FORESIGHTING REPORT
Sustainable Transport Fuels

Addressing technologies required for the next generation of biofuels

For Members Only

27th March 2008
V1.0

EXECUTIVE SUMMARY

Some three billion tons per year of liquid fuels are used for transportation worldwide supported by a very strong distribution infrastructure. Today, these essentially consist of fuels derived from fossil resources, which are by their nature finite and unsustainable.

There are numerous options in fuel type and feedstock and theoretically it is possible to obtain a suitable transport fuel from any available source of energy. However to be commercially successful any feedstock-fuel coupling must meet a number of requirements, such as:

- feedstock availability in large quantity and at competitive price
- low processing costs
- minimum modification/addition to existing infrastructure
- meeting or exceeding existing fuel specification for the targeted use
- represent a secure supply of energy

The production of fuels from biomass meets many of these requirements and has become a popular choice for a number of developers. Successful demonstration projects over the last few decades have led to implementation on a much larger scale. While this first generation of projects have been widely regarded as successful they have generated criticism that the associated detrimental effects on the environment and global standard of living, eg deforestation and increased food prices, will make further implementation unsustainable.

While some people are focusing on reducing the negative impacts of the first generation, through improved yields and more efficient processes, others are developing a second generation which has at its heart the need for sustainability. This is being pursued through:

- avoiding direct competition with food production, in particular competition for land and fresh water, through utilising existing agricultural residues
- significantly reducing the CO_2 life-cycle emissions or creating a completely self contained CO_2 capture/emission cycle
- respecting biodiversity and habitat

The successful implementation of the second generation faces many technical and economic challenges which offer opportunities for investment into research or diversification. This report will briefly summarise the status of the first generation of biofuels and report on the ongoing development of the second generation, with particular focus on marine algae as an alternative source of biomass that is now capable of delivering upon its potential. To conclude, this report will outline the emerging research into the subsequent generation of so-called 'Solar Fuels' produced by using micro-organism or photo-catalysts from the interaction between CO_2 and H_2O and sunlight.

TABLE OF CONTENTS

1 OVERVIEW

The worldwide consumption of transport fuels totals some three billion tons per year. At present these predominately consist of fuels derived from fossil resources, which are finite and therefore unsustainable in the long term. Increasing environmental (eg climate change) and political (eg energy security) pressures have generated global demand for alternative and more sustainable energy resources. This demand has generated a concerted research effort which, as can be seen on Figure 1, has resulted in the development of technologies that allow the production of transportation fuels from any available source of energy.

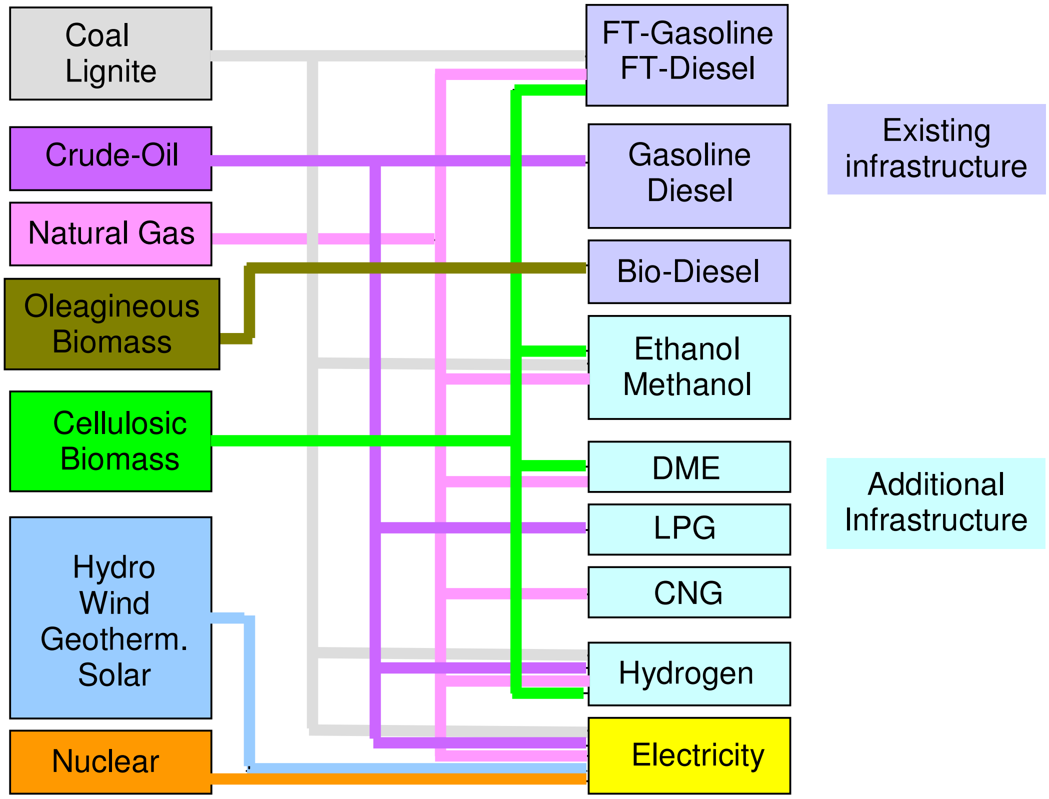

Figure 1: Possible routes from Primary Energy Sources to Fuels

While this technical development has been impressive these alternatives still face significant technical, economic and social challenges before they can be fully embraced by the market. The existing fuels market is supported by a very strong distribution infrastructure and the use of certain of these fuels would require significant modifications. Good examples of this include the proposed ethanol pipelines in the US and Brazil and the petrol station forecourt changes required to sell E85. Similarly in the case of hydrogen, a completely new infrastructure would be required, unless hydrogen is produced at the point of sale from existing fuels.

It is also possible to convert electricity generated from wind or marine mechanical energy into hydrogen or ammonia through electro-chemical processes. However, this route faces major infrastructure and efficiency hurdles, making such concepts unsuitable for large scale commercial application in the foreseeable future.

2 LIQUID BIOFUEL MARKET

Liquid biofuels; bioethanol and biodiesel are commodity products that are manufactured, shipped, blended and then sold to the end consumer via the existing fossil fuel infrastructure. To facilitate this market, contracts are traded on exchanges throughout the world, increasing the complexity of the market.

Economic rules of supply and demand apply to this market and key variables are:

- feed-stock cost, the CO_2 abatement costs or revenue and government subsides, on the supply side
- the oil price and the level of mandated biofuel blending, on the demand side

Plotting this onto the standard economic supply and demand graph (Figure 2) illustrates that the bio-fuel market is underpinned by government support, either through direct subsidy or mandated demand.

Obviously, the lowest cost producers are most profitable in a commodity industry, so it follows that prospective market entrants need to determine their costs of production relative to their competitors. Those developing technologies for the liquid bio-fuel market need to understand the cost reduction potential of their technologies to determine the possible market penetration.

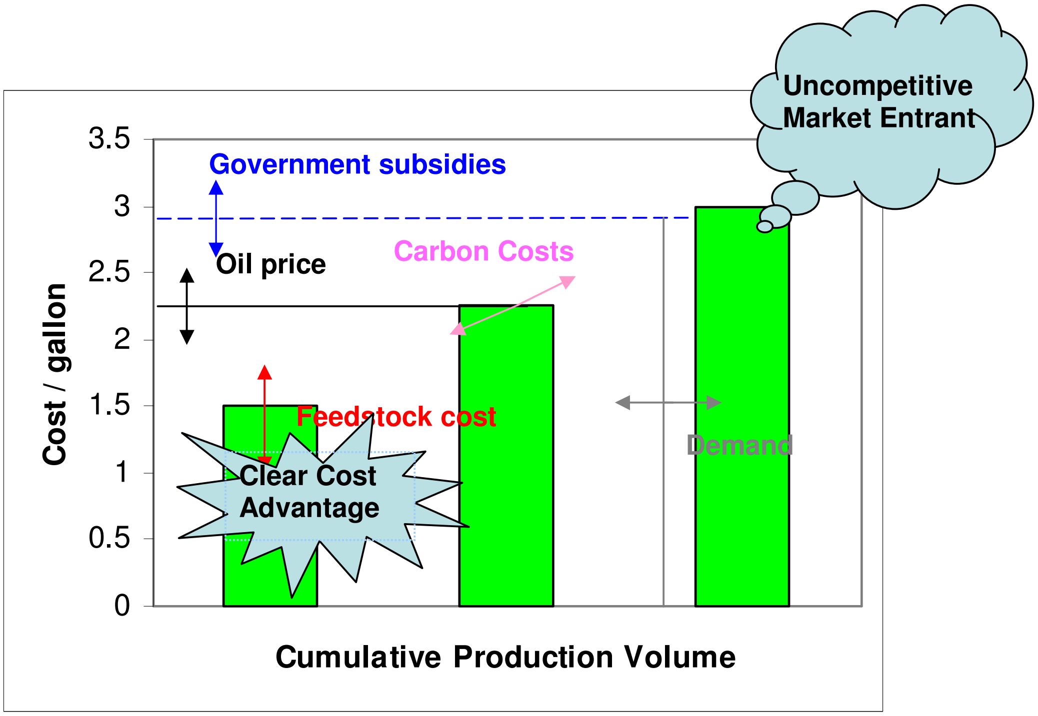

Figure 2: Supply & Demand model of Biofuel Market

Mandatory created demand for bio-diesel has resulted in an almost doubling of palm oil price over the last year, as shown by the following chart (Figure 3) of spot prices of crude palm oil traded on the Malaysia Bursa [1]. This has created a strong incentive to increase plantation acreage, in many cases at the expense of bio-diversity.

