

Marine Estate Research Report

**The potential of marine biomass for anaerobic
biogas production**



The potential of marine biomass for anaerobic biogas production:

a feasibility study with recommendations for further
research

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A report commissioned by The Crown Estate and supplied by the
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LIST OF ABBREVIATIONS / GLOSSARY

AD: Anaerobic Digestion

Biogas: Anaerobic bacteria break down or "digest" organic material in the absence of oxygen and produce "biogas" a mixture of methane (55-75%) and carbon dioxide (25-45%) with variable trace amounts of carbon monoxide, nitrogen, hydrogen, hydrogen sulphide and oxygen

CHP: combined heat and power

Ha: hectare

Ethanol: or ethyl alcohol (C_2H_5OH), suitable for use as fuel

HRT: Hydraulic retention time, a measure of the average length of time that a soluble compound remains in a constructed reactor

kW: 1,000 Watts of power

kWe: 1 kW electrical energy

kWh: work done by one thousand watts of power acting for one hour

kWth: 1 kw thermal energy

Macroalgae: marine seaweeds. Macroalgae are not 'plants', but are referred to as such for convenience in this document.

Methane (CH_4): is the major component of the "natural" gas used in many homes for cooking and heating. It is odourless, colourless, and yields about 1,000 British Thermal Units (Btu) [252 kilocalories (kcal)] of heat energy per cubic foot (0.028 cubic metres) when burned. Natural gas is a fossil fuel that was created eons ago by the anaerobic decomposition of organic materials. It is often found in association with oil and coal. The same types of anaerobic bacteria that produce natural gas also produce methane today.

MW: megawatt or 1000 kW

RTFO: Renewable Transport Fuel Obligation

SRT: solid retention time

T: one metric ton (1000 kg)

TS: total solids, the amount of solids remaining after heating the sample at 105°C to constant weight as defined by the NREL Determination of total solids in biomass Laboratory Analytical Procedure.

TW: Terawatt 1,000 (1 Gigawatt $\times 10^{12}$ Watts)

TWh: Terawatt hour

VS: volatile solids, expressed as a percentage of TS, the TS minus the weight of the inert material

Stoichiometry: the calculation of quantitative (measurable) relationships of the reactants and products in chemical reactions (chemical equations).

'The human race must make use of the vast ocean sea to yield more products for its benefit and a new era for the mariculture of seaweed for biomass will definitely come sooner or later'

C.K. Tseng, Institute of Oceanology, Academia Sinica, China, 1981.

EXECUTIVE SUMMARY

Concern over greenhouse gas emissions forcing climate change and dwindling oil reserves has focused debate and research effort on finding alternative sources of energy. Scotland has the capacity to generate much, or all, of its electrical energy needs from wind and hydropower and has the potential for offshore energy schemes generating from wind, waves and tidal streams. The route map to generating alternative transport fuels is less well defined. A relative shortage of good agricultural land, high rainfall and a low number of sunshine hours means there is little potential for producing biofuel (bioethanol or biodiesel) crops.

The Royal Commission on Environmental Pollution (RCEP) (2004a) however concluded that terrestrial biomass should play an important role in the renewable energy generation mixture. When energy crops are used as fuel the carbon does not contribute to net greenhouse gas emissions. Unlike most other renewable energy sources, biomass can be stored and used on demand to give controllable energy and is therefore free from the problem of intermittency, a particular problem for wind power. Also, unlike most other sources of renewable energy, biomass offers a source of heat as well as electricity. In fact in the RCEP (2004a) review, biomass is considered solely as a source of heat and electricity and not as a potential source of transport fuel; the RCEP report considers that there are three types of indigenous biomass only, forestry materials, energy crops e.g. willow and miscanthus, and agricultural residues. However the current document reviews the potential of another type of biomass, marine biomass, which has the additional benefit that it can be anaerobically digested to produce methane which, in turn, can be used to generate electricity, for heat or for transport.

Marine algae offer a vast renewable energy source for countries around the world that have a suitable coastline available. They are already farmed on a massive scale in the Far East and to a much lesser extent in Europe, primarily in France, and on a research scale in Scotland. Utilising marine as opposed to terrestrial biomass for energy production circumvents the problem of switching agricultural land from food to fuel production. In addition, the production of marine biomass will not be limited by

freshwater supplies, another of the contentious issues of increasing terrestrial biofuel production.

Various forms of terrestrial biomass are routinely used as feedstock in anaerobic digesters for the production of methane. In the 1970's and 1980's researchers in the US began to investigate the potential of marine biomass (seaweeds), as opposed to terrestrial biomass, as a feedstock for methane production. These studies still provide much relevant data for the assessment of the industrial production of methane from marine macroalgae and showed that marine algae are as good a feedstock for anaerobic digestion (AD) processes as terrestrial sources. Marine algae contain no lignin and little cellulose, demonstrate high conversion efficiencies, rapid conversion rates and good process stability. The residues are suitable for use as nutrient supplements for agriculture.

If marine biomass is a serious contender for supplying even a small percentage of our energy needs and if these seaweeds are to be cultured, rather than harvested from the wild, then it has to be accepted that a larger portion of the seas will be 'farmed'. While culture operations must be subject to their own environmental impact assessment, seaweed farms offer the possibility of increasing local biodiversity as well as removing a proportion of the nutrients which can lead to eutrophication. There is the potential to improve biomass yield and quality through selective plant breeding and for further mechanisation of the culturing process to streamline production and reduce labour costs. Before Scotland can seriously assess the potential of marine biomass there is a need to establish larger (hectare or more) pilot-scale farms both to learn how to manage such systems and to better understand the limits on productivity.

This report describes the anaerobic digestion (AD) process (Section 1), reviews the historical harvesting and present production methods of seaweed biomass (Section 2), its conversion to methane (and to a lesser extent ethanol) (Section 3) and the options for wild harvest versus culture in a UK and Scottish context (Section 4). A number of case studies have been used to exemplify the current state-of-the-art in AD and possibilities for energy production (Section 5) and an attempt has been made to forecast the macroalgal biomass required to produce a similar methane

yield equivalent to one of the given examples, the South Shropshire Biogas facility. While Section 5.3 does include some projected figures on methane production, energy obtainable, nitrogen availability and the costs of farming, this is largely conjecture and it would be useful to obtain hard data from scale field trials. The report includes 27 recommendations for future work, including the need for practical, development and demonstration projects to carry forward some of the concepts and the need for a government/industry forum to launch the concept (Section 6).

The further research recommendations can be categorised as those relating to 1) obtaining the seaweed biomass, 2) then optimising the methane (or other energy carrying) output from that biomass and 3) the economic aspects of installing the infrastructure required to farm at sea and to process the biomass and the socio-economics of large scale seaweed farms. As many of the factors in the first of these two categories will influence the last one, the emphasis in this report is on the research needs behind obtaining the biomass and optimising the methane output.

1. INTRODUCTION

Energy consumption throughout the world and particularly in the industrialised societies has been steadily increasing. Much of the energy consumed, 97% in the case of the UK (2003 figure; Royal Commission on Environmental Pollution (RCEP) 2004a), comes from non-renewable resources. The present rate of use of carbon-based non-renewable energy is unsustainable, not least because of the impact of the resultant carbon dioxide emissions on the global climate. Reduction in demand as well as alternative energy sources are part of the solution. The UK government has set a target of reducing domestic carbon dioxide emissions by 60% by 2050. This target figure is based on the contention that the maximum carbon dioxide concentration should not exceed twice the pre-industrial level. The production of crops for bioethanol or biodiesel in Scotland is unlikely to ever be competitive because of the wetter, cooler climate. The RCEP (2004a) however conclude that biomass, energy crops for thermal conversion, should play an important role in the UK's renewable energy generation. The carbon in biomass used as fuel, providing the biomass is re-established, does not contribute to net greenhouse gas emissions. Unlike most other renewable energy sources biomass can be stored and used on demand to give controllable energy, and is therefore free from the problem of intermittency, a particular problem for wind power. Also unlike most other sources of renewable energy, biomass offers a source of heat as well as electricity, in fact the RCEP (2004a), consider biomass solely as a source of heat and electricity.

The growth of terrestrial crops for biomass requires the use land and water and can have implications for both biodiversity and landscape. In the UK, the production of biomass will ultimately be restricted by the amount of agricultural land that can be turned over to this purpose. The RCEP report considers that there are only three types of indigenous biomass, forestry materials, energy crops e.g. willow and miscanthus, and agricultural residues such straw from cereal production and poultry litter. The most advanced energy crop for northern European conditions is short rotation coppice or SRC of Willow (*Salix* spp.). The coppice is established by planting 10-15,000 stems

ha⁻¹, it is pruned in the first year, and the first crop is harvested three to five years after planting. Willow and poplar perform best in wetter areas and miscanthus yields are higher in warm areas less prone to frost, so there are definable limits as to the amount of land that potentially suited to each type of crop. However, in the current document we review the potential of another type of biomass, marine biomass, which has the additional benefit that it can be used to generate transport fuels.

Although biomass-for-fuel technologies are only efficient where the demand for energy and the source of fuel are within economically viable distances of each other, biomass is successfully used as a source of energy across Europe, but has not become established in the UK. The reasons for this appear to be institutional rather than technological and there is no reason why the UK could not follow the route of Sweden, Denmark, Austria and New Zealand in increasing the dependence on biomass (RCEP, 2004a).

1.1 Scotland's energy needs

In 2002, Scotland consumed the equivalent of 175TWh of delivered energy (supplied by nuclear energy (34%), coal and oil (33%), gas (20%) and renewables (13%), and in the process emitted 12 million t of carbon. Of the 175TWh consumed 53% was used for heating, 27% for transport and 15% as electricity (Scottish Renewables, 2007). Scotland consumes more energy per head of population than the UK average. Scotland has 8.5% of the population but consumes 9.1% of the energy. This statistic reflects the greater need for heating in Scotland (Scottish Renewables, 2007).

Both the UK Government and the Scottish Government have signed relevant international protocols or directives, or have set unilateral targets for renewable electricity, biofuels for transport, combined heat and power systems (CHP), and reduction of carbon and greenhouse gas emissions. The most prominent targets are those that relate to carbon emissions. The Kyoto protocol commits the UK to cutting greenhouse gas emissions by 12.5% between 2008 and 2012. The UK Government has gone further and targeted

20% cuts by 2010. A recent report (Scottish Renewables, 2007) indicates that the former 12.5% target is likely to be met but that the UK is unlikely to hit the 20% target on time. The Scottish Government has estimated that Scotland has sufficient renewable energy resources to provide up to 75% of the UK's electricity needs. Today Scotland's renewable electricity sector is meeting around 16% of Scotland's electricity needs, primarily through hydro and wind power. However, it should be noted this figure is over optimistic in comparison with Scottish Renewables' statistics of the total present renewable energy generation capacity in Scotland, including heat as 2.6 TW (Table 1.1).

The Renewable Transport Fuel Obligation (RTFO) programme, from April 2008, placed an obligation on fuel suppliers to ensure that a certain percentage of their aggregate sales are made up of biofuels. The effect of this is to require 5% of all UK fuel sold on UK forecourts to come from a renewable source by 2010. This will help Scotland meet its climate change objectives as well as contributing to other Government objectives, including security of energy supply. The RTFO is modeled on the existing Renewables Obligation in the UK electricity supply industry. The transport sector is responsible for 25% of carbon emissions and through this initiative the RTFO expects to reduce the carbon emissions from road transport in 2010 by about 1 million t, equivalent to taking 1 million cars off the road. The 5% by volume target represents the maximum biofuel content allowed by European Specifications to be sold on the forecourts as standard petrol or diesel (Department of Transport, 2007).

Table 1.1 Renewable Energy Generation Capacity in Scotland (MW) 6th July, 2007: <http://www.scottishrenewables.com>

Hydro	Wind	Energy from waste	Biomass Electricity	Biomass Heat	Wave	Tidal	TOTAL
1357.57	1120.02	97.58	37.62	5	0.8	0	2618.59

The Department for Transport's web-site notes there are two main types of biofuel - biodiesel and bioethanol and describes biogas as a relatively 'niche

product'. So while the means for obtaining renewable electricity supplies is relatively well mapped out, the route to achieving renewable transport fuels is much less well defined.

1.1.1 Biofuel options:

Biodiesel: is generally produced from 'oily' crops like rapeseed, sunflower, oil palm etc, or recovered from used cooking oil. Because these oils are more viscous than fossil diesel, they require processing (transesterification) to make them usable. Biodiesel in the UK comes from a small domestic cottage industry that for the large part converts used cooking oil, or is imported, for example from Germany. Recently, a number of new plants have been established (e.g. the Argent plant in Motherwell, which is producing 50 million litres a year). It is currently available as a blend with fossil diesel at about 100 filling stations in the UK, including a number of Tesco stores in SE England (Department of Transport, 2007).

