



TamutechConsultancy

## Literature Review: State of the Art in Biorefinery Development (NFC 07/008)



A Report Prepared For the National Non Food Crops Centre  
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# 1. Report Context

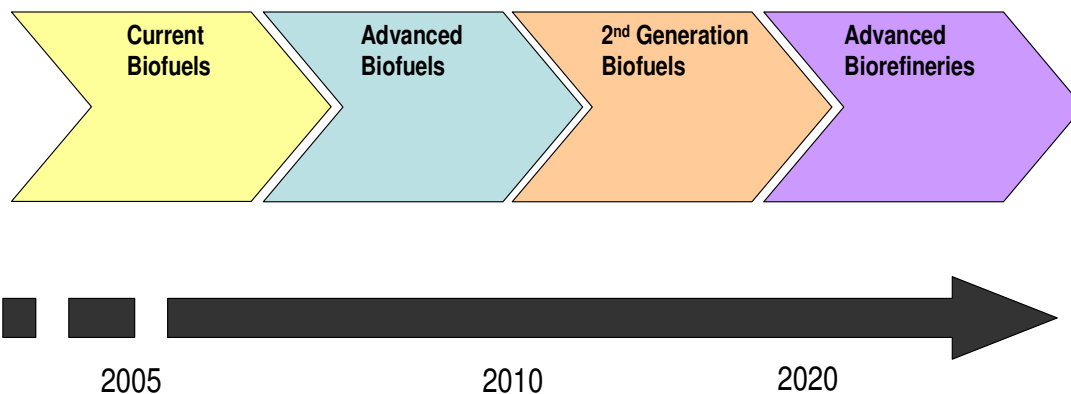
This report has been prepared by Tamutech Consultancy as part of the NNFFC project NFC 07/008 entitled “Mapping the Development of UK Biorefinery Complexes”. The overall aim of this project is to map out the development of two different biorefinery configurations within a UK context. This technology roadmap will help define and prioritise the multiple pathways possible for the implementation of UK biorefineries, identify the key technical barriers and the opportunities for technical innovation. This activity is intended to assist the NNFFC in developing a coherent strategy for engaging UK stakeholders and facilitating the development of biorefinery development.

The aim of this Literature Review is to provide an accurate picture of the current global landscape for biorefinery development and provide data for the mapping process. More specifically is to identify the:

- current commercial status of global biorefinery implementation
- technology barriers to commercialisation
- feedstock options within the UK
- UK actors in biorefinery development
- opportunities for transfer of best practise

It is likely that the commercial implementation of large complex advanced biorefineries will occur through incremental growth of existing biofuel infrastructure. Conventional biofuel facilities will become more sophisticated in exploiting lower value biomass streams for energy production and developing broader product portfolios to add increased value. In the medium term, second generation biofuels facilities utilising advantaged low cost lignocellulosic raw materials will be implemented to provide biofuels with even greater carbon dioxide reduction potential. In the longer term these developments will lead to the implementation of advanced biorefinery complexes.

**Figure 1 Timeline for Biorefinery Implementation**



Modelled on current oil refinery and petrochemical complexes, advanced biorefineries will maximise energy efficiencies and minimise production costs by fully exploiting highly integrated operations, huge economies of scale and whole-crop utilisation principles to produce a wide range of biofuels, renewable chemicals, biomaterials and renewable energy.

This literature review report is structured chronologically to reflect this transition towards biorefinery development and after covering UK feedstock options begins by addressing the relevant technology developments in conventional biofuel facilities. A summary of key findings is included at the end of the report.

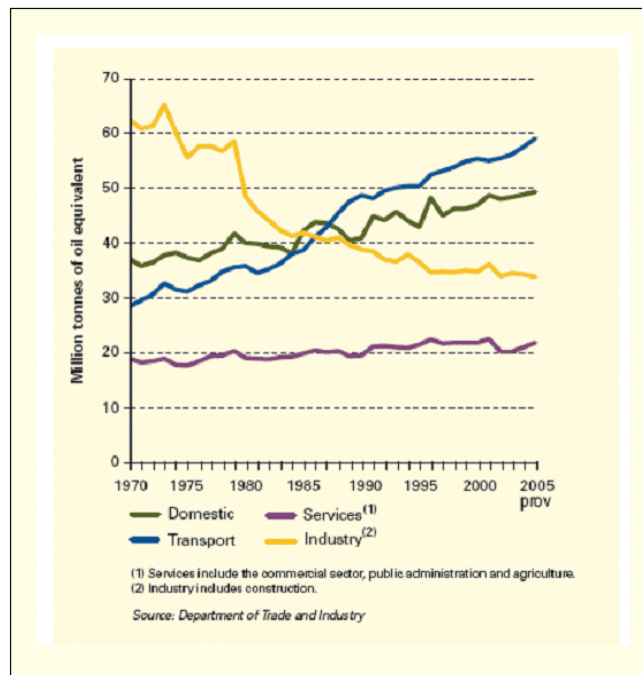
## 2. Introduction

The fossil fuels; oil, coal and natural gas are the primary energy sources that have powered modern industrial civilisation. In 2005 the global consumption of these resources was the equivalent of over 9 billion tonnes of crude oil [1]. The demand for these resources is set to increase even further given the dramatic economic expansion occurring in countries such as China and India. However, this trend is not sustainable. Fossil fuels, by their very nature are finite and in the case of oil we are rapidly approaching the point at which this resource is being consumed faster than it can be recovered from the ground. Recent times have seen the major oil companies fail to fully replenish their oil stock reserves and the tightening oil supply and demand balance has resulted in volatile crude oil prices. Energy security is now a primary concern for countries such as the United States that are primarily reliant on imported crude oil to meet their domestic energy requirements. In the UK, North Sea reserves are now becoming depleted. By 2020, the UK could be dependent on imports for three-quarters of its total primary energy needs. In addition to the issue of global energy security, it is now almost universally accepted that continued use of fossil resources at current rates will result in irrevocable damage to the environment. The effects of global warming caused by increased levels of greenhouse gases in the atmosphere are now evident.

To address these critical issues of climate change and energy security requires a concerted and multi-faceted approach. National and international governments have developed strategies and implemented far reaching policies to reduce demand for fossil hydrocarbon resources and stimulate low-carbon energy resource diversification. The European commission has recently released proposals for a common energy policy which calls for the adoption of binding targets on 20% green house gas reductions by 2020 [2]. The DTI “Energy White Paper”, released in 2003, set out the UK’s government policy on renewable energy and confirmed the 2010 target for 10% of all electricity generation to come from renewable sources [3]. Longer term targets of 20% renewable electricity generation by 2020 and a 60% cut in green house gas emissions by 2050 were described. A major element in the delivery of the low carbon economy is the innovative development of sustainable routes to efficiently utilise the world’s abundant biomass resources for energy, fuels, chemicals and materials production. In 2005, the European Commission released the Biomass Action Plan which builds upon existing directives in the Electricity, Heat and Transport sectors and aims to increase biomass utilisation from its current value of 4% of total EU energy requirements [4]. In the UK, the government commissioned a Biomass Task Force to identify and provide solutions to the obstacles that prevent further contribution of biomass resources to the attainment of targets on renewable energy [5]. In response to this study, a joint DTI/DEFRA biomass action plan was published last year [6].

The transport sector is the largest single energy consumer in the UK [7] and in 2005 contributed some 22% of the total greenhouse gas emissions (556 million tonnes of carbon equivalents) [8]. Figure 2 shows the relative contribution of each sector to UK energy consumption [7]. Unlike electricity and heat production, fuel diversification is somewhat constrained in the transport sector and this could present significant security of supply issues in the longer term as conventional petroleum supplies tighten. It is anticipated that the internal combustion engine will remain the dominant technology in the road transport sector and potential alternatives such as hydrogen fuel cell technology may not have significant market penetration until at least 2030. Biomass is currently the only renewable energy source that has the potential to produce significant volumes of

**Figure 2 UK Energy Consumption by Sector [7]**



transport fuels that have equivalent properties to conventional fuels and will require relatively little disruption to the existing supply infrastructure. The technology to produce biofuels such as ethanol and biodiesel is well established and utilises readily available commodity raw materials such as wheat, corn, sugar beet and oilseed rape. Countries such as Brazil and the United States have had large biofuels industries based on fermentation ethanol for many years. However, the relatively high cost of these biofuels dictates that subsidies are necessary if they are to compete with petroleum derived fuels. Emerging biofuel markets are now demonstrating tremendous growth rates and global production is estimated to exceed 35 billion litres per year. Driven by ambitious

production targets and facilitated by the implementation of fiscal incentives, regulatory infrastructures and other government support mechanisms, the biofuel industry is demonstrating tremendous growth. This trend is set to continue; the US president called for national biofuel production targets to be expanded to 35 billion gallons by 2017 so that a 20% reduction in gasoline consumption could be achieved over the next ten years [9]. In an extension of the biofuels targets set in 2003, the European Commission has recently proposed that 10% of all EU transport fuels be produced from biofuels by 2020 [10]. In addition to the existing tax derogation on biofuels, the UK government introduced a renewable transport fuels obligation which mandated that 5% (energy basis) of all fuels sold at the pump should of a renewable origin by 2010 [11]. These policies have successfully catalysed the development of an indigenous UK biofuels industry. In 2005, biofuels contributed some 0.24% of the total road fuel sales and the greater majority of the 118 million litres sold was imported into the UK. In contrast, in 2006 biodiesel capacity alone was estimated to be 500 million litres and bioethanol production is planned to commence in 2007 at a number of new facilities. The UK now has at least 15 ethanol and biodiesel production facilities either in operation, being constructed or at the planning stage with a combined biofuels capacity potentially exceeding 2 million tonnes.

Until recently biofuels markets were dominated by companies and cooperatives in the food and agricultural sectors. Now, big oil companies are developing strategic business activities in the area and investing significant capital in new biofuels infrastructure. Oil companies such as Neste, Total, BP and Shell are forming strategic alliances with both feedstock and technology providers to develop the next generation of biofuels. Car manufacturers are also now marketing vehicles that will run on higher amounts of biofuels in biofuel/petrol blends than currently possible in conventional cars. Saab and Ford have developed E85 flexible fuel vehicles that will run off a petrol/bioethanol mixture containing up to 85% bioethanol.

The two predominant commercial biofuels are bioethanol and biodiesel. Bioethanol is a biofuel substitute for petrol and can be used as a 5% blend in conventional vehicles as certified by the EU specification EN228. Bioethanol is produced via the fermentation of carbohydrate sugars derived from commodity agricultural products such as sugar cane, corn, wheat and sugar beet. Bioethanol production for transport fuel use is well established in countries such as Brazil, which implemented ambitious bioethanol programmes in the 1970's to reduce reliance on imported petroleum feedstocks. The United States, now the world's biggest producer of bioethanol, has for many years subsidised the bioethanol industry to help develop large production capability and reduce dependence on petroleum imports. In the US, bioethanol production is based on corn starch whilst the rapidly expanding bioethanol industry in Europe is predominantly based on cereals and sugar beet feedstocks.

Biodiesel, a substitute for mineral oil diesel, is generally utilized as a 5% (B5) blend in Europe and is covered by the EU specification EN14214. Higher blends of biodiesel can be utilised but this requires some vehicle modification. Biodiesel is a mixture of fatty acid methyl esters and is produced by the transesterification of vegetable oils with methanol. The major Biodiesel feedstocks are the commodity oil crops; oilseed rape, soy, sunflower and palm. Both bioethanol and biodiesel industries are well established and growing rapidly. International markets have developed and advantaged producers in tropical climates are gearing up production to export biofuels to Europe, the US and China. Conventional biofuels have made, and will continue to make, a significant contribution to reducing greenhouse gas emissions in the transport fuel sector. However, these conventional biofuels contain a number intrinsic limitations which may ultimately reduce their role to that of a transitory solution for reducing transport greenhouse gas emissions until more advanced biofuel technologies options can be developed and implemented. These issues are summarised below:

- Production technology for both bioethanol and biodiesel is mature and limited scope exists to provide a step-change improvement in the economics of these processes.
- Conventional biofuels utilise arable crops such as oilseed rape, cereals and sugar beet. Such food crops are relatively expensive and can display price volatility as supply and demand tightens. Crops in tropical climates such as sugar cane and palm oil present alternative lower cost feedstocks but there are serious issues concerning the environmental impact of a large scale expansion in the planting of such crops.
- The capacity to meet the rapidly growing market demands for bioethanol and biodiesel will be ultimately limited by the availability of arable land and competition for feedstocks from the food and feed industries.
- Arable crops, such as cereals and oilseed rape, require significant inputs of materials such as fertilisers, pesticides and herbicides. Life cycle analysis has demonstrated that the use of these inputs negatively impacts upon the overall greenhouse gas savings achievable with conventional biofuels.
- Bioethanol and biodiesel do not represent the optimum transport fuels. The differences in chemical composition, physical properties and energy content of these materials when compared to their fossil fuel counterparts present a number of issues that either limit the amount of biofuel that can be blended with conventional fuels or add complexity and cost to the supply chain infrastructure.

Ideally the optimum biofuel would utilise a low cost, high yielding renewable non-food feedstock that delivered the highest amount of greenhouse gas reductions, had a minimal environmental footprint and similar chemical and physical properties to existing petroleum fuels to ensure seamless substitution into the existing fuel supply infrastructure. There are a number of advanced biofuels in development that could address some of the drawbacks of conventional systems. BP has recently championed the virtues of biobutanol as a biofuel [12]. Biobutanol has many advantages over ethanol; it has a higher energy content being similar to that of petrol, it is less corrosive, less hygroscopic and can be blended to higher levels in petrol without the necessity for engine modification. BP is collaborating with DuPont and British Sugar and plans to demonstrate commercial scale production at the soon to be completed British Sugar ethanol plant at Wissington. Biobutanol is conventionally produced by carbohydrate fermentation although the currently available technology is limited and the process is unlikely to be commercially feasible at this moment in time. BP is currently collaborating with DuPont to develop improved fermentation technology for this route [12]. The DTI has also recently funded Green Biologics and EKB to develop advanced microbial process technology for cost competitive biobutanol production [13].

D1 Oils are active in the development of jatropha, a plant oil crop that can be used for biodiesel production. Jatropha is an oil bearing tree that grows in Africa, India and South East Asia. D1 Oils has successfully demonstrated that biodiesel meeting the EN14214 standard can be produced on a commercial scale using this feedstock [14]. Jatropha is drought resistant, can be grown on poor quality soils and is reported to have a high yield of oil (2.2 -2.7 tonnes per hectare). BP is also funding development work in India on the cultivation of jatropha as a biodiesel crop [15].

There are a number of other potential biofuel systems that address the majority of the issues associated with conventional biofuels but the technology required to deliver these so called “second generation” biofuels is complex, costly and not yet demonstrated at a commercial scale. Huge amounts of research funding is being directed towards this area and commercialisation of both second generation ethanol and biodiesel is likely to occur over the next few years. These advanced biofuel systems utilise adventitious low-cost lignocellulosic biomass feedstocks. Lignocellulosic ethanol is produced via sugars derived from the cellulose and hemi-cellulose polysaccharides present in biomass such as wood, agricultural residues and municipal waste. Synthetic diesel can be derived from biomass utilising gasification and Fischer-Tropsch technology, both processes well known in the refining and petrochemical industries. The resultant synthetic diesel, known as BTL Diesel after “Biomass to Liquids”, is chemically similar to state-of-the-art low sulphur synthetics diesels produced from natural gas or coal. Numerous life cycle analysis studies have shown that second generation biofuels can deliver increased greenhouse gas savings compared to traditional biofuels [16, 17].

The majority of the technology development for lignocellulosic ethanol is taking place in the US, with Europe taking the lead in the development of high temperature gasification and BTL technology development. It should be noted that the amount of concerted activity in both of these important areas in the UK is small and localised in only a few academic centres.

Although significant biofuel production capacity now exists and considerable technology development is being performed to develop improved biofuels, a radical step-change in the manufacture of plant-derived products remains elusive. Such a step-change is necessary to significantly increase the pace at which the UK transitions from an economy predominantly supported by fossil fuels to one utilising a more diverse energy and materials resource. One concept gaining momentum that could deliver such a radical-step change in the economics of biomass derived products is that of the biorefinery. The biorefinery concept describes a large highly-integrated processing complex that utilises a wide range of cost-effective biomass feedstock's to produce power, biofuels, renewable chemicals and biomaterials [18,19,20]. As with a modern day oil refinery, energy savings are maximised through process integration synergies and economies of scale are exploited for the cost effective co-production of chemical intermediates (platform chemicals). The Biorefinery will utilise a range of low cost biomass feedstocks which will undergo fractionation into lignin, hemicellulose, cellulose and starch components for processing into a suite of valuable products. The carbohydrate components will be converted utilising a combination of state-of-the-art biological and chemical process technologies. As practised in oil refineries, the efficient management of complex flows of materials and energy in the biorefinery complex will be paramount to utilise every element of the raw material feedstock and maximise integration benefits for improved energy savings and reduced processing costs.

In principle, current bioethanol and biodiesel production facilities can be considered as rudimentary biorefineries in that they produce a range of other valuable co-products in addition to the primary biofuel product. However, future advanced biorefineries will employ large economies of scale and advanced biofuels production technology will form the backbone of these large complexes. The realisation of advanced biorefineries will require a substantial and coordinated multidisciplinary approach to the development of essential enabling technologies. Large biorefinery complexes are a long term goal and many diverse challenges remain before they can become a commercial reality. Due to the large capital investment required for a stand-alone biorefinery complex and the immature status of its enabling technology, biorefinery development will likely occur through incremental advances in the existing biofuel infrastructure.

## 3. Biomass Feedstocks

### 3.1 Biomass Resources

Plant biomass represents a huge resource of mostly untapped sustainable carbon. Biomass can be described as material produced by the growth of micro-organisms, plants or animals which can be sourced directly or sourced from a wide variety of process streams from the food, feed and fibre industries. Plant biomass is predominantly composed of carbohydrates with smaller amounts of lignin, oils, proteins and other molecules arising from secondary plant metabolites. A large amount of the earth's biomass resides in tropical rainforests and marine plants. The vast majority of the plant biomass resource is lignocellulosic, the cellulose, hemicellulose and lignin being the major components of plant cell walls.

**Table 1 Important Sources of Biomass**

Sector	Biomass	Examples
Agriculture	Oil, Starch, Sugar Crops	Oilseed Rape, Cereals, Maize, Sugar Cane
	Energy Crops	Miscanthus, Switch Grass, Short Rotation Coppice
	Wastes	Cereal Straw, Rice Straw, Corn Stover, Sugarcane bagasse, livestock manure
Forestry	Hardwood, Softwood	
	Wood by-products	Chips, thinning
Industry	Various Biobased Wastes	Waste wood, sawdust, dried distillers grain, black liquor
Wastes	Green Wastes	Prunings, grass cuttings
	Municipal Solid Wastes	Paper, cardboard

The global reserves of sustainable biomass are reported to be in the region of 170 to 200 billion tonnes of oven dried material (odt) of which only around 6 billion tonnes is currently utilised [21,22]. A recent study funded by the US Department of Energy has estimated that by 2030 the US could potentially produce 1.3 billion odt of biomass feedstock per year without impacting on its ability to produce sufficient domestic food and feed [23]. On an energy basis, this amount of biomass is roughly equivalent to 440 million tonnes of crude oil or 3 billion equivalent barrels of crude oil per annum ( $3.2 \times 10^9$  boe). To put this biomass resource into context, the US consumed  $5.6 \times 10^9$  boe in 2005

over 60% of which was imported [24]. In a similar exercise it has been calculated that the EU could potentially produce 185 million odt of biomass by 2010 in a sustainable manner without impacting on domestic food production [25].

A diverse range of biomass streams are produced not only from agriculture but also as waste streams from a wide range of industrial operations. Some important sources of readily available biomass are detailed in Table 1.

### **3.2 Land Availability for Arable Feedstocks**

Being derived from arable crops, European bioethanol and biodiesel producers can take advantage of long established supply chains and commodity traded feedstocks. The EU-25 has a total area of 400 million hectares with over 95 million hectares of this being arable land [26]. In addition, there is a considerable amount of arable land designated as set-aside (6 million hectares in 2005). CAP reform has promoted the growth of crops for industrial purposes by decoupling income support, allowing energy crops to be grown on set-aside land and introducing the energy crops payment scheme. To meet the EU target of 5.75% biofuel substitution in 2010 through indigenous production (some 24 million tonnes) would require 16-18 million hectares of agricultural land. Improvements in agriculture and further liberalization of markets such as sugar reform are likely to increase the potential land available for biofuel crops. It has been estimated that there will be 33 million hectares of arable land available for non-food crops in 2040 [26].

In 2005, the total agricultural area under arable cultivation in the UK was 4.4 million hectares with a further 0.6 million hectares of set aside land [27]. Wheat is the predominant crop grown in the UK. It is generally accepted that there is more than sufficient arable land available to meet the UK target of 5% biofuel substitution through domestic production without impacting on food production [28]. Particularly if oilseed rape is planted on set-aside for biodiesel production and the UK current wheat export (2.5 - 3 million tonnes) is used for bioethanol production. However, more ambitious targets are likely to require the import of biofuels or biofuel feedstocks into the UK.

UK feedstocks for bioethanol production are wheat and sugar beet whilst biodiesel production utilises oilseed rape, imported palm oil, imported soybean oil, animal fats and waste cooking oils. The volumes of these arable crops grown in the UK for food, feed and non-food sectors are shown in Table 2 along with the potential biofuel yields of each crop.

**Table 2 UK Arable Biofuel Crops**

	Wheat	Sugar Beet	OSR
<b>Area cultivated (M ha)</b>	1.87	0.15	0.59*
<b>Yield (tonnes/ha)</b>	8	57	3.2
<b>Biofuel Yield (tonnes/ha)</b>	2.2 - 3	4	1 -1.2

Adapted from reference [29]

OSR = Oilseed Rape

\*Defra state that OSR area cultivated as energy crop in 2005 was 93,000ha [30]

### **3. 3 Current Bioethanol Feedstocks: Global Perspective**

**United States:** The US has recently overtaken Brazil as the largest global producer of bioethanol. The starch used for fermentation is derived from corn. In 2006, two billion bushels of corn, some 20% of the total crop, was converted into nearly 15 million tonnes of ethanol in 97 production plants [31, 32]. This output represents a threefold increase in volume since 2001 and there are currently 33 new ethanol production facilities under construction which will add a further 5.7 million tonnes of ethanol capacity. There is some debate about the maximum amount of corn that US agriculture can sustainably supply without negatively impacting on food, feed and export markets. The National Corn Growers Association suggests that US agriculture could potentially triple its current bioethanol output by 2015 provided that corn yield increases are maintained, biotechnology delivers higher starch yielding varieties and process conversion efficiency is increased [33]. Dried distillers grain, a significant by-product of ethanol production from corn, is sold into animal feed markets as a high protein supplement. Corn production also produces considerable volumes of corn stover residue, the waste stalks remaining in the field. It has been estimated that this presents a biomass resource of over 150 million tonnes

**Brazil:** The second biggest producer after the US and the world's biggest exporter of bioethanol. Nearly 13 million tonnes of bioethanol was produced in 2005 from 6 million hectares of sugarcane plantations. Sugarcane is a more efficient source of fermentable sugars than corn, sugarbeet or cereals. Sugar in the form of sucrose is directly extracted from the plant and fermented. Being a tropical grass species the yields of sugar are very high and at around 7 tonnes of ethanol per hectare, twice that produced by corn or wheat. It is due to this raw feedstock advantage that Brazilian bioethanol enjoys the lowest bioethanol production cost and is currently competitive with petrol even in the absence of state subsidies. Brazil initiated its national ethanol programme in 1975 to

offset reliance on imported petrol and has recently begun aggressively expanding its sugarcane planting and ethanol production to meet both domestic demand catalysed by large sales in flexifuel vehicles and burgeoning export demand. Bagasse is the fibrous residue remaining after sugar extraction from the plant and represents a huge biomass resource for Brazil (> 50 million tonnes). Modern bioethanol plants utilise bagasse as an energy source to provide power and heat for the process and also export excess electricity into the grid.

**China:** The third largest producer of bioethanol with over 1 million tonnes of capacity utilising corn, cassava and rice as starch feedstocks [34].

**Europe:** European bioethanol production has shown tremendous growth over the last few years. The production capacity in 2006 was of the order of 1.2 million tonnes, a 70% increase from the previous year. The major producing countries are Germany (340,000T), Spain (320,000T), France (200,000T) and Sweden (110,000T) [35]. The predominant starch feedstock is wheat and barley although sugar beet contributes to a significant amount of French bioethanol production. In France and Spain the majority of the bioethanol is converted into ethyl tertiary butyl ether prior to blending with petrol. Sweden utilises a range of feedstocks for bioethanol production including sulphite pulp liquor, corn and wine alcohol.