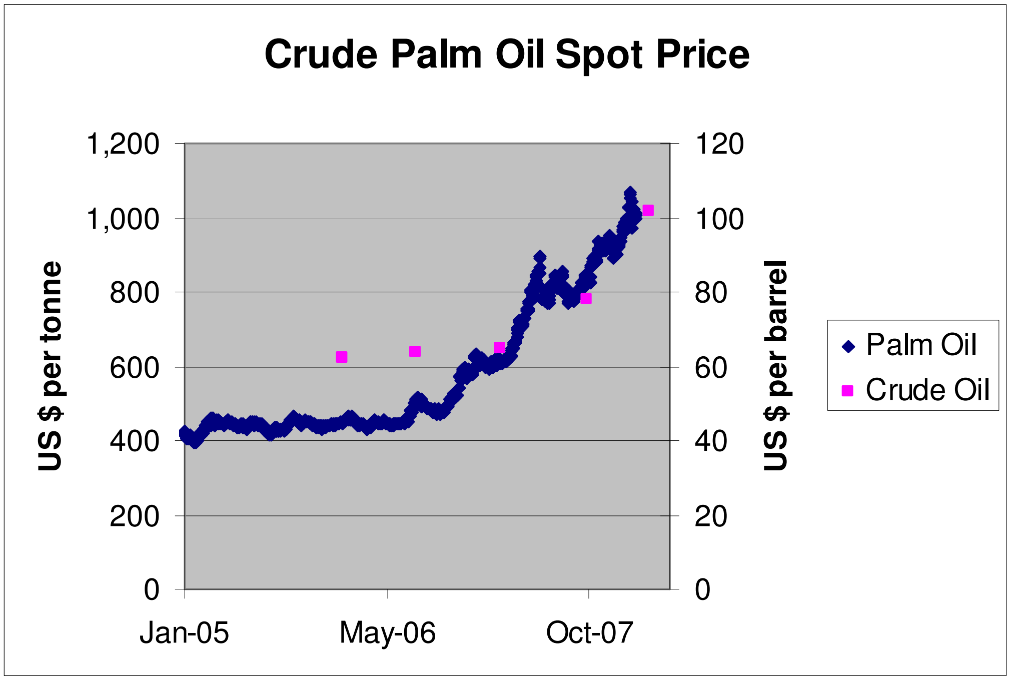

Figure 3: Crude Palm Oil Spot Price ($ / tonne)

The revenues associated with European bio-fuel markets are reported by Frost & Sullivan to be as follows:

- Bio-ethanol: US $642 million and growing at 33% per annum [2].
- Biodiesel: US $4.35 billion and growing at 20% per annum [3].

3 LIQUID BIOFUEL FEEDSTOCKS

In the wake of the development of ethanol from sugar cane in Brazil in the late 1970s, liquid bio-fuels have developed over the last decade – initially stimulated by government policies in Western Europe and the USA. Availability of excess agricultural land, recurring surplus in cereal production, and strong government incentives have led to the development of a significant market for ethanol and vegetable oil for use as transport fuel. Over the last few years, the increasing oil price has created additional incentive to accelerate the development of bio-fuels, not only in OECD, but also in large emerging countries such as India and China.

The road to sustainable production of bioethanol from Brazilian sugar cane began in 1978 when legislation was passed requiring the recycling of vinasse, the ethanol distillation residue. Today, ferti-irrigation utilises all of the vinasse and industrial wastewater, so that over half of the sugar cane cultivation in Brazil does not require irrigation. This recycling is so efficient that it is reported that Australia uses nearly 50% more fertiliser [4]. Sugar cane fields are burnt to facilitate harvesting, however the environmental impact of field burning has been recognised by the Brazilian Government who passed legislation in 1998 that reduces burning and prohibits the practice from 2018.

Although bio-fuel production and cattle feeding can complement each other in certain cases (soya, rapeseed), increased demand for bio-fuels has highlighted significant sustainability issues, such as:

- competition with food resources in the case of cereal for ethanol, with the price of wheat and corn being at an all time high in 2008
- increased deforestation of tropical forest in the case of palm oil for bio-diesel [5]

Figure 4: Annual Indonesian Palm Oil Production (million tonnes)

In Indonesia, the acreage under palm-oil plantation (Figure 4) increased by 50% between 2003 and 2007. This corresponds to repeated annual increases of about 3000 km^2, an area equivalent to that of the Western Isles. Over five years the acreage equivalent to two-thirds of the Highlands has been converted to palm-oil plantation, at the expense of natural forest.

To alleviate these pressures, much effort is currently devoted to developing a 'second generation of bio-fuels' that would have an improved sustainability foot-print. To reach this goal, industry and R&D organisations are pursuing a number of separate avenues, sometimes interlinked through the feedstock source and/or conversion technology into bio-fuels.

In addition to niche sources such as cooking oil or animal fat, the following sources can be considered as potentially sustainable:

- agricultural production (eg sugar plants) not resulting from dramatic change of land use (eg deforestation)
- vegetable oil from set-aside land, or from run-down lands (eg jatropha)
- woody crops or residues/thinnings from sustainably managed plantations
- agricultural residues (corn stover, straw)
- micro-algae developed on waste land or salted lakes
- macro-algae (seaweeds) sustainably cultivated in a marine environment

Sugar cane plantation would yield up to 10 ton/ha of sugar, providing up to seven ton/ha of ethanol. For each ton of ethanol produced, about three ton of bagasse (the residual fibre from the stems) has to be disposed of. Because of its high silica content, bagasse requires costly purpose-built boilers to be combusted and generate power. Torrefaction of bagasse is being considered as an alternative route.

Sugar beet would typically yield seven ton/ha of sugar, with all by-products being recycled as animal feed or organic fertiliser. However this requires some 120 kg/ha [6] of inorganic fertiliser which, together with the associated emission of nitrogen oxides in the field – N_2O is a gas with greenhouse effect 310 times [7] stronger than that of CO_2 – reduces the attractiveness of this feedstock for closing the CO_2 cycle.

The oil yield of vegetable oil plants is about one ton/ha (soya, rapeseed) and requires a three year rotation of crop to protect the soil nutrients. In the case of rapeseed, the total energy input required for planting, fertilisers, pesticides, harvesting and crushing, and processing the oil into bio-diesel, represents about a third of the energy content of the bio-diesel produced [8].

Palm oil plantation can reach up to five ton/ha, but there are significant biodiversity and sustainability issues to be dealt with.

Jatropha is able to grow in very different conditions and thus it is very difficult to estimate unequivocally its yield. It is claimed to reach up to three ton /ha under good growing conditions, with adequate level of rainfall and fertilisers. The plant can also withstand very poor soils and grow in saline condition, with lower yields then being achieved.

Making large quantities of transport fuel from the above crops requires a lot of land. In Brazil 10 million tonnes/year of ethanol are produced from 54000 km^2. To achieve the 5% blending target for the 200 million tonnes of diesel consumed annually in the EU, 10 million tonnes of bio-diesel will be required. This would require 100 000 km^2 of rape seed culture, an area equal to 20% of France or 20 000km^2 of palm oil plantation, equivalent to the area planted in Indonesia over the last six years.

To achieve the necessary increases in yield research has recently focused on micro-algae with high lipids content which can potentially reach up to 30 t/ha of bio-oil. However, capital and operating costs are still very high and reducing them constitutes a major opportunity for innovation. Similarly, sea-weeds are also being considered as a source of biomass for bio-gas or ethanol. This is further discussed in this report.

Three different types of process can be applied to biomass to produce a liquid or gaseous fuel.

1- oil extraction and mild chemical conversion
2- thermo-chemical conversion at high temperature
3- biochemical conversion using enzymes and/or yeast

The table below (Figure 5) provides a simplified map of which type of process is applicable to which feedstock. Green processes are proven, while blue processes are still being researched and developed. Scale of operation and related feedstock logistics have a significant impact on process economics for all routes above. In addition, each route has its own specific advantages and challenges.

	1st Generation	2nd Generation	
Biomass type	Mild Chemical conversion	Thermo-chemical processes	Bio-chemical processes
Sugar plants	🟩		
Oleaginous biomass			
Vegetable oil crops	🟩		
Micro-algae	🟦		
Ligno-cellulosic biomass			
Woody crops/residues		🟩	🟦
Agriculture crops/residues		🟩	🟦
Macro-algae (seaweeds)			🟦

Figure 5: Feedstock verses conversion technology comparison table

4. 1ST GENERATION MILD CHEMICAL CONVERSION

Bioethanol production from sugar cane or beet – and more recently from corn or wheat – is a commercialised process well documented elsewhere. In summary, the C6 sugars are converted to ethanol by yeast, through a batch process in a water medium containing up to 10% ethanol. Used yeast is filtered away, to be used for animal feed, while ethanol is separated from the water by distillation.