Bioethanol: Ethanol or ethyl alcohol (C_2H_5OH) is the principal fuel used as a petrol substitute for road transport vehicles. It is mainly produced by fermentation of sugars, although it can also be manufactured by the chemical process of reacting ethylene with steam and there is currently intense interest in converting cellulose to ethanol more efficiently. The main sources of sugar required to produce ethanol come from fuel or energy crops. These crops are grown specifically for energy use and include sugar cane, corn, maize and wheat. Increasingly other sources of carbohydrate are being used or investigated such as waste straw, willow and poplar trees, sawdust, reed canary grass, cord grasses, jerusalem artichoke, miscanthus and sorghum. There is also ongoing research and development into the use of municipal solid wastes to produce ethanol fuel (Energy Systems Research Unit, University of Strathclyde, 2007).

Ethanol fuel blends are widely sold in the United States. The most common blend is 10% ethanol and 90% petrol (E10). Vehicle engines require no modifications to run on E10 and vehicle warranties are unaffected by its use.

It can be used at higher blends (most Brazilian petrol is 23% ethanol), but not without some (relatively cheap) vehicle modifications. Ford and others are already producing 'E85 flexi-fuel vehicles' which can run on any petrol containing anywhere from 0 – 85% ethanol. It is more expensive to produce than petrol, especially from crops like wheat, but countries like Brazil can produce it very efficiently from sugar cane (prices as low as 7p per litre before import tariffs, which are currently around 20p per litre). As a consequence it is produced in huge volumes by Brazil and the US. Roughly three per cent of all US gasoline sales were bioethanol in 2005. Bioethanol is not produced at all in the UK although some companies, including British Sugar, have announced plans to do so. In March 2006, bioethanol sales amounted to some 8 million litres (about 0.4 per cent of total UK petrol sales) (Department of Transport, 2007).

Biogas: the methane element of biogas can be used as a transport fuel. It is suitable for use in vehicles designed to run on compressed natural gas (CNG) (of which there are only approximately 500 in the UK) (Department of Transport, 2007). However when considering the economics of the generation of biogas for transport fuel, one must also allow for the relevant inefficiencies of the internal combustion energy (20-38%, the rest being lost as heat, exhaust gas and friction) as opposed to, for example a CHP engine which can offer 85% efficiency.

1.2 General introduction to Anaerobic Digestion and the production of biogas.

Section 1.2 provides a basic insight into the process of anaerobic digestion, the main substrates and reactor types available and gives an overview of the current uses of biogas. It has purposely largely been confined to discussion of on-farm digesters and does not attempt to review the large body of information of the treatment of sewage sludge or the contribution of industrial or landfill digestion to renewable energy. For general descriptions of processes and definitions it draws principally from the sources Monnet F.

(2003), Friends of the Earth (2004), Lusk (1998) and Gracia (2005) which have recently reviewed the subject.

Anaerobic digestion (AD) is a biological process which occurs naturally in environments with little or no oxygen. The microorganisms which favour these environments degrade organic matter and produce biogas, primarily methane and carbon dioxide. However the term anaerobic digestion is also used to refer to the harnessed and contained process of anaerobic decomposition in an anaerobic digester, an industrial system of treating waste or a specially produced substrate to produce biogas that can then be used to power electricity generators, provide heat and produce soil improving material (Wikipedia, accessed 18.03.07). The unique ability of AD to provide both a treatment for organic wastes and a source of renewal energy is acknowledged in the DEFRA Waste Strategy document (DEFRA, 2007). The potential re-classification, in England, of digestate as a 'product' and not a 'waste' would remove another barrier to the uptake of this technology (McKendry, 2007).

Anecdotal evidence indicates that biogas was used for heating bath water in Assyria during the 10th century BC and in Persia during the 16th century. In 1808, Sir Humphry Davy determined that methane was present in the gases produced during the AD of cattle manure. The first digestion plant was built at a leper colony in Bombay, India in 1859. AD reached England in 1895 when biogas was recovered from a 'carefully designed' sewage treatment facility and used to fuel street lamps in Exeter (Lusk, 1998). However it has been the developing countries such as China and India, rather than Europe, that have truly embraced the AD technology in small scale energy and sanitation plants. It is estimated that in China there are between four and six million family-sized, low technology digesters used to provide gas for cooking, lighting and to sanitise manure (Garcia, 2005). However, in recent times, European countries have come under pressure to re-examine their AD options mainly because of increasing energy prices and more stringent environmental regulations.

Anaerobic digesters are commonly used for sewage treatment or for managing animal waste but almost any organic material can be processed in this manner, including waste paper, grass clippings, leftover food, sewage and animal waste. In the UK it is the process of choice for treating sewage sludges and an increasing percentage of the UK landfill sites recover anaerobically produced biogas for power generation. Anaerobic digesters can also be fed with specially grown energy crops to boost biodegradable content and hence increase biogas production. The material to be processed is often shredded, minced, or hydrocrushed to increase the surface area available to microbes in the digesters and hence increase the speed of digestion. The material is then fed into an air tight digester where the anaerobic treatment takes place. Anaerobic digestion has two key advantages compared to competitive renewable energies. These are that it can utilise waste (and therefore heterogeneous biomass) as a feedstock and secondly the process is completely unobtrusive, unless there are accidental gas emissions which are malodorous. The major disadvantage of anaerobic digestion, in common with other bio and fossil fuels, is the transport of feedstock and disposal of residuals after processing. Anaerobic digestion of solid biomass feedstocks will leave at least twice the amount of residue compared to the ash resulting from its combustion.

Biogas produced in anaerobic digesters consists of methane (50%–80%), carbon dioxide (20%–50%), and trace levels of other gases such as hydrogen, carbon monoxide, nitrogen, oxygen, and hydrogen sulphide. The relative percentage of these gases in biogas depends on the feed material and management of the process (Energy Efficiency and Renewable Energy, 2005)

The other product of AD is the digestate, also referred to as the sludge or effluent. It can be rich in nutrients (ammonia, phosphorus, potassium, and more than a dozen trace elements) and, depending on the substrate digested, an excellent soil conditioner. However any toxic compounds (pesticides, etc.) that are in the digester feedstock material may become concentrated in the effluent. Beneficial use of the residual is not always easy to achieve if sewage

or municipal wastes are involved. There are regional regulatory differences in Europe and also different attitudes from the sections of the food industry about the use of treated sewage sludge in agriculture in the UK. Where AD is used for waste management it is unlikely to be viable unless there is a use for both the biogas and the digestate (Monnet, 2003).

Biogas can be burned to produce electricity, usually with a reciprocating engine or microturbine. The gas is often used in a cogeneration arrangement, to generate electricity and use waste heat to warm the digesters or to heat buildings. Excess electricity can be sold to electricity suppliers. Electricity produced by anaerobic digesters is considered to be green energy and attracts a subsidy under the Renewables Obligation Certificate scheme. Biogas can also be used as a transport fuel and there are good examples in some European cities where public transport is being fuelled by biogas. Sweden has the world's first biogas powered train running on a 75 mile long coastal stretch between the cities of Linköping (south of Stockholm) and Västerås (Eastern Baltic). In Linköping another plant uses waste products from a local abattoir to produce biogas which fuels the city's bus fleet (Renewable Energy UK, 2007). An estimated 600 buses and 10,000 light and heavy vehicles are powered by biogas in Sweden (SUGRE, 2005)

Since the gas is not released directly into the atmosphere and the carbon dioxide comes from an organic source with a short carbon cycle, biogas does not contribute to increasing atmospheric carbon dioxide concentrations; because of this, it is considered to be an environmentally friendly energy source. From a single batch reaction the production of biogas is not a steady stream; it is highest during the middle of the reaction. In the early stages of the reaction, little gas is produced because the number of bacteria is still small. Toward the end of the reaction, only the hardest to digest materials remain, again leading to a decrease in the amount of biogas produced,

1.2.1 The biological process

Anaerobic microorganisms digest organic materials, in the absence of oxygen, to primarily produce methane and carbon dioxide. The process is best understood if considered in four main stages:

Hydrolysis where fermentative bacteria convert insoluble complex organic matter such as cellulose into soluble simple sugars, amino acids, and fatty acids with the addition of hydroxyl groups. Complex polymeric matter is hydrolysed to monomers.

Acidogenesis where acid forming bacteria further breakdown the products from the first stage to simpler molecules, i.e., volatile fatty acids (e.g., acetic, propionic, butyric, valeric) occurs, producing ammonia, carbon dioxide and hydrogen sulphide as byproducts.

Acetogenesis where the simple molecules from acidogenesis are further digested to produce carbon dioxide, hydrogen and mainly acetic acid.

Methanogenesis where methane is finally produced by methane forming bacteria in two ways: by cleavage of two acetic acid molecules to produce carbon dioxide and methane, or by reduction of carbon dioxide with hydrogen. The acetate reaction is the primary pathway because of the limited amount of hydrogen available.

It is important to note that some organic materials, such as lignin, remain effectively undigested, as of course does any non-organic material within the waste.

1.2.2 Stages of anaerobic digestion

There are two conventional operational temperature levels:

Mesophilic which takes place optimally around 37°- 41°C or at ambient temperatures between 20°- 45°C with mesophile bacteria

Thermophilic which takes place optimally around 50°-52° at elevated temperatures up to 70°C with thermophile bacteria.

In the thermophilic range, decomposition and biogas production occur more rapidly than in the mesophilic range. However, the process is highly sensitive to disturbances, such as changes in feed materials or temperature. While all anaerobic digesters reduce the viability of weed seeds and disease-producing (pathogenic) organisms, the higher temperatures of thermophilic digestion result in more complete destruction. Although digesters operated in the mesophilic range must be larger to accommodate a longer period of decomposition within the tank, the process is less sensitive to upset or change in operating regimen.

To optimize the digestion process, the biodigester must be kept at a consistent temperature, as rapid changes disrupt the bacterial activity. Some installations circulate the coolant from their biogas-powered engines in or around the digester to keep it warm, while others burn part of the biogas to heat the digester.

Other factors affect the rate and amount of biogas output. These include pH, water/solids ratio, carbon/nitrogen ratio, mixing of the digesting material, the particle size of the material being digested, and retention time. Pre-sizing and mixing of the feed material for a uniform consistency allows the bacteria to work more quickly. The pH is self-regulating in most cases. Bicarbonate of soda can be added to maintain a consistent pH; for example, when too much "green" or material high in nitrogen content is added. It may be necessary to add water to the feed material if it is too dry or if the nitrogen content is very high. A carbon:nitrogen ratio of 20/1 to 30/1 is best. Mixing or agitation of the digesting material can aid the digestion process. Antibiotics in livestock feed have been known to kill the anaerobic bacteria in digesters. Complete digestion of feedstock, and retention times, depend on all of the above factors.

The residence time in a digester varies with the amount of feed material, type of material and the temperature. In the case of mesophilic digestion, residence time may be between 15 and 30 days. Although the thermophilic phase the process can be faster, requiring only about two weeks to complete, it is more expensive, requires more energy and is less stable than the mesophilic process. Therefore, the mesophilic process is still widely in use. Many continuous digesters have mechanical or hydraulic devices to mix the contents and to allow excess material to be continuously extracted to maintain a reasonably constant volume.

1.2.3 By-products of anaerobic digestion

The principal by-products of anaerobic digestion are the biogas and the digestate. The biogas is comprised mostly of methane and carbon dioxide and small amounts of hydrogen sulphide. The digestate is a sludge-liquor mixture. Depending on the substrate digested, the sludge (acidogenic digestate) can be a stable organic material. Where woody or fibrous substrates have been digested it will be comprised largely of lignin and chitin, with a variety of mineral components, which can be used as compost or to make low grade building products such as fibreboard. The liquid (methanogenic digestate) is rich in nutrients and can be an excellent fertilizer, again, dependent on the quality of the material being digested.

If the digested materials include low levels of toxic heavy metals or synthetic organic materials such as pesticides, the effect of digestion is to significantly concentrate such materials in the digester liquor. In such cases further treatment will be required in order to dispose of this liquid properly. In extreme cases, the disposal costs and the environmental risks posed by such materials can offset any environmental gains provided by the use of biogas. This is a significant risk when treating sewage from industrialised catchments. The sludge liquor mixture has to be separated by one of a variety of ways, the most common of which is filtration. Excess water is also sometimes treated in sequencing batch reactors for discharge into sewers or for irrigation. Digestion can be either wet or dry. Dry digestion refers to mixtures which have a solid

content of 30% or greater, whereas wet digestion refers to mixtures of 15% or less.

