of less productive land? What effect will carbon trading have on plantations supplying biofuels? |
| Genetic engineering of crops as biomass crops                            | - What is possible in genetic engineering for low water requirement - the ability to thrive in high salinity conditions, rapid growth rates, inactive cellulase enzymes generated in planta to assist downstream processing, and physical characteristics that make harvesting easier and provide high biomass densities?  
- What are the benefits and negatives of genetically engineered non-food biomass crops? What are the risks?  
- What will be the regulatory requirements?                                  |
| Pretreatment and processing technologies for conversion of lignocellulosics to biofuels | - Technologies developed and tailored for conversion of Australian lignocellulose sources such as eucalyptus, acacias and grasses to fuels.  
- At present state of the technology, capital and operating costs for lignocellulosic fuels are high and possibly restricting commercial development. New technology advances directed at smaller infrastructure and lower requirement for pressure vessels, corrosion-proof vessels, electricity plants etc.  
- Efficiency improvement of conversion to fuel especially for enzymatic platform through breakthrough pretreatment or novel enzymes with enhanced activities, and consolidated bioprocessing. Improved thermochemical catalysts of cheaper material with improved tolerance of contaminants.  
- Increased efficiency of syngas conversion by micro-organisms. Improved technology for fractionation of bio-oil. |
| New transport fuels                                                      | - Butanol, hydroxymethylfurfural, methanol, synthetic diesel and ethers are some of the new fuels in the pipeline. What issues will these fuels generate in terms of infrastructure requirements, vehicle performance, tailpipe emissions, environmental impact of spills and cost?  
- What are the barriers to new fuel introduction?                           |
| Life cycle assessments and techno-economic modelling of lignocellulosic conversion in Australia | - Australian life cycle assessments of biomass growth, harvesting, conversion and use of the fuels to determine impacts of cycle under local conditions.  
- Locally based techno-economic modelling to assess the impacts on fuel cost and commercial viability of the industry of different technology choices and advances, and to predict fuel costs, greenhouse gas emissions savings and capacity for petroleum replacement |
| Integrated biorefineries                                                 | - Identify and develop biorefinery product streams that can value-add to the fuel production stream for lignocellulosics. |
12. Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amylose</td>
<td>A linear chain of glucose molecules connected (primarily) by α-1,4-glycosidic linkages.</td>
</tr>
<tr>
<td>Arabinose</td>
<td>A 5-carbon aldose sugar.</td>
</tr>
<tr>
<td>Cellobiase</td>
<td>A β-1,4-glycosidase enzyme that hydrolyses the β-1,4-glycosidic linkage in cellobiose to give two monosaccharide units.</td>
</tr>
<tr>
<td>Cellobiose</td>
<td>A disaccharide of glucose. Two glucose units joined by a β-1,4-glycosidic linkage (an ether bond). See Maltose for a comparison.</td>
</tr>
<tr>
<td>Cellulose</td>
<td>A straight (unbranched) glucose polymer typically containing 7,000 to 15,000 glucose units.</td>
</tr>
<tr>
<td>Dextran</td>
<td>A complex, branched polysaccharide made of many glucose molecules joined into chains of varying lengths (from 10 to 150 kilodaltons).</td>
</tr>
<tr>
<td>Disaccharides</td>
<td>Two monosaccharides covalently linked. Cellobiose, lactose, sucrose and maltose are all examples of disaccharides.</td>
</tr>
<tr>
<td>Endoglycosidase</td>
<td>An enzyme that cleaves a polysaccharide from an internal point. Examples are endoglucosidase, endoglucanase, endoxylanase etc.</td>
</tr>
<tr>
<td>Fructose</td>
<td>Fructose is the sweetest of saccharides. It most commonly exists in the five-membered ring state although it can form six-membered rings as well. It has a long and complex breakdown pathway in the body.</td>
</tr>
<tr>
<td>Glucan</td>
<td>A polysaccharide of D-glucose monomers linked by 1,3- and 1,4-β-glycosidic bonds.</td>
</tr>
<tr>
<td>Glucose</td>
<td>Glucose is the most common 6-carbon sugar. It can be either linear or cyclic.</td>
</tr>
<tr>
<td>Glucoside</td>
<td>A glycoside containing glucose.</td>
</tr>
<tr>
<td>Glucosidase</td>
<td>Any of a class of enzymes that hydrolytically cleave glucosides to give glucose and the corresponding aglycan.</td>
</tr>
<tr>
<td>Glucuronic acid</td>
<td>Exactly the same as glucose, however the 6th carbon is oxidised from an alcohol to a carboxylic acid.</td>
</tr>
<tr>
<td>Glycan</td>
<td>A generic term for any sugar or assembly of sugars, in free form or attached to another molecule, used interchangeably with saccharide or carbohydrate. Ie Galactan is a string of galactose molecules, glucon is a string of glucose molecules.</td>
</tr>
<tr>
<td>Glycoside</td>
<td>Any compound containing a carbohydrate molecule (sugar) convertible, by hydrolytic cleavage, into a sugar and a nonsugar component (aglycone), and named specifically for the sugar contained, as glucoside (glucose), pentoside (pentose), fructoside (fructose), etc.</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>A branched, mixed polysaccharide that, in addition to glucose, can contain a range of sugars including xylose, mannose, galactose, rhamnose, and arabinose. Hemicelluloses contain most of the D-pentose (5-carbon) sugars, and occasionally small amounts of L-sugars as well. Xylose is always the sugar monomer present in the largest amount, but mannuronic acid and galacturonic acid also tend to be present.</td>
</tr>
<tr>
<td>Mannan</td>
<td>A polymer composed of mannose sugars.</td>
</tr>
<tr>
<td>Mannose</td>
<td>A 6-carbon sugar that can exist in linear or cyclic forms.</td>
</tr>
<tr>
<td>Monosaccharides</td>
<td>Simple sugars with multiple hydroxyl groups. Depending upon the number of carbons in the sugar it is known as a triose (3), tetrose (4), pentose (5) or a hexose (6).</td>
</tr>
<tr>
<td>Pectin</td>
<td>A branched polysaccharide that has a backbone of poly-galacturonic acid. In region along the backbone, some of the galacturonic acids are replaced with L-rhamnose. Various neutral sugars such as D-galactose, L-arabinose and D-xylose form side branches from the L-rhamnose regions.</td>
</tr>
<tr>
<td>Reducing End</td>
<td>The end of a glycan where there is no further link through the hydroxyl oxygen that is part of the hemiacetal group.</td>
</tr>
<tr>
<td>(Reducing</td>
<td>Terminus)</td>
</tr>
</tbody>
</table>