In the case of vegetable oil, the plant has already done most of the job by converting sunlight, atmospheric CO2 and water into a liquid product close to the final fuel specification. Thus, the number of process steps is minimal and 1st generation bio-diesel production by trans-esterification quickly became an established technology.

Vegetable oils consist of tri-glycerides (fatty acids) which can be broken down and neutralised (esterified) by strong bases, such as caustic or potash. The resulting products, fatty acids methyl-esters (FAME), can be used as pure in (modified) diesel engines or blended to conventional diesel fuel in various amounts (up to 30%) with no engine modification.

FAME consists of a mixture of various esters with different chain length and properties. Certain characteristics such as the presence of three or more unsaturated double bonds, are unfavourable for fuel use. Challenges include gum formation at hot spots of the fuel injection system or during long periods of storage. For this reason, FAME have to meet certain specification, such as iodine index less than 120 or linolenic acid methyl ester content less than 12%.

Hydro-treatment is a radical way to deal with engine performance or fuel issues related to the use of vegetable oil as a feedstock. Over the recent years, industrial hydrogenation processes have been adapted to convert vegetable oil into diesel. For refiners, there is value in having catalysts able to hydro-process both traditional hydrocarbon and vegetable oil in the same reactor.

A number of process plants are already under development, with commercial operation already started in some cases.

- July 2006, Shell Canada published details of a Biofuels development that would involve rail shipments of canola seed oil being delivered to Shell's refineries, where the oil would be reacted with hydrogen to produce biodiesel
- May 2007, Neste Oil inaugurated its new 170 000 tonnes per annum biodiesel plant that uses their proprietary NExBTL technology, which combines hydrotreatment and isomeration
- June 2007, UOP announced a JV with Eni S.p.A. to build a 300 000 tonnes per annum production facility, utilising their registered catalytic hydro-processing technology called Ecofining™
- July 2007, Galp Energia announced a JV with Petrobras to build a 600 000 tonnes per annum production facility utilising Petrobras' H-Bio hydro-treatment technology

It is expected that hydrogenation will be the process of choice to turn oil from micro-algae into diesel. Initial patchy evidence indicates that algal oils tend to have not only high iodine values, but also relatively high sulphur content – in contrast to vegetable oil where this compound is virtually absent. Diesel specification requires sulphur content to be < 50 ppm. Obviously, characteristics of algal oil will vary depending on species and growing conditions and requires further investigation.

5. 2ND GENERATION THERMOCHEMICAL PROCESSES

These processes can be applied to all ligno-cellulose feedstock, but economics are strongly influenced by feedstock water content. Also, many process steps are required to move from ligno-cellulose to a transport fuel. After drying, biomass can be thermally converted into various products consisting of solids, liquids or gaseous, depending on the process conditions (temperature, residence time). For instance:

Torrefaction

Torrefied biomass is a product made by heating biomass at 250 – 300℃ for around one hour, leading to partial decomposition of the biomass polymeric structure. The resulting material is brittle and hydrophobic, can be easily stored, handled and milled without significant deterioration in quality.

The torrefied material can also be pelletised, bringing its energy density closer to coal. Because of a potentially huge sustainable supply and physical similarity to coal as a solid fuel, with no sulphur and virtually no ash, torrefied pellets (TOP) could become the future fuel of choice for space heating and co-firing with coal for power generation – provided the fuel can be produced and delivered at a competitive price. A fore-sighting study of torrefied biomass was published by ITI Energy in 2007.

Because of more consistent characteristics, and absence of light ends, torrefied wood could become a premium feedstock for making syngas, a mixture of CO and H_2 from which high performance diesel and gasoline can synthesised through the Fisher-Tropsch process.

Pyrolysis

Pyrolysis is the chemical decomposition of biomass in an oxygen deficient environment. Unfortunately, the bio-oil from pyrolysis is acidic, contaminated with solids, chemically unstable and viscous (hence the process is not commercialised). An additional issue is that the bio-oil is likely to have a high content of poly-aromatic compounds, such as anthracene, which are carcinogenic.

However TNO, a Dutch research organisation, has developed a patented system called PyRos – pyrolysis with integrated dust filtration and catalytic reaction. They claim that the process produces a solids and acids-free oil [9].

Gasification

In the 1990s much effort was devoted to the gasification of wood or woody biomass with air, to produce low heat content gas which could be fired in gas engines or (modified) gas turbines to generate electricity and heat. The gas is essentially a mixture of H_2, CO and CO_2 with nitrogen and traces of oxygen.

Alternative processes were also developed to avoid the use of air, by replacing it either by pure oxygen or steam in order to avoid the diluting presence of nitrogen.

An example is the Battelle sand cracking/steam gasification process for preparing medium heat content gas. A demonstration plant was operated in the USA from 1998 to 2002. The process mixes wood chips with very hot sand at a temperature of about 830℃ in a vertical steel cylinder called a gasifier. The hot sand breaks down the wood and, helped by the added steam, causes the resulting carbon, hydrogen and oxygen to form into combustible gases. The gases and sand leave the gasifier and the gas is cleaned for use as fuel. The sand is regenerated and re-heated, by burning the associated char, and recycled to contact the biomass again in the gasifier.

So far, these types of processes have failed to become commercial, essentially because of technical complexity and associated costs compared with simply burning the biomass/wood in a steam-boiler to generate electricity. Gas clean-up at high temperature, to meet turbine specification at an acceptable reliability and cost, has been one of the major challenges.

Producing higher value-added products, such as sustainable transport fuels rather than under-boiler fuels such as heavy fuel oil or coal, might justify further investigation of the biomass to syngas route. For example, the Carbo-V® Process that utilises endothermic char gasification creates pure synthesis gas, a mixture of CO and H_2, which can then be used to produce synthetic diesel or chemicals.

It is a three-stage gasification process (Figure 6) during which the biomass (with a water content of 15 – 20%) is first continually carbonized through partial oxidation with air or oxygen at temperatures between 400 and 500°C. This produces a gas containing tar (volatile parts) and solid carbon (char). The gas containing tar is post-oxidized into a hot gasification medium by using air and/or oxygen in a combustion chamber operating, below stoichiometric conditions, at temperature above the melting point of the ashes. The char is ground down into pulverized fuel and is blown into the hot gasification medium. The pulverized fuel and the gasification medium react endothermically in the gasification reactor and are converted into a raw synthesis gas. After clean-up, this gas can be fed into a Fischer Tropsh process for conversion into bio-diesel for instance.

Diesel from wood

The production of "Syngas" from biomass, a mixture of carbon monoxide (CO) and Hydrogen (H_2), is the first step for making synthetic bio-fuels.

The syngas has to be tar free before it can be processed into transport fuel (eg diesel) over a Fischer Tropsch catalyst. Much R&D has been performed in this area over the last decade.

In particular, Choren claims to have developed a process (Carbo V®) producing tar free syngas. Choren have formed a consortium with Shell and Volkswagen to develop and commercialise this process at industrial scale.

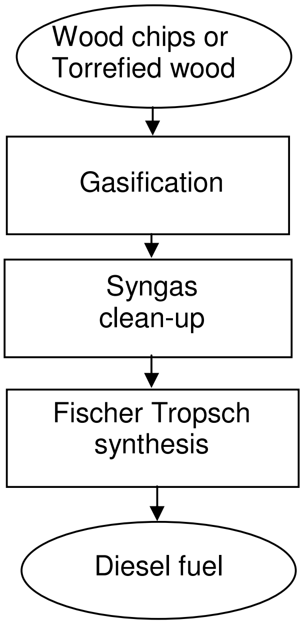

Figure 6: Synthetic diesel from wood (ligno-cellulose)

5.1 New Fuel - DME Dimethyl Ether

In addition to synthetic diesel, syngas from biomass could be a suitable feedstock for direct synthesis of DME. Dimethyl ether (DME) is a volatile organic compound which is non-toxic, non-caustic, non-carcinogenic, and non-mutagenic – hence research has been completed into the use of DME as a fuel. It is proposed that DME would be used directly as a fuel or as a blended component, in particular with LPG. DME can use the existing LPG infrastructures for transport and storage.

The technology for producing DME from syngas is proven. Development of pilot plants to produce ~35 kt/a of DME from syngas have been operational from 2003. At present the commercial development of plants in the range of 200 to 1000 kt/a is under way in China and Qatar. The plant in China will use coal as a feedstock to produce syngas. Currently, the least expensive way to produce syngas is by reforming natural gas but, technically, syngas can also be produced from biomass, although at a higher cost

Potentially, DME could become a suitable value-added outlet for smaller gas reserves located far from markets, where an LNG scheme is not feasible due to the minimum required plant size. Current alternatives to value these ‘stranded’ gas fields are production of ammonia or methanol.

Scouting work by ITI Energy indicates opportunities for developing appropriate catalysts to make DME the fuel of choice for fuel cells [10]:

- Electro-catalysts for the use of DME as fuel in Direct DME Fuel Cells (DDMEFC)
- Catalysts for the internal reforming of DME in Direct Internal Reforming Fuel Cells (eg DIR-SOFC)

6. 2ND GENERATION BIOCHEMICAL PROCESSES

Bio-chemical conversion can range from a simple fermentation once sugars have been extracted from the plant (eg cane or beet) or biomass residue (eg straw or forest residues), to complex chemical and/or bio-chemical treatment when processing ligno-cellulose feedstock into sugars.