1.2.4 Reactor types

The two main types of operations are batch and continuous. Batch is the simplest, with the biomass added to the reactor at the beginning and sealed for the duration of the process. Batch reactors can suffer from odour issues which can be a severe problem during emptying cycles. In the continuous process, which is the more common type, organic matter is constantly added to the reactor and the end products are constantly removed, resulting in a much more constant production of biogas. In continuously stirred tank reactors (CSTR) the content is continually charged and discharged and homogeneously mixed at all times. An agitator can be used to mix the contents, the power required for mixing varies according to the size and shape of the digester. Alternatively, in more innovative designs, mixing is performed by returning some of the biogas produced to the base of the reactor, so the bubbling gas causes the mixing (L. Lewis, Greenfinch Ltd., pers comm.), thereby eliminating the need for moving parts inside the digester. There are several benefits to mixing: inoculation of fresh substrate with digestate, maintaining contact between bacteria and the feedstock, even distribution of heat, avoiding scum and sediment formation, release of biogas bubbles trapped in the substrate.

For some feedstocks conventional reactor designs are being replaced by more innovative designs influenced primarily by the suspended solids content of the feed. The objectives are to increase the retention time of the solids and the microorganisms, to decrease reactor size and reduce energy requirements. For dilute low solid wastes (<1 %) attached-film reactors are used where the attachment of the microorganisms to an inert media permits low retention times without 'wash-out'. For feedstocks with intermediate solid contents (5 – 10 %), solids and organisms are recycled following settling in the digester or are digested in a separate secondary digester. For high solid content feedstocks (> 10%) high-solids stirred digesters or leach-bed systems

are being used (Chynoweth et al., 2001). The hydraulic retention time (HRT), the length of time the microorganisms have to digest the substrate inside the digester, depends on the nature of the substrate. Both output substances, the biogas and the digested material require a special storage tank. The gas tank is most usually connected to a gas or diesel gas engine where electricity and heat are produced.

1.2.5 Considerations - from Wikipedia (2007)

Endproducts: To be economically viable, there must be a market for the end products. Biogas can be sold or used in almost all parts of the world, where it will offset demand for fossil fuel stocks. The digester liquor is suitable for use as a fertilizer, although frequently supplemental nutrients need to be added. The sludge component, even when dried and available as a soil conditioner, is less easily disposed of. If not suitable for agriculture, it can have non-agricultural uses, such as on golf courses and as cover for landfills. In some localities, the sludge itself is used as a fuel in heating systems, and the residual ash is disposed of in a landfill.

Inhibition of methanogenesis & production of alcohols: Anaerobic digestion can be inhibited from reaching the methanogenic stage. The organic acids (i.e. carboxylic acids) from the acidogenic and acetogenic stages of the digestion can be recovered. The acids can then undergo further chemical transformations into useful chemicals or fuels.

Potential in the Hydrogen Economy: as anaerobic digestion is a renewable source of methane it offers the potential to contribute to the hydrogen economy: steam methane reforming (SMR) is the most common method of producing commercial bulk hydrogen. It is also the least expensive method. At high temperatures (700 – 1100 °C) and in the presence of a metal-based catalyst, steam reacts with methane to yield carbon monoxide and hydrogen. $[\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2]$. The US produces nine million t of hydrogen per year, mostly with steam reforming of natural gas. This process is different

from catalytic reforming, an oil refinery process that also produces significant amounts of hydrogen along with high octane rating gasoline.

1.3 Practical uses of AD in Europe: on-farm biodigesters

The development of solid waste biogas plants was stepped up during the second World War and by the end of the 1950's there were 48 large scale plants in operation in Germany and half of the gas production was used to fuel cars. Since then, with the increasing intensification of agricultural methods, the over-application of manure to the land has come to be seen as the major source of nitrates and phosphates leaching to groundwater and contaminating surface waters. Increasing awareness of pollution problems together with the inadequate management of animal manure and organic waste have been important drivers in creating environmental regulations that force the consideration of methods to reduce the impact of these products. In fact Garcia (2005) states that the most important reason for using AD is to reduce the environmental impact of organic waste.

In the mid-eighties the first biogas plants for the digestion of animal manure were built in Germany. Denmark and East Germany focused on large centralised biogas plants, whereas in West Germany mainly farm-scale biogas plants were constructed. German biogas engineers now have almost 20 years experience in the construction of biogas plants. Fischer et al, (2001) estimated at the end of 2001 there were 1,600 biogas plants in operation on farms, primarily due to investment funding and payment for each kWh delivered to the public energy grid. In Germany, over 2,500 on-farm digesters are currently in operation (Agri-Food and Biosciences Institute, 2007), compared with approximately 30 within the UK. A study in Northern Ireland in 1991 concluded that given oil prices and the capital costs for digesters, on-farm AD in Northern Ireland was not a viable economic proposition. But as current oil prices are considerably greater than those in 1991, on-farm AD may now be financially viable. In Germany, for example, the current economics of on-farm AD are favourable. This is as a result of the Renewable Energy Sources Act (EEG) 2000 and 2004 that guarantees (for 20 years) a

premium price for electricity generated from solar energy, hydropower, wind power, geothermal power and biomass. Furthermore, in Germany more than 90% of the digesters use energy crops as co-substrates to increase the gas yield (Bohn, et al., 2007).

Typical agriculturally based centralised AD (CAD) plants, such as those in Denmark, use farm products (livestock manures and crops) as the main feedstocks, as well as other organic material from, for example, food processing. Co-digestion can provide an additional source of income through gate fees and can improve the yield of biogas per unit of feedstock input. CAD plants can be thermophilic or mesophilic. Compared to typical on-farm plants, CAD plants are larger (0.1-1.0 MW_e), give economies of scale and offer better market opportunities for heat (for local industry and/or district heating) and fibre production. CAD schemes can involve a number of farms within a radius of about 10 km from the plant. All agriculturally based CAD schemes distribute digestate back to agricultural land, normally that of the supplying farms. The digestate is rich in plant nutrients (nitrogen, phosphorus and potassium) but must be applied to agricultural land in accordance with the crop requirements for plant nutrients. Nutrient management is a major issue for consideration when determining the feasibility of any AD scheme and CAD has major potential to assist in managing and redistributing plant nutrients in slurry. When redistributing digestate to farms it is very important to ensure biosecurity therefore all CAD schemes should include sterilisation of material prior to redistribution (Agri-Food and Biosciences Institute, 2007).

1.4 Fermentation processes, the production of bioethanol

Many types of biomass have been investigated as possible sources for bio-ethanol production. However, to date these have largely been of terrestrial origin and therefore have the disadvantages that if they come from agricultural land they will compete directly with areas of land that could otherwise be used to grow food. Another disadvantage is that they often contain large quantities of refractory materials (i.e. lignin and cellulose) that are not often amenable to fermentation or can lead to the formation of toxic by-products (e.g.

acetylated compounds, phenolics and furans) during pre-treatment processes. These by-products have been shown to cause significant detrimental effects on fermentation processes, ultimately limiting bio-ethanol rates and yields.

Macroalgae, however, offer an alternative source of biomass for producing bio-ethanol. Its cultivation and harvest from the sea would not impact on terrestrial agricultural activities, and importantly seaweeds do not contain any lignin and only low levels of cellulose. Their high level (25-30%) of easily degradable carbohydrates makes them a potential source for bio-ethanol production. Much of the work concerning the bioconversion of seaweeds has focused the production of methane (section 3) but recently, a Norwegian research group (Horn et al., 2000a, b) has shown the possibility of converting seaweed biomass into ethanol using selected microorganisms. Although the ethanol yields were relatively low compared to more established fermentation processes, this can be attributed to the relative infancy of the technology concerned in producing bio-ethanol from this completely new source material.

2. MARINE BIOMASS AS FEEDSTOCK FOR METHANE PRODUCTION

The term 'kelp' was first used in Scotland as a name for seaweed ash, and then became used as a name for the large brown algae generally. Today the term applies generally to any large, upright brown alga that forms dense forests in temperate regions. The general morphology of kelps (and most macroalgae) consists of the holdfast that is used to anchor the plant to the substratum and unlike roots of terrestrial plants does not play a large role in resource acquisition, the stipe that acts a "stem" or the "trunk" of the plant and the thallus which is the large flattened blade where most of the light and nutrients are harvested. The taxa to which kelps belong differ with geographical area; in the North Atlantic for example, kelps are mostly from the genus *Laminaria*, however in Pacific temperate waters the kelps are very often from the genus *Macrocystis*. *Macrocystis pyrifera* found on the North American Pacific coast is a perennial alga which can reach more than 30m in length and was the subject of the US harvesting and farming activities described below.

2.1 The history of kelp harvesting - from Neushal (1987)

For centuries European farmers made extensive use of seaweeds applied to crops as fertiliser. During the 17th and 18th centuries, as their forests dwindled, many European countries were forced to import the large quantities of soda and potash they required for making glass and glazing pottery, and for soap, alum and saltpetre respectively. France was the first country to use its kelp for soda, processing the seaweeds that grew in abundance along the coasts of Brittany. The industry spread to Scotland, the Orkney Islands and Norway. Historically Scotland's kelp industry flourished as a result of wars abroad, for example, when the American War of Independence limited Britain's supply of wood ash. Kelp continued to be a source of potash until 1814 when foreign imports and new technologies caused a decline in the industry. In 1841 the industry revived briefly when seaweeds were processed for their iodine content, but this again declined after the discovery of saltpeter mines in Chile; iodine being a by-product of the gunpowder manufacture.

It was the start of World War I that once again caused a revival in the kelp processing industry as at that time Germany was the world's largest manufacturer of chemicals and had a monopoly of mining potash. At the time US agriculture was heavily dependent on German imports of potash as fertiliser for crops such as corn, cotton, potatoes, beets and tobacco, as well as for glass, gunpowder, soap, matches and dyes. In fact it was feared an embargo on German imports of potash would affect the nation's agricultural productivity. In 1902, kelp had been identified as a source of potash and by 1911 many small companies were trying to make a profit from processing the seaweeds of California's giant kelp beds. With the outbreak of World War I the price of German potash doubled and US invested heavily in the struggling kelp industry and large companies such as the Hercules Powder Company and Swift & Co's. Kelps Works were founded on the Californian coast.

Mechanical methods of kelp cutting were developed to meet the demand; Swift & Co. built the largest harvester operated during World War I, the Alice

L, which was 45 m long and could carry 454 t of kelp. The cutting knives were 7 m wide and 2-3 m below the water surface. Kelp was an ideal source of materials for explosives, the potash being an ingredient of gun powder and the acetone, another kelp derivative, a key component of cordite, a smokeless powder used extensively by the British. By 1916, Hercules, which had developed a method for extracting the much sought after acetone from kelp, was running a plant occupying a 12 ha plot, operating 24 hours a day and employing 800 men in the harvesting and processing operations. Three giant harvesters, nine barges, four tow boats and a floating workshop conveyed 908 t of seaweed harvested daily to the plant. Although the company had the capability to produce a total of 54 chemicals from the kelp, their primary reliance on war materials led to their closure in 1919.

In 1881 E. C. Stanford, a Scottish chemist, discovered algin when experimenting with new methods for extracting potash and iodine from kelp in Scotland. The first successful commercial production of alginates began in San Diego in 1927. The company, which formerly made kelp meal for inclusion in livestock diets, was bought by Arnold Fitger in 1929, when he changed the name to Kelco. Fitger recognised the potential for algin as an ice cream stabiliser and by 1935 the firm was manufacturing alginates for this purpose. Kelco initially used harvesters similar in design to Swift & Co with a 3 m cutting bar and the cut kelp being automatically hoisted aboard by an inclined conveyor. During the 1950's the cutting mechanism was moved astern, allowing the vessels to retain a wedge-shaped bow and greater seaworthiness; their three vessels each harvested 272 metric t of kelp per load.

By 1939, and the start of World War II, demand for alginates rose as gelatine, also used as a food stabiliser, became in short supply as it was used to manufacture film needed by the armed forces. Kelco grew rapidly and as did the new technologies for using alginates in screen printing dyes to textiles, in treating paper to control ink penetration, in the manufacture of waxed paper and cardboard cartons and to stabilise latex. In 1950 staff at Kelco developed a modified alginate they called Kelcosol which became widely used in

desserts, beer, salad dressings and a multitude of other food products. In 1972 the now multi-million dollar company was purchased by the Merck Corporation. Whereas Kelco had proven to be technically proficient in developing new uses for alginates, they had paid less attention to the source of their raw material. The Californian kelp beds, which had once seemed inexhaustible, had been in decline since the turn of the century, and little attention had been paid to the actual cultivation of Californian kelp as a permanent solution to the shortage problem. In contrast, in the People's Republic of China, thousands of acres of seaweed farms were being developed, and Kelco became faced with the prospect of competition from Chinese alginate producers.