| **Rhamnose** | A naturally occurring 6-carbon deoxy sugar. Note the methyl side chain instead of the usual methanol. Occurs in pectins. |
| **Ribose** | A 5-carbon sugar |
| **Sucrose** | A disaccharide of glucose and fructose. Commonly known as table sugar. |
| **tpa** | Tonnes per annum |
| **tpd** | Tonnes per day |
| **Xylan** | Polymer of β-1,4-linked D-xylose molecules with short side chains. |
| **Xylanase** | A class of enzymes that break down the linear polysaccharide xylan (the main polysaccharide in hemicellulose). These enzymes can therefore break down hemicellulose. They are used in the chlorine-free bleaching of wood pulp and composting. The xylanase gene(s) from the shiitake mushroom were recently expressed in yeast. |
| **Xylobiose** | A disaccharide of xylose with each xylose being in pyranose (6 membered ring containing one ring-oxygen) ring forms. |
| **Xylose** | A five carbon sugar that is found in hemicellulose. |
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VIEWLS 2005 Shift gear to biofuels. Final report of the VIEWLS (Clear Views on Clean Fuels) project.


Lignocellulose is a collective term describing lignin, cellulose and hemicellulose that are components of plants and wood. Cellulose and hemicellulose are polymers of sugars that are among the most abundant natural polymers on earth and have the potential to supply a considerable proportion of low cost transport fuels if cost effective conversion processes are available.

This report outlines current conversion technologies of lignocellulosic materials to second generation biofuels. It considers the techno-economic aspects of the conversion technologies at a commercial scale and raises some fundamental issues arising from the use of lignocellulose such as its potential role in greenhouse gas mitigation and sustainable harvesting. The various transport fuels that can be obtained from these processes are also briefly described.

Australian and considerable international efforts in research, development and commercialisation of second generation biofuels production technologies have been summarised and a listing of the research and development needed to assist the establishment of a second generation industry in Australia is also presented.

Most of the information we produce can be downloaded for free from our website: www.rirdc.gov.au and books can be purchased online or by phoning 02 6271 4100.

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