A flow chart of the required steps for various type of feedstock is shown below (Figure 7). The green processing steps involved proven technologies that are operated commercially at 1st Generation bio-fuel plants. The blue processing steps are being actively researched, developed and demonstrated at pilot plant scales and represent 2nd Generation technologies.

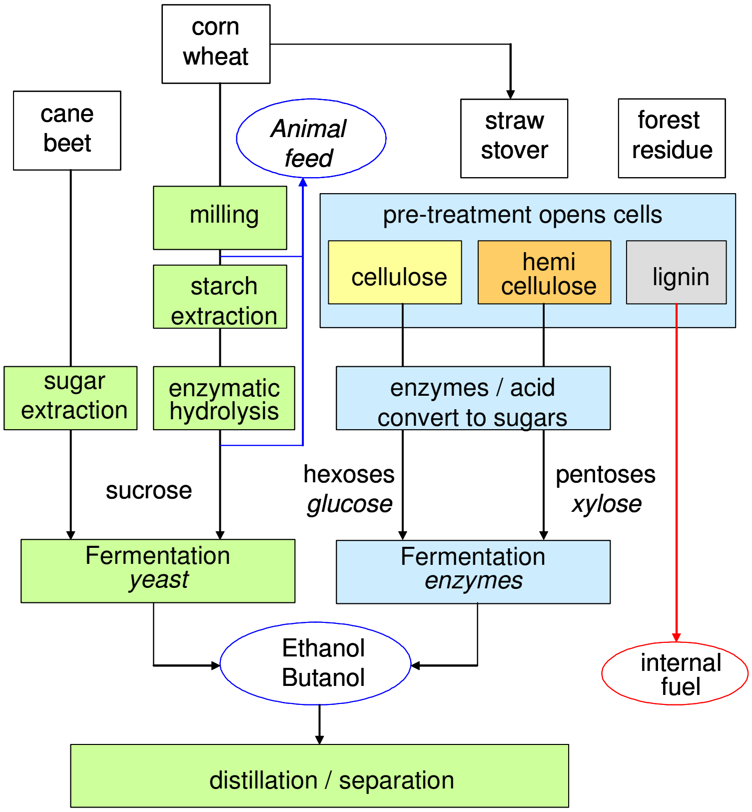

Figure 7: 1st and 2nd Generation Biochemical processes

In all cases, bio-chemical processes handle considerable amounts of water. This takes reactor space and the alcohols made in the process have to be separated by distillation, which is a fairly energy intensive process.

Soft biomass feedstock comprises a complex mixture of carbohydrate polymers from the plant cell walls (eg ~40% cellulose, ~15% hemi cellulose and ~10% lignin [11]). In order to produce sugars from the biomass, the biomass is pre-treated with acids or enzymes in order to reduce the size of the feedstock and to open up the plant structure. The cellulose and the hemi cellulose portions are broken down (hydrolysed) by enzymes, or dilute acids, into sucrose sugar that is then fermented into ethanol. The lignin which is also present in the biomass is normally used as a fuel for the ethanol production plant's boilers.

Fermentation of sugars by microbes (eg yeasts) is the most common method for converting these sugars into liquid fuels, such as ethanol. This process is well established for some sugars, such as glucose from cornstarch, and is now a mature industry producing more than10 billion US gallons per year (and growing rapidly) [12]. However, the efficient production of fuel ethanol from the mixture of sugars present in ligno-cellulosic biomass remains challenging, with many opportunities for improvement. Technologies for converting cellulosic biomass into fuel ethanol already have been demonstrated at small scale, and are being gradually implemented in pilot and demonstration plants. The primary challenge remaining continues to be the cost, with limiting factors such as process complexity, nature of the feedstock, and the limitations of current biocatalysts. Micro-organisms are needed with higher rates of conversion and yield to allow process simplification through the consolidation of process steps, which would reduce both capital and operating costs.

Some species of bacteria have been found capable of direct conversion of a cellulose substrate into ethanol. An example is C. thermocellum [13], which utilizes a complex cellulosome to break down cellulose and synthesize ethanol. However, this bacterial action also produces other products during cellulose metabolism, including acetate and lactate that lower the efficiency of the process. Some research efforts are directed to optimizing ethanol production by genetically engineering bacteria that focus on the ethanol-producing pathway. Although such a route could provide a major breakthrough by reducing the number of steps in the process, research is believed to be at an early stage.

6.1 Recent developments in pre-treatment

Pre-treatment to open cells and make them accessible to enzymes has attracted considerable R&D effort over the last decade. Both chemicals or enzymatic processes have been developed, or are under development. There is an array of technologies under investigation, with no clear winner. Also, the techniques are bulk processes and biomass specific.

A short review of the ongoing activity is presented below:

BlueFire Ethanol Fuels [14] holds an exclusive license to the Arkenol Technology Process, a proprietary concentrated acid hydrolysis capable of converting cellulosic agricultural residues into fermentable sugars. It deals with the cellulosic and hemi-cellolusic elements separately and is a good example of the classic approach. While they have addressed the issue of acid recovery, they do not mention if they have solved the problem of acid hydrolysis producing toxic degradation products.

NREL have developed a dilute acid pre-treatment developed and utilised for conversion of the whole straw crop to bioethanol. However the use of dilute acid requires high temperatures, which can degrade the sugars into furfurals which are toxic to fermentation micro-organisms and result in a reduced yield. Steam explosion techniques developed for the production of fibreboard greatly increases the surface area, thus increasing the rate of hydrolysis of treated cellulose. The biomass is subjected to high pressure 20-50 bar and high temperature 160-260°C steam for a few minutes and then decompressed to atmospheric pressure. However, steam explosion is an auto-hydrolytic process which can also produce furfurals.

The liquid hot water process uses superheated water to increase the surface area. However, this process liberates organic acids, which can lead to the sugar degradation products that are toxic to downstream fermentation micro-organisms.

Ammonia Fibre Explosion (AFEX) is a similar process to steam explosion, but the biomass is exposed to liquid ammonia at high pressure and temperature. This process results in a higher sugar yield and lower production of furfurals, but the capture and recycle of ammonia adds significant capital costs.

Alkali pre-treatment processes involve hydrolysis with an alkali to dissolve the lignin component of the biomass. Most research activity is focussed on the use of lime, due to its low feedstock cost and the fact that it can be precipitated out of solution after treatment. Reaction temperatures are lower than acid pre-treatments, but residence times are hours rather than minutes.

A number of companies are pursuing cost reductions in enzymatic pre-treatments where the cellulose is converted into glucose molecules by cellulase enzymes, eg Iogen Corporation [15]. This typically requires an initial pre-treatment stage to allow enzymatic attack, but leads to higher sugar yields. Genencor [16] and Novozymes [17] have received US DOE funding for research into reducing the cost of cellulase enzymes [18]. Dyadic International [19] are developing genetically engineered fungi which would produce large volumes of cellulose and hemi-cellulase enzymes.

Those looking at biotechnology to improve biomass pre-treatment include the Genomic GTL Bio-energy Centre in the US, the EU/USDA funded initiative EPOBIO researching plant cell wall saccherification and the UK funding council, Biotechnology and Biological Sciences Research Council (announced £13m funding for improved biofuel crops).

The USDA and DOE have formed a consortium called CAFI, which is attempting to develop robust comparative data for the application of each of the pre-treatment technologies listed above to a range of different feedstock.

UK organisations that are active in this field include: the Scottish Crop Research Institute (SCRI), the Centre for Novel Agricultural Products (CNAP), based at York University and the Forestry Commission.

6.2 Recent developments in fermentation

Traditional ethanol production in the brewery industry has relied on baker's yeast to ferment hexose feeds (6-carbon sugars). Due to the complex composition of the carbohydrates found in ligno-cellulosic biomass (eg corn stovers), a significant amount of xylose and arabinose (5-carbon sugars) is also present following pre-treatment. Thus, to increase the economic viability of cellulosic ethanol and biorefinery concepts, the ability of the fermenting micro-organisms to utilise the whole range of sugars (and, by extension, feedstocks) available is vital.

Yeast cells are particularly attractive for cellulosic ethanol processes, as they have been the workhorse of biotechnology for hundreds of years. They are tolerant to high ethanol and inhibitor concentrations and they can grow at low pH values, which avoids bacterial contaminations. In recent years, metabolically engineered yeasts which can effectively convert mixtures of sugars, have been reported [20][21]. Besides yeast derivatives, other micro-organisms such as Z. mobilis and E. coli have been modified through metabolic engineering for ethanol and bio-chemical production [22].

Given the scale and interplay of controlling factors, the economics of ethanol production for the biofuel market is still a matter of heated debate. However, it can be surmised that they are close to borderline at present. The primary aims of these developments is to reduce the cost of the existing process, via: allowing less expensive feedstocks, more efficient conversion or through simplification of the process.

A 2006 report, detailing the findings of a US DOE sponsored 'Biomass to Biofuels' workshop [24], provides a comprehensive review of the potential opportunities and challenges in this area. Discussions with some key Scottish organisations have highlighted some of these and indicated others [25][26].