#### **3.4 Current Biodiesel Feedstocks: Global Perspective**

In 2003 the worldwide production of soybean oil, palm oil, sunflower oil and rapeseed oil exceeded 80 million tonnes most of which was targeted for food, feed and oleochemical markets. Biodiesel represents a rapidly growing market for these oil crops and this sector is forecast to consume some 22 million tonnes of vegetable oils in 2007 [36].

**Europe:** is the largest producer of biodiesel utilising predominantly rapeseed oil as the feedstock. Oilseed rape (OSR) grows well in temperate climates and due to its relatively low levels of highly unsaturated fatty acid groups in the oil it is considered to be the optimum vegetable oil crop for biodiesel. EU OSR production in 2005 was around 15 million tonnes and forecasts suggest that 2010 production could be in the region of 18 to 23 million tonnes [37]. Defra reports that UK OSR production in 2006 was 1.87 million tonnes [38].

Biodiesel production capacity in the EU currently stands at just over 6 million tonnes. There are in the region of 120 plants in Europe in 20 different countries mostly located in Germany, France Austria, Italy and Sweden [38]. Germany is by far the largest producer with 2.68 million tonnes of capacity. The UK was reported as having 0.5 million tonnes of capacity in 2006 [39]. If all the UK biodiesel plants currently in planning were successfully implemented than UK production capacity would exceed 1 million tonnes.

**America:** The United States, Argentina and Brazil are the largest producers of soybean, the largest volume oilseed crop. The United States domestic market for biodiesel, which utilises soybean oil, is rapidly expanding. In 2004 the biodiesel production capacity was 25 million gallons by the end of 2006 there were 105 production facilities with a combined capacity of 864 million gallons [40, 41]. Brazil is also rapidly expanding its own biodiesel production capability. Feedstocks include soybean, castor-oil bean and palm oil. Biodiesel production is seen as a saviour to the ailing soybean market. However, increasing soybean production in Brazil is also thought to be culpable for the continued destruction/removal of Amazonian forests.

**South East Asia:** Increased palm oil production in South East Asia is now being directed towards biodiesel markets with the majority targeted at Europe. Oil palm gives very high yields of 5 tones per hectare (T/ha) relative to oilseed crops such as soybean (0.4 T/ha), sunflower (0.8 T/ha) and oilseed rape (1.1 T/ha). For this reason palm oil has historically been cheaper than rapeseed oil by some \$100-200/tonne. Relative to other oil crops, palm oil contains high levels of saturated palmitic acids. For this reason it must be blended with other vegetable oils to meet EU biodiesel specifications. The two largest producers of palm oil, Malaysia and Indonesia have ambitions to be large biodiesel producers [42, 43]. Malaysia has approved licenses for 52 production facilities with a combined biodiesel capacity of 5 million tonnes.

### **3.5 Drivers for Non-Food Feedstocks**

It is widely accepted that indigenous biofuel production can meet the 5% target for biofuel substitution by 2010 [28] and provide greenhouse gas savings equivalent to the removal of one million cars of UK roads [44]. However, there are limitations to the use of arable based crops for biofuel feedstocks. Many years of plant breeding and agronomy improvements have resulted in a steady increase in the yields of crops such as wheat and oilseed rape. However, the biofuel yields of these crops on a per hectare basis are still relatively low. This fact, coupled with the relatively small amount of available arable land in the UK, suggests that achieving biofuel substitution rates of 10% by 2020, as recently agreed by EU members, will be difficult to attain with domestic production alone.

This shortfall in domestic biofuel production could be supplemented with either biofuel or biofuel feedstock from countries such as Brazil or Malaysia that benefit from the very high sugar and oil yields achievable with tropical plants. However, the rapid expansion of biofuel crops in Brazil and South East Asia has been linked to increasing rates of deforestation. Converting rainforests and grasslands to cultivated land not only removes valuable habitat but also results in a large loss of soil carbon to the atmosphere. This effect may well negate any of the beneficial greenhouse gas reductions associated with the biofuel crops grown on such land [45]. These issues concerning the sustainability of biofuel feedstocks are attracting considerable focus. A recent plan to convert a UK

power station to palm oil fuel was cancelled after a sustainable supply of raw material could not be guaranteed [46]. Governments are now assessing how feedstock sustainability can be incorporated into future biofuel policy. Current UK biofuel policy does not discriminate against any differences in the carbon intensity of the biofuel. Government has committed to developing such sustainability accreditation systems for piloting during the RTFO reporting period [47]. To assist in this matter, the Low Carbon Vehicle Partnership is developing a carbon certification system to provide assurance on individual biofuels against a number of sustainability criteria [48].

Numerous “well to wheels” studies have demonstrated that biofuels derived from oilseed rape, wheat and sugarbeet offer greenhouse gas savings over conventional fossil fuels [16, 17, 49]. Such greenhouse gas savings are intrinsically limited due to the high inputs required for the cultivation of these arable crops. Such inputs, particularly nitrogen based fertilisers, require considerable fossil derived energy to manufacture and hence reduce the potential carbon benefits of the final biofuel.

Raw materials represent a considerable percentage of the production costs for biodiesel and bioethanol. Cereals and oilseed rape, being essentially food crops, are relatively expensive for transport fuel feedstocks. In the absence of subsidies only biofuels using advantaged feedstocks, such as Brazilian bioethanol and biodiesel produced from waste cooking oils, are competitive with petrol and diesel at current crude oil prices. Grain and oilseed prices are now experiencing high prices due to the huge demand generated by the rapidly expanding biofuels markets and competition from the food sector. Recently rapeseed oil prices have risen dramatically compared to other vegetable oils and palm oil, historically the cheapest oil feedstock reached a eight year high of \$620/tonne in early 2007 [50]. Similarly, corn prices in the United States have hit a ten year high in early January 2007 [51].

Raw material costs can be reduced by developing higher yielding wheat and oilseed rape crops that perform better under low input regimes. In the longer term, genetically modified crops delivering high yields of starch and oils with compositions specifically tailored for end industrial applications could become a commercial reality. For the foreseeable future however, it is clear that the use of arable food crops for biofuels production presents a relatively expensive option for greenhouse gas mitigation in the transport sector. In contrast, lignocellulosic biomass offers the potential of biofuels with greatly improved greenhouse gas reduction capacity at lower cost.

### **3.6 Lignocellulosic Feedstocks**

The use of lignocellulosic biomass as a raw material for biofuels production could potentially resolve many of the issues associated with the use of conventional arable crops. It is an abundant, potentially cheap source of carbohydrates and is available from a great many sources (Table 1). When cultivated as an energy crop, significantly higher

yields of biofuel per hectare can be achieved and relatively little inputs are required. It is for this reason that significant government and industrial research funding is being directed towards the development and demonstration of process technologies that can effectively utilise lignocellulosic biomass to produce the so-called “2<sup>nd</sup> generation biofuels”. First generation biofuels utilising arable crops are being recognised as an interim solution to greenhouse gas reduction for the transport sector until improved lignocellulosic derived biofuels become commercially viable. The implementation of these advanced biofuels will accelerate when government policies directly correlate the fiscal incentives available with the greenhouse gas reduction capability of the biofuel.

At present second generation biofuels only offer the potential of being cost competitive with fossil derived fuels. A number of significant technological barriers remain to be resolved before these benefits can be realised. A number of these challenges can be related to the resilient or “recalcitrant” nature of the biomass raw material. To explore this in more detail it is important to consider the structure and chemistry of lignocellulosic biomass.

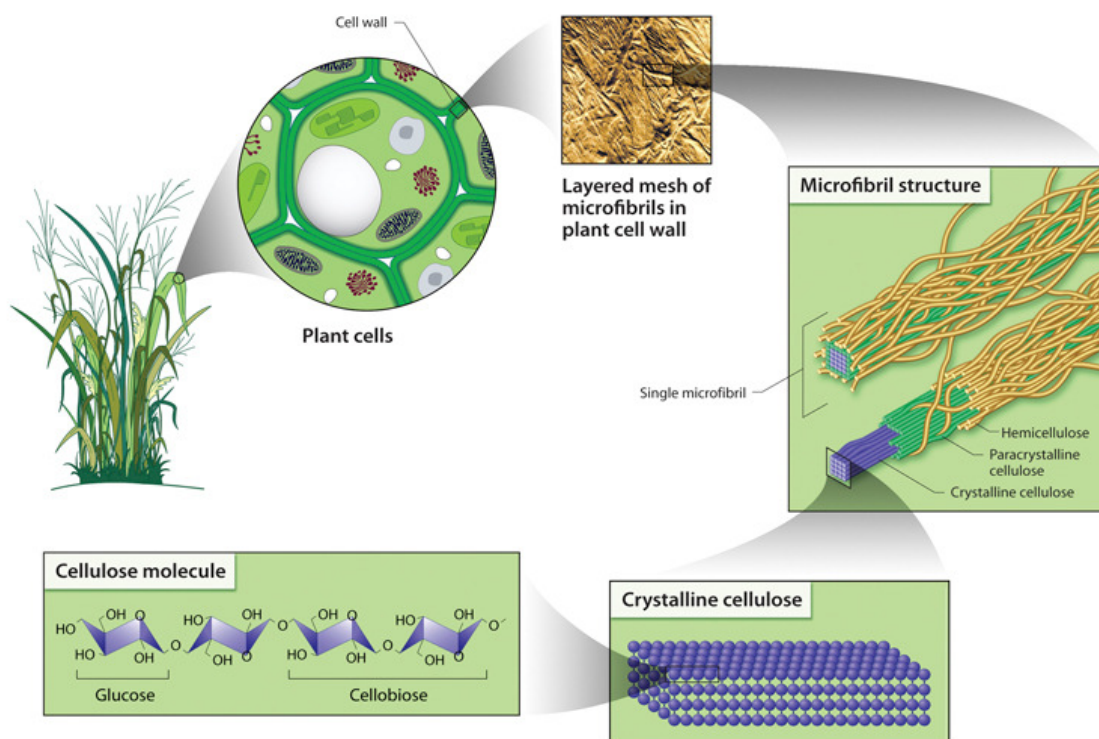
### **3.6.1 Chemistry of Lignocellulosic Biomass**

As discussed in section 3.1 the greater majority of the globally available biomass consists of lignocellulosic material. Lignocellulosic material contains cellulose, hemicellulose and lignin along with smaller amounts of other material such as proteins, minerals and secondary metabolites. The amounts of lignin, cellulose and hemicellulose can vary depending on the biomass source (Table 3).

**Table 3. Composition of Lignocellulosic Biomass Composition**

Component	Percentage %
Cellulose	30-50
Hemicellulose	15-30
Lignin	10-25

Both cellulose and hemicellulose are polysaccharides. Cellulose is a linear crystalline polymer containing glucose sugar monomer units. Cellulose polymer chains contain 7000 – 15,000 such monomeric units and are of the order of 100 – 400,000 nanometres long. As shown in Figure 2, these chains are joined together through hydrogen bonds to form microfibrils of 2-20 nanometre diameter. Due to the strength of the specific bonds ( $\beta 1 \rightarrow 4$  glycosidic bonds) between the monomer sugar units, cellulose is difficult to break down into its constituent sugars through hydrolysis. There are a relatively small number of bacteria systems in nature which can break down cellulose into sugars, examples of these include such the bacteria present in the stomach lining of ruminants and certain fungi. These bacteria contain cellulose enzymes which hydrolyse the cellulose.

**Figure 3 Structure of Cellulose**

(Graphic source: Genome Management Information System, Oak Ridge National Laboratory <http://genomics.energy.gov>.)

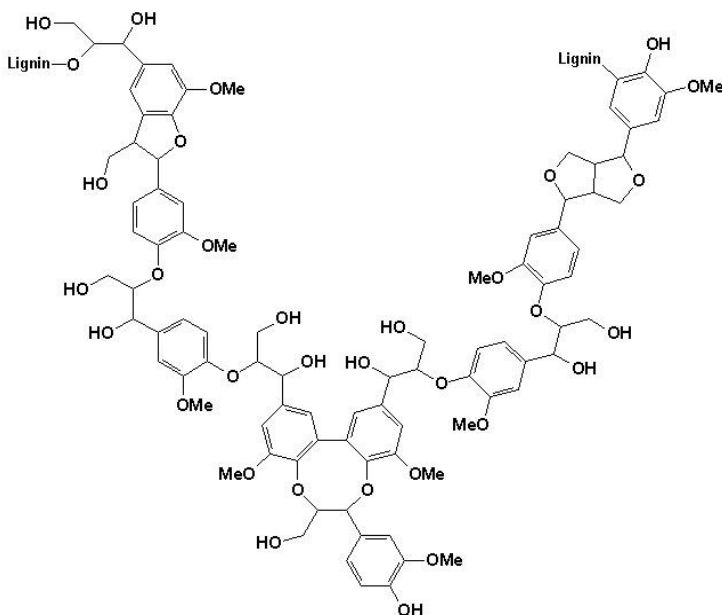
In contrast to cellulose, hemicellulose is a highly branched amorphous polymer that is readily hydrolysed by weak acids, bases and a wide variety of enzymes. Hemicellulose is a heteropolymer being composed of both six carbon sugars (glucose, mannose and galactose) and five carbon sugars (xylose and arabinose). The chain lengths of hemicellulose polymers are much shorter than those of cellulose being about 200 monomer units in length.

Lignin is a large complex non-carbohydrate mononuclear aromatic polymer containing both phenyl propane and methoxy groups (Figure 4). The lignin polymer contains a variety of substructures which repeat in a random fashion and are linked by a variety of different functional groups. The nature of these linkages is dependent on the lignocellulose source. Lignin encrusts the plant cells, cementing them together and strengthening the entire plant. Lignin provides robustness to the plant and is only degradable by a few organisms. Lignin contents vary depending on the plant source; perennial grasses such as switchgrass contains relatively low levels of lignin whilst woody biomass contains high levels of lignin.

In plant cell walls, the hemicellulose and lignin associate with the cellulose microfibrils to provide strength and resistance to biological, chemical and physical attack.

There are two main process routes under development to convert lignocellulosic material to liquid biofuels. The first involves the extraction of the fermentable sugars from the lignocellulosic biomass and conversion of these to bioethanol. The second route is to

**Figure 4 Lignin Sub Structure**



use the lignocellulosic material as a source of renewable carbon and gasify it at high temperatures to produce synthesis gas which can then be converted into hydrocarbons using known process chemistry. These two different approaches are discussed in sections 5 and 6.

Lignocellulosic materials have long been known as a potential source of low cost sugars however, the plant wall structure presents a very effective barrier to accessing these valuable structural units. To access the cellulose sugars the plant cell wall structure must be deconstructed. Forcing conditions such as high temperatures or strong chemicals are required to break the linkages in lignocellulose so that hydrolysing agents can access the cellulose. A number of pretreatment technologies have now been developed that aim to cost effectively modify the lignocellulose feedstock such that downstream saccharification of the cellulose is possible and these are discussed in section 5.

### **3.6.2 UK Resources**

A number of reports have reviewed the nature and scale of the various lignocellulosic resources available in the UK for biomass energy [5,52,53]. The recent Biomass Task Report has put the available biomass resource at around 20 million tonnes (odt) per annum [5]. The UK biomass resource can be broken down into the following different categories:

**Forestry Products:** Forestry products are seen as a critical biomass resource to meet the UK's renewable energy needs. This resource includes all material harvested from woodland areas, by-products of this harvesting and poor quality residues left in the field. The 2005 volume for production of wood in the UK was 9.4 million odt per annum [54]. Most of this volume has existing markets but demand from the pulp and construction industries is reported to be declining [53]. A further source of wood is that arising from arboricultural cuttings which amounts to around 0.67 million odt per annum [55].

The current forestry resource potentially available as biomass energy or biofuel raw material is around 1.0 – 1.4 million odt per annum [5, 52, 53]. The Forestry Commission has recently reported a strategy for bringing an additional 2 million odt of wood into the marketplace for biomass energy by 2020 [56]. The total potential volume at 2020 is reported to be of the order of 10 MT [5, 53]. Around 60% of the UK forestry resource resides in Scotland and the capability of this to contribute to the Scottish renewable energy portfolio has recently been reviewed [57]. Regional activities for the development of forestry biomass supply chains have been described in the Government response to the Biomass Taskforce Report [6].

**Waste Wood:** Waste wood materials are generated from a wide variety of sectors including waste from primary processing operations and downstream sectors such as construction, packaging and furniture manufacture. The waste arising from the primary processing of wood is reported to be 0.86 million odt per annum [55]. These waste materials mostly have existing markets and the amounts actually available for biomass energy and biofuels are limited. The total volume currently available is of the order of 3 million odt [5, 52].

**Agricultural Residues:** Straw represents an important biomass resource for the UK. Straw consists of stalks and leaves of crops such as wheat, barley and oilseed rape left in the field after harvesting. In 2003 it was reported that the UK produced some 15MT of straw of which 50% was used for animal feed and bedding [58]. Since legislation against straw burning in the field was introduced conventional farming practice is to plough surplus straw back into the soil. A report by the Bioregional Group detailed the potential availability of wheat straw for alternative markets [59], it was reported that out of the 10 million tonnes of wheat straw produced some 3 - 4.6 million tonnes could be available for alternative markets. The Biomass Task Force report quotes a figure of 3MT of cereal straw potentially available for biomass energy [5]. The yield of straw from

oilseed rape varies from 1 to 3 tonnes per hectare depending on weather conditions and harvesting method [59] this puts the oilseed rape straw resource roughly at around 1 million tonnes. This could also provide a significant contribution to the agricultural residue used for biomass.

**Municipal Waste:** The UK produces about 28MT of municipal waste per year the majority of which is landfilled. Compliance with EU landfill directives will require the diversion of considerable amounts of biodegradable waste away from landfill. The biodegradable fraction of the MSW represents an untapped renewable biomass resource. There are a relatively small number of energy from waste plants that utilise around 4 million tonnes of this municipal waste feedstock in the UK [60]. Approximately half the energy content of an average MSW stream can be derived from animal or plant matter although the complex matter of sorting these streams may limit the amount of renewable material that can be effectively recovered. The total biomass resource available from MSW for energy production is reported to be 7.6MT per annum [5].

**Energy Crops:** Energy crops are generally defined as perennial crops such as trees and grasses. Annual crops such as oilseeds, cereals and sugarbeets could also be classified as energy crops if grown specifically for energy and fuels. Perennial crops offer significant benefits over conventional arable crops for biomass production in that they produce very high biomass yields and require relatively little in the way of inputs. Short rotation coppiced willow [61] and *miscanthus* grass [62] are the two most well developed energy crops in the UK, whilst coppiced poplar and switchgrass remain at the development stage. Incentivised by government grants for crop establishment and EU energy crops payments, both SRC willow and *miscanthus* cultivation is expected to grow from the 443 hectares planted in 2003 to over 15,000 hectares by end of 2007 [30].

SRC willow grows well in Northern European conditions and can give biomass yields of 7-12 odt per hectare [61]. The first harvest takes place 3-4 years after the initial planting and following harvests every three years after. Commercial SRC willow operations are well established in Scandinavia where machinery for both planting and harvesting/chipping has been developed. The UK has world leading expertise in the breeding of improved SRC willow variants. Defra is currently funding a £2 million project with Rothamsted Research Centre and the University of Southampton who are utilising specialised breeding and genomic techniques to develop willow genotypes with improved yield and pest resistance [63].

*Miscanthus*, a perennial grass, has a high biomass yield generally producing 12-14 odt per hectare [62]. In contrast to SRC willow, *miscanthus* cultivation does not require specialised farming equipment and is therefore less capital intensive. *Miscanthus* has potentially a much biomass higher yield than SRC willow but is yet to be demonstrated in the field. Bical Ltd, a producer group dedicated to *miscanthus* production, has been

contracted to supply 300 thousand tonnes of *miscanthus* biomass fuel to the Drax power station to help meet its renewable energy commitments [64]. Significant government funding has been directed towards improving *miscanthus* biomass yields and current activity includes research work at the Institute of Grassland and Environmental Research Centre [65].

Assuming a conservative yield of 12 tonnes per hectare from energy crops and a set aside land area of 680 thousand hectares the potential biomass production for energy crops is of the order of 8 million odt in the UK.

**Other Biomass Sources:** There are a number of other significant biomass sources such as animal manure from poultry, cattle and pig operations. This resource amounts to around 3 million tonnes per annum [5]. However, because of the high water content of animal manures and sewage sludges, transport limitations will dictate that the scale of conversion of these feedstocks will be relatively small. Of the different conversion options for these animal slurries, anaerobic digestion presents the best option for small scale production of biogas for heat and CHP.

**Summary:** It is clear that there is a considerable renewable biomass resource available in the UK for biofuel production. A biomass resource of 20 million odt translates to a biofuel capacity of around 4-6 million tonnes of either bioethanol or synthetic diesel. This biomass resource could be increased with further cultivation of high yielding energy crops. The actual resource available for biofuels will be less due to competition for this feedstock from existing markets and the growing renewable energy sector. In fact, power stations are now operational that utilise only biomass feedstocks such as the Elean Power station which uses 200 thousand tonnes of straw and the 38.5 MW Thetford power station which utilises 420 thousand tonnes of poultry litter [66].

Advanced biofuel production facilities will require large volumes of biomass to achieve economies of scale and be cost competitive. To achieve this will require highly developed and efficient biomass supply chains. The UK biomass infrastructure that could supply such volumes is not yet developed to the same extent as other countries and, other than the forestry and waste wood sectors, the UK has few biomass supply intermediaries that could deliver at the scale required [52]. Such a feedstock supply risk presents a barrier to project financing. To address this, a number of government and regional initiatives are underway to develop integrated biomass supply chains [6]. In addition, co-firing of biomass in large power stations may provide a platform for the development of such supply chains.

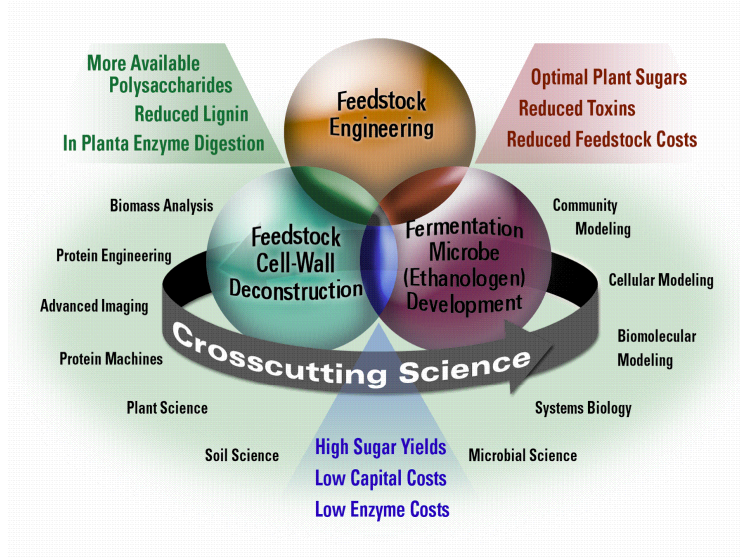
Biomass is generally harvested in the form of a low density solid which is both difficult and expensive to transport. This feedstock will need to be delivered to the biofuel factory gate at minimum cost and with minimal environmental impact. The ability to supply

sufficient amounts of biomass feedstock may well constrain the scale of the biofuel facility and dictate its location. In the longer term, this problem could be resolved through the development of technology for the conversion of biomass into more readily transportable solid pellets or pumpable liquids.

### 3.7 Exploiting Advances in Biotechnology for Plant Feedstocks

Advances in Biotechnology are driving the development of a sustainable bio-based economy utilising natural raw materials and sophisticated bioprocesses [67]. The successful development of integrated biorefineries utilising lignocellulosic feedstocks will require the development and application of a diverse range of tools cutting across many biotechnology disciplines (see Figure 5). Such a multidisciplinary approach, spanning both Green and White biotechnology, incorporates the design and engineering of crops with desirable specific traits and the utilisation of novel biocatalysts for the conversion of sugars to fuels and chemicals.

**Figure 5 Cross cutting biotechnology tools for 2<sup>nd</sup> generation biofuels**



(Graphic source: Genome Management Information System, Oak Ridge National Laboratory <http://genomics.energy.gov>.)

The successful development and application of biotechnology could deliver plant feedstocks with:

- **Higher yields (increasing output per hectare)** higher yields of starch, sugar and oils from cereals and oilseeds and also higher biomass yields of perennials crops.
- **Reduced Inputs (reduced environmental impact)** crops with reduced need for fertiliser, herbicide and pesticides that deliver biofuels with reduce carbon footprint.