2.2 Energy from marine biomass in the US: an historical perspective

In 1968 Howard Wilcox, then a physicist and consultant to President Johnson's Commission on Ocean Resources proposed development of open ocean macroalgal farms as sources of food, animal feeds, fertilisers and energy. Research began in 1973, led by the Californian Institute of Technology and funded by the US Navy; ten years of research activity followed. An oceanic farm was defined as a structure held in locations where the water depth was too great for kelp to occur naturally and where the physical and chemical conditions approximated oceanic environments. In a review of the research North (1987) lists the criteria for seaweed species suitability for biomass production as that it should:

- Display high productivity
- Tolerate long exposure to full sunlight
- Be coppiceable
- Be easily harvested by mechanical means
- Be amenable to culture, transplanting and reproduce prolifically in the farm environment
- Be structurally able to withstand water motion in high energy environments
- Have a chemical composition with good potential for conversion to fuel

- Have increased nutrient translocation ability to enhance productivity and permit culture at high biomass densities
- Be a long-lived perennial to avoid the need for frequent replacement
- It was also thought the farmed species should attract and support a community of useful organisms so the farm could also be used to provide food as well as fuel.

Certain characteristics were recognised that would favour the seaweeds' ability to prosper in the oceanic environment, where nutrient levels might be limiting. For example, large surface-to-area ratios would facilitate nutrient uptake. The selected plant should be able to maintain a high productive capacity even when tissue concentrations of growth limiting nutrients are low. It should have simple nutrient requirements and exhibit luxury uptake, storing reserves when external nutrients are high and utilising these when external concentrations are low. The species should be amenable to mooring or restraining devices.

Macrocystis ranked favourably with respect to many of the above criteria and a series of experiments followed, attempting to measure its growth and performance when attached to a variety of man-made structures. The first structure, deployed in 1973 was offshore of San Clemente Island, California, occupied an area of 3 ha and was made up of polypropylene ropes spaced a 3 m intervals forming a grid. It was moored 10 m below the surface in a depth of 125 m. *Macrocystis* plants were attached by a knitting-needle like rod to pull a cord through the base of the plant and around the grid lines. The farm did not survive its first winter however as a corner anchor line broke loose. The grid floated to the surface and was thought to have been destroyed by passing shipping. Despite this early engineering failure, because of the potential for generating biomass for biofuel, Wilcox was able to secure a further 2 billion \$US funding from the then American Gas Association to continue the research. In a three phase programme Wilcox envisaged a marine farm covering 40,000 ha of open ocean producing valuable foods, liquid and gaseous fuels, lubricants, waxes, plastics, pharmaceuticals, and

fertilisers as its principal products. A further two attempts with grid-style farms followed, the first being much smaller at 35 m a side, was moored in 47 m of water, but was lost when a float failed causing the farm to sink. A second farm was installed in 1975 was destroyed by a storm, but in each case a limited amount of information was gathered on plant growth and performance before the farms were lost. Important lessons had been learnt regarding the necessity to avoid contact between kelp plants and the solid components of the farms, a difficult proposition given the differential buoyancy of the plants and the structures to which they were attached. Rapid vertical movements of offshore structures can occur at exposed sites, causing the underlying farm to 'overtake' the buoyant plants which subsequently become wrapped around the underlying cables. Similarly contact with any part of the hard substrate, particularly once it had been colonised by sharp edged encrusting organisms, caused chaffing and loss of biomass.

Subsequent farm designs included an upwelling system, bringing water from a depth of 350 m and rich in nutrients to plants held in a cone shaped structure and later a modular structure, the quarter acre module. This consisted of a single buoy with radiating spars, anchored by three 6.8 t anchors. The buoy contained a diesel pump to bring up nutrient rich water and contained an electrical system to power navigation lights. The substrate support bars were poles of stainless steel. Unfortunately, the pitching of the quarter acre module in storm waves did not match the floatation responses of the lax kelp fronds which wrapped themselves around the spars and support lines. A further design called the hemisphere attempted to culture plants in an enclosed structure supported by a floating tubular steel ring, and supplied with upwelling nutrient rich water; in this case the confined environment proved ideal for bacterial growth which destroyed all the kelp plants.

It was in 1981 that a subsequent near shore grid farm at Goleta, California, funded by General Electric finally survived long enough to allow the required growth data to be collected. The farm consisted of two 0.2 ha plots on which 700 plants were attached to grids of rope and chain anchored by concrete blocks. The plants were arranged in three different densities, the experimental

plot was fertilised with nutrient enriched seawater sprayed from a small boat while a control plot remained unsprayed. Yield data was obtained by hand-harvesting plants every three months and weighing the biomass produced. The results from these short term experiments indicated that growth rates on large scale oceanic farms could be at least equivalent to that on coastal kelp beds. Growth rates of adult transplants ranged from 5.4 – 7.2 % per day, within the normal range for *Macrocystis* in coastal waters.

In summary, providing nutrients were provided by upwelling water in nutrient-deficient offshore sites, the biggest challenges the ocean farming programme encountered were those of designing equipment capable of withstanding the extreme weather conditions of the offshore sites. Small plants were observed in varying abundance on three of the farm structures suggesting continued growth was possible; there was a clear relationship between favourable nutrient conditions and the appearance of small plants on structural components of the farm. Artificial upwelling of deep water appeared to be a suitable method of supplying nutrients to the kelp plants.

2.3 Seaweed culture in the far-east: history to present day scale

The use of seaweeds for medicines and foods dates back at least 1,500 years and over 100 species are used for food, in medicine, or as fertiliser and in the processing of phycocolloids and chemicals (Tseng, 1987). China is the world's largest producer of cultivated seaweed. *Laminaria japonica* known as haidai or 'sea-strap' is the most important species economically enjoying popularity as a food article and a drug; it is not native to China, having been introduced from Japan originally. It was the first seaweed to be subjected to the entire process of seeding, tending and planting out and to have the status of a marine plant crop (Tseng, 1987). Now its biomass production, per unit area in a large scale operation, is larger than any other seaweed.

In the 1940s, Japanese experts associated with Chinese experts began kelp farming experiments in Shandong Province. Large-scale kelp farming was not established until the early 1950s, when the three key problems that hindered it

before were resolved: 1) fertilizing the sea, greatly expanding the farming area; 2) breeding summer instead of autumn seedlings, prolonging the growth period; and 3) the southward introduction of commercial cultivation beyond its natural distribution on the China coast to Liaoning, Shandong, Jiangsu, Zhejiang, and Fujian provinces (FAO, 2007). In addition to the countries mentioned above, Russia is now producing *L. japonica* in its far eastern region. The culture methods of this seaweed are reviewed in detail by the FAO (2007) in their Cultured Aquatic Species Information Programme CASIP.

In the commercial cultivation of haidai in China there are two phases, the indoor cultivation of the sporelings and the field cultivation of the large sporophytes. In the summer the seeding process takes place in shallow tanks where the mature plants shed their spores. The swimming zoospores are allowed to settle on spore-collectors, which are frames carrying the seeding strings. The string can be made of natural or synthetic fibres. The adult kelp blades are removed once a given spore density has been achieved (approximately 10 spores per x 100 field of view under the microscope). The seeded strings are arranged in shallow tanks containing filtered seawater enriched with nitrogen, phosphate and iron and kept between 8-10°C in a specially cooled greenhouse. There is a partial exchange (20%) of the refrigerated seawater through the tanks every day. In modern practice the light intensity and temperature is carefully controlled by shading the greenhouse roof and the input of nitrogen, phosphate and iron has been precisely defined. The zoospores germinate to gametophytes and resultant zygotes germinate to sporelings in around 12 days (see section 4 for lifecycle details and terminology). In the autumn, when the sporelings are 1- 2cm high and the ambient seawater temperature has fallen below 20°C the strings are transferred to the field. The sporeling frames are hung from floating rafts until the plants are 10 -15cm (1 – 1.5 months) and then they are transplanted to the final growing position on lines of 8 mm diameter synthetic ropes. In North China the growth period is 6 -7 months for transplanted kelps to reach lengths of 3-6 m.

In Sangou Bay, in the Yellow Sea, the kelp harvest is from April to the end of July, as after this the water temperature is unfavourably warm the kelps start to degrade. During the harvest teams of workers, starting at first light, leave for the culture areas, which in Sangou Bay stretch for more than 10 km out to sea. A lead vessel pulls up to eleven barges, each barge is manned by two workers. In the bottom of the barge there is a loose net; 2-3 t of cultivated seaweeds are stripped from the culture lines and piled in each barge before the motorised vessel tows them to port where the harvest is lifted from the barge by the net using the cranes along the quay. The seaweed is transported by tractor to the processing units (Figs 2.2 a-d).

The development of the 'floating raft' cultivation method was considered key to the success of the industry, but now the most popular method in the Yellow Sea is to suspend the seaweeds between the buoyed up parallel long lines (Fig 2.2e), known as the horizontal raft method. The one-dragon method (a continuous culture string attached at intervals to the horizontal top rope) is used where the currents are stronger (H. Liu, YSFRI, pers. comm.). In the floating raft method the strings bearing the seaweeds are 70 – 140cm apart depending on the conditions and the total number of kelp plants in one hectare on a modern commercial farm averages 1,500,000 – 3,000,000. Formerly the seaweed cultures were fertilised in the field cultivation phase by means of porous clay bottles filled with ammonium sulphate hung at intervals from the rafts, the porosity of the earthenware effectively controlling the diffusion of the fertiliser. However later studies showed that *L. japonica* can absorb nutrients very quickly and then hold them in large quantities in the vacuoles of its cells and grow normally for several days without further fertilisation. So the labour intensive clay-bottle method was replaced by spraying a fertiliser solution from a boat at intervals (Tseng, 1987). Although, fertiliser is still provided during the first month after seedlings are put out to sea, this practice has ceased for on growing period now in favour of integrated aquaculture methods where fish, shellfish and seaweeds are cultured in the same water body and the nutrients excreted by the animals serves to fertilise the plants (H. Liu, YSFRI, pers.com.).

Production in the Yellow Sea region according to Tseng (1987) was 15 t dry ha⁻¹. More recently figures of 25 t dry (163 wet weight) ha⁻¹ have been reported (H. Liu pers.comm. citing China Fish Annals, 2003). However in an experiment with very dense planting and harvesting in separate lots in different periods a production as high as 60 t ha⁻¹ dry kelp has been reported, although production costs were high and the quality of the material produced was poor (Tseng, 1987).

In addition to these achievements, a programme of strain selection has been in operation since the 1960's and strains selected for the production of broader and longer fronds, higher iodine content and higher biomass have been produced. Selective breeding for fast growing and high-temperature tolerant haidai strains has also achieved significant progress in the last ten years. Currently gametophyte-cloning techniques are used in the selective breeding programme to conserve good strains (F. Wang, YSFRI, pers.comm.)

In his account Tseng (1987) also mentioned inverting culture ropes to even out productivity in the vertical-line cultivation methods, as seaweeds at the top grow better than at the bottom of the ropes, although this is no longer practiced as the culture ropes are slung between the horizontal long lines and are no longer vertical drops.

Tseng (1987) also mentions several diseases affecting the cultured *L. japonica* including white rot, caused by increased light intensity. Tip-cutting was formerly used to enhance productivity and reduce loss due to white rot disease. However, this method is not used today, primarily as it is labour intensive and therefore too costly. The method to control white rot now is to lower the long line to deeper waters at times of high light intensity in certain cultivation areas, and 'Alternation Harvesting' is practiced through April to May in order to reduce white rot loss. Tseng (1987) also reported the malformed sporeling disease caused by hydrogen sulphide producing bacteria, twisted frond disease caused by a mycoplasma and detaching disease caused by several types of bacteria. It was stated that measures have been found for their control (Tseng, 1987), but with no indication as to

what these might be. However, there is almost no report of these diseases now owing to the achievements of genetic breeding and improvements in cultivation methods (H. Liu, YSFRI, pers. comm.).

In his account Tseng (1987) also considered that haidai, in the future, may even serve as a source of energy. He commented that to lower the costs of production a series of problems had to be solved as the eventual rise in the standard of living in China would mean that labour costs would increase. He suggested increased mechanisation to lower labour costs, and highlighted that the intensive planting, required for energy production, may increase disease problems and that drying was another labour intensive part of the production process. Outdoor drying is still widely practiced nowadays, since the energy cost of this processing method is minimal, while more sophisticated processing methods are also deployed to produce high-valued haidai products, such as various shaped fast-food haidai, kombu, seaweed powder, seaweed tablets, other health foods and seaweed soaps etcetera.

Today in China nine species of seaweed are cultured including *Sargassum* and *Macrocystus*, the latter being cultured as food for abalone. Over 800,000 t of dry *L. japonica*, equivalent to approximately 8 million t wet weight were produced in 2005, making this the largest single species aquaculture crop in the world (Table 2.3), although it should be noted there is some discrepancy between these values and the figure of four million t quoted by FAO (2006) section 4.

Table 2.3 Main cultivated species in China (tonnage and area) 2003. (F. Wang, YSFRI, pers. comm.)

Seaweed	<i>Laminaria</i>	<i>Undaria</i>	<i>Porphyra</i>	<i>Gracilaria</i>	Total
Yield t (dry)	818,768	172,613	72,753	59,536	1,383,790
Area Ha	35,859	7,047	28,427	4,323	80,699
Seedlings	85 x 10 ⁹		2.8 x 10 ⁹		



Fig.2.2 . a) Seaweed cultivation area in Sangou Bay, where some 50,000t (dry weight) are produced annually b) seaweed harvesting barges c) the harvesting barge d) transport to processing e) the seaweeds are cultured suspended between the horizontal long lines.