These include:

- Ethanol tolerance – The ability of the micro-organism to survive in higher concentrations of alcohol, allowing intensified streams and greater throughput
- Feedstock flexibility – The ability of the micro-organism to handle a range of different feedstock compositions without degradation in production
- Feedstock specialisation – The use of micro-organisms that naturally exist with the particular biomass and would require less modification
- Higher value products – The conversion of some of the biomass to more valuable chemicals [27]. Lignin would be an ideal material, as it is a good natural source of aromatics and is typically burnt – but as the saying goes 'you can make anything out of lignin, except money' [28]
- Process simplification – The combination of some of the process stages, eg the use of a micro-organism that both deconstructs the biomass and ferments the sugars to produce the ethanol
- Inhibitors – Reducing the effect of natural microbial inhibitors, such as furfural, either through greater process selectivity or improved microbe resistance

Given the maturity of fermentation technology for simple sugar streams, a cursory overview of the patent landscape isn't particularly instructive. While there is undeniably scope for innovation through incremental improvements, as detailed above, a more rewarding approach might be to target as many of these areas as risk/finances allows. If successful, this could result in an end to end process for converting organics wastes to fuels and higher value products.

6.3 New Fuel - Butanol

Butanol is being considered as a fuel component which could be made from bio-mass, as it can be blended with both gasoline and diesel – hence is fully compatible with the existing fuel infrastructure.

Gasoline is a mixture of carbon chains from C4 to C12. Butanol with a four carbon chain has some properties which are closer to those of gasoline (Table 1). Ethanol has a two carbon chain.

Gasoline	115 000 BTU / gallon
Butanol	110 000 BTU / gallon
Ethanol	84 000 BTU / gallon

Table 1: Energy content of liquid fuels

These advantages have caught the interest of major actors BP and DuPont, as well as start-ups such as Green Biologics, W2 and Gevo. It is claimed that existing ethanol capacity might be cost effectively retrofitted to biobutanol production, as only minor changes may be required in the fermentation and distillation stages.

Conclusion

Fermentation to produce ethanol is an established technology, but is not sufficiently efficient or cost effective to provide a suitable fuel with certain biomass feedstocks (eg agricultural wastes). There are areas of research that could provide suitable cost reductions or additional high value product streams. These could be developed with Scottish expertise and exploited globally.

There is a great deal of existing expertise located in and around Scotland relating to fermentation, biomass and microbial research, including:

- Scottish Crop Research Institute (SCRI) – biomass and microbes
- Scottish Association for Marine Science (SAMS) – biomass and microbes
- International Centre for Brewing and Distilling (ICBD) – fermentation
- Green Chemistry Centre of Excellence for Industry – green processes
- Process Intensification and Miniaturisation Group, Newcastle University – biofuel process intensification

However ethanol production from cellulosic biomass has featured on research agendas for many years. Although this 2nd generation process is not yet commercialised, ITI predicts that it will be in the near to mid term.

On several organisations' mid term horizons is a new 2nd generation feedstock; algal oil. The discontinued US Aquatic Programme, 1978 to 1996, demonstrated that it was possible, but uneconomic, to grow algae in raceway ponds, extracting algal oil with high lipid content that would be suitable for conversion to bio-diesel.

With further research and development, coupled with the DNA breakthroughs in the last decade, increased oil prices and a need to fix CO_2, it maybe possible to economically grow algae for biodiesel production.

The time to market, and the technical challenge, for the next generation of biofuels are summarised in the chart below (Figure 8).

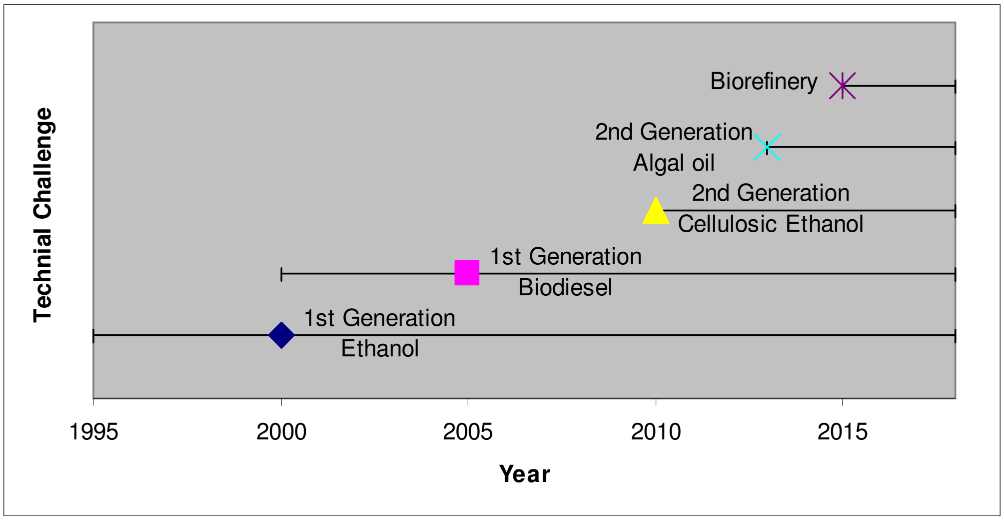

Figure 8: Comparison of the technical challenges associated with the next generation of Biofuels

Since 2nd generation algal oil is further from market and less developed, it represents the best opportunity to research Sustainable Transport Fuels for ITI.

6.4 Future concept - Biorefinery

The concept of the Biorefinery has several interpretations and has been mooted since the 1980s. The concept is analogous to the petro-chemical refinery, where a range of value-added intermediary feedstocks are manufactured from crude oil. However, the extraction and separation of the complex aromatic molecules within biomass may, perhaps, suit fine chemical production rather commodity energy products. The National Renewable Energy Laboratory [29] has several research programmes investigating the potential of biorefineries.

7. 2nd Generation – Sustainable biofules from algae

7.1 Introduction

An extreme analysis of the food verses fuel debate reveals that land use is critical. To avoid land use and still provide large quantities of biomass feedstock it makes sense to turn to the marine environment.

The marine environment can be harnessed to provide suitable feedstocks for biofuels that do not directly compete with land-based food crops. The concept consists in converting sunlight, nutrients and CO_2 into bio-fuels through the use of algal biomass. Algal biomass can be subdivided into microalgae (eg plankton) and macroalgae (eg sea weeds/vegetables) which have very different properties, as can be seen in Table 2.

Product	Typical macroalgae [30]	Microalgae [31]
Proteins	< 40%	15 to 55%
Lipids/oils	< 5%, generally about 2%	20 to 55%
Carbohydrates	Soluble fiber (agar, carrageenan & alginate) < 50% Insoluble fiber (cellulose, xylans & others) < 8% Oligosaccharides, sugars & sugar alcohols: up to 20%	15 to 65%
Minerals e.g. Ca, P, Mg, Fe, Na, K, & Cl.	<36%	~15%

Table 2: Chemical composition of Macro and Micro algae

The useful oil content of microalgae (as much as 70% oil [32]) is comparable with the best crops used for biodiesel production and potential yields per surface area are expected to be significantly higher, but yet to be economically proven. While the growth and harvesting of the microalgae offer a completely different series of challenges, the collected and dried material can be pressed in a similar manner to extract the natural oil which can then be converted into biodiesel. The remaining cellulosic residue can be directly utilised in a power plant, or processed to produce alcohol – which may be fed into the biodiesel production process. At present, the only microalgae grown at scale is Spirulina for the health food market, due to its high protein content (~70%); annual global production in 2004 approaching 6000 tons [33].

Macroalgae are a traditional food source in many parts of the world, particularly in Asian countries where many millions of tons are grown and harvested each year [34]. Macroalgae are also the primary source of three industrially important hydrocolloids. Alginate, agar and carrageenan are water-soluble carbohydrates that are used to thicken aqueous solutions, to form gels of varying degrees of firmness, to form water-soluble films, and to stabilize some products (such as ice cream). In 2003 approximately 1 million tons of wet seaweed were harvested and processed to produce about 55000 tons of these hydrocolloids, with a value of $585 million [34].

Given the low oil content, the processing of macroalgae to biofuels would utilise the sugar and cellulosic elements (presently a waste stream from the hydrocolloid production) through fermentation to bio-ethanol or higher alcohols.

In 1978 the US Department of Energy initiated The Aquatic Species Program, in an attempt to find the optimal species (predominately micro-algae) and conditions for algal oil production [35]. Over a period of almost 20 years the programme funding waxed and waned in relation to the oil price until the mid-1990's when, following a protracted slump, it was eventually terminated. By the end it had consumed roughly $25 million (equivalent to $100 million today), almost 6% of the US annual biofuels budget. As well as producing a comprehensive database of species and their characteristics, it had achieved a number of key milestones, including the development of a low cost harvesting bio-flocculation process and the construction of a 0.2 hectare demonstration facility.

In Japan a major R&D programme, totalling over $250 million in joint funding, was undertaken in the 1990s to investigate the bio-fixation of CO_2 by micro-algae as a route to greenhouse gas abatement. Despite significant cross-governmental and industrial involvement, the project was not continued. This is believed to be mainly due to the high cost of the closed photo-bioreactors which formed the core of the research efforts [36].