- **Improved downstream processing (reduced biofuel processing costs)**  
Crops that deliver starches and oils with specific traits so that downstream processing requirements are reduced. Lignocellulosic crops containing plant cell walls which are more readily deconstructed to allow ready access to the valuable carbohydrate constituents in downstream conversion processes. The potential of this approach has been demonstrated; transgenic trees with significantly reduced lignin content have been produced that could ultimately be beneficially employed as feedstocks for the pulping industry [68].

It should be noted that conventional plant breeding and improved agronomy have delivered continued increases in food crop yields and reduced crop input requirements. Indeed, wheat varieties yielding high bioethanol productivities are now available [69]. However, recent advances in biotechnology now allow targeted modifications at the genetic level and offer the potential of a step-change in the ability to design improved crops for biofuels. At present, the development of designer biofuel feedstocks remain a medium to long term goal; such capability requires a deeper understanding of the fundamental processes involved in plant biology and the development of improved tools such as analytical and combinatorial techniques. The development of improved biofuel feedstocks will necessitate the coordination of a wide range of bioscience disciplines such as genomics, microbial and plant biology, proteomics and computational biology. Considerable activity in the United States is currently being directed towards the coordination of these activities into a coherent strategy for the development of lignocellulosic bioethanol technology [70]. In addition, \$250 million in funding has recently been committed to the development of Genomic GTL Bioenergy Centres to be the focus of these activities [71]. The importance of biotechnology towards the development of a long term European biofuel capability has also been acknowledged and incorporated into strategic technology platforms [72, 73]. The EU/USDA funded EPOBIO initiative has designated plant cell wall saccherification to be a critical area for biorefinery development [74].

The UK is recognised as being at the forefront of plant bioscience particularly in the field of genomics [75]. The BBSRC recently announced £13M of funding to exploit advances in plant science including the development of improved biofuel crops [76].

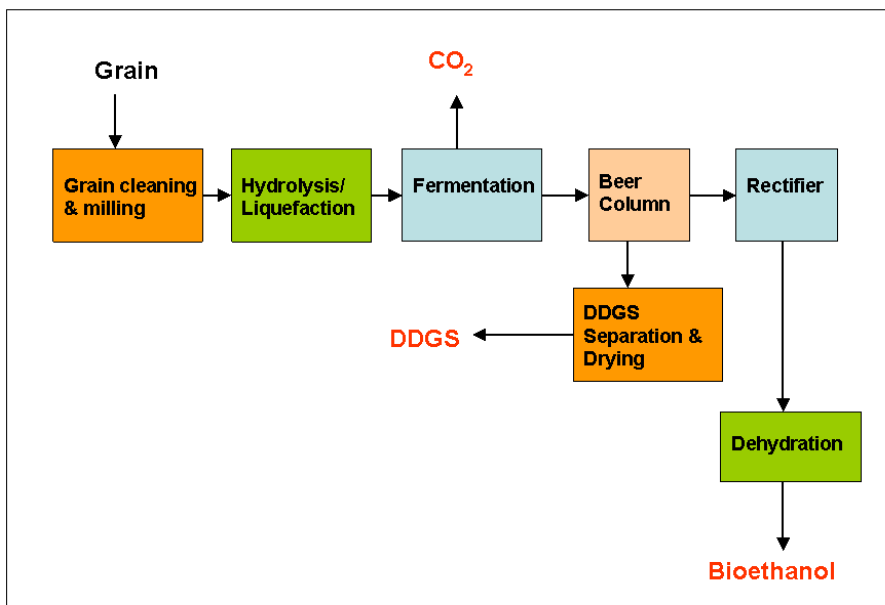
## 4. Current Biofuel Process Technology

This section gives a brief outline of the existing process technology and production costs for both bioethanol and biodiesel including the associated by-products and markets. The transition to large biorefinery complexes producing a suite of biofuels, chemicals, materials, heat and power will likely occur through incremental improvements to existing biofuel processes. This is already occurring with the integration of biomass CHP technologies within bioethanol plants to promote whole crop feedstock utilisation and reduce fossil fuel inputs. Furthermore, the valorisation of co-product and waste streams in current biofuel processes through improved chemical and biotechnical conversions will benefit plant economics and bring new bio-based chemicals into the marketplace. These issues are discussed below with regard to existing process technology for bioethanol and biodiesel. In both cases the process technology described is in the context of UK operations

### 4.1 Bioethanol Process Technology

Bioethanol production is a mature technology based on the fermentation of six carbon sugars by yeast. The sugar feedstock can be directly extracted from sugarcane or sugarbeet or derived from the starch component of cereal crops such as corn or wheat. World scale capacity for a modern bioethanol plant is of the order of 300 thousand tonnes per annum. There are a large number of process technology suppliers, including Delta-T, Vogelbusch, Katzen and Lurgi PSI [77]. A simplified schematic of a grain based bioethanol plant (dry mill) is shown in Figure 6.

Figure 6 Schematic of a Grain Based Bioethanol Plant



The process can be broken down into a number of simple process operations:

- Milling of the wheat grain to produce flour (meal)
- Liquefaction of the meal to produce the mash (~100C)
- Hydrolysis and saccherification of the starch using amylase enzymes (~100C)
- Fermentation of the glucose sugars using yeast (~30C)
- Separation of the product (beer) into solids (stillage) and ethanol
- Rectification and molecular sieve drying to dewater the bioethanol
- Drying of the stillage to produce distillers dried grain with solubles (DDGS)

In terms of product yields, a typical bioethanol plant will convert 1 tonne of wheat grain into 0.3 tonnes of bioethanol, 0.35 tonnes of DDGS and 0.3 tonnes of carbon dioxide.

A process based on sugarbeet feedstock is somewhat simpler in that the sugars are directly extracted from the sliced beets by hot water treatment.

#### 4.1.1 Bioethanol co-products

**Dried Distillers Grains and Solubles (DDGS):** Valuable high protein fibrous solid sold into animal feed markets. Generates considerable by-product credit and competes with rape meal and imported soy meal in the animal feeds market. The drying of the wet distillers grain represents a sizeable amount of the energy utilised during the entire process.

**Carbon Dioxide:** Sold to specific compressed gas markets, such as the beverage industry, but plant needs correct location and logistics otherwise carbon dioxide vented to atmosphere.

#### 4.1.2 Process Economics

There are a large number of reports that give detailed breakdown of bioethanol production costs [78, 79, 80]. Due to the maturity of the bioethanol process technology, production costs are heavily dictated by feedstock price and the value of by-product credits. Production costs for bioethanol produced from wheat or sugarbeet range from £380 to £570/tonne (30-45p/litre) depending on feedstock cost and plant scale. Production costs for sugarcane derived bioethanol produced in Brazil are significantly cheaper however this difference is reduced somewhat after transport costs to the EU and EU import tariffs are applied.

### 4.1.3 Potential Advances in Process Technology

As discussed, the bioethanol process technology is mature; however the potential for incremental improvements still exist particularly with regard to reducing energy consumption in the various processing steps. Energy intensive steps include the starch cooking section (liquefaction and saccherification), ethanol dewatering (rectification and molecular sieve drying) and DDGS drying. A range of diverse technologies are under developments that have the potential to address these issues. Some examples include:

- Improved enzymes that reduce energy requirements in the liquefaction and saccherification steps [81, 82].
- Advanced distillation column design and thermal integration [83, 84].
- Genetically modified yeasts with greater tolerance to substrate inhibition that deliver higher fermentation rates [85].
- Novel thermophilic bacteria that facilitate higher temperature sugar fermentation for increased reaction rates and the potential of continuous ethanol removal. The UK has world leading scientific capability in this area in academia and industry. TMO Biotec based in Guildford, is developing such thermophiles and has licensed technology to BER for bioethanol production [86]. TMO Biotec and Novacta Biosystems have recently been funded by the DTI to develop thermophiles for cellulose bioethanol technology [87].
- Development of pervaporation membranes that allow continuous separation of bioethanol from bioethanol / water mixtures [88].

### 4.1.4 Co-generation

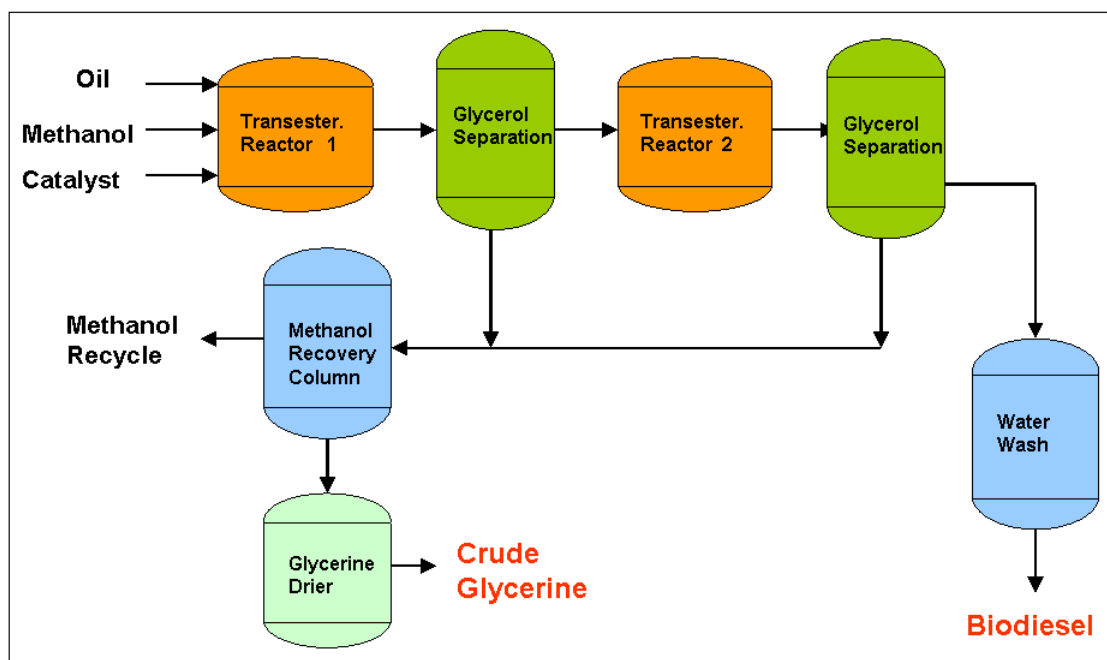
Bioethanol producers in Brazil generate considerable cost savings and energy efficiencies by utilising the waste sugarcane bagasse as a biomass energy source to power the bioethanol conversion process and supply excess electricity to the national grid. This “whole crop” approach towards integrated processing significantly reduces the greenhouse gas emissions associated with sugarcane bioethanol relative to that made from corn or wheat [89]. Grain based bioethanol producers are now evaluating the potential of utilising the stillage, or the DDGS co-product, as a biomass energy resource to power their plants. Bioethanol Rotterdam (BER) has announced that their new 100 thousand tonne plant will have the facility to combust the produced stillage to generate power for the plant and for export to the grid [86]. An alternative to combustion or gasification is to produce biogas via the anaerobic digestion of the stillage or its components. The biogas can then be combusted in a steam or gas turbine to produce electricity [90][91]. This approach is particularly beneficial in that the energy intensive DDGS drying step is minimised. Co-generation provides a valuable alternative market

for the DDGS co-product. At present animal feed prices are significantly higher than biomass fuel prices however, this could change as the amount of DDGS entering the marketplace rapidly grows.

#### **4.2.0 Biodiesel Technology**

Biodiesel technology is relatively mature having been developed in the oleochemicals sector many years ago. The relatively simple process is based on the base-catalysed transesterification of vegetable oils and animal fats with methanol. Due to its simplicity the biodiesel process also lends itself to small and medium scale production. Although there are a large number of process technology suppliers, the market is dominated by Lurgi and Desmet Ballestra. World scale biodiesel plants are now up to 400 thousand tonnes capacity.

**Figure 7: Schematic of a Generic Biodiesel Plant**



A simplified schematic of a generic biodiesel plant is shown in Figure 7. The process can be broken down into a number of individual steps:

- Methanol, rapeseed oil and an alkaline catalyst (sodium methoxide or potassium hydroxide) are reacted together to produce biodiesel and glycerine. More than one reactor with interstage separation is generally used to circumvent equilibrium limitations on feedstock conversion.

- Biodiesel product is separated from the glycerine phase which contains unreacted methanol and catalyst
- Biodiesel is further purified with a water wash to remove entrained glycerine and methanol
- Methanol is removed from the glycerine phase by distillation and recycled back to the reactor
- The Glycerine is dried by distillation to produce a crude glycerine product (~ 90% purity)

In terms of product yields from the process; 1.0 tonne of rapeseed oil will yield approximately 1.0 tonne of biodiesel and 0.13 tonnes of crude glycerine.

#### 4.2.1 Biodiesel By-products

**Glycerine:** Glycerine production from the oleochemical and biodiesel sectors has now completely replaced the synthetic route from propylene. Crude glycerine produced from the biodiesel process is around 90% pure. Due to the cost of transporting crude glycerine, further refining is usually performed on site however this adds significant capital investment to the plant. Refined glycerine is used in a wide variety of markets from personal care products, pharmaceuticals, alkyd resins, foods and beverages. The rapid increase in European biodiesel production has resulted in a glut of crude glycerine entering the marketplace. Prices for crude glycerine have consequently collapsed and are approaching waste value whilst prices for refined glycerine have reduced dramatically over the last three years. The market for refined glycerine is still relatively strong in the US and Asia and this is encouraging glycerine exports from Europe although this is unlikely to be sustainable in the longer term. The low price of glycerine now makes it attractive as a chemical feedstock. Glycerine is a highly functionalised chemical molecule with the potential for conversion to a vast number of important chemical intermediates such as polyols. Much industrial and academic attention is now focussed on developing new conversion processes and markets for glycerine. There are a number of excellent reviews on these activities, for example [\[92\]](#)[\[93\]](#). In addition there are a number of UK academic groups active in the development of new catalytic and biotechnical routes to transform glycerine, for example [\[94\]](#).

**Rapeseed meal:** Rapeseed meal is the solid residue remaining after oilseed crushing to remove the oil. Although, not directly produced as part of the biodiesel process which utilises the refined oil, it is a valuable product in its own right. Like DDGS, the meal is a high protein solid sold into the animal feed market and competes with imported soy

meal. Alternative markets for rapeseed meal are being explored such as the utilisation of the meal proteins to make novel products such as biodegradable plastics, adhesives and coatings [95, 96].

#### 4.2.2 Economics

There are a number of reports which provide a breakdown of biodiesel production costs [79, 80, 97]. When compared to bioethanol, the biodiesel process has much lower capital costs but significantly higher feedstock costs. For this reason total biodiesel production costs are even more sensitive to feedstock cost. Production costs are in the range 30p to 45p/litre depending on the feedstock price.

#### 4.2.3 Advances in Biodiesel Process Technology

Although biodiesel production technology is mature there are a number of new production technologies some of which are currently being commercialised:

- Novel fixed bed process using an heterogeneous catalyst [98].
- Use of highly active enzyme transesterification catalysts [99].
- Solvent based process that reduces mass transfer limitation [100].

Research in the Process Intensification Group at Newcastle University is evaluating novel oscillatory flow reactors and heterogeneous catalysts for biodiesel production [101]

#### 4.2.4 Co-generation

As with bioethanol facilities, steam and power for the biodiesel plant could be provided by combusting or gasifying the reaction co-products, or associated crop residues, to provide energy self sufficiency, reduce fossil fuel requirements and promote a whole crop biorefinery approach. Crude glycerine value is rapidly approaching that of a waste and could be viable as energy source. It has been proposed, for instance, that crude glycerine could be fed to an anaerobic digester to provide biogas to power a biodiesel plant [102]. It should be noted that glycerine has relatively low calorific value compared to other biomass fuels.

Rapeseed meal has high value as an animal feed, however this price will come under pressure as more meal enters the market place with increasing biodiesel production. Rapeseed meal has been mooted as a biomass resource for co-firing and pyrolysis although studies at Aston University have shown that the meal is a relatively poor pyrolysis feedstock [103]. Increased greenhouse gas reduction benefits for biodiesel have been demonstrated when the meal is co-fired [104].

Significant amounts of rape straw are generated during oilseed rape cultivation (approx 1 tonne of straw per tonne of oilseed). Little of this is harvested although some may find value as animal bedding. This remains an untapped biomass energy resource.

## 5. Lignocellulosic Ethanol Production

The next two sections concern the two main technology platforms for producing liquid biofuels from lignocellulosic feedstocks; fermentation and gasification. These two radically different conversion technologies will become the backbone of advanced biorefinery complexes.

Considerable research activity has been directed towards the development of lignocellulosic routes to bioethanol over the last twenty five years [22,105,106,107]. Over this period, a number of large scale pilot projects have demonstrated the technical feasibility of producing bioethanol from lignocellulosic material. However, it is only now with continued improvements to conversion technology and the right economic climate for capital investment that commercialisation is seemingly imminent. One of the reasons for this long lead time is the presence of a number of challenging technical hurdles. The whole conversion process can be broken down into a number of key individual steps:

- Feedstock Pretreatment
- Liquefaction and Saccharification of the polysaccharides
- Fermentation of the resultant sugars to bioethanol.

In principle these steps are the same as those present in the conventional dry-mill process that converts grain starch to bioethanol. However, each of these steps presents a different technical challenge when lignocellulosic feedstocks are considered:

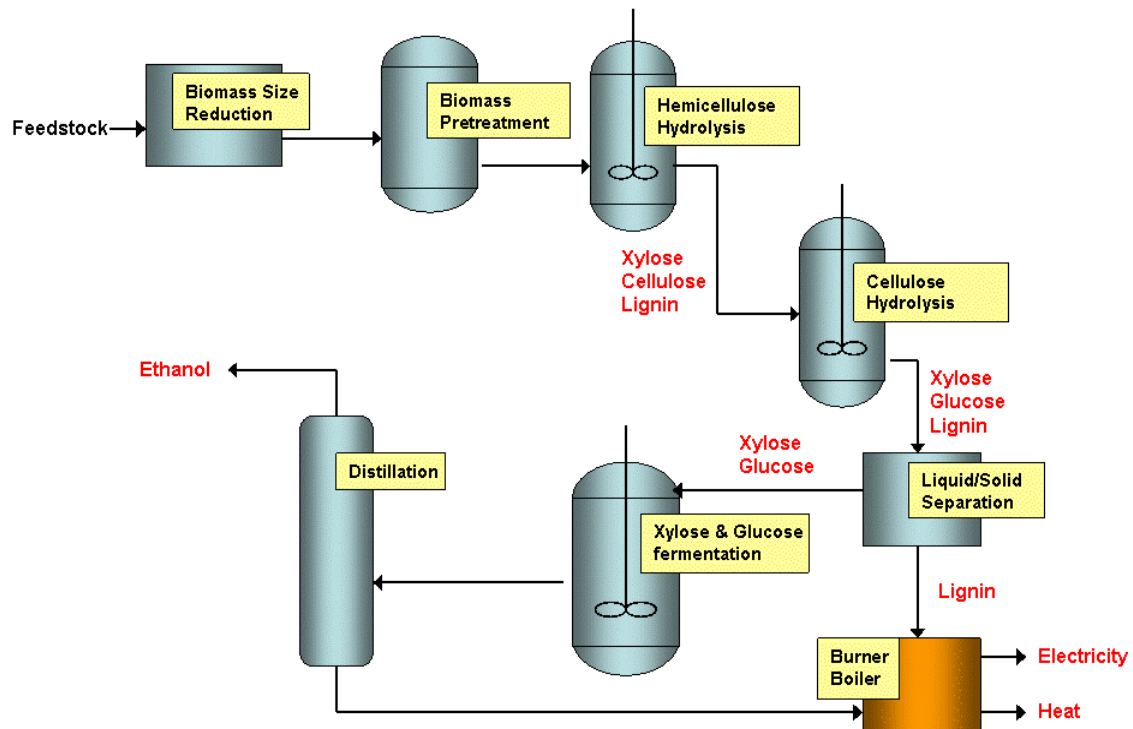
- Due to the recalcitrant nature of the lignocellulosic feedstock, forcing conditions are required to sufficiently pretreat the feedstock so that the polysaccharides can be accessed for conversion.
- Unlike starch, cellulose is not hydrolysed by conventional amylase enzymes and requires the application of sophisticated cellulase enzymes to complete saccharification.
- Unlike glucose, xylose sugars extracted from hemicellulose can not be fermented with conventional bakers yeast and require the application of novel microorganisms.

It is only with recent advancements in biotechnology that improved microorganisms and enzymes have been designed with sufficient activity for commercial cellulose hydrolysis to be considered credible.

### **5.1 Lignocellulosic Ethanol Process**

A wide variety of process designs are now being developed through to commercialisation. It is clear that considerable scope still remains for process efficiency

and cost reductions in the overall conversion process. Further research is being directed towards process integration and consolidation of different operations. The individual process operations are now considered in more detail. To aid discussion, a schematic of a generic lignocellulosic ethanol process is shown in figure 8. It should be noted that a number of the individual operations below can be combined together into single processes. Indeed such process consolidation is a feature of current process development. The individual operations are now discussed in more detail.



**Figure 8 Schematic of a Generic Lignocellulosic Ethanol Process**

### 5.1.1 Biomass Size Reduction

After cleaning, the biomass feedstock will require chipping or milling to reduce its size to smaller particles. Size reduction is necessary to provide a pumpable slurry and to increase the biomass surface area so that mass transfer effects are minimised during the downstream processes [106,108]. Techniques for size reduction include hammer, disk and knife milling. This step is considerably more involved than that utilised in conventional grain milling. Depending on the biomass feedstock used, the milling step can add considerable cost to the overall bioethanol production cost due to its energy intensity. Some pretreatment techniques claim not to require biomass size reduction.

### 5.1.2 Biomass Pretreatment

The purpose of pre-treatment step is to further increase the surface area of the lignocellulosic material, disrupt the structure of the lignocellulose such that the cellulose component is accessible to hydrolysing agents and reduce the crystallinity of the cellulose to further facilitate hydrolysis [106,108,109]. Depending on the nature of the pretreatment technology selected this step can also include solubilisation of the lignin or the hemicellulose component. Due to the recalcitrance of the lignocellulose structure these treatments are generally severe in nature and are combinations of either physical, chemical, biochemical or thermal treatments. Consequently, the pretreatment process represents a significant cost element of the whole lignocellulosic bioethanol process.

The performance criteria for an optimum pretreatment technology are:

- Maximise the yield of both hexose and pentose sugars in downstream processing
- Facilitate the recovery of lignin for valorisation
- Minimum production of chemicals that inhibit downstream enzymatic processing such as furfural and hydroxymethyl furfurals.
- Flexibility with regard to the nature of lignocellulosic feedstock
- Does not require expensive biomass size reduction (milling)
- Utilise low cost chemicals and minimise waste
- Low energy requirements and low capital intensity

The pretreatment processes considered to be the most advanced are as follows:

**Acid Pretreatments:** The use of acids to pretreat biomass and to hydrolyse the resultant hemicellulose and cellulose sugars has been known for many years and was a central part of early chemicals manufacture from wood [21]. More recently, both dilute and concentrated acid biomass pretreatment technologies have been developed for bioethanol production. Of these the most well known is the NREL dilute sulfuric acid process [110,111]. This process operates at 180-200°C with a residence time of around 1 minute. The hemicellulose fraction is hydrolysed into pentose sugars and the downstream hydrolysis of the cellulose is improved. The biomass is chipped prior to pretreatment. The use of dilute acid requires high temperatures which can degrade the sugars into chemicals such as furfurals. Not only does this reduce the yield of fermentable sugars but such degradation products are toxic to downstream fermentation microorganisms. To circumvent this, the process can be staged at two temperatures; a lower temperature to remove the more easily hydrolysed hemicellulose components which are then removed prior to a higher temperature treatment to hydrolyse the

remaining hemicellulose component. This ensures that the majority of the hemicellulose derived pentose sugars are not exposed to unnecessary high temperatures and thereby maximises the sugar yield [112]. An alternative is to run a countercurrent reactor which ensures that hemicellulose sugars once formed flow directly out of the reactor [112]. Furthermore, studies have shown that a pressurised hot water wash directly after the pretreatment process improves the overall process by removing soluble lignin species and degradation products which may hinder downstream processing [113].

As discussed, the disadvantage of the dilute acid pretreatment process is its propensity to produce sugar degradation products that are toxic to downstream fermentation microorganisms. Attempts to remove these inhibitors after the pretreatment step invariably leads to reduction in the sugar yields. Additionally, the dilute acid process requires expensive reactor construction materials and a downstream acid neutralisation unit which adds capital cost. Acid neutralisation is usually performed with calcium hydroxide which creates a waste disposal issue with the resultant gypsum.