2.4 Tank culture of seaweeds for biomass

In 1975 a research programme was initiated at Harbour Branch Oceanographic Institute, Florida, to assess the potential of macroalgae as a source of biomass for conversion to methane (Hanisak, 1987). Forty-two species of seaweeds were screened for their biomass production capability but most of this research was conducted on the red algae *Gracilaria tikvahiae*, more commonly cultured for its agar content. The growth of the algae in tumbling, aerated cultures was tested in a variety of tanks, troughs and pond designs. Yields from *G. tikvahiae* in the experimental tanks were among the highest for any plant, including terrestrial plants, but such yields were only obtained under exact experimental conditions and it was hard to reproduce these on a commercial scale. Also the experimental conditions were very energy intensive, requiring large amounts of flowing water and aeration which could not be employed at a commercial scale because of economic considerations. The intensive methods was however scaled up successfully to larger tanks (29 m² surface area and 24,000 l volume) and over a seven year period the mean annual productivity was 80-91 dry t ha⁻¹ yr⁻¹. Most of the research was conducted with one particular clone of *G. tikvahiae* 'ORCA', the clone reproduces itself vegetatively through fragmentation of the thalli and not sexually. Such sterile clones are useful in culture as they can be maintained for long periods without change to their genetic makeup.

Non-intensive cultivation methods were also attempted, in PVC-lined earthen ponds. To alleviate epiphyte problems a method of supplying nutrient in fortnightly pulses was developed. Unlike the epiphytes, *Gracilaria* can take up enough nutrients at once for two weeks of non-nutrient limited growth. Yields from the ponds were 18-29 dry t ha⁻¹ yr⁻¹. Other methods included spray-culture, where the seaweeds were held on trays and literally only sprayed with seawater, in-situ cage culture and rope culture.

The large amounts of sea water required for tank or enclosed *Gracilaria* culture are not related to a need for nutrients but to the fact that the cultures become carbon dioxide-limited under low flow rates. As with the nutrients, it

was determined that pulses of aeration (15 mins hr⁻¹ for 6 hours a day) were as beneficial as constant aeration and allowed significant energy saving. Aeration allows the redistribution of the seaweeds to maximise photosynthetic efficiency through absorbance of light and to minimise self-shading, it also increases nutrient uptake by reducing diffusion boundary layers and increases the availability of metabolic gases. Aeration systems can also be used to dislodge and flush out competing algal spores, thereby reducing the epiphyte problem.

Hanisak (1987) also highlights the difference between growth rates and yield in cultivation systems and the relationship of these factors with the density of the culture. For *G. tikvahiae* the specific growth rate is negatively correlated with density while the response of yield to density is a bell-shaped curve. This is most likely explained by the fact that at low densities the cultures are not light or nutrient limited, but as density increases yield begins to plateau as nutrients are utilised and ultimately density increases until the detrimental effects of self-shading mean that the net production is zero. Fortunately, it is easy to manage culture density and once the optimal density range is determined, any incremental growth above optimum should be harvested as frequently as possible. In *G. tikvahiae* cultures in Florida the practice was to stock cultures at 2 kg wet weight m⁻², to maintain this density the cultures were harvested every week in summer and every two weeks in winter.

G. tikvahiae has been successfully fermented to produce methane, with gas production and bioconversion efficiencies similar to that of other biomass substrates. Experiments were performed to determine the efficiency of recycling nutrients found, in both the liquid and solid residues of the digestion process, by adding various amounts to the *G. tikvahiae* cultures. Cultures grown in digester residue grew as well as those grown in inorganic fertiliser. Average nitrogen recycling efficiencies (the proportion removed as a percentage of the amount available) ranged from 62-83%. Levels of assimilation were dependent on the ammonium content of the residues. Ammonium comprises 40-70% of the total nitrogen content of the residues.

The percentage ammonium is a function of the residence time in the digester (Hanisak, 1987).

During the initial screening of seaweeds for rapid growth rate (Hanisak, 1987) species of the green algal genera *Enteromorpha* and *Ulva* were also grown. These species had higher initial yields than *Gracilaria* but the yields were not sustainable for significant periods as the species would become reproductive and shed spores. As each cell in the thallus can become reproductive, it was not unusual for an entire culture to sporulate and be lost overnight, leaving only empty cells. A search was initiated for sterile strains, as *Ulva* in particular lends itself to digestion with high methane yields because of its favourable carbohydrate and protein content.

3. BIOCONVERSION OF SEaweEDS

Morand et al. (1991) provide an overview of the variety of methods, research and commercial scale trials of the bioconversion of seaweeds for energy. At this time Europe had a substantial algae industry, principally for alginate production, with centres in France, the UK and Portugal. Apart from cultured and harvested seaweeds the authors highlight the potential for using nuisance seaweeds produced by proliferation in disturbed waterways (proliferation of macroalgae being the equivalent to a bloom of microalgae). Proliferation is characterised by the accumulation of seaweeds in confined areas such as lagoons and bays and/or their stranding along the shore. These authors also speculate over the potential to increase the available macroalgal biomass through selective breeding programmes and the fact the yields can be greatly enhanced by providing the optimum nutrients in the growing regions, for example the natural productivity of seaweeds is 1 t dry weight ha⁻¹ year⁻¹ in nutrient poor water but can be increased to as much as 40 t dry weight ha⁻¹ year⁻¹ in good conditions. *Laminaria japonica* has been cultured at 60 t dry weight ha⁻¹ yr⁻¹ under experimental conditions in China. Further, the authors suggest an integrated approach would assist in attaining economic viability, so seaweeds grown for biomass are simultaneously used as a means of pollution abatement, coastal protection, fertiliser production and the production of other high value raw materials or food.

3.1 Thermal conversion methods

Macroalgae have been tested for their suitability to conversion methods other than anaerobic digestion. These methods include thermal methods such as:

- Combustion: the burning of biomass which is oxidised and produces heat. Combustion of air-dried macroalgae was originally carried out in pits from which a thick ash was recovered. Once cooled and solidified this constituted soda or *kelp* and was used in the glass industry, for iodine and numerous other useful products. Combustion processes tend to be uneconomic because of the high temperature required.

- Gasification: an endothermic process where biomass is transformed inside a reactor to simple gases such as carbon monoxide and hydrogen but a process best suited to substrates which have low water content.
- Pyrolysis-carbonisation: the thermal decomposition of organic materials in an oxygen free or oxygen deficient environment to produce charcoal, gas and pyroligneous liquor. Since Stanford first discovered (1862) that the dry distillation of seaweeds produced an oily substance, many compounds have been extracted by like processes. In 1919-1920, in the US, compounds including oil, creosote, pitch, ammonia, char, phenols, acids, amines, hydrocarbons, and alcohols were being produced from the harvested *Macrocystis*. Tupholme (1926) (cited in Morand, 1991) was commissioned by the British Fuel Research Board to investigate the carbonisation of seaweeds in an attempt to provide employment in rural areas. The pyrolysis of air-dried *Laminaria* species at 600°C produced hydrocarbons, tar, mixed liquor and ammonium sulphate. However the pyrolysis of seaweeds suffers a series of problems affecting its economics, these include the high water content of the seaweeds, costs associated with bulk handling and transport and the difficulty of separating the complex mixtures of chemicals.
- Hydrolification: the transformation of biomass to liquid fuels using high temperature and pressure.

3.2 Methanisation

Morand et al. (1991) and Chynoweth et al. (1987) summarise the results of seaweed methanisation by numerous research workers. This research has included the effect of several variables on AD including separation of the juice and non-juice fractions, temperature, inoculum, nutrients, freshwater versus seawater dilution and non-dilution. Later the research focused on advanced digester designs, process optimisation and kinetics. In general the brown algae are more easily degraded than the green algae, and the green are more easily degraded than the red. There are exceptions, such as the brown algae *Sargassum* for which methanogenesis is inhibited, probably by the presence

of phenolic compounds or the oxygen from undamaged pneumatocysts. Because at least two very distinct microbial consortia are involved in AD, some investigators have proposed separating these organisms into two separate phases. Whether methane production is performed within combined or separate phases, the process is strictly anaerobic and must be performed in the absence of air (Chynoweth et al., 1987). The non-methanogenic acid producing bacteria are relatively robust and fast-growing organisms, the methanogens are by contrast fastidious and slow growing. The complexity of the numerous bacterial species involved has prevented identification of all of these organisms.

Controlled AD for producing and recovering methane is performed in digesters or reactors designed with the major objective of keeping the costs low. Low costs require high methane yields (volume of methane kg feed⁻¹) and high production rates (volume of methane, volume⁻¹ day⁻¹). Generally high methane yields are obtained through long solid retention times (SRTs) while high organic loading rates and resultant short HRTs along with high methane yields promote high methane production rates (Chynoweth et al., 1987).

3.2.1 Pre-treatment

Algae as semi-solid substrates need pre-treatment, indeed hydrolysis is the limiting factor in their methanisation. Mechanical treatment from simple chopping to ultrasonic grinding is always used for the digestion of entire macroalgae. Operational costs determine the type of pre-treatment applied. Some treatments such as enzymatic, heating, or milling/crushing to reduce particle sizes to 1 – 5mm, for example, can increase the accessibility of the biomass and accelerate substrate conversion. However some thermal and thermochemical treatments can be unsuccessful and each algal substrate must be carefully studied for determination of the optimum pre-treatment. Spontaneous pre-treatments can be advantageous, exploiting the natural pre-degradation of the algae. Percolation or the natural hydrolysis of the algae as been used successfully with the green algae *Ulva*; simple storage at 4°C for a month increased the methane yield by 45%.

3.2.2 Biomass variability

Research conducted by the Institute of Gas Technology was concentrated on the brown algae *Macrocystis pyrifera* and to a limited extent *Laminaria* spp. *Macrocystis* had a higher ash content and therefore a lower volatile solids (VS) content compared to *Laminaria* spp (mainly *L. saccharina*); it contained algin and mannitol as its principal organic components. Biomass composition within species was also shown to vary considerably depending on growth and time of harvest; several batches of *Macrocystis* were compared and the mannitol, C:N ratio, heating value and stoichiometric methane yield showed considerable variation. It is likely mannitol content varied with nutrient availability and the bioconversion of *Macrocystis* was shown to be highly correlated with the mannitol content of the batch studied. Levels of light and the addition of fertilisers to seaweeds in culture may also affect their biodegradability and methane yields (Chynoweth et al., 1987). The differences in composition between lots of the same species can dramatically affect the performance and stability of the digestion process.

3.2.3 Toxicity

Inhibition of methanisation can result from high concentrations of substances such as phenols, heavy metals, sulphides, salts and volatile acids. However, acclimation is a feature of the process in reactors: when a toxic element is brought into the medium slowly, much higher levels are tolerated than if it is introduced suddenly. To achieve acclimation, retention time of the microorganisms is important, and can be adjusted depending on whether the toxins are in continual supply or transient. Sulphur, an element needed for methanic fermentation can also act as an inhibitor. The green algae, *Ulva*, can contain large quantities of sulphur under certain conditions. The presence of sulphur is not a problem reported in the AD of brown algae.

3.2.4 Salt

Salt can have an inhibitory effect on methanisation, although acclimation can allow successful functioning at concentrations, which if introduced suddenly, would cause perturbation. However in some trials, desalting has led to a decrease in methane production, probably due to the loss of fermentable products along with the salts. So in conclusion, it should be noted that it is not possible to generalise over particular results because many factors influence the ability of bacteria to tolerate a potentially toxic substance.

3.2.5 Inoculum:

Some authors (as reviewed by Morand et al., 1991) report that a marine inoculum has no greater final effect than one from domestic sewage sludge, although the marine inoculum caused the process to start faster. Others observed that some marine bacteria are able to digest specific phycocolloids which accelerated and increased biogas production when added to the digester with the inoculum. The use of marine sediments from an area of decaying seaweeds was reported to give a fast start to the digestion process.

3.2.6 Temperature

Little or no justification for the use of thermophilic bacteria has been reported for digestion of seaweeds. Salt appears to inhibit the thermophilic process, with only a partial adaptation of thermophilic bacteria (Chynoweth et al., 1981). Several authors (as reviewed by Morand et al., 1991) state that a constant temperature is required, for example low biogas production from *Cladophora* in Senegal was attributed to a drop in temperature overnight.