The continued global interest in this area from governments and private companies led in 2000 to the formation of an International Network, which promoted the research and development of microalgae-based greenhouse gas abatement technologies over a ten year time horizon [37]. This Network has published a technology roadmap outlining many of the challenges and has, more recently, sponsored an independent assessment on the technical and economic viability by TNO [38].

In 2004, Michael Briggs of the University of New Hampshire estimated that the entire transportation needs of the United States could in theory be met with 15,000 square miles of microalgal ponds [39]. While a large number, this is only ~12% of the area of the Sonora desert in the south-western US and less than 1% of the land allocated to US agriculture.

This wealth of background knowledge has proven fertile ground for companies in the private sector, seeking to unlock algae’s potential as a fuel source. Despite this, commercial algae biofuels production is still in a nascent stage, with only a small number of companies close to deploying their respective technologies on a reasonable scale, thus highlighting the challenges and opportunities that this area offers.

7.2 Existing developers

There is a growing number of players in this area and the recent review by Mora Associates [40] provides a good list. The companies mentioned below are included to provide an example of the range of different technical solutions and applications available.

GreenFuel's [41] Emissions-to-Biofuels technology is a system where CO_2-rich flue emissions feed into tubes filled with water and nutrients, where the microalgae are suspended. The rapidly growing algae are continuously removed from the system. The technology has been demonstrated at the MIT power plant and, in the next 18-24 months, several pre-commercial pilot projects are scheduled.

The GreenShift CleanTech system [42], developed from the work of David Bayless of Ohio University, uses solar collectors to concentrate sunlight. The system then directs the light into a closed chamber and distributes it over glow plates with a large surface area enriched with CO_2 from a nearby power plant. Between the glow plates are growth media, over which water and a nutrient solution flow, and microalgae grow. When the algae are ready to harvest, an increase in water pressure separates them from the growth media for collection.

Solix Biofuel [43] in Fort Collins, Colorado, has partnered with Colorado State University to develop an alternative bioreactor. While most of the other applications take CO_2 from power plants, the Solix demonstration site sits adjacent to the New Belgium Brewery where the fermentation process yields enough CO_2 to feed the microalgae. Long, narrow tanks sealed with plastic sheeting contain microalgae, water, nutrients, and CO_2 that are pumped from the nearby brewery. In order to ensure that the microalgae have sufficient light, a roller passes back and forth over the tank to mix the contents.

The other common method for cultivating algae uses an open pond design. Open ponds, such as Aquaflow [44] Bionomic's open pond design, uses carbon and nutrient rich effluent streams from waste water treatment plants to grow their microalgae. Unlike the closed photo bioreactor, enough carbon is present in the effluent stream that additional CO_2 doesn't need to be added. While currently under development, Aquaflow hopes that the process will sufficiently filter the wastewater for re-use in other applications, like irrigation. To demonstrate the potential of their technology, the company drove the energy minister of New Zealand around using a B5 blend of their microalgae-based biodiesel.

While research into algae for the mass-production of oil is predominately focused on microalgae, due largely to its less complex structure, fast growth rate, and high oil content, macroalgae may offer other subsidiary benefits (eg pharmaceuticals and other bio-chemicals). Global interest in this area appears significantly smaller than microalgae, with it being seen as more of a nuisance than potential feedstock [45][46].

As well as these smaller, independent players there is growing evidence that the potential of algal biofuels is being taken seriously by a number of major oil companies, eg Chevron [47] who are in the early stages of initiating research programmes. While this increases the competitive nature of research in this field, it clearly indicates the willingness of the majors to potentially adopt advances in this technology.

7.3 Economics

The economics of algal production are sorely contested by supporters and critics. The NREL close out report in 1998 provided illustrative production values for open pond microalgal biofuels between $70/barrel to $230/barrel (in today's dollars). With the price of crude oil now having broken through the $100 mark, many have focussed on this lower 'optimistic' figure – claiming that advances in both the understanding of the algae biology and the aquaculture technology makes it a realistic proposition. The counter argument states that the increases in raw materials, eg steel, have markedly accelerated the rise in EPC (engineering, procurement, construction) costs which will push the values closer to the more pessimistic case. This point of view is strengthened by the recent TNO report, which states that a fuel-only process is not economically viable without other revenue streams – such as higher value products or the ability to claim carbon credits.

However, some of the start-ups firms claim otherwise. Table 3 below represents PetroAlgae's estimated cost of production [48].

	Rapeseed	Soybean	PetroAlgae
Raw oil $/gallon	$3.38	$2.63	$1.73
Conversion cost	$0.52	$0.52	$0.52
Biodiesel Cost	$3.90	$3.15	$2.25

Table 3: Comparative costs of production for biodiesel

The cost of feedstock is the major component of fuel costs. Micro-algae would show a strong advantage if the high yield observed at bench scale level can be scaled up to industrial production. The conversion cost quoted by PetroAlgae is based on trans-esterification. Because of its sulphur content, it is likely that algal oil will need to be hydro-treated which could result in a higher processing cost.

A potential real world example could be given by the cost of producing spirulina microalgae in large, open raceway tracks for sale in the natural food market. However, because of the fundamentally different market drivers, its sale price (~$110/kg [49]) is many times the price of algal biofuels [50]. The production costs of biofuels in this instance would also be different since less expensive sources of CO_2 (such as industrial exhaust or effluent) could be used.

Another approach favoured by many of the recent start ups is the use of closed photo-bioreactors, which concentrate the available sunlight and maximise the available area. Headline grabbing claims of yields and productivity of 30-100 times that of typical agricultural crops have been claimed [51], but there is some debate regarding the financial benefits of such an approach [52][53]. The costs of open pool can be <$10/m^2 with single day yields of up to 50 g/m^2 [30], while photobioreactors have reported peak yields of 170 g/m^2 [51] – but costs of >$100/m^2.

Whichever arguments are correct, the economics offer small margins and demand an intensified and inexpensive source of CO_2 and nutrients. This 'restricts' the initial application of the technology to locations such as fossil fuel power plants and waste-water treatment facilities. While this is not necessarily a problem, it raises the issue that the majority of the algal biofuels market, as presently imagined, is locked into a synergistic (green carbon capture) relationship with the combustion of fossil fuels, as opposed to a standalone green fuel.

> A micro-algae bio-fuel plant located next to an oil refinery could potentially results in zero CO_2 emissions for the refinery as the emission has been displaced to the fuel end user (eg the motorist). In the case of a power plant, the CO_2 emitted by the plant would be displaced to the bio-fuel end user. The fuel producer would need to obtain carbon credits from the power generator and transfer them to the fuel end user. A market related mechanism for sharing carbon credits between power generators and fuel producers would need to be established. For the power producer the economic benefits would have to be compared with transport and sequestration of CO_2.

7.4 Scope for development

A number of commentators have indicated that the key to a successful algae biofuels industry lies in finding optimal algae strains, proper technologies for growth/culturing, and efficient oil extraction. The commercial developers have stressed the need to lower current production costs to be competitive in the larger market, and have highlighted opportunities to reduce costs by harnessing carbon and heat sources from manufacturing facilities and power plants. Figure 9 and Figure 10 respectively illustrate the process pathways for both the micro and macroalgae and indicate some of the potential challenges and opportunities. They can be defined at a high level as follows:

A. Micro-algae:
A1 – value chain
A2 – feedstock
A3 – strain developments
A4 – reactors
A5 – harvesting
A6 – separation
A7 – products
A8 – downstream processing

B. Macro-algae:
B1 – value chain
B2 – plant selection
B3 – harvesting
B4 – products
B5 – downstream processing

The original NREL reports indicated that the cost of algal strain optimisation would be very expensive, but discussions with the Scottish Association for Marine Science (SAMS) have suggested that this may not necessarily be the case [54]. They stated that while significant research had been undertaken on predominately terrestrial microalgal biomass, there was significant potential in investigating marine species [55]. This could improve efficiencies through relatively inexpensive selection and breeding to allow production at economic levels. It could also provide subsidiary benefits (eg pharmaceuticals and other bio-chemicals) as they investigate the characteristics of previously unstudied algae.

Indeed, searching for a purely genetic engineering solution is perhaps not the best ay forward as the utilisation of such a GM organism becomes more complex. This is mainly because it would require a more costly closed reactor system, to prevent the organism being out-competed by wild strains. There is also the question of the acceptability of genetic modification. It can be argued that the consumers would potentially not have the same objections to a genetic modified fuel, given that the existing source cannot be considered particularly ‘natural’ or environmentally friendly. However, there would undoubtedly be concerns and objections raised to the utilisation of GM organisms by lobby groups which, given the Scottish Government's public opposition to GM crops [56], could be a potential roadblock.

Further conversations with SAMS have highlighted the particular potential of macroalgae biomass. As seaweed contains no lignin, a much larger proportion of the harvested biomass is available for processing compared with land-based energy crops. Advances in pre-treatment, processing (eg specific microbes for fermentation) and conversion technologies could integrate with the existing seaweed market, particularly the utilisation of the waste sugars from alginate production, in the short term. Meanwhile, work could be done towards reducing the logistical burden of fuelling coastal or island communities.