Groups in Sweden have also been active in the development of dilute acid pretreatment processes for many years. Sekab in collaboration with a number of Swedish Universities are developing wood cellulose bioethanol processes that can be integrated with existing pulp manufacture [114, 115]. This consortium operates a 400 litre per day bioethanol plant utilising dilute acid pretreatment technology.

A pretreatment process utilising concentrated sulphuric acid has also been developed in parallel. The concentrated acid process has the benefit of being able to operate at much lower temperatures and thereby reducing the formation rate of sugar degradation products. The concentrated acid pretreatment hydrolyses both the hemicellulose and the cellulose components of the biomass [116,117]. If this process is to be economic the concentrated acid must be recovered and recycled, usually by ion exchange resins. As with the dilute acid route, downstream neutralisation also produces a gypsum waste disposal issue.

Arkenol [117], Losonoco [118] and Masada [119] have developed concentrated acid biomass pre-treatment processes, all reportedly close to commercialisation. Both Losonoco and Masada plan to utilise their technology on municipal solid waste feedstock.

**Steam Explosion Techniques:** Steam explosion is a well known biomass pretreatment process having been used for many years in the production of fibreboard. Steam explosion entails subjecting the lignocellulosic material to high pressure steam at 20-50bar pressure and 160-260C temperature for a few minutes before rapidly decompressing back to atmospheric pressure [106,108,109]. The subsequent explosion greatly increases the surface area of the biomass material and increases the rate of

hydrolysis of the treated cellulose in downstream processing. The beneficial affect of steam explosion are reported to depend on the nature of the biomass feedstock and are considered very effective for hardwoods but not for softwoods [109]. Chemical reactions occur during steam explosion and the hemicellulose fraction is partly hydrolysed to produce oligomers, sugars and degradation products. A water wash is required to remove the degradation products from the pretreated biomass prior to downstream processing. Such washing, however leads to loss of solubilised sugars and the yield of xylose sugars is reported to be only 45-65% using steam explosion [106, 109]. Steam explosion is an autohydrolysis process and can produce inhibitory by-products such as furfurals, organic acids and phenolic derivatives. The most efficient means to deal with these compounds is either to perform a water wash on the pretreated material or neutralise it with calcium hydroxide. Addition of dilute sulphuric acid to the steam explosion process is reported to be beneficial in increasing pentose sugar yields to around 70% [106].

SunOpta, a Canadian based engineering group, has developed a continuous steam explosion process which will be utilised in the Abengoa bioethanol demonstration plant in Spain [120]. SunOpta (previously Stake Technology) have supplied a steam explosion pilot plant to the ENEA Research Facility in Southern Italy [121]. Iogen has developed its own acid-catalysed steam explosion pre-treatment technology for its straw to bioethanol process [122].

**Liquid Hot Water:** An alternative autohydrolysis technique to steam explosion is to expose the lignocellulosic material to superheated water (180 – 230C) maintained in the liquid state by high pressure [108, 123]. Liquid hot water treatment is reported to need little particle size reduction before treatment. This treatment completely dissolves the hemicellulose fraction and renders the cellulose fraction highly receptive to enzymatic hydrolysis. The process liberates organic acids, such as acetic acid, from the biomass which catalyse further hydrolysis. As with steam explosion, sugar degradation products are formed which are toxic to downstream fermentation microorganisms. A number of different process configurations have been developed to maximise sugar yields and beneficial operation has been demonstrated by controlling the pH of the process by adding potassium hydroxide. This process is still at the development stage.

**Ammonia Fibre Explosion Pretreatment (AFEX):** This process is similar to that of steam explosion in that the lignocellulosic material is exposed to liquid ammonia at high temperature and pressure and then the pressure is rapidly reduced [108, 109, 124]. The ammonia is heated to 90C and the residence time is around 30 minutes. In contrast to steam explosion, the hemicellulose fraction is not significantly solubilised to monomeric sugars and the composition of the solid remains the same after pretreatment. The AFEX treatment results in the rupture of the lignin- hemicellulose bonds and some hydrolysis of the hemicellulose to produce oligomers. There is also greatly reduced production of

furfural and hydroxymethylfurfural compared to other pretreatments but some organic acids are liberated which are toxic to downstream fermentation microorganisms [125]. Ultimate sugar yields are high using AFEX. The disadvantage of AFEX is the need to capture and recycle the ammonia which adds significant cost to the overall capital of the pretreatment process. This process has been under development for over 20 years and is pioneered by Bruce Dale at Michigan State University.

**Alkali Pretreatment Process:** Alkali treatments involving hydrolysis with ammonia, calcium, sodium or potassium hydroxide are similar in nature to the Kraft process in that the lignin component of the biomass is dissolved [108,109]. Most activity is concentrated on the Lime pretreatment technology being developed by Holtzapfle at Texas A&M University [126]. The digestibility of the lignin depends on the severity of the process conditions used and the nature of the biomass feedstock. The residual hemicellulose and cellulose can then be hydrolysed and fermented downstream. Lime is generally the alkali used due to its lower cost and the fact that it can be readily precipitated out from solution after treatment. In contrast to acid based pre-treatments, reaction temperatures are low and residence times tend to be of the order of hours rather than minutes.

**Others:** Other pre-treatment processes still at the development stage include the use of organic solvents to fractionate the lignocellulose into different streams for upgrading. Examples of such process developments include the Lignol Process which uses ethanol to solubilise the biomass [127] and the ACOS process which utilises acetone as the solvent [128]. Both of these process offer potentially high yields of sugars and in contrast to the pre-treatment technologies described above produce a unique refined lignin co-product which could have market value above that of its energy value.

#### **Pretreatment Summary:**

The benefits of the respective pretreatment technologies can be summarised as follows (see table 4).

It is clear that there are a large number of biomass pretreatment technologies at varying stages of development but no obvious winners at this stage. Each individual pretreatment technology has its own strengths and weaknesses. It is also apparent that there is no universal biomass pretreatment system and each process technology has beneficial attributes for certain feedstocks. For instance, the concentrated acid process is most suitable for the pretreatment of municipal solid wastes.

One of the issues with the development of improved biomass pretreatment processes is a lack of the fundamental understanding of some of the chemistry and kinetics involved. Another issue affecting selection of the most appropriate technology is the lack of rigorous comparative data on each system. To address these issues the USDA and latterly the DOE have funded a consortium activity, entitled CAFI, which brought together

**Table 4 Qualitative Evaluation of Selected Pretreatment Technologies**

Pretreatment Process	Reduced Inhibitor Production	High yield of Fermentable Sugars	Chemical Recycling	Waste Disposal	Investment Cost
Dilute Acid		√√	√		√
Concentrated Acid		√√			
Steam Explosion	√	√	√	√	
AFEX	√√	√√		√	√
Solvents	√√	√√		√	
Lime Treatment	√	√√			√

Adapted from reference [129]. The √ symbol indicates a positive attribute

the leading US exponents of each pretreatment technology to develop robust comparative data and a better fundamental understanding of each process when applied to a specific feedstock [130, 131]. The biomass feedstock chosen for the first part of the activity was corn stover.

The closest pretreatment technologies to commercialisation appear to be the dilute acid, concentrated acid and the steam explosion processes. All of these processes represent a significant capital cost element towards the overall bioethanol production cost from lignocellulosic feedstocks. The capital cost of a dilute acid pretreatment process for a 56 million gallon bioethanol plant is of the order of \$25 million. The production costs of bioethanol increase in the following order: dilute acid < AFEX < lime [130, 131].

The greater majority of technology development in this area is occurring in the United States funded by the USDA and DOE with some activity in Canada and isolated pockets in Europe in Italy and Sweden.

The pretreatment section of the lignocellulosic process remains an area with significant potential for improvement and current processes moving forward to commercialisation are suboptimal in terms of cost and performance. The severity of the different processes reflects the recalcitrant nature of the lignocellulosic feedstocks and imparts a large capital and operational cost to the overall bioethanol process. Different biomass feedstocks are suited to different pretreatment technologies. A greater fundamental knowledge of the structure–activity relationships between the components of lignocellulosic is required and a detailed understanding of the kinetics of the different

reaction pathways during pretreatment is necessary before improved systems can be designed.

### **5.1.3 Cellulose Hydrolysis**

A biological route to cellulose hydrolysis offers significantly more potential in reducing process costs than the use of liquid acids. Enzymatic hydrolysis is preferable due to its milder operating conditions, reduced by-product formation and the non-corrosive reaction medium. Cellulose hydrolysis is the rate limiting step in bioethanol production [132] and to be successful an enzyme catalyst (cellulase) must overcome a number of challenging barriers [133]:

- Unreactive crystalline cellulose
- Presence of lignin blocking reactive sites
- Low substrate surface area
- Low hydrolysis rates
- Substrate inhibition
- Product inhibition

Improved biomass pretreatment processes may beneficially address the first three of these issues but improved cellulase systems are required to address the later three barriers and considerable effort has been directed towards the identification and development of improved microorganisms and enzymes for cost effective processing. Both bacteria and fungi can produce enzymes for cellulose hydrolysis but the majority of research has concentrated on aerobic fungal systems such as *Trichoderma reesei* [132,133]. Logans who are close to the commercialisation of straw based bioethanol process have a proprietary cellulase system based upon a genetically modified *T. reesei* system [134]. Due to the ability of termites to digest cellulose, many groups are active in the identification of cellulase genes present in the termite hindgut and their exploitation in designing new cellulase biocatalysts [135, 136]. Anaerobic bacterial systems such as *Clostridium* offer the potential of both cellulose hydrolysis and glucose fermentation in one step [132].

Cellulase costs have in the past been prohibitively expensive; contributing some \$5 to the production cost of each bioethanol gallon [137]. One of the difficulties in developing new cellulases is the fact that they comprise a cocktail of different enzymes. These enzymes have specific roles within the cellulose saccharification process including the creation of free cellulose chains ends, cutting these chains to free cellobiose units (glucose dimers) and finally hydrolysis of cellobiose to produce glucose [109]. In 2000 the US DOE contracted both Genencor and Novozymes to genetically engineer improved cellulase enzymes and meet a target of a ten fold reduction in enzyme costs [138]. Both programmes have delivered successful outcomes with Genencor and Novozymes each reporting 30 fold reductions in cellulase enzyme costs such that

enzyme now contributes of the order of \$0.1 to \$0.2 to the cost of a gallon of bioethanol [139, 140]. However, further cellulose cost reductions are still required if lignocellulose bioethanol is going to be cost competitive, a realistic target for this would be an enzyme cost of \$0.03/gallon [141][142]. These systems were specifically designed for corn stover biomass that had been pretreated using the dilute sulphuric acid process. New enzyme packages are likely to be needed for different biomass feedstocks and pretreatments. Recent research at VTT in Finland and Lund University in Sweden has been concerned with the development of thermophilic cellulase enzymes that can operate at higher temperatures than conventional cellulases [143]. Such systems offer potential benefits in increased reaction rates, higher yield and higher integration potential.

The manufacture of cellulase enzymes is now big business and many of the enzyme manufacturers are now forming strategic collaborations with key players in the developing lignocellulosic bioethanol sector:

- Both Novozymes and SunOpta have formed a collaboration with a Chinese Bioethanol producer (CRAC) to develop lignocellulosic technology [144]. Novozymes cellulase enzymes will be evaluated in the Abengoa bioethanol plant [145].
- Diversa have entered into collaboration with Syngenta to develop novel enzymes for lignocellulosic bioethanol [146] and have also formed a collaboration with Celunol [147].
- Dyadic International, a genomics company who have a proprietary fungal strain has formed collaborations with both Royal Nedalco to develop enzyme systems for utilising wheat bran [148] and with Abengoa to develop novel enzymes for utilising straw [149].

#### **5.1.4 Pentose Fermentation**

The efficient fermentation of all the sugars streams released from the pre-treatment and hydrolysis steps is a prerequisite for economic conversion of biomass to bioethanol. However, conventional bioethanol yeasts such as *Saccharomyces cerevisia* nor *Zymomonas mobilis*; a bacteria with potential for bioethanol production, can ferment the pentose sugars released from the hemicellulose fraction [150, 151]. This has represented a considerable barrier to the commercialisation of lignocellulosic bioethanol production. More than twenty years research has been directed towards the development of improved microorganisms for the fermentation of the pentose sugars. For cost effective processing, such organisms must be able to co-ferment both glucose and xylose streams together. Recent advances in metabolic engineering have led to a spate of proprietary microorganisms for xylose fermentation.

Considerable effort has been directed towards the genetic engineering of the bacteria; *E. Coli* and *Z. Mobilis* to selectively introduce pathways for the fermentation of arabinose and xylose sugars to bioethanol [152]. One of the first examples of this was the work by Ingram's group at the University of Florida [153]. Since that time a number of other groups have also developed engineered strains of *Z. Mobilis* for xylose fermentation. Research at NREL has successfully introduced pathways for xylose and arabinose metabolism into *Z mobilis* by incorporation of *E. Coli* pentose metabolism genes [154]. The performance of the NREL microorganism was demonstrated on a commercially realistic hydrolysate feedstock from the Arkenol concentrated acid process [155]. Celunol have exclusive license to the fermentation organisms developed at the University of Florida based upon genetically engineered *E Coli* bacteria [156].

Microorganisms exist in nature that utilise xylose as a substrate. An example of this is the yeast *Pichia stipitis* which is present in the gut of wood eating beetles [151]. Although itself ineffective for commercial fermentation, its genetic information can be utilised to improve the xylose metabolism of more appropriate microorganisms such as *S. cerevisia* and *Z. mobilis* . The successful sequencing of the *P. stipitis* genome was recently reported [157]. Researchers have sought to develop improved mutants of *P stipitis* [158, 159]. Other groups have incorporated *P stipitis* genes into recombinant *Saccharomyces* yeasts to improve its xylose fermentation capability [151]. Research workers at the Delft University of Technology have incorporated the gene from a fungus (*Piromyces*), found in elephant dung, into *Saccharomyces* yeasts and demonstrated highly promising performance for xylose fermentation [160].

UK company, Agrol Ltd has developed proprietary genetically engineered thermophilic bacteria *Bacillus Stearothermophilus* for the fermentation of pentose and hexose sugars [161]. Agrol is collaborating with Colusa Biomass Energy Corporation in the US, who plans to use the bacteria in a proposed lignocellulosic ethanol plant to be built in Sacramento [162]. Research work on thermophilic *Bacillus* bacteria is also being performed at Imperial College [163].

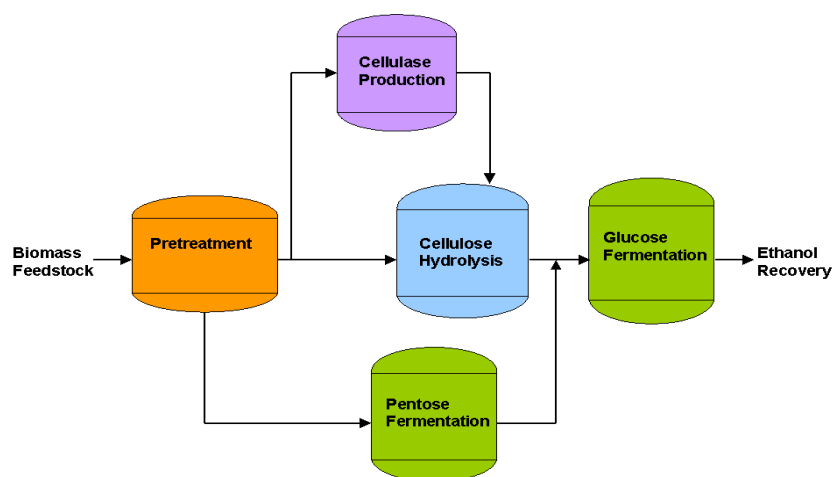
Although there are a large number of engineered microorganisms for the co-fermentation of glucose and the pentose sugars, issues such as product inhibition, sensitivity to inhibitors and the production of unwanted by-products remain concerns until these systems are demonstrated at a commercial scale.

## **5.2 Process Integration and Consolidated Bioprocessing**

Due to the large number of individual processes in the overall conversion of lignocellulosic biomass into bioethanol considerable scope exists for process integration and capital cost reduction. To aid discussion, Figure 9 shows a rudimentary process flow scheme for a lignocellulosic bioethanol process. This process scheme depicts separate pentose and glucose fermentation operations. In this case, the two fermentations are

performed individually due to the lack of available technology to perform effective co-fermentation of the two sugars. However, separate processing of the glucose and pentose sugars provides greater options for flexible processing. For instance, the pentose sugars can be converted into valuable chemical intermediates such as xylitol or levulinic acid. In the flow scheme depicted in Figure 9, the pre-treatment process produces a separate stream of pentose sugar hydrosylate. In principle, the pentose fermentation unit could also be configured downstream of the glucose fermentation unit provided that the presence of pentose sugars did not inhibit glucose fermentation and there was intermediate removal of the bioethanol product prior to the pentose sugar fermentation unit. This flow scheme also contains a dedicated cellulase production facility; such units are reported to consume 2-6% of the feedstock to grow the cellulose

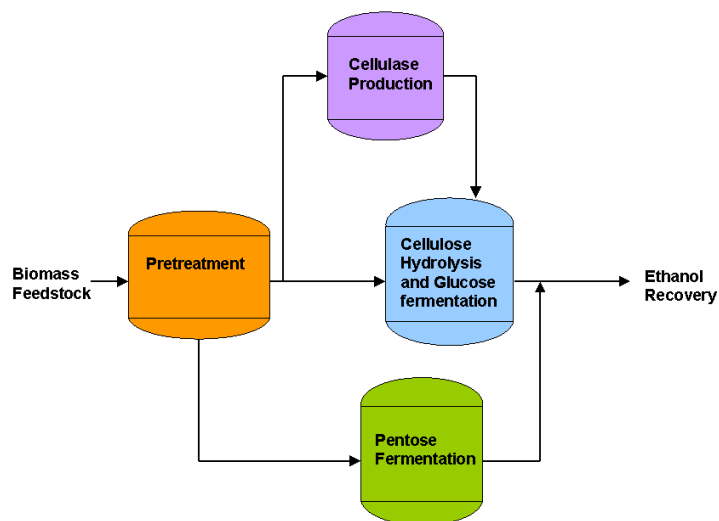
**Figure 9 Lignocellulosic Ethanol Process Flow Scheme (SHF)**



enzymes [105]. Such a flow scheme depicted in Figure 9 is often referred to as Separate, or Sequential, Hydrolysis and Fermentation (SHF).

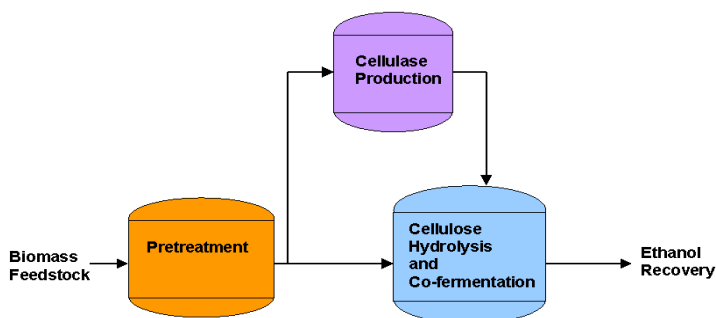
Figure 10 shows a process flow scheme in which the separate cellulose hydrolysis and glucose fermentation units are combined. Not only does this reduce the number of reaction vessels but it also minimises the problem of product inhibition affecting the hydrolysis reaction because product glucose sugars are removed by the fermenting microbes. This process is known as Simultaneous Saccherification and Fermentation (SSF). However to combine cellulose hydrolysis and fermentation requires microorganisms that operate under similar conditions. Current *Saccharomyces* yeasts operate optimally at 37C, whilst cellulases operate optimally at 55C [152]. As a result, considerable research activity has been devoted to the development of thermophilic enzymes that will ferment glucose and pentose sugars at temperatures required for hydrolysis conditions. The majority of this work has been performed on microorganisms

**Figure 10 Lignocellulosic Ethanol Process Flow Scheme (SSF)**



such as *Clostridium thermocellum* [164,165,166]. Further process consolidation can be achieved by utilising a thermophilic bacteria that can ferment both glucose and pentose sugars; this is known as Simultaneous Saccharification and Co-Fermentation (SSFC) and is shown in figure 11.

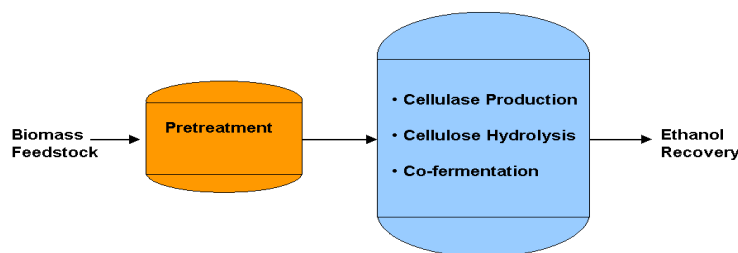
**Figure 11 Lignocellulosic Ethanol Process Flow Scheme (SSFC)**



The logical end point of this process integration is known as Consolidated Bioprocessing (CBP) and is shown schematically in Figure 12. In CBP all enzymes are produced by a single microbial community in a single reactor operating under the same conditions. This process is championed by Lynd's group at Dartmouth College [167, 168]. Lynd is a co-

founder of Mascoma Corporation, a lignocellulosic ethanol company pursuing advanced bioprocessing technology.

**Figure 12 Lignocellulosic Ethanol Process Flow Scheme (CBP)**



Calculations suggest a potential fourfold reduction in processing costs is achievable when moving from a SSFC to a CBP system. Lynd reports a decrease in production costs of bioethanol from 18.9 ¢/gallon to 4.23 ¢/gallon when shifting to CBP [167]. If successfully developed CBP could potentially produce bioethanol at a cost of 63 ¢/gallon with a biomass feedstock price of \$40/tonne [167].

Such technology is some way from the marketplace and significant R&D is still required not only in metabolic engineering of improved and more cost effective microorganisms for simultaneous processing but also chemical engineering to address issues such as high solids loading in fermentation processes. As discussed previously, SSCF and CBP are strategies to maximise the production yield of bioethanol from lignocellulosic feedstock and as such negate the potential of generating value from a multi-product, biorefinery approach utilising the different hydrolysate sugar streams.

### **5.3 Commercial Activity in Lignocellulosic Ethanol Production**

Although lignocellulosic ethanol facilities have been in development for many years, it is only now that a number of these are close to commercial realisation. In part, this can be related to continued improvements in biotechnology and reductions in processing costs. Such processes however remain highly capital intensive and currently are not competitive with conventional bioethanol production from food crops. As such, these 2<sup>nd</sup> generation bioethanol processes present significant risk for venture capital investment and government assistance, such as capital loans or tax allowances, is necessary to facilitate the implementation of the first wave of lignocellulosic ethanol plants. The US government has recently pledged \$385M of funds to support the construction of six lignocellulosic ethanol plants [169]. Other proposed lignocellulosic ethanol plants in the United States are receiving significant financial support from state governments.

Table 5 lists the global lignocellulosic ethanol plants under construction, or in planning. A number of these processes are differentiated by the proprietary microorganisms used for sugar fermentation. In addition to these plants, there are a large number of demonstration/pilot plants around the world. A production capacity of 10 million gallons (~30 thousand tonnes per annum) is considered to be the threshold for commercial scale. Although not of this scale, Bioethanol Japan is reported to be the first company to produce lignocellulosic ethanol on a commercial basis. The Celunol plant in California is likely to be the first operational facility in the US.

#### **5.4 Process Economics**

There are a large number of reports that detail projected economics for the production of ethanol from a variety of lignocellulosic feedstocks [22, 79, 129, 170, 171]. Projected lignocellulosic ethanol production costs have reduced from over \$4 per gallon to \$0.5 per gallon with improvements to process integration and reductions in cellulose enzyme costs. To illustrate this further three studies are highlighted below:

- Detailed studies have been performed by NREL on the economics of a 180 thousand tonne per annum bioethanol plant using corn stover as the biomass feedstock [170,171]. The total forecast investment was \$200M and the ethanol price calculated to be \$1.28/gallon. Corn stover feedstock at \$35/dry tonne accounted for 34% of the cost contribution. It should be noted that this price incorporated future reductions in enzyme costs and at current enzyme costs the ethanol price would be closer to \$1.5/gallon. This figure is line with the quoted production costs for ethanol produced from cereal straw in the logen process (\$1.44/gallon ethanol) [172].
- A study by Royal Nedalco, ATO-BV and the University of Delft [129] reported that a 150 thousand tonne per annum capacity bioethanol plant utilising a range of biomass feedstocks would require an investment of the order of €235-313 million (wheat straw = €235M, verge grass = €313M). The bioethanol product cost was calculated to be 0.75 €/litre for wheat straw and 0.92 €/litre for verge grass.
- A study by EEDA [78] estimated that a 150 thousand tonne per annum capacity bioethanol plant utilising UK biomass feedstock would require a capital investment of the order of £134 - £143 million and the bioethanol costs would be 80p/litre for miscanthus, 78p/litre for SRC, 74p/litre for forestry residues and 54p/litre for wheat straw.