3.2.7 Elemental ratios, inorganic nutrients

Chynoweth et al.(1987) report the nutrients required for AD are, in decreasing order of importance, nitrogen, sulphur, phosphorus, iron, cobalt, nickel, molybdenum and selenium. Nitrogen is the major nutrient, other than carbon

sources, that is needed for AD. In a study using *Macrocystis* methane production rapidly fell off as C:N ratios increased. Similarly when Chynoweth (1987) studied the methanisation of *L. saccharina* he found the biogas production was highest when the C/N ratios were low (14:1) and fell off as they increased to 24:1. However this is not the case with all algae, for example, with *Ulva*, when the algae are low in nitrogen the soluble carbohydrate concentration is augmented, increasing biogas yields.

The impact of modifying C/N/P ratios through mixing seaweed biomass with other substrates, such as municipal sludge waste or manure has been examined with mixed results. Some mixtures improved the process while others proved negative, in a similar way co-digestion of mixed seaweed species often proved difficult because of differences in the digestion speeds of the algal species, metabolites released by one inhibiting methanisation in another.

3.2.8 Reactor types

Continuously stirred tank reactors (CSTRs) were reported by Chynoweth et al. (1987) as being unsuitable for energy production systems as the high loadings required resulted in reduced biomass conversion and system instability. In order to reduce the limitations of CSTRs a non-mixed vertical flow reactor (NMVFR) was developed with a view to increasing microorganism and solid retention as a means of increasing biomass loading potential of the system. Feed is added at the bottom and effluent extracted from the top of this non-mixed vessel. Solids are passively concentrated by settling resulting in longer solid than liquid retention times. The data collected was interpreted as the bioconversion process only being limited by the quality of the feedstock and not by the design of the reactor. Chynoweth et al. (1987) also report data from a two phase NMVFR where effluent from the first phase which had a poor methane yield but was rich in volatile acids was fed into a second reactor operated as a NMVFR methane phase digester. This digester had a methane yield of over 75% and significantly exceeded that previously observed with undiluted kelp. Seaweeds have not been trialled in the state-of-the-art

commercial CSTR systems such as those designed and developed by the Shropshire based company Greenfinch Ltd.

3.2.9 Methanisation of polysaccharide residues

Residues of extraction of seaweed polysaccharides have been trialled as a substrate for methanisation. Bird et al., (1981) (cited in Morand et al., 1991) attempted methanisation of *Gracilaria tikvahiae* followed by agar extraction, but found the gelling properties of the resulting agar much reduced. The reverse procedure, methanisation of residues after agar extraction has also been abandoned. However using flotation sludges from alginic acid extraction in an infinitely mixed digester gave results close to those that can be obtained with the entire algae. Fermentation of solid residues proved difficult and that of flocculated residues impossible, except when mixed with mineral solutions or pig manure.

3.2.10 Use of residues

Early work also proved that the liquid and solid residues of the red algae *Gracilaria tikvahiae* were an excellent source of nutrients for the cultivation of the seaweed itself. Freeze dried methanisation residues were also tested as fertilisers on terrestrial plants. Residues from the intertidal brown seaweed *Ascophyllum nodosum* gave good results on lettuce plants, but *Laminaria* spp. produced a negative effect. An original idea (reported in Morand et al., 1991) for the use of *Laminaria* spp. methanisation residues was to improve the mechanical qualities of peat blocks, increasing the strength after compression and allowing the peat to be usable for seed growing.

3.3 Biological gasification – Case studies: Morocco, France, Tokyo

SOPEX Methanisation in Morocco: A reactor of 800m³ was constructed in Morocco by the Belgian company SOPEX in order to treat 12 t of daily waste generated by the agar production from the algae *Gelidium* (as reported in 1988 by Goes, quoted in Morand et al., 1991). The total cost of the plant was

BFr 6 million and the production of biogas was expected to be of the order of 100,000m³ per annum worth BFr 1 million. The plant served to eliminate a form of environmental pollution and to produce fertiliser (which had yet to be marketed at the time of the report).

Methanisation of Laminariaceae in France: A full scale experiment on *L. digitata* methanisation was carried out in 1984 in Brittany, during a summer period and using a reactor that normally functioned on manure. At the time it was the only experiment of its type carried out on this scale in the world. The results should be treated with caution as only two HRT were completed and conclusions are more generally drawn on stability of a process after four HRT. The infinitely mixed reactor had a usable volume of 30 m³, the total seaweed mass was 48 t, the seaweed and juice being introduced to the reactor after a slight grinding leaving blades 20 cm long, and at the rate of 1 m³ per day for the first 25 days and increasing to 1.5 m³ per day for the next 31 days. During the last 21 days a methane production of 29.8 m³ day⁻¹ was obtained, the biogas composition was 61.2% methane, 38.3% carbon dioxide, 0.5% hydrogen. The methane yield of 0.5 m³ kg⁻¹ VS (volatile solids) was therefore approximately equal to the maximum theoretical yield calculated from the composition of *L. digitata*. However, the experiment should be repeated as it is possible that products with long retention degradability times remained from previous loadings of manure.

Methanisation of Ulva sp. and Laminaria sp. in Japan: Japan has had a long interest in the concept of seaweed biomass as biofuel. In 1982 the Japan Ocean Industries association produced a report examining the feasibility of marine biomass crops (Brinkhuis et al., 1987). Current research in Japan, as reported by Matsui et al. (2006) is associated with the chronic problem with 'green tides', green seaweeds (mainly *Ulva* sp.) washing up on seashores and rotting. This nuisance seaweed has historically been collected and incinerated by local governments. Seaweeds have also recently been cultivated to remediate local nutrient pollution in the sea and to protect fish habitats from waves. The disposal of this seaweed, usually from the genus *Laminaria*, is also a growing problem. One solution is to use this seaweed as feedstock for

anaerobic conversion to methane. The Tokyo Gas Company Ltd. has built a 1 t day⁻¹ methane fermentation plant combined with a gas engine power generator to convert the biogas produced into electricity. The company has selected methane fermentation (AD), rather than gasification for example, as the proper process to convert seaweeds to gas fuel because of the high concentration of water (about 90%). This field test plant consists of four parts (pre-treatment, fermentation, biogas storage and generation). In the pre-treatment part, the seaweeds are passed through a cutter/separator, cleaned of foreign objects, smashed and diluted with water to suppress the effect of salt and to make an appropriate slurry. In the fermentation part, there are two processes (pre-fermentation and methane fermentation) for higher efficiency. The seaweed slurry is first treated by pre-fermented (acid production) in a 5 m³ tank for 2 to 3 days to increase the concentrations of organic acids. This organic acid rich solution is then fermented for 15-25 days in a separate methane fermentation tank (30 m³) which contains a porous matrix for immobilizing bacterial cells. The biogas is refined (de-sulfured) and stored in a gasholder (30 m³). The residue from the fermentation process is dried and used as fertiliser. The biogas is then mixed with city gas and fed to a co-generation system where a generator (10 kW) produces electricity and excess heat from the engine is used to heat the fermentation tanks.

When using *Laminaria* sp. as a test material for gas conversion it was continuously supplied at a rate of 0.2 t to finally 1 t per day. The TS content after adding the dilution water was 1 to 5%. Retention time of the pre-fermentation was 2 to 3 days. The temperature was controlled at 25-35 °C. Total concentration of produced organic acid (mainly acetic, lactic, and butyric) was 1000 to 5000 ppm. In the case of the methane fermentation, retention time was 15 to 25 days and temperature was controlled at 55 °C. The concentration of ammonium ion was low (under 150 ppm), higher levels can prevent methane fermentation. Biogas was produced continuously, of a composition of 60 % methane and 40 % carbon dioxide, it also contained several thousands ppm hydrogen sulphide which was removed by iron oxide in this plant. Results of tests at varying pH showed the optimum for

maximising was over pH 7.5. One t of seaweed yielded 22 m³ methane gas, produced continuously for over 150 days.

The *Ulva* sp. collected on seashore was also tested. These seaweeds contained sand which did not affect fermentation directly but does decrease the available volume of the tanks. Therefore they were washed with water and any foreign bodies removed before they were used for fermentation tests.

Ulva was supplied to the digesters at 0.6 t per day (TS=3%) and the conditions of the fermentation were same as for the *Laminaria* sp. Organic acid was produced in the pre-fermentation tank at a concentration of 1000 to 3000 ppm, and then fed to the methane fermentation tank. The ammonium ion concentration was about 500 ppm, and did not affect the methane fermentation. The composition of the biogas was again 60 % methane and 40 % carbon dioxide, and the yield was 17 m³ t⁻¹ of seaweed, lower than the yield of the *Laminaria* sp. It was assumed that the *Ulva* sp. had more components not decomposed easily by bacteria. The biogas was continuously produced for over 70 days and the yield of methane gas was stable.

These results of these tests show it is possible to produce biogas from seaweeds (*Laminaria*, *Ulva* sp.) in practical conditions. The quantity and composition of collected biogas changes with the source of materials, conditions at sea and the weather, as well as with the fermentation conditions. Thus it is most effective to use the biogas mixed with other fuel, such as natural gas, and by controlling the ratio of natural gas to biogas it is possible to keep the engine operation stabilised. Adding natural gas to the biogas helps control the heat value of the fuel gas, by reducing the overall concentration of carbon dioxide in the fuel gas, an obstruction to combustion, and therefore increasing the thermal efficiency of the gas engine. The thermal efficiency of the gas engine supplied with mixed biogas and natural gas is over 10% higher than when using biogas alone.

3.4 The study of biological degradation of brown seaweeds in Norway

In Norway two species of seaweed are commercially harvested, *Ascophyllum*

nodosum and *Laminaria hyperborea*. In a study to identify factors that may limit the biological degradation of these seaweeds, knowledge of which is important to the bioconversion of seaweed biomass, Moen (1997) and Horn et al. (2000) examined the degradation efficiency in small batch reactors by measuring (among other parameters) methane and carbon dioxide (biogas) production. *L. hyperborea* (stipes) had a higher degradation than *A. nodosum*. This difference was attributed to the higher polyphenolic content in the latter. Polyphenolics were found to have non-specific negative effects on the degradation of algal material, inhibiting the microbial consortia used and forming recalcitrant complexes with the algal material, proteins and the alginate lyases. The complexation of the alginate lyases were significant because of the reliance on these enzymes to render the alginates (the major component of algal cells) available to biological degradation. This inhibitory effect of polyphenols was removed by the addition of small amounts of formaldehyde. The large differences in the type of alginate present in the two species of seaweed had little effect on their biological degradation. Mannitol, the main sugar in the seaweeds was readily degraded without prior hydrolysis.

3.5 Ethanol production

Brown seaweeds contain two main storage sugars, mannitol and laminaran, which can be relatively easily extracted from milled seaweed. The Norwegian researchers (Moen et al., 1997) showed that these are the best substrates in seaweeds for the production of bio-ethanol. They are also both waste by-products of the alginate extraction industry. Initial attempts using microbes for converting these sugars into bioethanol have shown promising results (Horn et al. 2000a, 2000b). Bioconversion of these sugars into ethanol can be made possible by either (i) employing a two-step process using two different microorganisms, each optimised for maximum ethanol yield from each sugar substrate; or (ii) using a single-step process with one organism that can utilise both substrates to yield maximal ethanol yields. This possibility was only recently shown to hold promise by the same Norwegian research group who, for the first time, demonstrated that both sugars could be converted into

ethanol, and that this was possible with the use of one single organism, the yeast strain *Pichia angophorea* (Horn et al., 2000). Although ethanol was produced at reduced yields, the demonstration of this bioconversion is significant. Interestingly, in another report by the same authors the bacterium *Zymobacter palmae*, isolated from palm sap, was shown to have ethanologenic properties in its capacity to ferment seaweed-derived mannitol to ethanol. Phylogenetic studies later classified this bacterium to belong to the *Halomonas* genus, of which SAMS' has a collection of the marine representatives of these species in its strain library. Both of the microbes used in these Norwegian studies were of terrestrial origin (the yeast *P. angophorea* and the bacterium *Zymobacter palmae*) and, as expected, were found to produce less than sub-optimal conversion rates and yields of bio-ethanol. This is possibly attributable to the incompatibility of these terrestrial origin microbes to degrade a marine-based biomass. The relatively high concentrations of salts present in seaweed biomass limiting the conversion of this feedstock to biofuel.

The economic potential of bioethanol production from seaweed is enhanced by the facts that (i) the raw feedstock could be derived from the waste products of the alginate industry which is highly enriched in the sugars mannitol and laminaran, thereby cutting down on initial costs; (ii) the time taken to achieve optimal bioconversion rates and yields of bioethanol from seaweed is estimated to be years rather than decades as many technological hurdles have been overcome in the past 50 years of experience into converting bioethanol from lignocellulosic materials; (iii) the cost of enzymes for digesting complex biomass to make it more amenable to fermentation has fallen considerably, thus making ethanol from biomass more affordable and technologically less daunting.

Uchida & Murata (2004) reported ethanologenic bacteria on the surfaces of *Ulva* species for the first time. This finding is significant in that it not only identifies a new source for isolating the microbes with the relevant potential but the fact that these strains are of marine origin implies that they would likely tolerate the high salt concentrations present in raw seaweed feedstock,

hence eliminating the need for any pre-washing and thereby cutting down on processing costs.