Further expansion toward a vision of the large scale cultivation (~millions of hectares) of offshore farms (capable of supplying a significant fraction of the UK's energy requirements) are heavily dependant on the development and implementation of cost-effective aquaculture technologies (eg rope farms).

A review of the various technologies, and cursory analysis of the patent landscape, suggests that there is potential for optimisation of the various stages in the microalgae to biodiesel process. There is a danger that these may be only incremental improvements and risk being overly specific. There also appears to be limited opportunity for the development of high value, platform technology. This danger can be mitigated by investigation of new strains as potentially valuable, cross applicable characteristics (eg route to higher value products) may be uncovered.

It could be argued that there is value in the development of a carbon capture and storage infrastructure to mitigate the need for location-specific intensification. While while interesting concepts have been proposed, they are outwith the scope of this report.

7.5 Summary of findings

- Microalgae concept has been proven, with basic (open pools, paddle wheels) existing technological solutions proving sufficient
    - Issues regarding cost effective harvesting partially addressed, eg autoflocculation and bioflocculation, but remains primary R&D priority
- Microalgae economics necessitate specific locations for implementations (typically ready supply of CO_2 and nutrients) and demand simple solutions eg 'open' pools, paddle wheels
- Scope for optimisation of existing terrestrial strains, but predominately incremental improvements on theme as opposed to game-changing research Strong potential for the investigation of marine strains which may provide ancillary benefits
- Potential to develop sustainable biofuel pathways from traditional macroalgae crops

7.6 Conclusions

Microalgae technology is already finding both application and private funding, because of the high oil price. However, the level of activity and funding remains low, relative to other energy technologies, and the challenges to be overcome – especially in terms of cost reduction – are still considerable. Considering both the availability of marine resources and the strong market opportunity present in Scotland, there is a strong argument that ITI Energy should rise to this challenge.

Similarly, there appears to be an opportunity in applying biofuel concepts to the existing macroalgae value chain. In the short term this could fit within Scotland's existing chemicals markets – and within global energy markets in the longer term. The logistics and economics of such a concept are not readily transparent and understanding these would be a priority.

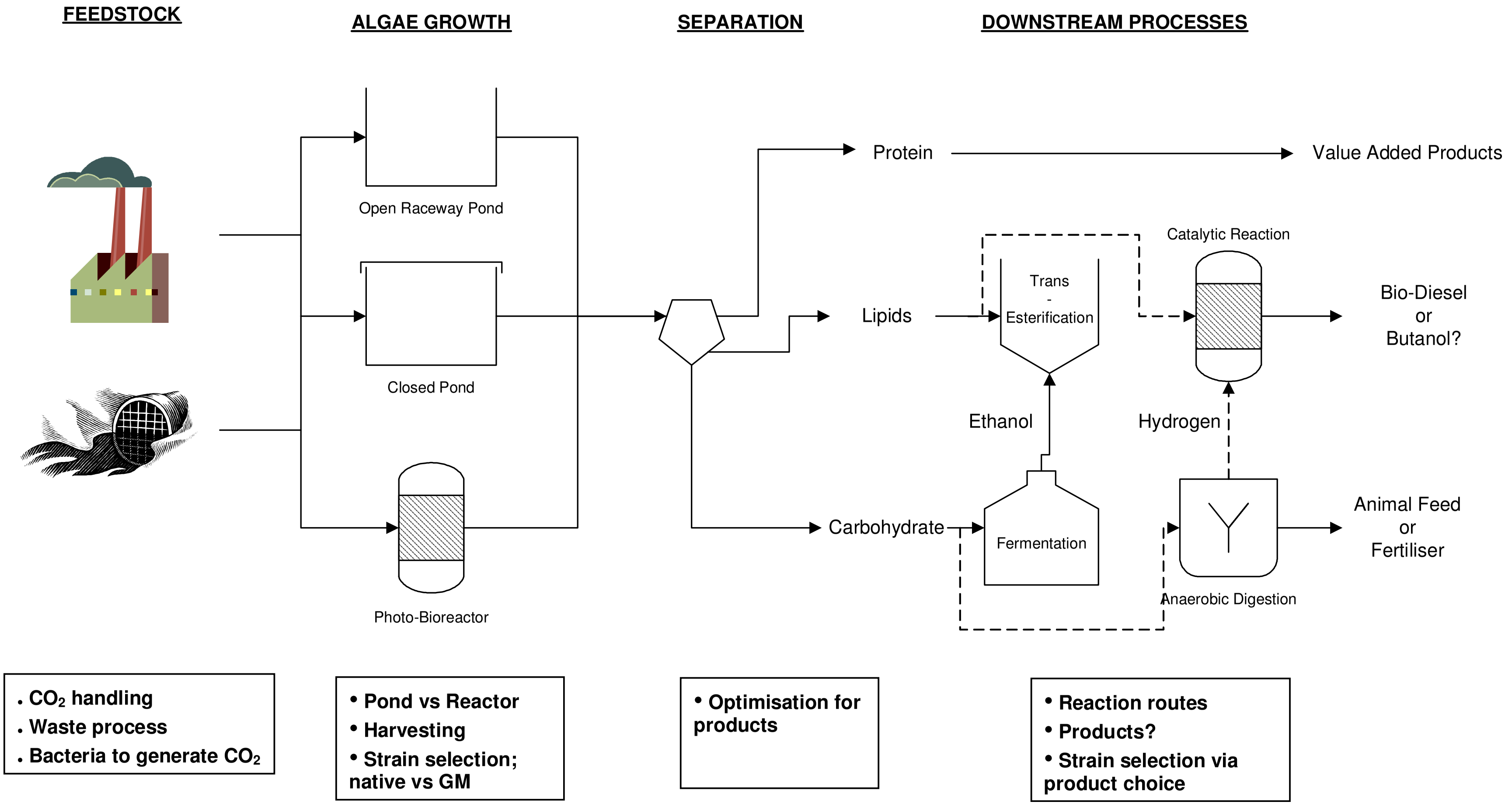

Figure 9: Microalgae process/value chain

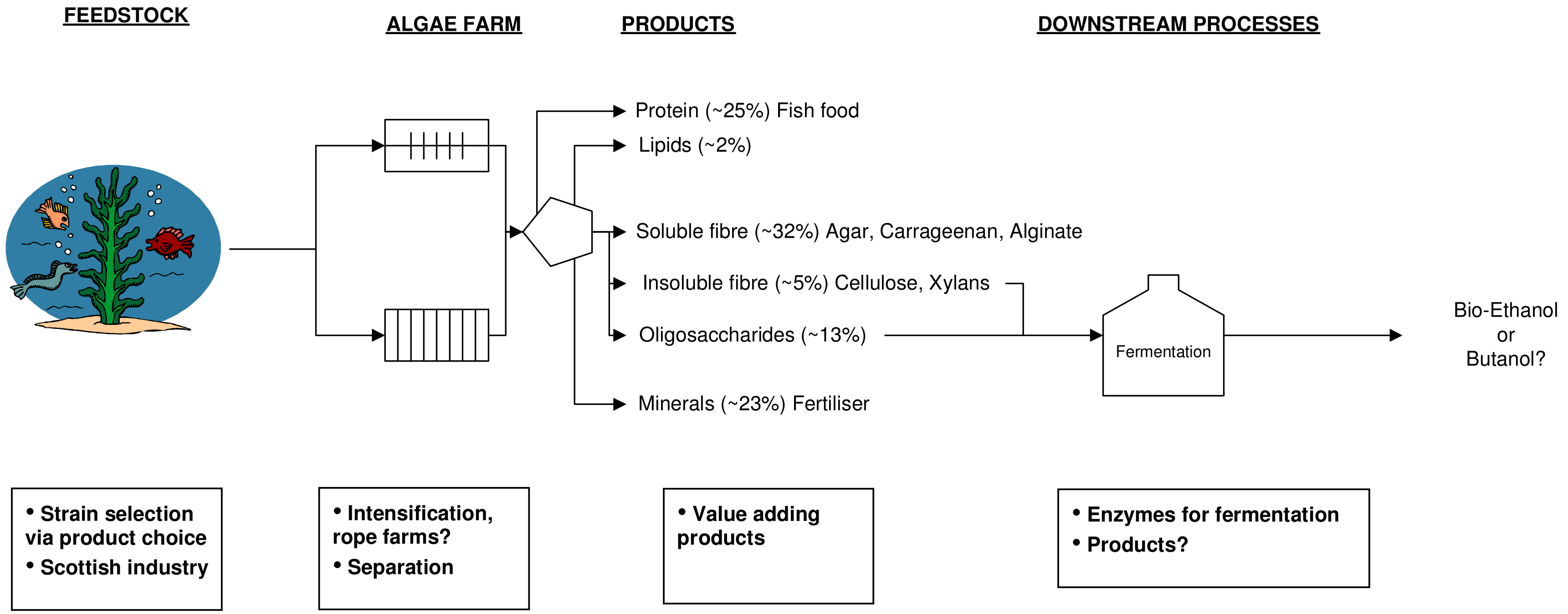

Figure 10: Macroalgae process/value chain

8. 3RD GENERATION SOLAR FUELS; DREAM OR NEXT DECADE REALITY?