**Table 5 Proposed Lignocellulosic Ethanol Plants**

Company	Scale Ktpa	Location	Process	Feedstock	Timing
Abengoa	34	Kansas	SunOpta	Mixed	2010
Alico	42	Florida	Syngas fermentation	Wood, wastes	
Celunol	90	California		Sugar Cane Waste	2007
Colusa	30	Califronia		Rice straw	2008
BlueFire Ethanol	57	California	Arkenol	Green & wood waste	
Broin	94	Iowa		Corn stover	2009
logen	54	Idaho	logen	Mixed	2008*
JGC Corp	24	California	Arkenol	Wood waste	2009
Range Fuels	120	Georgia	Syngas catalytic	Wood wastes	
Xethanol	150	Georgia		Wood	2007
Greenfield Ethanol	32	Ontario/Quebec	SunOpta	Wood Chips	
Abengoa	4	Salamanca Spain		Straw	2006/7
Losonoco		Merseyside, UK		MSW	
Royal Nedalco	150	Sas van Gent Netherlands			2008
CRAC	5	Heilongjiang Province	SunOpta		2007
Bioethanol Japan	1.1	Osaka	Celunol	Wood waste	now

\*start construction

Although benefiting from considerably cheaper feedstocks, the lignocellulosic processes currently do not appear competitive with bioethanol produced from starch and sugar feedstocks. The increased capital and variable costs associated with lignocellulose processing can be traced a number of key elements of the process namely:

- High cellulose enzyme costs
- High capital and operational costs of the pretreatment section
- Long residence time associated with hydrolysis and fermentation

These elements remain the focus of continued R&D to improve the cost competitiveness of the lignocellulosic ethanol routes. Another important area of focus is the generation of higher value from the various co-product streams that exist in such processes.

## 6. Thermochemical Processes

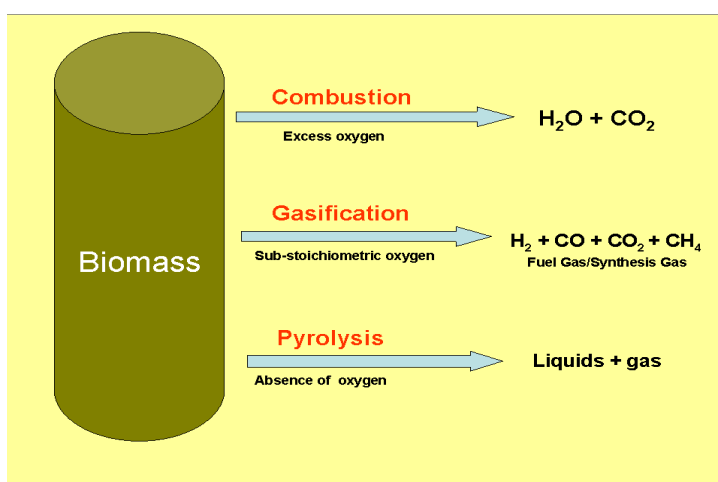
This section is concerned with thermochemical routes to convert biomass to power, fuels and chemicals. In contrast to the biochemical routes discussed in the last section, process technology for thermochemical conversions are, for the most part, well established and in some cases have been practised commercially for many years.

Although there are a number of routes for the thermochemical conversion of biomass (see figure 13), emphasis in this section will be placed on high temperature gasification processes that generate synthesis gas, a mixture primarily consisting of carbon monoxide and hydrogen, and the conversion of the synthesis gas into transport fuels. Gasification is a very flexible process with regard to feedstock and, in principle, many different carbon sources can be utilised to produce synthesis gas. Historically, gasification technologies have been developed for coal feedstocks for both power and synthetic diesel production. Recent attention has focused on the gasification of natural gas, particularly as a platform for utilising the vast reserves of stranded gas in remote locations. The conversion of stranded gas into synthesis gas which can then be converted into either synthetic diesel or methanol produces a transportable liquid product which can be shipped to market locations. These “gas to liquid” (GTL) processes are operated on a vast scale and are now being implemented in regions such as Qatar, Trinidad and Alaska. The gasification processes themselves are highly capital intensive and often represent more than 50% of the total capital costs of a GTL plant. Driven by government policies and fiscal incentives, biomass gasification technologies are now being developed for the production of renewable heat and power, biofuels and chemicals. The gasification of biomass to synthesis gas presents a number of technical challenges resulting from the different physical nature and chemical composition of the feedstock compared to natural gas and coal. However, downstream of the biomass gasification processes, technology for the conversion of the synthesis gas to biofuels and chemicals can be considered, for the most part, commercially established.

There are three main primary thermal processes for converting biomass; combustion, gasification and pyrolysis. All of these processes differ in the amount of oxygen present during thermal conversion (Figure 13). The primary products from these processes can be utilised to generate heat and/or power in downstream energy conversion processes or, in the case of gasification and pyrolysis, utilised as a feedstock for transport fuels and chemicals. Considerable technology development is being focused on high pressure biomass gasifiers that can operate at the large scale necessary for economic production of synthesis gas feedstock. It is well documented that the major remaining technical barrier to the commercialisation of biomass gasification technology for biofuels

production is the requirement for high purity synthesis gas and the development of effective gas clean-up technologies.

Although technology development for energy production (heat and power) is well established for biomass combustion and to a lesser extent biomass gasification, pyrolysis of biomass is still at the development stage. The pyrolysis of biomass, particularly fast pyrolysis techniques, produces a dense “bio-oil” which can then be used in other conversion processes. Pyrolysis offers great potential for the realisation of an easily transportable biomass derived liquid fuel and chemical feedstock. In the longer term it may be possible to convert the bio-oil directly into a diesel range products by catalytic hydroprocessing.



**Figure 13 Primary Thermal Conversion Processes for Biomass**

Synthesis gas is an important chemical feedstock and is currently produced on a vast scale from coal, oil-residues and natural gas. The major outlet for synthesis gas is in the hydrogen market, where the separated hydrogen is used predominantly in the ammonia industry and also in refining operations. Synthesis gas is also used to manufacture methanol on a large scale with a global market approaching 40 million tonnes. As shown in Figure 14, a number of other valuable chemicals can be potentially manufactured directly from synthesis gas or from methanol.

The development of new thermochemical biomass routes to transport fuels requires a multidisciplinary approach at national and international level. This is reflected in the number of coordinated activities in this area; the IEA Bioenergy activity within the International Energy Agency has a number of tasks dedicated to the thermochemical conversion of biomass including gasification (task 33) and pyrolysis (task 34) [173]. In the United States, the Department of Energy has a large thermochemical biomass conversion activity coordinated through the NREL laboratories [174]. In the UK, the Supergen programme is a coordinated activity to develop sustainable power and supply

systems. Biomass, biofuels and energy crop utilisation is one of the Supergen themes and is led by Aston University [175]. In contrast to the biochemical processes discussed in the last section, thermochemical technology development is being led by Europe rather than the United States. A recent DTI funded global watch mission recorded the status of technology development in second generation biofuels from thermochemical routes in Finland, Netherlands and Germany [176].

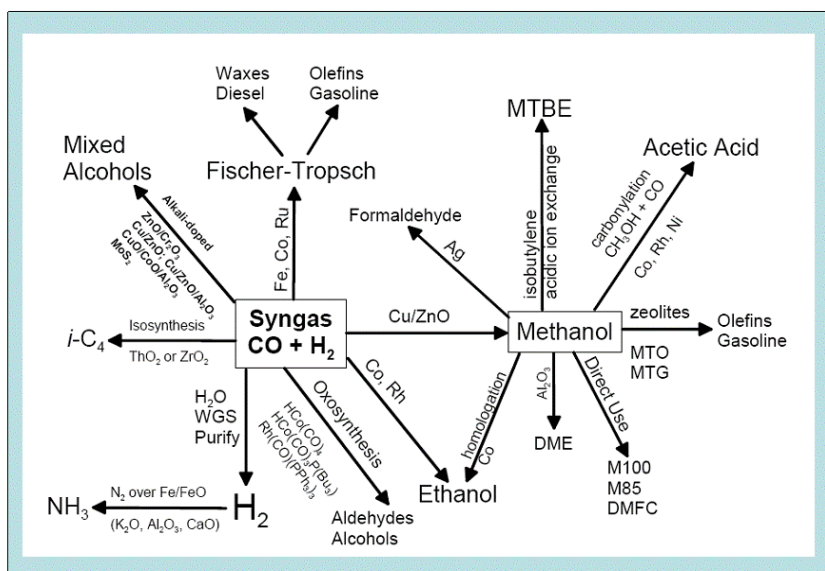


Figure 14 Synthesis Gas and Methanol Platforms

(source: R P Overend, 2004 [http://gcep.stanford.edu/pdfs/energy\\_workshops\\_04\\_04/biomass\\_overend.pdf](http://gcep.stanford.edu/pdfs/energy_workshops_04_04/biomass_overend.pdf))

## 6.1 Biomass Energy

There are a number of important differences between biomass fuels and conventional fossil fuels. These distinctions are important when considering biomass energy generation:

- The calorific value of biomass (LHV = 15-18MJ/kg) is much lower than that of fossil fuels such as coal (LHV ~ 30MJ/kg) and natural gas (LHV ~ 53 MJ/kg).
- Biomass invariably contains retained moisture and also relatively high amounts of minerals such as potassium and sodium and in addition can contain high amounts of halides that can lead to acid gases.
- Biomass has a low volumetric energy density, is difficult to transport and requires significant energy to mill/chip to smaller particle sizes.

All of these factors can combine to add complexity to process engineering when generating energy from biomass, particularly large scale heat and power generation.

Of the primary processes shown in figure 13, combustion is the most established technology for deriving energy from biomass. Considerable biomass is used in this manner for small scale domestic heating, larger scale combined heat and power applications (2–10MWe) and stand alone power plants (20 – 100's MWe). Replacement of fuel oil boilers with biomass heating boilers is relatively straightforward and both economically and environmentally attractive for renewable heat production [52]. Heat produced in this fashion can have very high efficiencies and typically 80-90% of the LHV (lower heating value) of the biomass fuel can be recovered [53].

Electricity is produced from biomass combustion by generating steam at high pressure and directing this through steam turbines or steam engines. The 36MW straw-fired power station at Ely is an example of this. Generating electricity in this fashion is inefficient and considerable energy is lost as waste heat. Modern coal-fired combustion plants typically have an energy efficiency of 40%, biomass-fired plants considerably less. If the hot exhaust gases from the steam turbine are used to generate hot water for heating or steam for industrial use then energy efficiencies can be increased to around 80%. This is known as Combined Heat and Power (CHP) and examples of large biomass CHP plants in the UK include Sembcorp's £60 million 30MWe Wilton10 plant and Eon's £90 million 44MWe power plant at Lockerbie both utilising wood fuel and due on stream later this year [177,178].

Combustion technology is well developed for biomass combustion and includes fluid bed burners for larger plants. CHP units are commonplace in Northern Europe due to many years of successful facilitation by governmental policies [52]. The worlds largest biomass CHP plant is the Alholmens Kraft Power Plant in Finland which has a steam capacity of 55MW and a electrical capacity of 240MW [179]. The situation is different in the UK with output-based government support only applicable to electricity generation rather than combined heat and power [5]. In addition, finding suitable CHP sites with a market for both the power and the associated heat is not straightforward [53].

Due to limitations associated with the steam cycle, greater efficiencies in electricity generation can be achieved using gas turbines or gas engines. In this case the biomass feed is gasified with air to produce a fuel gas which can then be combusted. The resultant crude synthesis gas mixture is known as producer gas. Due to the use of air as the oxidant, producer gas contains large amounts of nitrogen and has a relatively low calorific value (3-5 MJ/m<sup>3</sup>). If the biomass is gasified using oxygen the synthesis gas is not diluted with nitrogen and has a higher calorific value (12-15MJ/m<sup>3</sup>). For the production of electricity, producer gas is fully combusted downstream and the hot pressurised combustion gases used to drive a gas turbine. This process can deliver

efficiencies in electricity generation of 22-37% (steam turbines generate 10-15%) [180]. Small scale biomass gasification plants utilise gas engines or modified diesel engines rather than gas turbines. The DTI has funded research aimed at the development of biomass microturbines that can be utilised at this small scale [181,182,183]. Gasification technology is more complex and capital intensive than combustion processes for heat and power production and therefore more suited to large scale applications. Biomass gasification processes are at a relatively early stage of development and are particularly complex due to the extra requirement for gas clean-up.

There are a number of small ~ 100kWe biomass gasification plants in the UK utilising gas engines including the 130kWe CHP plant at BedZED [184] and the 75kWe CHP plant at the ECOS Millennium Centre in Ballymena [185]. A much larger 8MW biomass gasification plant based in Yorkshire (ABRE Project) was built in 2001 utilising state-of-the-art integrated combined cycle gas turbine technology. However, the plant ran into technical difficulties during commissioning and was abandoned after the project was declared insolvent. The UK scene for biomass gasification was summarised in 2004 by Future Energy Solutions as part of the IEA Bioenergy activity [186].

## **6.2 Biomass To Liquids (BTL)**

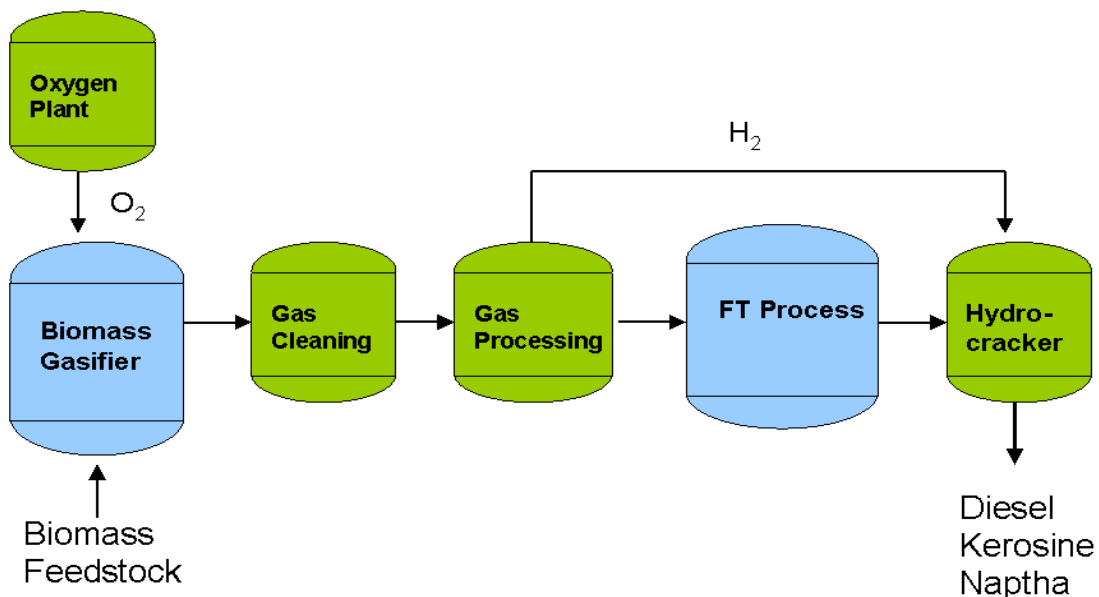
Synthesis gas can be converted to synthetic diesel via the Fischer-Tropsch reaction; this process has been practised for many years and was first demonstrated in the 1930's. The Fischer-Tropsch process is complex and utilises a number of highly integrated process and separation steps. The product slate is not limited to diesel but can be tuned to produce a portfolio of products from diesel, kerosene, naphtha and chemical intermediates such as linear alpha olefins and solvents. The synthesis gas feedstock for the Fischer-Tropsch process has historically been produced from coal (CTL: coal to liquids process) and in more recent times natural gas (GTL: gas to liquids process) but now attention is focusing on the use of biomass as the source of the synthesis gas, this process is known as Biomass to Liquids (BTL process).

Irrespective of synthesis gas source feedstock, the Fischer-Tropsch process produces a synthetic diesel that has a higher cetane value and much lower sulfur content than conventional diesel. However, the synthetic diesel has somewhat lower lubricity and lower density than conventional diesel. For these reasons, the market entry for synthetic diesel is likely to be as a blendstock to improve fuel quality.

Being based on fossil resources themselves, CTL and GTL derived synthetic diesels offer little environmental benefits compared to conventional crude oil derived materials. In fact, synthetic FT diesels produced from coal or gas feedstocks have increased greenhouse gas emissions relative to conventional diesel. However, BTL synthetic diesel can deliver considerable greenhouse gas reductions producing only 7% of the carbon dioxide emissions associated with conventional diesel [176]. This is also a

significantly better performance than FAME biodiesel which generates some 63% of the greenhouse gas emissions of conventional diesel. BTL synthetic diesel being closer to conventional diesel in chemical composition and energy content presents a smoother transition to renewable fuels than biodiesel. BTL diesel is likely to be less restricted on blending levels, has higher chemical stability in storage and will suffer less from consistency issues. It is for these reasons that a number of car manufacturers and oil companies are championing the introduction of BTL synthetic diesel. This is particularly the case in Germany, where Volkswagen, Shell and Choren are collaborating on the development of new BTL process which is reportedly close to commercial implementation.

By utilising the established Fischer-Tropsch platform, the greater majority of the process technology required for BTL implementation is available off the shelf. However, the production of synthesis gas from biomass with the required purity and composition for downstream catalytic processing is yet to be demonstrated at a commercial scale. Although gas and coal gasifier technology is well established, biomass as a feedstock presents a range of specific technical challenges due its physical form and chemical composition. A BTL process scheme will comprise a large number of integrated individual process units. Figure 15 shows a schematic of a generic BTL process. The individual elements will now be discussed in more detail

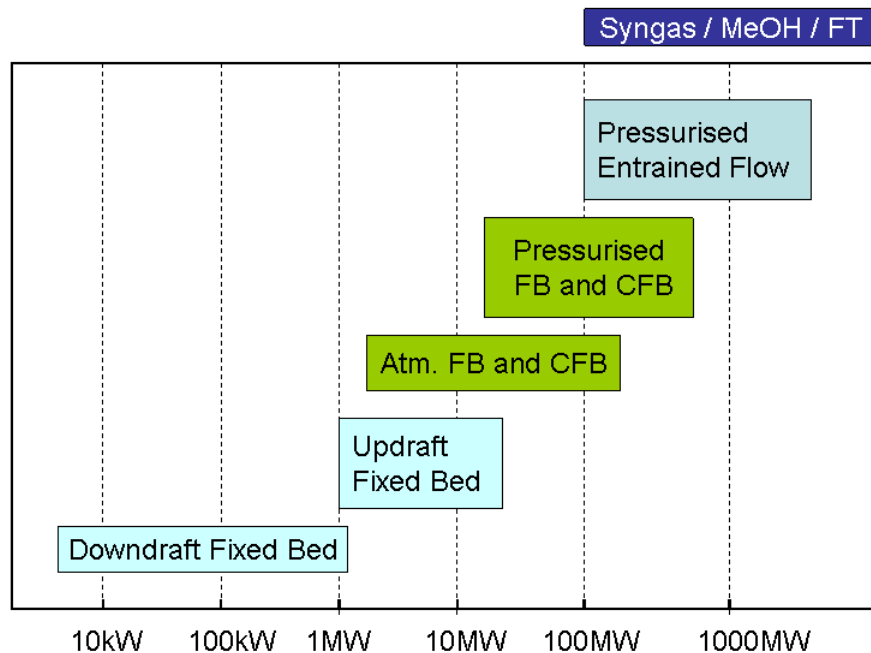


**Figure 15 Schematic of a Biomass to Liquids Process**

### 6.2.1 Biomass Gasification for Synthesis Gas Production

Although there are a wide variety of biomass gasification options for energy production, the very specific requirements for large scale Fischer-Tropsch process limits the gasification options to large, high pressure, oxygen blown fluidised bed and entrained flow reactors [176,187,188]. These choices are mostly dictated by the ability to manage the large scale of synthesis gas production required for economic fuels and chemicals production (see figure 16).

The use of higher pressure (15-60 bar) reduces the scale of the gasification reactor and the downstream processing equipment. The high pressure and also reduces the downstream compressor requirement necessary to operate at the higher pressures required for the Fischer-Tropsch synthesis. Oxygen blown processes are necessary to produce the diluent free synthesis gas feedstock for Fischer-Tropsch synthesis. Air blown gasification processes produce a synthesis gas feedstock with significant nitrogen diluent; this inert diluent would build up in the Fischer Tropsch recycle stream necessitating large purge streams and significantly impacting the economics of the process. A disadvantage of oxygen blown processes is the requirement for an air separation plant which adds significant capital cost to the overall investment. Once through Fischer-Tropsch processes that can operate with nitrogen containing synthesis gas from air blown systems are under development by companies such as Syntroleum but as yet not commercially demonstrated [189].



**Figure 16: Gasification Technology Scale vs Market Requirement**

Adapted from E Rensfelt et al

([www.ecotraffic.se/synbios/konferans/presentationer/19\\_maj/gasification/synbios\\_rensfelt\\_erik.pdf](http://www.ecotraffic.se/synbios/konferans/presentationer/19_maj/gasification/synbios_rensfelt_erik.pdf))

Successful development of biomass gasification technology for BTL processes will need to overcome a number of challenging barriers including; inefficient biomass handling and feeding systems, ash sintering and slagging and tar removal from the synthesis gas. Of these issues, gas clean-up (tar removal) is widely recognised to be the biggest issue [190]. Both fluidised bed and entrained flow systems have advantages and disadvantages when addressing these aspects of biomass gasification [191]:

- Fluidised bed gasifiers are operated below a temperature of 1000C to guard against problems with ash slagging and sintering in the reactor. Under these conditions, significant amounts of methane are present in the product synthesis gas stream along with medium amounts of tar. To maximise, the carbon efficiency of the gasification process the unreacted methane must be converted to synthesis gas in a downstream catalytic reforming step.
- Entrained flow gasifiers are already demonstrated at a large commercial scale for coal gasification. These reactors operate at temperature around 1300C and ash slagging is accommodated in the reactor design. At these high temperatures, methane and tar concentrations in the reactor outlet are greatly reduced relative to the fluidised bed system. However, entrained flow reactors require very fine particles of biomass feedstock. Unlike coal, biomass is very difficult to pulverise and grind down to the required particle size.

As described in the section 5.1, biomass feedstocks present significant issues regarding solids handling. Biomass milling and chipping adds a significant energy cost to the process and pressurised gasification reactors require specialised feed systems. A number of groups are developing biomass pyrolysis and torrefaction pre-treatments to produce feedstocks that can be more readily fed into pressurised reactors. Difficult to handle biomass feedstocks, such as straw, can be converted into a bio-oil/char slurry and then fed into an entrained flow gasifier; this approach is being pursued by FZK in Karlsruhe, Germany [192]. FZK have developed a twin-screw reactor system to perform the pyrolysis, the heat being supplied by recirculating hot sand. The resultant bio-oil/char slurry can be milled to produce a pumpable liquid. The FZK slurries have been evaluated in the Future Energy 5MW entrained flow gasifier demonstration plant in Freiberg [176]

An alternative to pyrolysis is torrefaction, which involves heating the biomass at 250-300C to produce a brittle, easy to grind material, that has physical properties similar to coal ("Bio-coal"). This route is being developed by ECN in the Netherlands to enable biomass to be more easily fed to entrained flow gasifiers [193]. Choren has developed a different route to overcome the problems associated with entrained flow gasifiers in their unique Carbo V process [194,195]. In this process the biomass feedstock is subjected first to slow pyrolysis to yield solid char and gases, the gas is then fed to the gasifier and converted whilst the char is pulverised and injected further downstream in the reactor to

react with the hot gases. The resulting synthesis gas product is cooled down to a temperature of around 1000C as a result of the endothermic gasification of the char. Utilising the CARBO-V process Choren claims a synthesis gas product completely free of tar and with very low levels of methane. To commercialise this technology Choren have formed a collaboration with Shell and Volkswagen and are in the process of commissioning a large scale 45MW demonstration (Beta) plant in Freiberg [176].

Fluidised bed biomass gasifiers are being developed by a number of research institutes: VTT in Finland are developing this technology using a 500kW demonstration plant [196] and as part of a large EU FP6 “Renew-Fuel” project, the CUTEC-Institute in Germany has a 400kW demonstration plant in addition to a 2 litre Fischer-Tropsch pilot plant [197]. A large 5 year EU funded project entitled “Chrisgas” started in 2004 to commercially develop biomass gasification for synthesis gas production. The project has a funding of 15 million euros and contains 16 partners from 7 EU member states [198]. There are no consortium members from the UK. The ultimate goal of this activity is to convert the existing air blown 18MW gasifier at Varnamo in Sweden to an oxygen/steam blown system for pure synthesis gas production. This activity will also incorporate the retrofitting of a complete gas clean-up and processing section.