At SAMS researchers have successfully compiled a large collection of marine bacteria, many of which are un-described strains, isolated based on their potential to degrade hydrocarbons. The biotechnological application of this collection has been exemplified by the filing of an international patent application [PCT/GB2005/003421] and the publication of peer-reviewed papers describing novel marine bacterial polymers with functionalities as hydrocolloid stabilizers and emulsifiers (Gutierrez et al., 2007a; Gutierrez et al., 2007b). This strain collection, together with new isolates, could act as a platform for screening and identifying novel marine microorganisms with the capacity to convert seaweed biomass into ethanol.

4. BIOMASS AVAILABILITY

In temperate seas the brown seaweeds or the Phaeophyta generally dominate the flora in terms of biomass. The patterns of seaweed species distributions differ among geographical regions and on smaller spatial scales, species distributions also change with, for example, the height on the shore and environmental conditions. In the North Atlantic the inter-tidal – or those areas that are covered by water at high tide and exposed during low tide- are dominated by the wracks (species from the genus *Fucus* and the species *Ascophylum nodosum*). The sub-tidal, defined as areas below the mean low water mark, is dominated by large upright brown species of algae colloquially called kelps. The depth to which kelps grow is limited by light and they are mostly not found below 20 m of water. This section of the review will focus on the kelps because of their large biomass and the ease of using them as feedstock for biofuels (see Section 3). In the North East Atlantic kelps are generally from the genus *Laminaria* and/or the species *Sacchoriza polyschides* and *Alaria esculenta*. By far the most dominant species found in kelp forests of the UK is *Laminaria hyperborea*. Kain (1979) provides an extensive review of the biology of kelps from the genus *Laminaria* and reviews specific to *L. hyperborea* are contained in a series of papers by Kain (e.g. Kain, 1976, 1977). Moreover, the FAO Fisheries Synopsis series contain reviews of biology *L. hyperborea* (Kain, 1971) and *Saccorhiza polyschides* (Norton, 1970).

4.1 Standing stock of seaweeds in Britain

The seaweed resources of the UK and in particular Scotland are some of the most extensively and intensively surveyed in the world. The shortages of raw materials caused by the Second World War prompted an investigation of Britain's seaweed resources in the 1940's and 50's. A survey of the entire coast of Britain showed that the majority of kelps in commercially harvestable densities are found in Scotland (Chapman, 1948). Subsequently, surveys of the coast of Scotland were conducted by the now defunct Scottish Seaweed Research Association.

4.1.1. Subtidal Seaweeds

The standing crop of sub-tidal seaweeds in Scotland is reported in a series of papers for the Scottish Seaweed Research Association by Walker (1947-1955). The surveys were conducted using a combination of aerial photography and an intensive sampling programme. Sampling was done from boats using a spring loaded grab that was especially designed for the task. Over a period of ten years approximately 100,000 quadrats were taken using the spring grab. This intense sampling effort was conducted along about 8500 km of Scottish coast, and included the Outer Hebrides, many of the Inner Hebridian islands and in the north the Orkney and Shetland Islands. The study estimated that there was 8,000 km² of seaweed habitat in the Scottish sub-littoral. Within this habitat it was estimated that in total approximately 10 million t of algae was growing between the depths of 0 -18 m. The biomass of kelp growing along the Scottish coast was found not to be evenly distributed and Walker deemed that only about 1000 km² of the habitat to have sufficient densities to be commercially harvested. The main centres of seaweed biomass occurred on the offshore islands of Shetland, the Outer Hebrides and Orkney (see Table 4.1).

Walker found that the dominant species in the subtidal was *L. hyperborea*. Species found in lower abundances included *L. digitata* in the shallower habitats, giving way to *L. saccharina* and *Saccorhiza polyschides* in deeper habitats. The average density of seaweed was 3.7 kg m⁻². There was a strong relationship between depth and density of seaweeds with higher densities in shallow water, 6 kg m⁻² at 1 m, dropping down to 3 kg m⁻² at 5 m and the lowest densities in deep water, 1.2 kg m⁻² at 10 m. A later, in-depth exploration of the effect of depth on biomass and growth of *L. hyperborea* can be found in Kain (1977).

The validity of using the results from Walker's surveys to assess the current standing biomass of seaweeds depends on whether the techniques used were accurate and whether the abundance and distribution of seaweeds has

changed in the last fifty years. More recent surveys of seaweed biomass (Jupp and Drew, 1974; Kain, 1977) offer a way of assessing the first of these criteria. One of the main criticisms of using a grab to assess biomass is that it only collects a sub-sample of the biomass leaving behind many whole seaweeds and parts of plants. Using SCUBA to hand collect seaweeds from a known quadrat ensures that all of the biomass is surveyed and predictably, this method always give a higher estimate of standing stock than using a grab. Studies that have used SCUBA to sample *L. hyperborea* by hand have found densities of 20 kg m⁻² in 3 m of water in western Scotland (Jupp and Drew, 1974) and 10-20 kg m⁻² at 5 m depth around the Isle of Man and the Outer Hebrides (Kain, 1977). These results are similar to those from other countries, for example Sjøtun et al. (2004) found that in Norway at 3-5 m the standing stock of *L. hyperborea* was between 6-16 kg m⁻². These results are about 3-5 times the density found in Walker's original surveys. Extrapolating these estimates to the whole coast of Scotland would increase the total sublitoral biomass from Walker's estimate to 30-50 million t. However, it has been argued by Kain and Holt (1998) that while Walker's estimates are almost definitely an underestimate of total seaweed biomass they provide a good estimate of the harvestable biomass as it approximates the yields that would be obtained using conventional seaweed harvesting technology which leaves behind smaller plant and parts of mature plants (Christie, 1998).

Assessing whether there has been a shift in distribution and abundance of seaweeds since the 1940's and 50's is more difficult. Recently, shifts in the distribution of seaweeds on decadal scales have been documented for fucoids in the UK (Davies et al., 2005) and for Laminarians in Japan (Kirihiro et al., 2006). Both studies have shown decreases in these seaweed populations which are correlated to increases in winter temperatures that may be consistent with climate change models. It is unknown whether there has been any large scale change in subtidal seaweed biomass in the UK. For Scottish kelp communities one thing that is clear from Walker's data is that during the time of the surveys there was considerable natural variability in the Laminarian standing stock. Walker's surveys were done annually from 1946-55 and many sites were resurveyed enabling analysis of how the seaweed

biomass changed from year to year. During this time both the proportion of different species and the total biomass significantly changed (Walker, 1956). For example, when the total density of seaweeds between 0 and 9 m was averaged there was almost a five fold difference among years. Large fluctuations in biomass may be a characteristic of kelp forests. For example, Dayton et al. (1992) found similar fluctuations in Californian *Macrocystis* forests that were attributable to large scale climatic events (El nino-Southern Oscillation), severe storms, and variation in herbivore grazing. All of these factors will no doubt play a role in structuring subtidal communities in the UK, overlaid on this will be the increased uncertainty of the effects of climate change.

In conclusion the standing stock of subtidal seaweed in Scotland has been extensively studied and offers a prodigious amount of biomass that could be utilised. However, doubt remains about the natural inter-annual variability of this resource. This may impact any attempts to measure longer term changes in biomass caused by harvesting or climate change.

4.1.2: Intertidal seaweeds, fucoids and *Ascophylum*

The high polyphenolic content of inter-tidal seaweeds render them unlikely to make good feedstock for energy production. However, as technologies develop this situation may change. There has been a recent comprehensive review of the standing stock, sustainability of harvesting littoral seaweeds in the Western Isles (SNH, 1994) including a summary of current and historic seaweed utilisation and harvesting in the UK and beyond. Walker (1945-46, 1947) conducted surveys of the intertidal seaweeds of Scotland similar to those he conducted on subtidal seaweeds. Intertidal seaweeds are currently harvested, on a small scale in the Western Isles (Hebridean Seaweed Company) thus any future harvest of this resource for fuels will encounter issues related to sharing a currently commercially utilised resource.

Table 4.1. Standing crop of kelp at localities in Scotland sorted by density of kelp per hectare. Data recalculated from Walker (1947).

Locality	Standing crop of kelps (tons)	Area (hectares)	Length of coast (km)	Density (tons/hectare)
Orkney	1088400	22663	805	48
W. Kintyre and Gigha	181400	4452	80	41
Outer Hebrides	634900	16593	137	38
Crail	19954	526	11	38
Skye	272100	7285	354	37
E. Kintyre	36280	1052	35	34
Loch Eriboll	18140	526	21	34
Tiree and Coll	273914	8094	93	34
Dunbar	45350	1376	18	33
Islay	45350	1619	18	28
Luce Bay	18140	648	6	28
Shetland	553270	22663	1127	24
Girvan	39908	1700	34	23
Colonsay	18140	809	10	22
Mull	18140	931	24	19
Arran	50792	2752	77	18
Helmsdale	19954	1174	16	17
Tarbat Ness	9070	648	13	14
Enard Bay - Lochlash	110654	9713	257	11
Fraserburgh	54420	7285	97	7

4.2 Sustainability of wild harvest

A review of the literature of the potential impact of harvesting kelp in Scotland was done by Wilkinson (1995) for Scottish Natural Heritage, it contains a thorough treatment of the older literature and reviews of some primary Norwegian language reports.

There is currently no large scale harvesting of subtidal seaweeds in the UK. The best data on the sustainability of the wild harvest of the dominant subtidal

seaweed in Scotland, *Laminaria hyperborea*, is from Norway. Norway currently harvests between 130 000-180 000 t of *L. hyperborea* a year, it is estimated the standing stock is more than 10 million t (Jensen, 1998). The harvest is highly regulated and is sourced from four geographical regions. Each of these regions is further divided into five areas that are harvested on a five year cycle (before 1992 this was a four year cycle) (Briand, 1998). Between 6-17% of each of these sub-areas is harvested every five years. The trawl harvesting methods used clears the entire adult canopy of *L. hyperborea*, but leaves behind a high density of smaller sub-canopy plants from several age classes (Christie et al., 1998). Growth of these understory plants is quickly stimulated by the increased light resulting from removal of the canopy. The high density of the understory plants shades the substratum and effectively inhibits the recruitment of other species of algae. The mixed age classes in the understory means that the recovery of the kelp bed is not reliant on one year's recruitment. Thus the recovery of the kelp bed is not sensitive to the time of year that the harvest takes place. These two factors, the high density and mixed age class of understory plants, combine to make *L. hyperborea* kelp forests very stable and highly resistant to disturbances such as intensive harvesting.

According to Norwegian industry capture records the biomass at trawled sites recovers within the five year trawling cycle (Briand, 1998). However, recovery in the size of *L. hyperborea* after trawling can be dependant on location. For example, Christie et al. (1998) found that at one location the plants at a trawled site reached the height of plants at a control un-trawled site after two years and the size of plants three years after trawling surpassed the size of plants at the control site. At another more northerly location the plants at the trawled site had not reached the height of the un-trawled site after six years. Other indicators of the effect of trawling on the kelp forest show mixed results. The community of epiphytic algae on the stipes of the *L. hyperborea*, an important habitat in itself, show good recovery in terms of abundance diversity and percentage cover after two to three years. However, full recovery of this community is not achieved within six years (Christie, 1998). The recovery of invertebrate fauna in the hold fasts of *L. hyperborea* also shows good signs of

recovery after one year (Christie, 1998) but the currently available data are not sufficient to assess the true effect of trawling on the wider communities living kelp forests.

There are some data available on the effect of removing *L. hyperborea*, in a Scottish context. However, the studies were not intended to investigate the effect of harvesting so the way the plants were removed and thus the amount of seaweed removed may be significantly different than would be expected from a commercial harvest. In one of the first reported manipulative studies on kelp Kitching (1941), removed *L. hyperborea* (*L. cloustoni*) from the Sound of Jura, using shears and after 12 months a very dense covering of new plants 1 m high had re-grown. Kain (1975) in a series of experiments removed all of the kelp growing on concrete blocks of a seawall, including scrubbing the blocks with a wire brush and monitored the recolonisation macroalgae. This treatment removed the under story *L. hyperborea* plants that maintained the resilience to colonisation in the Norwegian studies cited earlier. The result was that the successful regeneration of *L. hyperborea* depended on the time of year that the removal took place and often the kelp *S. polyschides* colonised the cleaned area. Notably, the *L. hyperborea* always replaced the *S. polyschides* after two years and the biomass in the shallow treatments reached control site biomass after three years.

The available data indicate that *L. hyperborea* forests are generally robust to disturbance by harvesting on a five year cycle. However, data on the effects on the wider kelp community, the sensitivity of different locations to harvesting, and data set in a Scottish context are poor or lacking. Norway is estimated to have a similar standing stock of kelp to Scotland and to sustainably harvest 130,000-180,000 t per year.