The conversion of sunlight into a fuel (a transportable energy vector, eg hydrogen, hydrocarbons) can be approached from three primary directions:

- development of improved chemical analogues of photosynthetic processes, eg bio-mimetic reaction centres and photo-systems
- modification of organism to produce suitable fuel
- combination of discrete photo-catalytic and electrochemical process

Research into the fundamental photosynthetic processes, with a goal to develop artificial photosynthesis, is undeniably exciting and technically challenging but is perhaps too early stage to be of commercial value. By contrast, there are clear signals that a microbial or a photo-catalytic approach to making solar fuels is somewhat closer to commercial exploitation, as illustrated by the following examples:

LS9 researchers are using a combination of standard recombinant DNA techniques and synthetic biology (redesigning known genes with a computer and synthesizing them) to insert genes into the microbes. The resulting modified bacteria make and excrete hydrocarbon molecules that are the length and molecular structure the company desires. The company claims to be able to make hundreds of different hydrocarbon molecules. The process can yield crude oil which would go to a standard refinery to be processed any petroleum product.

Chemists at the University of California, San Diego, have developed a device to split carbon dioxide which utilizes a semiconductor and two thin layers of catalysts. It splits carbon dioxide to generate carbon monoxide and oxygen in a three-step process. The first step is the capture of solar energy photons by the semiconductor; the second step is the conversion of optical energy into electrical energy by the semiconductor; the third step is the deployment of electrical energy to the catalysts. The catalysts convert carbon dioxide to carbon monoxide on one side of the device and to oxygen on the other side.

There is undeniably scope for research and creation of new commercial IP in each of these areas, a point echoed by the top-level conclusions of the 'Basic Research Needs for Solar Energy Utilization' report by US DoE, reproduced below, and supported by a recent joint EPSRC/BBSRC workshop:

"*The efficient production of clean solar fuels presents many scientific challenges. Yet progress in this field to date provides a strong argument that this goal is achievable.*

The major scientific challenges that will need to be addressed are:

(1) understanding biological mechanisms for the efficient production of fuels from biomass;
(2) developing a detailed knowledge of how the molecular machinery of photosynthesis captures and converts sunlight into chemical energy;
(3) discovering how to use this knowledge to develop robust, bio-inspired chemical systems to carry out photo-conversion;
(4) developing catalysts that use photo-generated chemical energy to efficiently produce such fuels as CH_4 and H_2;
(5) developing an integrated photo-driven system for solar fuels formation with optimized performance and a long functional lifetime."

ITI Energy is currently mapping these fields and investigating this area in more detail. This research will be published to Members as a separate fore-sighting study that will seek to answer whether Solar Fuels are only a dream – or a real possibility within the next decade?

REFERENCES

[1] http://www.bursamalaysia.com/website/bm/market_information/market_statistics/derivatives/downloads/FCPO_spo_mth_av.pdf

[2] Frost & Sullivan European Bioethanol and Feedstock Markets Analysis August 2007

[3] Frost & Sullivan *European Biodiesel and Feedstock Markets Analysis* May 2007

[4] Masmi Kojima and Todd Johnson "*Potential for Biofuels for Transport in Developing Countries*" October 2005. World Bank ESMAP. Energy Sector Management Assistance Programme.

[5] Data is from Foreign Agricultural Service/USDA. Available at http://www.fas.usda.gov/psdonline/circulars/oilseeds.pdf

[6] http://www.fwi.co.uk/Articles/2008/02/13/109374/new-fertiliser-recommendations-for-sugar-beet-announced.html

[7] http://www.geocraft.com/WVFossils/greenhouse_data.html

[8] ADEME, Ecobilan, July 2006

[9] Gerrit Brem "*Catalytic Pyrolysis of Biomass for the Production of Green Oil*" presentation at Next Generation Biofuel Markets conference, October 2007

[10] Olivier Bordelanne "*Emerging Fuel – The DME Case*" presentation ITI internal report

[11] Hideaki Yukawa, '*Technologies for mitigating global warming and the role of Japan*' 2007 RITE International Symposium, 18 January 2007

[12] www.ethanolproducer.com

[13] www.rochester.edu/news/show.php?id=2803

[14] bluefireethanol.com

[15] www.iogen.ca/cellulose_ethanol/what_is_ethanol/process.html

[16] www.genencor.com/cms/connect/genencor/products_and_services/agri_processing/renewable_fuels/new_products_ethanol/cellulosic_ethanol_en.htm

[17] www.novozymes.com/en/MainStructure/ProductsAndSolutions/Fuel+ethanol/Fuel+ethanol.htm

[18] www1.eere.energy.gov/biomass/cellulase_cost.html

[19] www.dyadic.com/wt/dyad/biofuels

[20] T.W. Jeffries, Y-S. Jin, *'Metabolic engineering for improved fermentation of pentoses by yeasts'* Applied Microbiology & Biotechnology, 63 495-509 (2004)

[21] K. Karhumaa, B. Wiedemann, B. Hahn-Hägerdal, E. Boles and M-F Gorwa-Grauslund, *'Co-utilization of L-arabinose and D-xylose by laboratory and industrial Saccharomyces cerevisiae strains'* April 2006, available from - www.microbialcellfactories.com/content/5/1/18

[22] Eliora Z. Ron, *'The energy crisis - how can microorganisms be put to work'* Energy Biosciences Strategy for India Workshop, 10-11th September, 2007, New Delhi

[23] www.rochester.edu/news/show.php?id=2803

[24] J. Houghton, S. Weatherwax, J. Ferrell, '*Breaking the Biological Barriers to Cellulosic Ethanol'* US DOE Office of Science, DOE/SC-0095 June 2006

[25] Meeting with Scottish Association for Marine Science (SAMS) – 12th October 2007

[26] Meeting with Scottish Crop Research Institute – 16th October 2007

[27] John Pierce, DuPont 'A perspective on sustainable energy & materials' Energy Biosciences Strategy for India Workshop, 10-11th September 2007, New Delhi

[28] http://www.floridaenergycommission.gov/UserContent/docs/File/EthanolProducerMag0907.pdf
[29] http://www.nrel.gov/biomass/biorefinery.html
[30] www.surialink.com/infomedia/Monographs/comp_veg.htm
[31] D.A. Feinberg, '*Fuel Options from Microalgae with Representative Chemical Compositions'* Solar Energy Research Institute, July 1984
[32] Y. Chisti, '*Biodiesel from microalgae'* Biotechnology Advances, 25 (2007) 294–306
[33] www.engineeringnews.co.za/article.php?a_id=49447
[34] D.J. McHugh, *'A guide to the seaweed industry: FAO Fisheries Technical Paper 441'* Food And Agriculture Organization Of The United Nations, Rome, 2003 available at www.fao.org/docrep/006/Y4765E/y4765e00.HTM
[35] J. Sheehan, T.G. Dunahay, J.R. Benemann, P.G. Roessler, J.C. Weissman, '*A Look Back at the U.S. Department of Energy's Aquatic Species Program: Biodiesel from Algae'*, National Renewable Energy Laboratory, July 1998, NREL/TP-580-24190
[36] J.R. Benemann, '*Biofixation of CO_2 and Greenhouse Gas Abatement with Microalgae – Technology Roadma*p' International Network on Biofixation of CO2 and Greenhouse Gas Abatement with Microalgae, January 2003
[37] http://www.co2captureandstorage.info/networks/Biofixation.htm
[38] T. van Harmelen, H. Oonk, '*Microalgae Biofixation Processes: Application and Potential Contributions to Greenhouse Gas Mitigation Options'*, TNO, May 2006
[39] http://www.unh.edu/p2/biodiesel/article_alge.html
[40] Leonard Wagner, '*Biodiesel from Algae oil'* Mora Associates Research report July 2007
[41] www.greenfuelonline.com
[42] www.gs-cleantech.com
[43] www.solixbiofuels.com
[44] www.aquaflowgroup.com
[45] aiche.confex.com/aiche/2006/preliminaryprogram/abstract_73948.htm
[46] www.tokyo-gas.co.jp/tgminutes/51.pdf
[47] http://www.nrel.gov/news/press/2007/535.html
[48] PetroAlgae Business Overview presentation available at http://www.xltg.com/archive/PetroAlgae_Overview.pdf
[49] www.spirulina4nutrition.com
[50] www.earthrise.com
[51] O. Pulz, '*Performance Summary Report – Evaluation of Greenfuel's 3D Matrix Algae Growth Engineering Scale Unit'* September 2007, available from www.greenfuelonline.com
[52] K. Dimitrov, '*Greenfuel Technologies: A Case Study for Industrial Photosynthetic Energy Capture'*, March 2007, obtained from algae-thermodynamics.blogspot.com
[53] www.theoildrum.com/node/2541
[54] Telephone conversation with Ian McFarlane, Scottish Association of Marine Science, 8th August 2007
[55] Meeting with SAMS Blue Energy team, 12th October 2007
[56] news.bbc.co.uk/1/hi/scotland/6268556.stm www.maesanturio.org – 'Greenbox' technology

ACKNOWLEDGEMENTS

ITI Energy would like to acknowledge the following parties for providing permission to use their information in this report:

PetroAlgae LLC, 1901 South Harbour City Boulevard, Suite 300, Melbourne, FL 32901, USA www.petroalgae.com