### **6.2.2 Synthesis Gas Cleaning and Conditioning**

The biggest challenge in the development and commercialisation of BTL processes is the integration of the biomass gasifier with the downstream Fischer-Tropsch process. Fischer-Tropsch catalysts are very sensitive to poisons and there are very strict requirements for the synthesis gas purity and composition. Such requirements place great emphasis on a highly effective synthesis gas clean up. A wide range of contaminants can be present in the synthesis gas on leaving the biomass gasifier including:

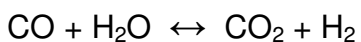
- Heavy hydrocarbons (tars)
- Particulates: soot, ash
- Acidic gases: HCl, H<sub>2</sub>S, COS..
- Basic gases: NH<sub>3</sub>

As a rule of thumb, Fischer-Tropsch synthesis gas feeds must have ammonia and sulphur containing gases reduced to levels below 1ppmv and halides and alkalis reduced to below 10ppbv [199]. Tars must be reduced to such a concentration in the synthesis gas such that no condensation occurs in the Fischer Tropsch reactor. Due to the wide range of impurities present a highly integrated multi-step approach is taken to synthesis gas cleaning. As the majority of these impurities are present in synthesis gas streams produced from coal and oil-residues, commercially available technologies exist for their removal. Both hot gas and cooled gas cleaning options are available. Particulates can be removed by cyclones, electrostatic filters and wet scrubbers. Acid

gases can be removed by wet scrubbing. Zinc Oxide filters, or a Rectisol unit, can be employed to remove hydrogen sulfides.

Although there is a considerable amount of activity in the area of tar removal, as yet there is no effective commercially demonstrated technology that exists for this purpose. Tars are generally composed of heavy polynuclear aromatic hydrocarbons and create huge problems by condensing out in downstream heat exchangers, filters and other areas. Tars can be removed by wet scrubbing, thermal decomposition and catalytic reforming. However, wet scrubbing suffers from long term operational issues and more importantly presents a serious waste disposal issue with the resultant condensate. An alternative to wet scrubbing is thermal decomposition of the tar, this avoids disposal issues because the tar species are destroyed however very high temperatures are required (>1000C) which can result in soot formation [190]. Consequently, most work has focused on catalytic reforming as the likeliest option for effective tar removal. Research has concentrated on two catalytic systems; non-metallic calcined dolomites (natural calcium/magnesium oxides) and nickel based catalysts [200,201,202]. Dolomite catalysts have been evaluated in fluidised bed reactors but can suffer from severe catalyst attrition and low activity. Nickel based catalysts are well known for other steam reforming processes and have proven to be highly active for both tar destruction and methane reforming. However, nickel based catalysts are significantly more expensive than dolomite systems and are susceptible to catalyst poisoning by sulphur compounds and deactivation under reaction conditions. VTT in Finland is active in developing new tar reforming catalysts based on nickel monoliths and more stable zirconia's [203].

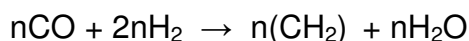
The synthesis gas produced from the gasification of biomass has a H<sub>2</sub>/CO ratio close to 1.0; this is too low for Fischer-Tropsch synthesis and needs to be increased to a value closer to 2. The synthesis gas H<sub>2</sub>/CO ratio is readily adjusted using the Water Gas Shift Reaction which reacts carbon monoxide with water to produce carbon dioxide and hydrogen.



The water gas shift (WGS) process operates at around 300C and 15-25bar and is a common process unit in petrochemical refining. In addition to increasing the H<sub>2</sub>/CO ratio the WGS reaction also increases the carbon dioxide content of the gas. Carbon dioxide is an inert diluent in the Fischer-Tropsch process and will build up in the recycle loop. To avoid this, the carbon dioxide content can be reduced in the synthesis gas by commercially available solvent extraction processes such as Rectisol and Sulfinol. These extraction processes will also remove other contaminants in the synthesis gas such as hydrogen sulphide.

### **6.2.3 Fischer Tropsch Synthesis**

The production of synthetic diesel via the Fischer Tropsch reaction is well established and has been practised for many years. The Fischer Tropsch process converts synthesis gas into a mixture of linear hydrocarbons with varying chain length. The basic reaction can be represented as follows:



The products are a wide range of linear alkanes and alpha-olefins. The distribution of the hydrocarbons is determined by the reaction conditions, catalyst type and the H<sub>2</sub>/CO ratio of the synthesis gas. The reaction is performed at an operating pressure of 20 – 40bar and a temperature range of either 200 -250C or 300-350C. The lower temperature range produces waxy products which can be hydrocracked to diesel whilst the higher temperature range produces more gasoline range products. The catalysts employed for the reaction at lower temperature are either iron or cobalt based. Cobalt catalysts are more selectivity to wax products, more attrition resistant and have higher activity whilst iron catalysts are less easily poisoned and deactivate less quickly. An advantage of iron catalysts is that they have intrinsic water gas shift activity and can process synthesis gas with low H<sub>2</sub>/CO ratios. The Fischer-Tropsch reaction is highly exothermic and a number of reactor designs have been developed to accommodate this feature including fixed bed, fluid bed and slurry phase reactors. More detailed information on Fischer Tropsch synthesis can be found in the following papers [204,205,206,207].

The waxy product from a Fischer-Tropsch process can be broken down into a range of valuable hydrocarbon products such as diesel, kerosene and naphtha. This process is performed using hydrocracking, a standard refinery operation. In principle, the hydrocracking process can be switched from diesel to kerosene mode depending on market conditions.

The Fischer Tropsch process has been practised by SASOL in South Africa since the 1950's using coal as the synthesis gas feedstock. More recently, the Fischer-Tropsch process has been identified as a means to convert remote gas into easily transportable liquid products. Shell built the first such GTL plant in Malaysia in the early 1980's with a relatively small production capacity of 12,000 barrels per day of product [208]. A second larger GTL plant with 30,000 bbd capacity was brought on stream in 1993 by South African company, PetroSA at Mossel Bay [209]. Now most of the oil majors are involved in developing and constructing significantly larger plants in countries such as Qatar (GTL) and China (CTL). These plants are vast in scale, with the proposed Shell plant in Qatar having a production capacity of 140 thousand barrels a day of Fischer-Tropsch products (7 million tonnes per year) [210].

Although BTL is as yet commercially unproven it has been demonstrated at a large scale. By far, the most advanced of these activities is the work performed by Choren [194, 195]. Utilising their proprietary Carbo-V biomass gasification process and Shell FT technology, Choren have demonstrated BTL at a 1MW pilot plant scale and are currently commissioning a 45MWth, 15,000 tonne capacity demonstration plant at Freiberg which will process some 75,000 tonnes of biomass per annum. Choren has stated that it intends to build five commercial BTL scale plants each with 200,000 tonne per annum product capacity in Germany [211]. The first plant is likely to be constructed on a former nuclear power station site in Lubmin and is planned to come on stream in 2011 [212].

A large amount of BTL research is currently being performed under an EU FP6 funded activity named Renew [213]. This is a 4 year activity started in 2004 and aims to develop BTL technology and other thermochemical routes to bioethanol and biomethanol. The German institute CUTEK is operating a BTL pilot plant facility as part of this activity. The consortium contains 33 companies and organisations from 9 EU member states. The ultimate aim is to take a slipstream of synthesis gas from the Gussing Power station in Austria and feed it into a Fischer-Tropsch reactor. The UK is not represented in this consortium activity.

#### **6.2.4 BTL Economics and Scale of Production**

Fischer-Tropsch facilities are large, complex and highly integrated multi-process facilities. Such complexes are constructed at a vast scale to maximise economy of scale benefits. As an example, calculations have shown that a small GTL plant with less than 10,000bpd product capacity would have a CAPEX cost on a daily capacity basis, double that of a larger GTL plant with 35,000 bpd capacity [214]. The three major capital plant items for GTL are the air separation unit to produce the oxygen, the gasification plant and the Fischer-Tropsch process representing 30%, 20% and 25% of the ISBL cost respectively [215]. The industry target for GTL capital cost is in the region of \$20,000 per barrel of daily capacity. Currently, GTL plants are thought to cost in the region of \$25,000 to \$40,000 per barrel of daily capacity [216]. It was recently reported that the investment cost of the “Pearl” GTL plant under construction in Qatar had tripled from its original estimate and now was likely to be as high as \$18 billion when completed [217]. The economics of GTL processes are very sensitive to the price of natural gas; GTL is considered profitable at a crude oil price above \$40 barrel and a gas price between \$0.5 per million Btu to \$1.0 per million Btu [216]. CTL plants are more capital intensive than GTL plants due to the extra complexity associated with solids handling and feeding, the use of an entrained flow gasifier rather than a natural gas reformer and the need for a Rectisol unit to remove CO<sub>2</sub> after synthesis gas conditioning. Capital costs for CTL plants are reported to be in the range of \$50,000 to \$70,000 per barrel of daily capacity [216]. BTL plants are similar in nature to CTL plants in terms of gasification plant requirements and the need for more involved gas cleaning. A range of capital costs have been reported for BTL processes. A world scale BTL plant of 34,000bpd product

capacity is reported to have a CAPEX of \$52,000 per barrel of daily capacity [215] whilst others have reported BTL CAPEX at €30,000 to €40,000 per daily barrel capacity for a small BTL plant (1000-2000 bpd capacity) [218] up to capital costs as high as \$140,000 per barrel of daily capacity [216]. On a comparable basis BTL plants are more expensive than CTL plants and considerably more expensive than GTL plants.

Vast feedstock reserves are required to support GTL and CTL plants, natural gas reserves of 4 to 5 trillion cubic feet and coal reserves of 2 to 4 billion tonnes respectively are necessary for plants of capacity 70,000 -80,000 bpd [216]. Unlike coal and natural gas, biomass resources are not so densely concentrated in one area, nor so easily transported. The physical nature of biomass (low energy density) and its dispersion over a larger area introduces significant feedstock logistics issues for a BTL plant. The increased transportation and storage costs of the biomass feedstock may limit the scale of a BTL plant and thereby restrict the opportunity to maximise capital efficiency through economy of scale. Choren have stated that their commercial BTL plants of 4000 bpd product capacity will access the required one million tonnes of biomass feedstock within a 30km radius of the plant [194]. A number of groups have reported on the effect of BTL plant scale on capital cost and diesel product production cost. In one case it was demonstrated that the specific CAPEX costs (\$/bpd) and BTL diesel production cost increased dramatically below a BTL plant scale of 2000 MW<sub>th</sub> (17,000bpd capacity) [215]. In this particular study the optimum BTL plant scale was determined to be of the range 2000 to 4000 MW<sub>th</sub> (16,000 to 32,000 bpd). It should be noted that even at the lower range of BTL plant scale of 2000 MW<sub>th</sub>, a biomass feedstock supply of some 4 million tonnes per annum would be required to support the plant.

Two different scale scenarios have been proposed for potential BTL plants; a local scale model and a global scale model. In the local scale model the BTL plant is situated close to the biomass feedstock and transportation costs are minimised whilst in the global scale model the much larger BTL plant is situated close to a river or sea port and accesses internationally traded biomass supplies [219]. The advantages and disadvantages of both BTL models are summarised in Table 6.

From a financial viewpoint, the benefits of economy of scale are likely to outweigh the extra transport costs incurred by extending the catchment area of the biomass feedstock. This is particularly the case if the biomass feedstock can be shipped to the BTL plant and densification strategies such as torrefication or pyrolysis can be employed. A recent study evaluated the feasibility of positioning a large global scale BTL plant in the port of Rotterdam in 2020 to supply EU markets [220]. The Rotterdam BTL plant of 75,000bpd product capacity would require 50,000 tonnes of biomass per day. The supply chain logistics of delivering the huge biomass requirements of this plant were investigated and shipping in wood from the Baltic States was considered a feasible option.

**Table 6 BTL Plant: Local vs Global Scale**

	Local Scale	Global Scale
Production Capacity (tonnes)	Limited to hundreds of thousands	Millions of tonnes
Plant site logistics	Site near to biomass feed. Exploit existing infrastructure ie pulp mill, power station	Site near to diesel markets, exploit existing infrastructure by siting on oil refinery
Transport costs	Relatively low	Relatively high
Feedstock flexibility	Probably tied into one feedstock. Opportunities for very cheap niche feedstock	Flexible, access commodity biomass feedstocks
Economy of scale	Relatively Poor	Good
Portfolio of products	Limited	Wide variety possible
Investment (\$)	500M to 1Bn	Many Bn's (prohibitively expensive?)

Both small and large BTL plants can benefit from integration into existing infrastructure. For instance, small BTL plants can be integrated into existing pulp mills by replacing Tomlinson Boilers with black liquor gasification systems (see later) whilst large BTL plants can benefit from co-locating with existing oil refinery infrastructure. Major benefits in energy efficiency and process economics can be accrued by integrating both power generation and BTL fuel production, this can be achieved by utilising the off-gas (light hydrocarbons) from the Fischer-Tropsch process to generate heat and electricity [218, 221, 222]. The production of biofuels, heat and steam is known as tri-generation or polygeneration. The integration of power production within the BTL process also allows the possibility other process configurations [223]. The Fischer-Tropsch unit operates on a relatively low conversion per pass of synthesis gas with large recycles. With integrated power production it becomes feasible to operate the Fischer Tropsch unit on a once-through basis and feed the unconverted synthesis gas to a gas turbine for heat and power generation.

A large number of studies have reported on the production costs of BTL synthetic diesel some of this data is summarised in Table 7

**Table 7 Various Production Costs Reported for BTL Liquids**

Production Cost /litre	Comments	Reference
€ 1.1 to € 0.55	Plant scale from 50MWth to 8,500MWth, feedstock cost contributes 0.26 €/litre to cost	213
€ 0.7	EU FP6 Renew Project Target for BTL	211
\$0.7 to \$0.5	Choren BTL plant improvement from 2009 to 2020 with feedstock cost reducing from 0.28€/litre to 0.22€/litre and plant increasing in scale	193
\$0.4	Large 75,000bpd plant Rotterdam in 2020, feedstock costs 0.25 \$/litre	218
£0.32 to £0.54	Utilising short rotation coppice feedstock, advanced FT technology. No co-product value included	16
€ 0.3	Large scale BTL with tri-generation (heat & power production). Electricity price set at 6 € cent/kWh	220

Short to medium term costs for BTL liquids are around triple that for conventional mineral oil diesel. However with technology development and economies of scale, these studies show that at high crude oil price and favourable fiscal incentives tax incentives, BTL synthetic diesel can be competitive against mineral oil diesel.

### **6.3 Other Biofuels Derived from Synthesis Gas**

In addition to synthetic diesel, synthesis gas can be converted into a wide range of other transportation fuels (Table 8). Hydrogen produced from biomass represents the lowest cost biofuel derived from synthesis gas. The hydrogen content in synthesis gas can be maximised through the water gas shift reaction and then extracted using separation techniques such as pressure swing absorption. Although the majority of hydrogen production is used for chemicals manufacture (mostly ammonia) and oil refining processes, its potential major long term use is as a feedstock for PEM fuel cell vehicles. Life cycle analysis studies have shown that biomass derived hydrogen used in fuel cell cars delivers the highest greenhouse gas savings for a renewable transport fuel. However, a number of challenging technical and logistical issues remain to be resolved before hydrogen powered fuel cell vehicles become a commercial reality.

Synthesis gas can be catalytically converted into a range of oxygenate chemicals which can either be used directly in transport fuels or converted into more conventional hydrocarbon transport fuels. These chemicals will now be discussed in more detail.

**Table 8 Other Transport Fuels produced from Bio-derived Synthesis Gas**

Energy Carrier	Energy Conversion
Hydrogen	ICE , Fuel Cell
Higher Alcohols	ICE gasoline oxygenate
Methanol	ICE Gasoline oxygenate, Fuel Cell
Ethanol (synthesis gas fermentation)	ICE gasoline oxygenate
DME	ICE, LPG substitute

### **6.3.1 Biomethanol**

Methanol is a major commodity chemical produced from natural gas. The global market for methanol is well over 35 million tonnes, the majority of which is used to manufacture formaldehyde for use in the construction sector. Methanol production technology is mature and exploits economy of scale in huge plants (Mega-methanol plants) with production capacities measured in millions of tonnes. Methanol is produced from synthesis gas utilising copper/zinc based catalysts at temperatures of 220C- 300C and pressures of 50 -100 bar. Methanol synthesis is an exothermic reaction and reactor design is based on efficient control and removal of heat from the process [224]. The synthesis gas feedstock is currently produced from natural gas and methanol competes with both GTL and LNG (liquefied natural gas) processes from the valorisation of natural gas in remote sites.

Methanol has a long history of use as a replacement for petrol. Throughout the 1980's and 1990's, petrol blended with methanol was commercially trialled in various US States [225]. Methanol has a number of advantages as a transport fuel including its high octane rating and cleaner burning characteristics. However, a number of critical issues such as its immiscibility with petrol and toxicity have led to methanol now being largely discounted as a transport fuel.

Methanol itself can be derivitised to produce a wide range of transport fuels. Methanol is used to manufacture the petrol additive methyl tertiary butyl ether (MTBE), although the use of this additive is now in decline. Methanol is also used as a component of biodiesel. Methanol is an excellent platform molecule and can be derivitised to produce

a wide range of other chemical intermediates. With the oil shocks of the 1970's considerable industrial research was directed towards the conversion of methanol to hydrocarbon fuels and petrochemical intermediates. This activity culminated in the commercialisation of the Mobil Methanol to Gasoline (MTG) process which was commercialised in New Zealand in the early 1980's [226]. This process was abandoned due to the rising cost natural gas which made the process uneconomic. The MTG process relied on a highly selective solid-acid zeolite catalyst. By changing the catalyst and process conditions, the MTG process can be modified to produce either light olefins or a mixture of gasoline and diesel [227, 228, 229]. Although not commercially practised both of these processes have been demonstrated at commercially relevant scale and are considered to be "off the shelf" process technology. If the synthesis gas used to produce the methanol is derived from the gasification of biomass then these methanol processes represent alternative synthetic routes to biofuels. However, the MTG process produces a gasoline range product with a very high aromatics content which does not conform to current petrol specifications. It is for this reason that most interest, particularly in Germany, has focused on the methanol to gasoline and diesel process (MOGD) utilising bio-derived methanol feedstock.

The production of biomethanol via biomass derived synthesis gas has been considered for some time particularly as a means to upgrade low value black liquor streams in pulp and paper mills. However, large scale stand alone bio-methanol plants are now being planned [230]. Some of the synthesis gas output from the Schwarze Pumpe gasification plant in Germany is used to produce around 100,000 tonnes of methanol, this process converts mixed wastes including woody biomass and plastics into synthesis gas for power and chemicals production [231]. The process is economic due to the fact that the waste feedstock commands a gate fee of €150/tonne [176]. In many ways bio-methanol synthesis is more straightforward than BTL, it is a more selective reaction and there are fewer requirements for downstream separation and upgrading. The energy efficiency of biomethanol synthesis is greater than that of the BTL liquids process [232]. Although this difference in energy efficiency will be reduced if the bio-methanol is converted into hydrocarbon fuels via a MTG or MOGD processes.

The catalysts used for methanol synthesis are susceptible to poisoning by impurities such as sulphur compounds so it is essential that the synthesis gas derived from biomass is of sufficient purity. As with the BTL process considerable economic and energy efficiency benefits can be realised by integration of methanol synthesis with heat and power production. A number of authors have reviewed the potential of producing methanol from biomass [232, 233]. Production costs for bio-methanol have been evaluated by a number of groups and have been compared by Spath et al [226]; depending on the plants scale and biomass feedstock costs (\$38/odt to \$46/odt) biomethanol costs ranged from \$9/GJ to \$19.6/GJ (approximately \$200 to \$445/tonne). A recent presentation [234] detailed the cost of bio-methanol delivered to Rotterdam

harbour from different countries and hence different biomass feedstock costs. The price of natural gas derived methanol has risen recently with high natural gas feedstock price, the October 2006 European spot price was reported to be €400/tonne (€17.6/GJ). It seems feasible therefore that biomethanol could be competitive against methanol at current market prices.

Black liquor produced during pulp manufacture represents a very large biomass resource for biomass energy and chemicals production. Conventionally black liquor is combusted in Tomlinson boilers to recover the inorganic pulping chemicals and provide steam for power generation. These Tomlinson boilers are now slowly being replaced by, or augmented with; more efficient air-blown gasification technology supplied by companies such as Chemrec [235] and ThermoChem Recovery International [236]. A number of groups have assessed the potential of utilising oxygen-blown entrained flow gasifiers for black liquor conversion to synthesis gas and subsequent conversion to methanol. The biomethanol potential for this route is around 4 million tonnes in Sweden and 28 million tonnes in the US [237]. The BLGMF (Black Liquor Gasification with Motor Fuels Production) project which included consortium members from Chemrec, Methanex, and Volvo concluded that biomethanol produced from black liquor in a modern integrated pulp mill could be produced with high efficiency and be cost competitive against conventional methanol [238]. Because of the sulphite chemicals used in the pulping process, synthesis gas produced from black liquor contains relatively high amounts of sulphur compounds. These sulphur compounds need to be removed prior to methanol synthesis to avoid catalyst deactivation. The available technology required for effective black liquor synthesis gas clean up has been reviewed [239].

As discussed previously biomethanol can be converted into a range of other biofuels using established technology. Work at the Technical University Bergakademie, in Freiberg (TUB-F), Germany is focused on demonstrating large scale biomass conversion to gasoline and diesel utilising a 10 bar fluid bed gasifier combined with methanol synthesis and methanol conversion to gasoline and diesel [176, 240]. The methanol conversion process will utilise the Lurgi MtSynfuel technology [227].

Methanol can be readily dehydrated to form dimethyl ether (DME). DME is similar in properties to LPG and has a high cetane number; consequently it has been promoted as an alternative transport fuel [226]. In addition to the methanol dehydration route, DME can be produced directly from synthesis gas. The Swedish government is funding research at Volvo for the development of DME powered truck engines [241]. The aim of this activity is to exploit the large volumes of black liquor available in Sweden for biofuels production.

The use of hydrogen carriers and on-board reforming for hydrogen powered fuel cell vehicles may provide a transition option until technology is developed for effective

hydrogen storage. Biomethanol represents a suitable carrier for renewable hydrogen for onboard reforming and has advantages over other potential carriers such as ethanol and hydrocarbons.

### **6.3.2 Mixed alcohols and ethanol**

The production of mixed alcohols from synthesis gas is well known and many processes have been developed to large demonstration scale over the last thirty years. Such processes are similar to methanol synthesis but differ in catalyst type and process conditions [226]. Such processes produce a mixed alcohol stream containing methanol, ethanol, propanol, butanols and smaller amounts of heavier alcohols. The original driver for mixed alcohol production was to find an alternative oxygenated transport fuel for blending with gasoline. However, none of these processes were commercialised due to the deficiencies in catalyst performance, fluctuating crude oil price and the subsequent use of MTBE and bioethanol as oxygenated additives for gasoline. A number of research groups have attempted to selectively produce ethanol from synthesis gas with varying degrees of success with most suffering from poor economics due to low catalyst selectivity. Interest in both mixed alcohol and ethanol production from synthesis gas has been rekindled recently due to the increased profile of biofuels. A number of companies are now pursuing the commercialisation of mixed alcohols synthesis from bio-derived synthesis gas. Pearson Technologies in the US are reported to be developing a biomass to ethanol process via the synthesis gas route [242, 243]. Recently Syntec have claimed to have developed a proprietary catalyst that delivers unique performance for ethanol production from synthesis gas [244].

In contrast to high temperature catalytic routes, the conversion of synthesis gas to ethanol can also be accomplished by fermentation with anaerobic bacteria such as *Clostridium ljungdahlii* [245]. This system was identified by workers at the University of Arkansas in the early 1990's and is now being commercialised by BRI [246]. BRI who have benefited from DOE research grants totaling some \$2.4 million, now plan to construct the first plant in Tennessee utilising municipal waste as the biomass feedstock. The process produces 75 gallons (0.23 tonnes) of ethanol per tonne of biomass [247, 248].

## 7. Renewable Chemicals

A significant change is occurring in the Chemicals Industry as increasing attention is being directed towards crops as a valuable source of raw materials. This change is being driven by environmental and economic factors coupled with the rapid advances in biotechnology. Raw materials derived from crops and biomass offer the potential of cheaper feedstocks, less intensive processing and highly functionalised starting materials for conversion to innovative and differentiated chemical products and intermediates.

Specific components of plants such as carbohydrates, vegetable oils, plant fibre and complex organic molecules known as primary and secondary metabolites can be extracted and utilised. Indeed some sectors, such as the oleochemicals industry has been harnessing the unique functionalities of plant oils for many years. Plants can synthesise highly complex bioactive molecules often beyond the power of synthetic chemists and a range of chemicals are currently extracted from plants for a wide range of markets from crude herbal remedies through to very high value pharmaceutical intermediates. However, it is only recently that large production facilities have been constructed to convert agricultural crops into bulk commodity chemicals such as polymers.

Current manufacture of bulk chemicals is based predominantly on crude oil and natural gas feedstocks. The Petrochemicals Industry has developed in tandem with Oil Refining and has flourished by successfully exploiting cheap and abundant mineral oil resources. The Petrochemical Industry accounts for around 8% of the total volume of liquid and gaseous hydrocarbon consumed. Petrochemical complexes are often integrated with oil refineries and have evolved into large, flexible and highly efficient manufacturing operations that maximise the synergistic opportunities of co-location to exploit the various energy and raw materials streams for cost effective chemicals production. This manufacturing model will form the basis for future biorefinery complexes. Petrochemical complexes produce primary chemical intermediates such as ethylene, propylene, butylenes and aromatics, which are further converted into intermediates for the plastics, textiles, solvents and detergent markets. Of these primary products, ethylene is the largest volume petrochemical with over 75 million tonnes produced globally. Interestingly, bioethanol can be readily dehydrated into ethylene, which in turn can be converted into propylene, butylenes and aromatics, and in principle therefore could form the basis of an entire chemicals complex based on renewable resources.

In addition to bioethanol, there are a number of other renewable chemicals that can be transformed into a variety of potentially useful chemical intermediates. These chemicals

are known collectively as “platform chemicals” and are analogous to the petrochemical building blocks. Platform chemicals will form an integral part of future biorefinery complexes.

These aspects will now be discussed in more detail. Particular emphasis will be placed on the production of large volume commodity chemicals, the potential platform chemicals of the biorefinery.

### **7.1 Bioprocessing**

White Biotechnology, the use of biotechnology in industrial applications, is seen as a critical platform for a future sustainable and competitive chemical industry utilising natural raw materials as feedstocks [249,250]. The application of biotechnology for chemicals production is well established in the pharmaceutical, fine and speciality sectors and has demonstrated a number of compelling advantages over conventional chemicals production. In contrast, the use of biotechnology for bulk chemicals manufacture has had relatively little commercial impact. However, recent progress in the fundamental understanding and application of new biotech areas coupled with the desire for more environmentally benign and differentiated polymers has facilitated the commercialisation of a number of new innovative processes that use agricultural raw materials. Derived from corn starch, both polylactic acid [251] and propanediol [252] processes have been commercialised. These new processes have arisen from advances in fermentation technology, genomics, molecular genetics, metabolic engineering and biocatalysis. The use of biotechnology for the manufacture of renewable bulk chemicals has been extensively reviewed [253,254,255, 256].

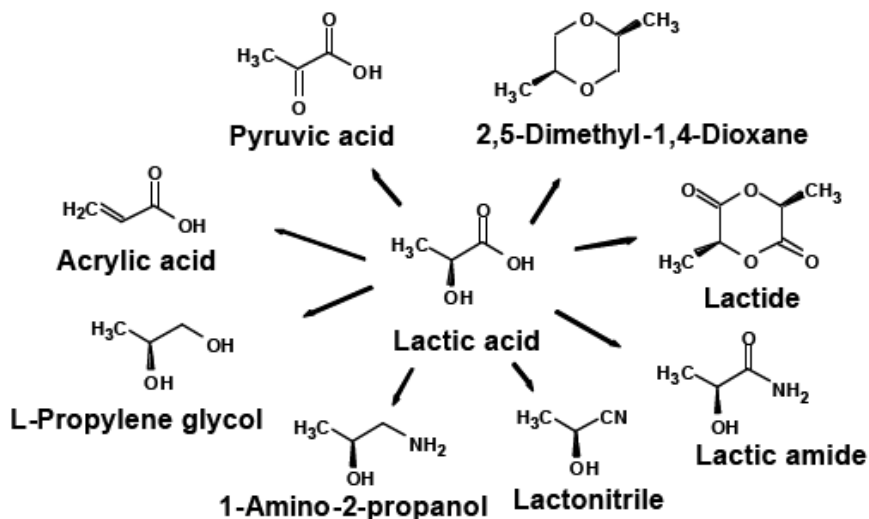
The complex nature of developing new biocatalysed routes for plant based chemical production dictates a large degree of multidisciplinary. To accomplish this chemical companies are forming partnerships with agricultural, food and specialised bioscience sector companies to access vital core skills. For example Cargill have partnered with Codexis to develop biotechnology platforms for the production of 3-hydroxypropionic acid and DuPont collaborated with Tate & Lyle and Genencor to develop their new process for 1,3 propanediol.

The continued development of bioprocessing technologies requires a considerable and coordinated activity at national and international level across a wide variety of academic and industrial groups. The UK is recognised as having core fundamental skills in this field and this was strengthened by the recent implementation of CoEBio3; a Centre of Excellence in Biocatalysis, Biotransformation and Biocatalytic Manufacture [257]. To ensure that new developments in bioprocessing are fully commercially exploited, a new Knowledge Transfer Network, the Bioscience for Business KTN, was formed by the DTI to facilitate the transfer of technology into the marketplace [258].

## 7.2 Platform Chemicals

Platform chemicals are functionalised chemical molecules that are produced from plant derived raw materials and can be readily derivitised into a range of valuable intermediates for use in the polymers, solvents and detergent markets. They are analogous with the petrochemical building blocks. An example of a platform chemical is shown in Figure 17; Lactic acid, produced by the fermentation of starch sugars, can be derivitised into a wide range of valuable intermediates with potentially significant market volumes. For example, acrylic acid could be converted into acrylic esters and polyacrylate polymers whilst lactide is converted into the new biodegradable polymer, polylactic acid. In many cases, these platform chemicals are difficult to manufacture using conventional petrochemical routes and often require complex and costly high temperature catalytic processes.

Two major reports have highlighted the potential of platform chemicals and their current status of development. A 2004 study by the US Department of Energy identified the twelve most important chemicals that could be produced from sugars either by fermentation routes or via the intermediate production of synthesis gas [259]. Chemicals selection was based on their strategic fit within a future large biorefinery complex.



**Figure 17: Lactic acid, an example of a platform chemical**

A more recent report published in September 2006, details the output of the EU funded BREW Project which reviewed the potential of white biotechnology to economically produce bulk chemicals [260]. The BREW project looked in detail at the technical, economic, societal and environmental factors that would influence the potential market

impact of a wide range of bio-based chemicals from the current time up until the year 2050. After screening, a total of 21 potential bio-based chemicals were identified as having greatest potential. A number of chemicals were identified by both studies as being of particular importance; these include glycerine, 3 hydroxypropionic acid, succinic acid, xylitol and sorbitol. Table 9 shows examples of some potential platform chemicals, for illustrative purposes representative 3, 4, 5 and 6 carbon platform chemicals are chosen.

Current research involves the development of improved routes to platform chemicals from crop derived feedstocks via both biotransformations and conventional catalytic processes. In parallel, new routes for the conversion of platform chemicals to higher value derivatives is also being explored. A number of UK academic groups are active in this field including the Satake Centre for Grain Process Engineering at the University of Manchester, the Green Chemistry Centre of Excellence at York University, the University of Cardiff and Imperial College. A recent DTI funded activity, coordinated by BHR, performed a mapping exercise for the catalytic conversion of plant raw materials in the UK [261]. Industrial activity in this area is increasing and a number of Chemical companies are now committing to substitution of conventional oil derived products with bio-based chemicals. DuPont for instance has set a target of 25% of revenue generation from renewable sources by 2010. Roquette currently operates its manufacturing processes on a biorefinery principle where a wide range of polyol products are produced from cereal starches [262]. Roquette is leading a large consortium activity (€98M funding over 7 years) to develop the Bio-Hub concept for cereal grains to chemicals [263].

### **7.2.1 Glycerine as a feedstock for Chemicals.**

Considerable focus is now being directed towards the conversion of glycerine to higher value chemicals. The huge growth in biodiesel capacity, particularly in the EU, has resulted in a glut of crude glycerine entering the marketplace. As a result the crude glycerine price has collapsed and is now worth little more than waste value. The crude glycerine can be refined into a high purity material, but this involves a complex and capital intensive distillation step and therefore only available to the big biodiesel manufacturers. Refining of glycerine is only likely to be a short term solution because markets for refined material are expected to be saturated in the not too distant future as extra biodiesel capacity comes on stream, particularly in the US. The depressed price of glycerine has prompted a huge interest in the application of innovative bioprocessing technologies for its derivatisation to higher value chemicals [264,265,266]. Glycerine is an excellent platform chemical with over 1500 derivatives and a number of companies are developing commercial processes based on glycerine feedstock: Both ADM and Cargill are developing separate routes to produce propylene glycols [267, 268] and Solvay has just brought on stream (6<sup>th</sup> April 2006) its new 10 thousand tonne capacity plant for producing epichlorohydrin. The product known as “Epicerol” is used as a feedstock for epoxy resin manufacture [269].

**Table 9 Selected Examples of Platform Chemicals and Their Derivatives**

Platform Chemical	Potential Derivatives	Applications	Market Size
<b>Lactic Acid</b>	Poly lactide	PLA biodegradable polymer	Currently 140KT (capacity) but could be 3.5MT by 2020
	Ethyl lactate	Solvent	Currently ~ 20KT could be >100KT as a green solvent
	Acrylic Acid	Acrylates, coatings, super absorbent polymers, adhesives	Currently ~ 2.5MT
	Propylene Glycol	Antifreeze, polyesters, detergents	Currently ~1.3MT
<b>Sorbitol</b>	Ascorbic acid	Vitamin C	80KT
	Sorbitan	Emulsifiers, detergents, personal care products	50KT
	Polyetherpolyols	Polyurethanes	~ 2MT
	Isosorbide	Small pharmaceutical at present but could be polyesters and plasticizers	Small but potentially large
<b>Succinic Acid</b>	1,4- Butanediol	Solvent, coatings, resins,	~ 0.9MT
	Tetrahydrofuran	Solvent, speciality polymer	~ 0.5MT
	2-Pyrrolidinone	Solvent, plasticizer, speciality polymer	20-30KT
	Itaconic acid	Additive, speciality polymer	Small but could be large as a methyl methacrylates substitute
<b>Levulinic Acid</b>	Methyl tetrahydrofuran	Solvent, possible fuel oxygenate	Could be very large
	Delta-amino levulinic acid	Novel Biodegradable Herbicide	
	Diphenolic acid	Possible Bisphenol A substitute in polycarbonates	Bisphenol A ~ 3MT market
	Ethyl levulinate	Possible fuel oxygenate	Could be very large

## 8. Biorefineries

Considerable attention is now being focused on the concept of the biorefinery. National and International strategies have been developed to facilitate the delivery of this concept and ultimately realise radical improvements to both the economics and energy efficiencies of biomass processing. The biorefinery concept can be described as follows [19, 20, 21]:

***The biorefinery concept describes a large highly-integrated complex incorporating individual processes that synergistically convert biomass feedstocks into power, biofuels and value-added chemicals.***

A generic biorefinery schematic is shown in Figure 17. The biorefinery concept is based on the modern day oil refinery where energy savings are maximised through process integration synergies and economies of scale are exploited for the cost effective co-production of power, fuels and chemical intermediates. By basing biorefinery concepts on current oil refinery models, the biomass industry can exploit more than 200 years of development. There are a number of interesting analogies that can be drawn between the biorefinery and the oil refinery:

- As with crude oil, biomass feedstock is a complex mixture of components that requires separation on introduction to the refinery. Crude oil is simply fractionated using distillation whilst biomass requires more complex physical and chemical fractionation methods.
- The oil refinery uses a wide array of high temperature catalytic processes. The biorefinery will utilise both high temperature catalytic processes and state-of-the-art biochemical processes to provide greater flexibility in the choice of product slate. In the majority of cases the oil refinery uses highly efficient catalytic technology that is mature with the prospect of incremental improvements over time. The biorefinery will apply novel and innovative biocatalytic routes with scope for radical improvements over time.
- Over the years oil refinery processes and product slates have changed to meet market demand. Biorefineries should be designed with the same principle. State-of-the-art biochemical process may allow more flexible processing and the potential for multi-product synthesis from common process units.
- Crude oil is extracted from the ground and its composition is fixed within certain boundaries that change from location to location. Biomass feedstock is grown and

ultimately could be tailored for both optimum processing and end market application through the utilisation of both plant breeding and genetic modifications.

- Oil refineries have huge processing capacities to achieve maximum economy of scale. A typical oil refinery processes around 200,000 barrels of crude oil per day, some 10 million tonnes per year. Biomass feedstock logistics are likely to limit biorefinery processing capacity but volume should be maximised to gain economy of scale benefits.
- In an oil refinery every element of the crude oil barrel is utilised to manufacture products or power processes. In a biorefinery, every component of the biomass feedstock will be similarly utilised.

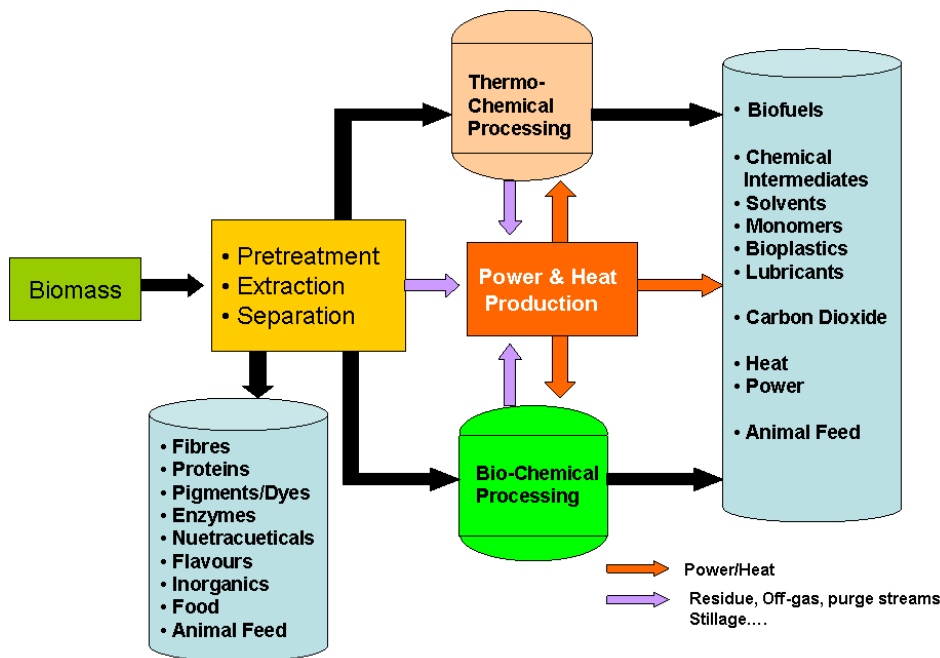


Figure 17 Generic Biorefinery Complex

If biorefinery complexes are to aspire to oil refinery economics and conversion efficiencies then they should be designed on complimentary principles. These can be summarised as follows:

- A biorefinery should have a large throughput capacity to maximise economy of scale benefits.

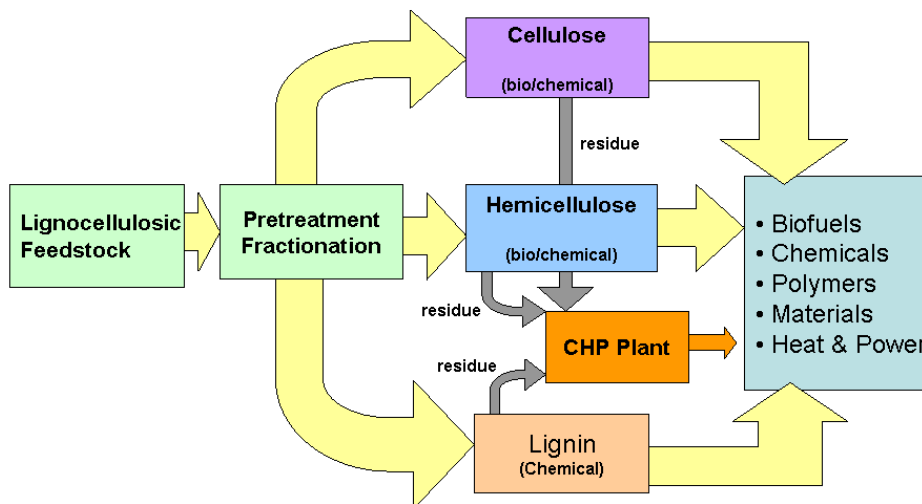
- A biorefinery should have world-scale biofuel production capacity to provide a sustainable economic platform over the lifetime of the investment by supplying product to a vast commodity market. The large biofuel production capacity of the plant will also generate sufficient volumes of ancillary biomass feed streams at minimal cost for value added co-product production.
- A biorefinery should produce a wide spectrum of products. Operational design will incorporate flexible processing such that individual product stream flows can be optimised to match external market requirements and maximise overall economics of biomass conversion.
- A biorefinery should maximise synergies through integrated processing and holistic operation on one large site. The various biomass feed streams should be joined by pipe.
- The biorefinery should be self sufficient in heat and power, deriving all its needs from the biomass input. Additional value can be generated through export of renewable electricity to the grid.

## **8.1 Conceptual Biorefinery Systems**

Four different conceptual advanced biorefinery systems have been described by Kamm et al [21]; the lignocellulosic biorefinery, the whole crop biorefinery, the green biorefinery and the “two platform concept” biorefinery. The “two platform concept” biorefinery is an amalgamation of the sugar and thermochemical platforms described by NREL.

### **8.1.1 Lignocellulosic Biorefinery (LCF - Biorefinery)**

Of the biorefinery systems described, the LCF-biorefinery is probably the most advanced in terms of technology development. A schematic of a lignocellulosic biorefinery is shown in figure 18. The lignocellulosic biorefinery utilises “naturally dry” biomass feedstocks such as wood, agricultural residues, energy crops and municipal waste. Such feedstocks are optimum in terms of reduced cost, resource flexibility and low inputs. The concept represents a logical progression of a 2<sup>nd</sup> generation lignocellulosic bioethanol facility towards a more advanced biorefinery system producing a broader array of co-products. In the lignocellulosic ethanol plant all of the pentose and hexose sugars are converted into ethanol to maximise biofuel production. In contrast, the hexose and pentose sugars are separated in the LCF-biorefinery and individually converted into bioethanol and higher value chemicals. Lignin itself represents a potentially valuable resource for aromatic chemicals, such as phenols, but limitations in conversion technology suggests that it will initially be utilised as a fuel to provide heat and power for the LCF-biorefinery.



**Figure 18 Lignocellulosic Biorefinery Schematic**  
(adapted from ref [21])

The individual steps of the LCF-biorefinery can be summarised as follows

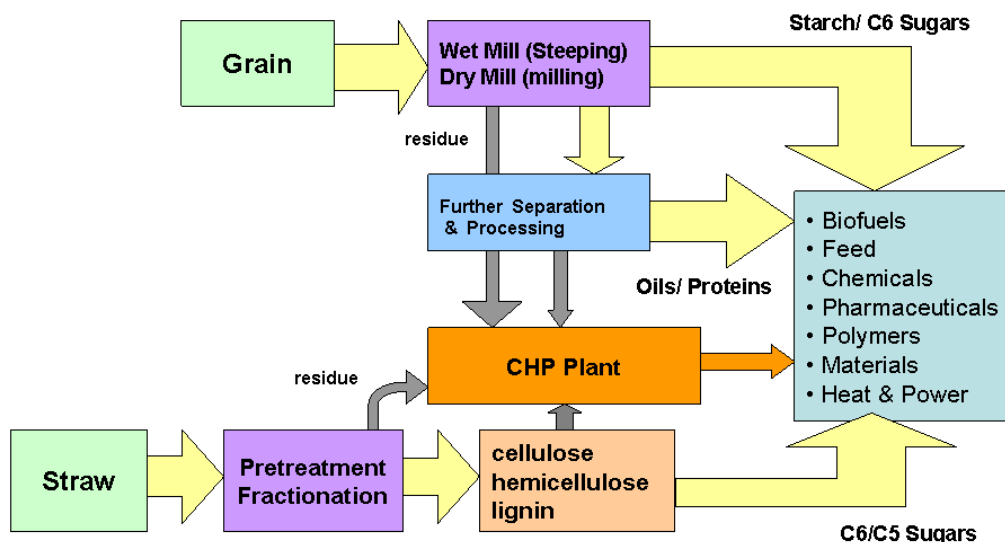
- Extraction of primary products from the lignocellulosic feedstock
- Fractionation of the lignocellulosic biomass into its component parts; cellulose, hemicellulose and lignin
- Hydrolysis of the cellulose and hemicellulose polysaccharides to fermentable glucose and xylose sugars
- Conversion of glucose sugars to biofuels/chemical intermediates such as ethanol, butanol, organic acids (succinic acid, lactic acid, levulinic acid..) using both fermentation and conventional chemistry
- Conversion of xylose sugars to biofuels/chemicals such as ethanol, xylitol, furfurals using both fermentation and conventional chemistry
- Conversion of lignin and other residue streams in a gasification combined cycle gas turbine to provide heat and power for the biorefinery and export of excess power to the grid.

Examples of LCF-Biorefineries are the Integrated Forest Biorefinery (IBFR) which process wood and wood wastes and lignocellulosic ethanol plants producing ethanol and co-products from municipal wastes.

### 8.1.2 Whole-Crop Biorefinery

The Whole Crop Biorefinery concept utilises cereal crops such as wheat and corn. In contrast to current bioethanol facilities, the entire crop including the straw and corn stover is used as the biomass feedstock. This concept could also be expanded to include vegetable oil crops. The utilisation of both straw and the grain at the same processing facility may provide a platform for the development of improved harvesting, storage and transport systems through whole crop harvesting and fractionation at the biorefinery. This concept was first explored in the early 1990's by the BIORAF consortium; an EU funded activity which looked at both wheat and oil seed rape whole crop processing [270].

The realisation of the Whole Crop Biorefinery concept is dependent on the efficient fractionation of the cereal grain or corn kernel into primary raw materials for upgrading into valuable products. A wide range of valuable chemicals, polymers and materials can be produced from the starch, proteins oils and non-starch polysaccharides that can be extracted from cereals. The whole crop biorefinery can incorporate either dry or wet milling operation to provide the primary fractionation of the cereal grains. Considerable work in this area has been performed at the Satake Centre for Grain Processing at Manchester University who are developing novel dry milling technologies to optimise fractionation of grains into raw material streams for chemicals manufacture [271,272,273]. Similar activities are being performed in the US [274, 275].



**Figure 19 Whole Crop Biorefinery Schematic**  
(adapted from reference [21])

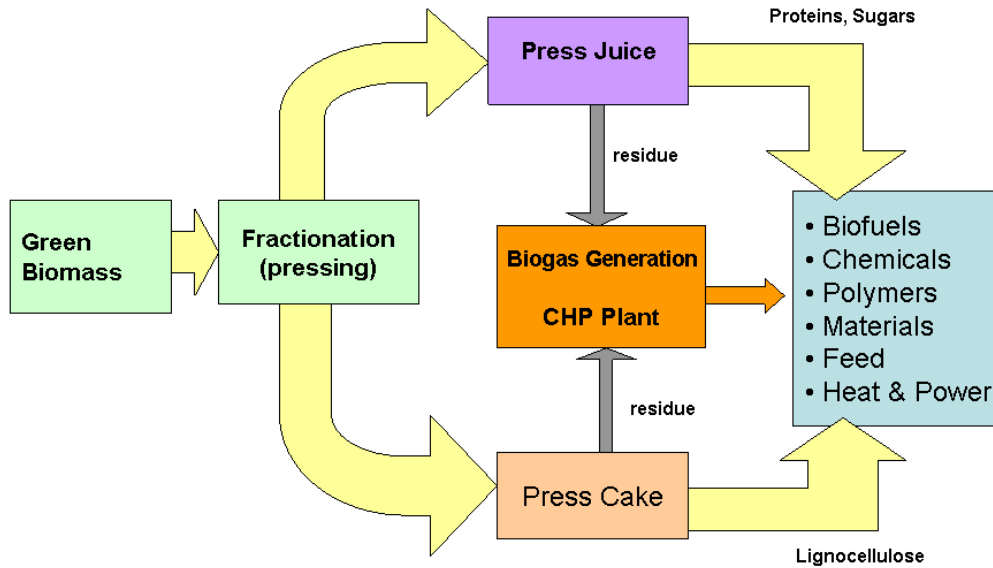
A simplified schematic of the Whole Crop Biorefinery concept is shown in Figure 19. The steps can be summarised as follows:

- The grain is fractionated either by dry milling and separation of the flour components into raw materials or by steeping and subsequent wet milling.
- The starch is hydrolysed to provide glucose sugar streams for fermentation /chemical processing to produce bioethanol and other chemicals such as lactic acid and succinic acid.
- Further extraction and separations are performed on the remaining components of the grain to provide protein, oil and non-starch polysaccharides raw materials for upgrading into high value polymers, pharmaceutical intermediates and specialities.
- The agricultural residue from the crop (wheat straw, corn stover...) is fed to a pre-treatment section for fractionation into lignin, cellulose and hemicellulose components. These streams could then be processed in much the same fashion as described in the LCF-Biorefinery. Transitional whole crop biorefineries will utilise the agricultural residues to provide heat and power for the whole facility.

### 8.1.3 Green Biorefinery

The Green Biorefinery utilises green plant matter, particularly grasses, to produce a diverse range of products. In contrast to the previous biorefinery models, the feedstock used is “nature-wet”. The typical feedstocks for a Green Biorefinery are forage and amenity grasses, these materials are relatively low cost and potentially available in large quantities. Primary processing of green plants consists of pressing and separation into a filter cake and press juice. The press cake is a source of fibres, animal feed or feedstock for anaerobic digestion. The press juice is a source of concentrated proteins. Secondary products can then be extracted from the two fractions. The press juice contains valuable proteins and amino acids and can also be used as a fermentation feedstock for lactic acid or bioethanol production.

Considerable effort has been directed at the Green Biorefinery concept throughout Europe particularly in the Netherlands and Austria. Work in the Netherlands started in the mid 1990's [276] and led, in 2002, to the construction of a pilot plant in Veendam operated by AVEBE [277]. This work has now halted. Research workers in Austria have also been active in Green Biorefinery development at the Joanneum Research Institute [278] although this work is primarily aimed at the use of silage grass predominantly for the production of lactic acid, amino acids, proteins and biocomposites rather than bioethanol. This area was recently reviewed by the Biocomposites Centre [277] and the market potential of a UK Biorefinery was assessed by Agros Associates in 2004 [279].



**Figure 20 Green Biorefinery Schematic**  
Adapted from reference [21]

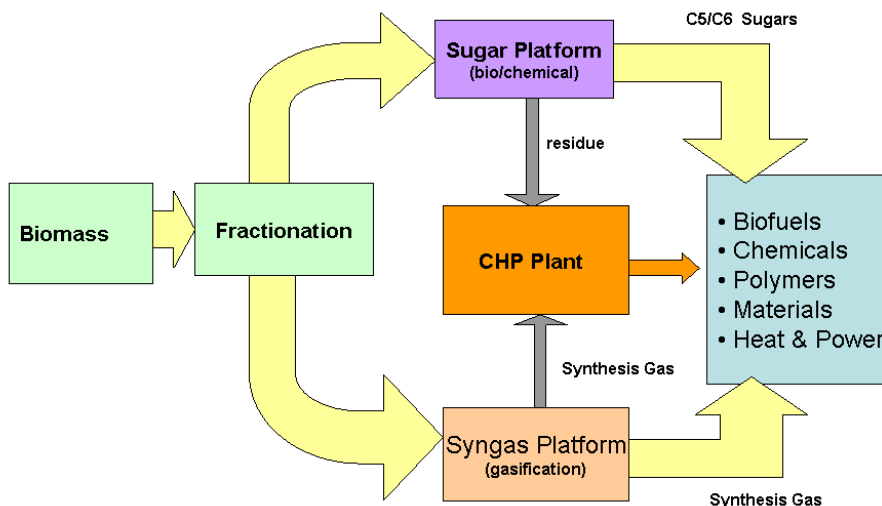
A simplified schematic of a grass biorefinery is shown in Figure 20. Residue streams from the secondary processing of the press cake and the press juice would be fed to an anaerobic digestion plant for the production of biogas which in turn is used to provide the facility with heat and power.

The green biorefinery has a number of advantages: The feedstock is abundant and low cost, the lignocellulose present in the press cake is less recalcitrant than that present in woody crops and can be more easily fractionated into its components. A number of high value proteins and sugars can be produced as secondary products such as lysine and inulin. However to become a commercial reality higher value markets need to be developed for primary products such as the grass fibres and further improvements in separation technologies need to be developed for cost effective separation of the high value components from the dilute press juice streams .

#### 7.1.4 Two-platform Biorefinery Concept

This biorefinery concept integrates two biomass conversion platforms; the sugar platform and the thermochemical platform. These platform strategies were developed at NREL to facilitate coordination of US research activities. The sugar platform concerns the production of fermentable sugars from lignocellulosic materials [280] whilst the thermochemical platform concerns the high temperature gasification of biomass to synthesis gas and its subsequent conversion to fuels, chemicals and power [281]. The

thermochemical route also incorporates other high temperature conversions such as the production of bio-oil by pyrolysis. The combination of these two platforms in one integrated biorefinery complex provides tremendous flexibility with regard to the biomass feedstock and the suite of products possible. The two-platform biorefinery concept also raises the possibility of combined bioethanol and synthetic diesel production. A schematic of the two platform biorefinery complex is shown in figure 21.



**Figure 21 Two-Platform Biorefinery Concept Schematic**  
Adapted from reference [21]

Two-platform biorefinery concepts have been proposed for the production of ethanol and mixed alcohols from corn stover and lignocellulosic feedstocks [282].

## **8.2 Biorefinery Development**

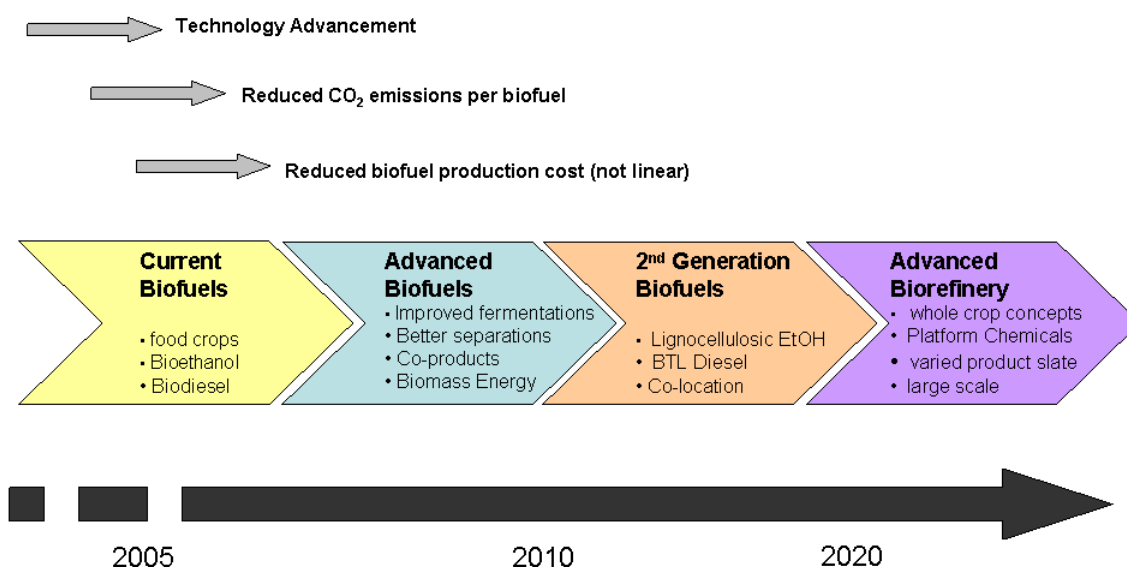
The principles discussed in the introduction to this section describe the aspiration for a future biorefinery complex. The implementation of such an advanced biorefinery will be constrained in the short to medium term and most forecasts put advanced biorefinery implementation beyond the 2020 timeframe [283]. This long lead time for implementation can be related to a number of factors including:

- Inefficient feedstock supply chains and feedstock cost
- Current status of process technology and modelling tools
- Volatile crude oil and natural gas price
- Large capital investment required for a large complex on a greenfield site
- Uncertainties in investment community due to concerns over longevity of favourable governmental policies towards biofuels.

Economic evaluations of both lignocellulosic ethanol and BTL plants reveal capital investment costs significantly higher than those of an equivalent oil refinery [216]. It is therefore likely that biorefinery development will be incremental in nature and will exploit existing infrastructure such as sugar factories, conventional bioethanol and biodiesel production facilities and pulp/paper mills.

Such a transition is occurring now in conventional bioethanol and biodiesel facilities. This first steps towards biorefinery operation involve the use of biomass feedstock residue and low value product streams produced in the facility or harvested in the field to provide indigenous heat and power to fuel the biofuel process operations. This has been the norm for many years in the Brazilian bioethanol industry and is now being designed into future bioethanol plants in the US and Europe [284]. The second step is the development of a broader portfolio of products from existing biofuel production facilities with new conversion processes being integrated onto site to exploit co-location benefits. This could incorporate the extraction of high value chemicals from primary feedstocks, such as proteins from rapeseed meal, and the production/derivatisation of platform chemicals such as glycerol. Another example of this approach is the technology currently being developed to extract corn oil from DDGS in bioethanol dry mills and

**Figure 22 Timeline for Advanced Biorefinery Implementation**



convert it into biodiesel. The remaining DDGS residue can then be converted into heat and power for the plant [285]. Such technology could be valuable if DDGS animal feed markets become saturated.

An alternative approach to upgrading existing biofuel facilities is to incorporate biofuels production into other existing facilities, such as sugar factories and pulp mills that potentially have large streams of biomass feedstocks available.

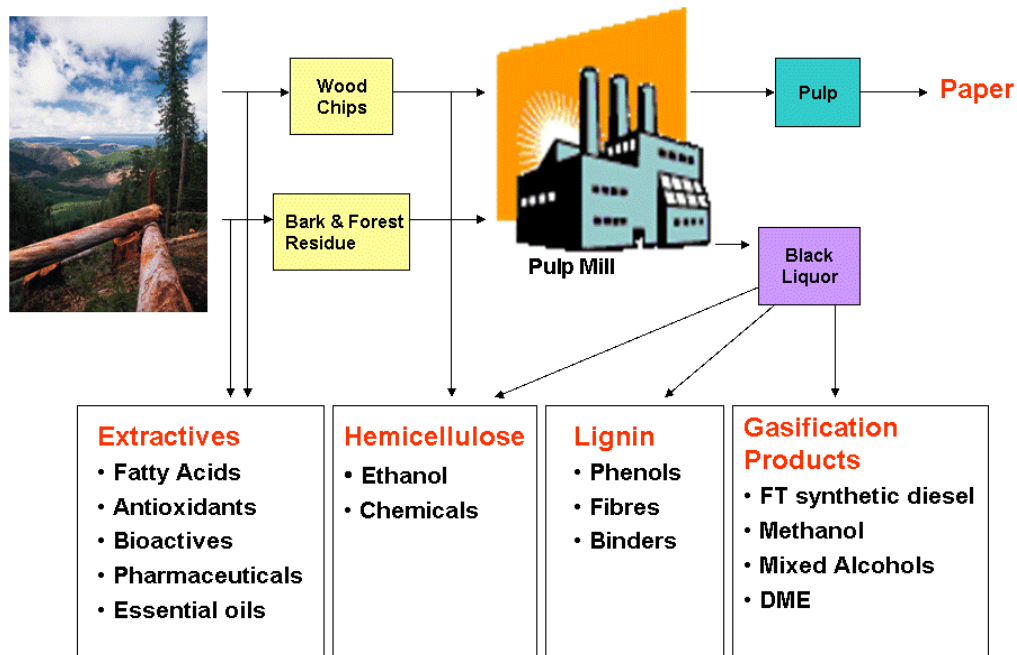
The next stage in biorefinery development will be the commercial implementation of second generation bioethanol and BTL diesel facilities. Again this development could be facilitated by co-location with existing infrastructure such as conventional biofuel plants, pulp mills and power stations [286, 287]. The case of pulp mills will be specifically addressed in the next section.

The timelines for advanced biorefinery implementation is represented in Figure 22.

### **8.2.1 Paper and Pulp Mill Biorefineries**

The pulp and paper industry is amongst the largest producers and users of biomass energy today and considerable scope exists to extend the operation of these facilities to produce renewable chemicals and biofuels. A typical Kraft pulp mill contains a number of biomass resources streams that could be more effectively utilised to provide a more economic and environmentally beneficial plant operation. Such resources include the bark, wood residues and the black liquor stream. Declining profits and government incentives are now driving the pulp and paper industry, particularly in Scandinavia and the US, to improve biomass resource efficiency and evaluate the development of pulp mill biorefineries [288,289].

Historically, Kraft pulp mills have produced a variety of valuable by-product chemicals such as tall oil and turpentine. A greater range of valuable co-products can now be envisaged by the application of innovative extraction, fermentation and gasification technology (see figure 23). As discussed previously, pulp mills can be converted into more resource efficient operations by replacing existing Tomlinson boilers with black liquor gasification and combined cycle turbine technology. The synthesis gas can be used for methanol or FT diesel production. Bark and forest residues can be used to provide extra feedstock for the biomass gasifier. Hemicelluloses, normally combusted in the Tomlinson boiler can potentially be extracted from the wood prior to pulping or from the resultant black liquor stream [290]. Such hemicellulose streams can be converted into bioethanol or other valuable chemicals. In the longer term, lignin can be precipitated from the black liquor and utilised for the production of high value chemicals such as phenols and polyurethanes.



**Figure 18 Possible Product Slates from a Integrated Pulp Mill Biorefinery**

Larson et al [291] have performed an extensive cost benefit analysis of seven different pulp mill biorefinery configurations producing FT diesel, mixed alcohols and DME via gasification of black liquor and woody residues. The work funded by the USDOE and the American Forest and Paper Association revealed that a number of the biorefinery scenarios could be economically attractive in the future.

In Europe, an EU FP6 project entitled “WaCheUp” is developing concepts for the valorisation of low value pulp mill biomass resource streams through conversion into a wide range of valuable chemicals [292]. The project costing nearly 3 million euros will complete in mid 2007 and is coordinated by STFI-Packforsk in Sweden.

### **8.2.3 Utilising Existing Oil Refinery Infrastructure**

A solution to the huge capital investment costs required to implement new biorefinery complexes is to exploit existing oil refinery infrastructure for the conversion of biomass into fuels and chemicals. This has already been demonstrated successfully by Neste Oil who has converted vegetable oils and animal fats into “renewable synthetic diesel” using conventional hydroprocessing technology [293]. The NexBTL process is now being commercialised at the Neste refinery in Finland with the construction of a 170 thousand tonne per annum plant. The plant which cost €100M is scheduled to be operational in June 2007. The synthetic diesel product is very different to a conventional biodiesel and more closely resembles a GTL synthetic diesel. The fuel is promoted as having the

environmental benefits of biodiesel with the fuel performance benefits of GTL synthetic diesel.

In work funded by the USDOE, UOP evaluated the conversion of vegetable oils in conventional oil refinery processes such as Hydrotreating, Hydrocracking and Fluid Catalytic Cracking using modelling and laboratory reactors [294]. This research demonstrated that products such as diesel, gasoline and olefins could be successfully produced using vegetable oils provided that a low cost source of feedstock could be identified. To address this aspect further, UOP reviewed the potential of using bio-oils generated by pyrolysing biomass, in refinery operations. Their work concluded that bio-oils could be successfully utilised as refinery feedstocks if the high oxygen content of the material could be reduced effectively and economically. PyNe, the global pyrolysis network funded by the EC and coordinated by Aston University, is also focusing effort towards the identification of biorefinery configurations incorporating biomass pyrolysis technology [295].

A novel hydrothermal process for converting wet biomass to a liquid “bio-crude” is being developed at TNO-MEP in the Netherlands [296]. This process subjects wet biomass, such as sewage sludge, to high temperatures (350C) and pressures (> 100 bar) to produce a liquid product. The bio-crude, after some fractionation, could be used as a feedstock for a refinery hydroprocessor to produce a diesel product (HTU-diesel). The “bio-crude” produced by hydrothermal upgrading has a lower oxygen content than pyrolysis bio-oils and may be a more appropriate feedstock for hydroprocessing (global watch report).

### **8.2.3 Biorefinery Modelling**

Oil refineries and petrochemical complexes maximise economic performance through efficient allocation and distribution of the myriad of raw material streams to individual processing units. To a certain extent this feedstock distribution and product allocation can be tuned to match external markets. Similarly, the efficient management of these complex flows of materials and energy in the biorefinery complex will be essential to maximise integration benefits for improved energy savings and reduced processing costs.

Mathematical optimisation tools are now being developed to provide information on the optimum configurations for biorefinery complexes both for economic and environmental performance. Such models will provide information on:

- Cost benefit analysis of different biorefinery configurations
- Sensitivity analysis to external market perturbations
- Sensitivity analysis to technology development

Such information can be used to set R&D targets for economic biorefinery development. NREL is developing an excel based biorefinery optimisation model “Biorefine.xls” with the University of Pittsburgh [297]. In a separate US study performed at Dartmouth and Princeton, detailed ASPEN modelling of various biorefinery configurations was performed and economic and environmental performance data derived [298]. Biorefinery modelling is also being undertaken in the UK at the Cranfield Institute [299] and the University of Manchester [300].

#### **8.2.4 Biorefinery Demonstration Activities**

There are a number of large pilot plant/demonstration scale projects concerning the demonstration of biorefinery concepts. Some recent examples are summarised below:

##### **Biocoup**

FP6 funded project (€13.3M project, 5 year programme)

Start Date: 1/5/2006

Coordinated by VTT in Finland (17 project members)

**Aim:** Integration of pyrolysis bio-oil raw material streams within existing oil refinery operations. Energy and oxygenated chemicals will be co-produced. The overall innovation derives from integration of bio-feedstock procurement with existing industries and processing of upgraded biomass forms in existing mineral oil refineries. It will allow a seamless integration of bio-refinery co-processing products to the end consumer for products like transport fuels and chemicals, and provide an important stimulus to biomass acceptance and technological development of biomass production routes.

##### **IBUS**

EC funded project (€13.6M project, 5 year programme)

Start Date: 1/12/2002

Coordinated by Elsam Kraft A/S (4 project members including TMO-Biotec)

**Aim:** Develop supply chain for a Whole Crop Biorefinery system utilising cereals, straws and MSW. Bioethanol production performed using novel thermophiles. Both 100kg/hr and 1000kg/hr pilot plants constructed and operated. Major products are bioethanol and electricity

##### **A Second Generation Dry Mill Biorefinery**

USDOE funded project (\$4.5M)

Start Date 1/1/03

Coordinated by Broin and Associates Inc (others NREL, South Dakota State University)

**Aim:** Expand product portfolio of Dry Mills by developing efficient separation and processing of bran, germ and endosperm from corn kernels and efficient upgrading of components to valuable products.

**A New Biorefinery Platform Intermediate**

USDOE funded project (\$6M)

Start Date 5/1/03

Coordinated by Cargill (Codexis and Pacific Northwest National Laboratory)

Aim: Develop new microorganisms for the production of the platform chemical 3-hydroxypropionic acid. Develop new routes for derivatisation of 3-hydroxypropionic acid to other chemicals such as propanediol and acrylic acid.

**Making Industrial Biorefining Happen**

USDOE funded project (\$26M)

Start Date 1/3/03

Coordinated by Natureworks LLC (Others: Genencor, Iogen, Shell)

Aim: Develop and build pilot scale biorefinery that produces lactic acid, ethanol and other chemicals from grains. Utilise novel genetically engineered microorganisms for sugar fermentation to products.

**Integrated Corn Based Biorefinery**

USDOE funded project (\$18M)

Start Date 4/1/03

Coordinated by DuPont (Others: Diversa, NREL, Michigan State University)

Aim: Develop Integrated whole-crop biorefinery for the production of ethanol and platform chemicals such as 1,3 Propanediol .

**Advanced Biorefining of Distillers Grain**

USDOE funded project (\$17.7)

Start Date 1/2/03

Coordinated by Abengoa (Others: Novozymes, VTT, NREL)

Aim: Develop pre-treatment process for conversion of DDGS to high value products whilst maintaining a high-protein animal feed. Large scale pilot plant to be built in Nebraska

**BioSynergy**

EC FP6 IP Project

Start Date: 2007

Partners include: ECN, Greencell, Dow, VTT, Aston, IFP, Joanneum Research, Delft University of Technology.

Aim: Development of competitive and environmental friendly bio-product chemicals and/or materials together with the production of secondary energy carriers for transportation fuels, power and/or CHP through the biorefinery approach, combining both biochemical and thermo-chemical pathways, and process development from lab-scale to demonstration at pilot-scale.

## 9. Conclusions

This review has revealed a huge volume of current R&D activity, both in industry and in academia, focused on developing biorefinery operations for biofuels and renewable chemicals manufacture. Although the implementation of large biorefinery complexes remains a long term target (>2020) considerable progress is being made in developing enabling technology that will facilitate the commercialisation of second generation biofuels and ultimately accelerate the implementation of biorefinery complexes.

The commercialisation of second generation biofuel technology appears to be imminent particularly in the US where a number of facilities are being planned, or under construction, to convert corn stover and other agricultural residues into ethanol. This progress has been achieved through impressively coordinated and concerted project activities involving a diverse range of industrial and academic consortia heavily funded by the US Department of Energy. Of particular note, is the increasing role of innovative bioprocessing technologies in the development of lignocellulosic ethanol processes. A number of small UK biotechnology companies are actively contributing to these commercial developments particularly in the application of proprietary thermophilic microorganisms.

However, it appears that a number of technical barriers to commercialisation still remain including the inefficient pretreatment technology for lignocellulosic feedstocks and the relatively high cost of cellulase enzymes. The potential of new xylose fermenting microorganisms is yet to be demonstrated under commercial scale conditions. It is also apparent that these technologies demonstrate very high specificity to individual biomass feedstocks. These barriers may well be addressed in the medium term with improved biotechnology and engineering, but in the short term it appears that the various lignocellulosic ethanol processes may not be competitive with conventional bioethanol. To encourage uptake of second generation biofuels, the United States government is providing significant financial assistance to early adopters of this technology.

In contrast to lignocellulosic ethanol routes, the technical barriers facing the implementation of BTL synthetic diesel technology are not insurmountable and most of the enabling technology is considered "off the shelf". Choren plans to commercialise this technology in 2011. However, the significant capital investment required for BTL facilities and the difficulty in achieving the appropriate economy of scale due to biomass feedstock supply constraints may delay the wider implementation of this technology. This can be addressed to a certain extent by exploiting existing infrastructure as demonstrated by plans in the US and Scandinavia to convert existing pulp mills to small lignocellulosic biorefineries.

The application of biorefinery principles is now taking place in conventional bioethanol plants where agricultural residues and low value waste streams are being utilised as renewable energy sources to provide heat and power to fuel process operations. Driven by the high price of natural gas, a number of companies, in the US and Europe, are evaluating the potential of using the stillage/DDGS as a renewable energy source rather than sell to the animal feeds markets. In the longer term innovative separation technologies are being developed to provide new feed streams from dry milling operations for conversion to added value chemicals.

The UK has a potential biomass feedstock resource of over 20 million tonnes but there is likely to be competition for this from the renewable energy sector. Current biomass supply chains are not sufficiently developed in the UK to supply large biorefinery conversion facilities. Providing sufficient biomass feedstock to the biorefinery complex so that it can be of sufficient size to exploit economy of scale economics will be critical for commercial feasibility. Literature suggests that biomass feedstock rates below 2000 tonnes per day of biomass would not be economically feasible. A more realistic figure for even a small biorefinery complex would be a minimum of 5000 tonnes per day of biomass feedstock. With this in mind the biorefinery complex will need to incorporate high feedstock flexibility. In the longer term, the successful development of biomass densification technologies, such as pyrolysis and torrefaction, may resolve this issue by expanding the feedstock catchment area of the biorefinery.

Coordinated activities and programmes at the National and International level have been implemented to foster a multidisciplinary approach to the development of essential biorefinery technologies and to promote the formation of functioning supply chains across relevant sectors. A number of countries now have established national bodies to provide coordination and focus for biorefinery development and ensure stakeholder engagement. For instance, the Netherlands recently formed a Dutch Biorefinery Network and held its first workshop in June 2006. The United States has developed a thorough, structured and coherent strategy to develop biorefinery complexes and meet its long term targets for indigenous biofuel production and energy security. Similar programmes in Europe appear to be more fragmented, particularly so in the UK. Although there are a small number of individual UK centres actively engaging in this area, the lack of broad engagement of UK organisations in international biorefinery activities should be of concern.

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