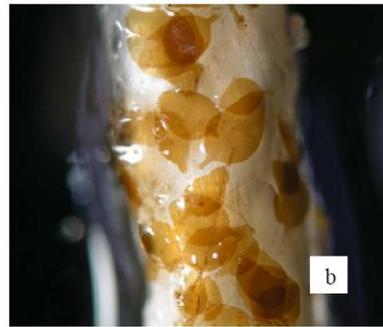


Figure 4.2 Seaweed cultivation in Scotland (SAMS), a) *Laminaria saccharina* sporelings on culture strings b) *L. digitata* sporelings at 6 weeks c) Juvenile plants on culture strings (strings 1-2mm thick) d) transplanted *L. saccharina* after 2 months at sea d) *L. saccharina* plants produced from 10 cm section of culture string e) individual *Sacchoriza polyschides* plants, grown in a single season.

4.3 Culture

4.3.1 Extent of culture

The cultivation of seaweeds is well established and extensive, indeed the cultivation of aquatic plants accounts for 23.4% of the total tonnage of the world's aquaculture production (FAO, 2006). Seaweeds tend to be a high volume, low value crop compared to other aquaculture species, aquatic plants only account for 9.7% of the total value of the world aquaculture production, despite being ranked second behind fish in terms of volume (FAO, 2006). Seaweeds are the fourth most valuable crop behind fish, crustaceans and molluscs. Most of the world's seaweeds are grown in China where more than 4 million t of one plant, *Laminaria japonica*, alone was produced in 2005 (FAO, 2006). The rest of Asia and Pacific region is responsible for most of the rest of the world's production (Fig 4.3). This trend where Asia and specifically China is the centre of cultivated seaweed production mirrors aquaculture production in general.

Seaweed culture in Europe is very limited. The most significant grower is France producing about 25 t seaweed per year (FAO, 2006), mostly on the Brittany coast. *Laminaria* spp. and *Alaria esculenta* are the main species produced in France. In the rest of Europe there have been and are currently several trials of seaweed culture. These have included growing *L. saccharina* in the open ocean in Germany (Buck and Buchholz, 2004), *Palmaria palmata* and several strains and hybrids of *Alaria esculenta* in Ireland (S. Kraan pers. comm.). In the UK in the 1980s *L. saccharina* and *A. esculenta* were successfully grown and sold for a few years (Kain and Dawes 1987), but attempts at growing *Sacchoriza polyschides* and *P. palmata* were less successful.

Currently, the Scottish Association for Marine Science has an ongoing research programme investigating the culture of seaweeds. They are cultivating several species of seaweed including *S. polyschides*, *Laminaria hyperborea*, *L. saccharina* and *P. palmata*. The main thrust of this research is testing whether integrating the growth of seaweeds in open water fish culture is an effective way of sequestering waste nutrients produced by the fish farm

and indeed whether seaweeds can be cultivated as feed stock to produce biofuels.

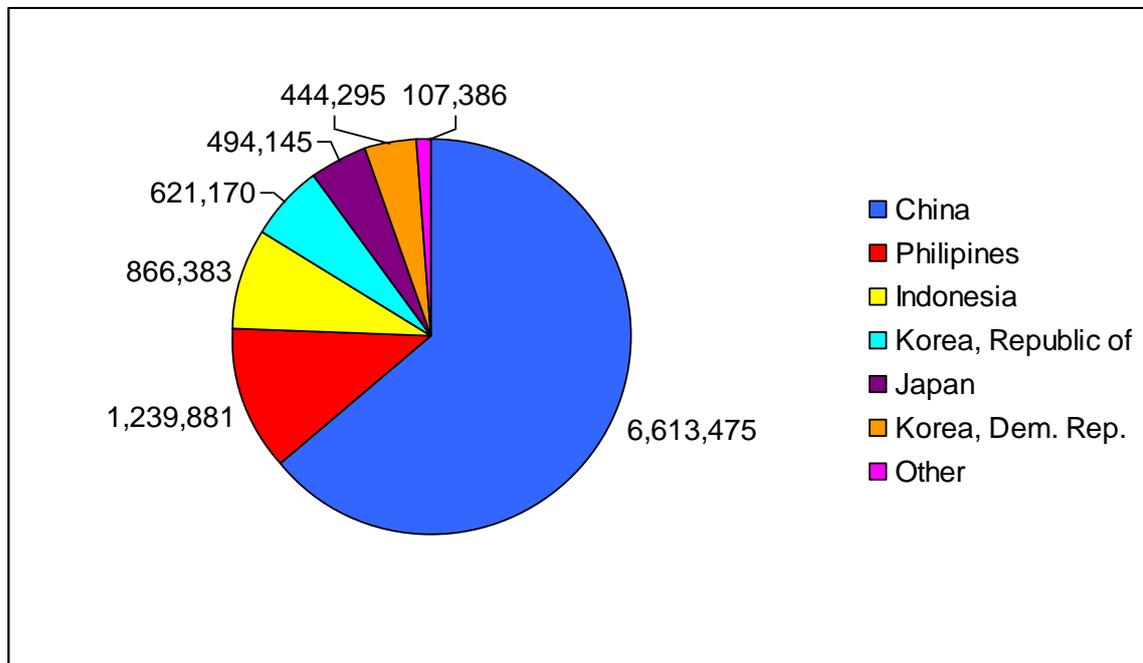


Fig. 4.3 World seaweed aquaculture. The proportion of the total volume of seaweeds produced by the six seaweed growing countries (data are given as tonnes). Source: fishstat, (FAO 2006).

4.3.2 Productivity in culture

Seaweeds are extremely productive plants. The productivity of natural stands of large brown algae has been estimated to be in the range of 16-65 kg m⁻² yr⁻¹ wet weight (wwt) (3-11 kg m⁻² yr⁻¹, dry weight (dwt) (Gao and McKinley, 1994). However the actual harvestable weight would be much less. For example, Scotland has at most 10-20 kg m⁻² standing stock in the shallow subtidal that may be harvested at an absolute maximum every five years giving a productivity of 2-4 kg m⁻² yr⁻¹. To put this in perspective, sugar cane (the most productive plant under cultivation) has a productivity of between 6-18 kg m⁻² yr⁻¹ (wwt) (Gao and McKinley, 1994), (note that these figures are not directly comparable as wet weights, energy and carbon content, etc, will differ between sugar cane and algae). However, cultivated seaweeds are much more productive than natural beds of seaweeds and arguably the most

productive systems known. In China for example *Laminaria japonica* is regularly cultivated at $15 \text{ kg m}^{-2} \text{ yr}^{-1}$ (wwt) and at up to $60 \text{ kg m}^{-2} \text{ yr}^{-1}$ (wwt). In the UK seaweeds have never been cultivated to the extent of that in China but data from experimental farms can be extrapolated for comparison. In Ireland hybrids of *Alaria* spp. have produced up to $8 \text{ kg m}^{-2} \text{ yr}^{-1}$ (wwt) (S. Kraan, pers. comm.) and *Alaria esculenta* was cultivated in the 1980's at up to $5.6 \text{ kg m}^{-2} \text{ yr}^{-1}$ (wwt) (calculated from Kain and Dawes 1987). At the Scottish Association of Marine Science several species have recently been grown in experimental plots near fish farms to take advantage of the dissolved nutrients (Sanderson, 2006; Dworjanyn, unpublished data). They found that the red algae *Palmaria palmata* can be cultivated at (at < than $1 \text{ kg m}^{-2} \text{ yr}^{-1}$ (wwt)) and that the long lived kelp *L. hyperborea* achieved productivity of just over $2 \text{ kg m}^{-2} \text{ yr}^{-1}$ (wwt), a value similar to the estimates for harvested wild *L. hyperborea* above. In comparison opportunistic species such as *L. saccharina* was grown at $10 \text{ kg m}^{-2} \text{ yr}^{-1}$ (wwt) and the annual kelp *S. polyschides* was grown at up to $17 \text{ kg m}^{-2} \text{ yr}^{-1}$ (wwt) (Sanderson 2006, Dworjanyn unpublished data).

4.4 Selection of species for culture in the UK

For reasons of biological security only species native to the UK should be considered for cultivation. The selection of suitable UK seaweeds to cultivate for biomass will depend on, a) the chemical composition of the alga and the effect that this has on the efficiency of bioconversion and b) the efficiency with which a species can be cultured. Data on the efficiency with which UK seaweeds can be used for fuel production is scant, much of which is reviewed in this document. What is known is that polyphenolics, a class of chemical ubiquitous in the brown algae (Ragan and Glombitza, 1986) reduce the efficiency of bioconversion by binding proteins and inhibiting bacteria (Moen, 1997). The intertidal seaweed species, i.e. *Ascophyllum nodosum* and *Fucus* spp. have much higher polyphenolic content (up to 14%) than the subtidal kelps (generally less than 2%) (reviewed by Ragan and Globmbitza, 1986) and thus can initially be ruled out. Of the kelps both *L. saccharina* and *L. hyperborea* (as well as other laminariacea) are known be good substrates for bioconversion (Moen, 1997; Chynoweth, 2001; Matsui, 2006). The chemical

composition of many species of kelp is known and this can change predictably between species and with season. For some chemical metabolites these changes and the effect on fuel production can be predicted. For example, the kelp sugars, mannitol and laminarian rise in kelps during summer from a winter low (Loban and Harrison, 1997) and the efficiency of ethanol production will be directly related to these changes (Horn, 2000). However, for most seaweed metabolites there is not enough known about the complex interactions in the bioconversion process and the natural variations in the seaweeds to form a basis for species selection. The variation in seaweed metabolites and the effect on fuel production is a key area of research that needs to be addressed.

There are several seaweed species that have potential to be grown as feedstock for biofuel production in the UK. If selecting species using the criteria of fast growth rates in cultivation, the productivity rates quoted above indicate that the kelps especially *L. saccharina*, *S. polyschides* and *Alaria* spp. would be prime candidates. However, comparisons of growth rates of different species under the same culture conditions are not available. Moreover, seaweed cultivation is in its infancy in the UK and methods to increase productivity, including selecting fast growing strains, should be investigated before any meaningful assessment of which seaweed would be the most efficient producer of biomass under culture conditions.

4.5 Methods of culture for the UK

All of the potential species that would be cultured in the UK for biomass are kelps and have very similar life histories and thus methods to cultivate them are almost directly interchangeable. They have a life cycle called an 'alternation of generations' where the large macroscopic plants (sporophytes) we know as 'kelp' release spores that grow into microscopic plants (gametophytes). These microscopic filamentous plants are either male or female and produce eggs or sperm that when fertilised grow into another large kelp plant. Thus the kelp alternates between large macroscopic (diploid) plants and microscopic (haploid) filaments. When culturing kelps the

microscopic phase takes place in the laboratory and the macroscopic kelp stage is cultured in the field.

The methods used for cultivating kelps are all variations on those used in China and other Asian countries to produce many millions of tons of kelp every year. Sporophytes can be collected from the field or cultivated. For wild sporophytes, specific times for maturation vary between species and between geographical areas (eg Kain 1989). However, in general they become sexually mature after the summer growth has slowed. Fertile kelps are easily identified as groups patches of sori (cells containing spores) are visible as raised areas on the kelp blades (thallus). Obtaining enough spores should never present a problem as spores are very small (6-8 μm long), and the sori each containing 32 or more spores are packed very tightly on the surface of the thallus. As many as 50 million spores are produced per square centimetre of thallus (Kain 1975). The fertile sections of kelp are first cleaned, by wiping the surface of the plants and/or applying antibiotic solution. The cleaned damp seaweeds are placed a fridge for 24h or more after which they spontaneously release spores on immersion in seawater. The spores are settled onto a substrate, usually string wound onto a spool or frame, onto which they attach within 24h and germinate into gametophytes. These microscopic filamentous plants when kept under the specific light and temperature conditions release eggs and sperm that after approximately six days results in the sporophytes. The sporophytes re-attach to the substratum provided and are allowed to grow for a few weeks to months in the laboratory until they are between 0.5 – 1 cm in length and are ready to be transplanted to the field.

An alternative method maintains gametophytes under specific culture conditions that encourage them to grow indefinitely without producing gametes. For many Laminarians this entails keeping them under red light. When needed the vegetative gametophytes are formed into a suspension and are sprayed onto the seed strings that are then kept under normal culture conditions to allow sporophytes to develop. This technique is of particular use when gametes need to be produced out of season, for breeding programmes

where specific lines need to be crossed or where a particular line needs to be produced in large numbers.

In the field the sporophytes are grown using variations of the same theme. In general they are attached to floating structure, usually longlines that are anchored to the sea floor and kept on the surface using buoys. The sporophytes are either grown on these horizontal surface longlines or in clearer water grown on weighted vertical lines (called droppers) attached to the longlines at regular intervals. The sporophytes are either a) allowed to grow in the field on the original strings they were settled on in the laboratory until they are 10-15 cm and then individual plants are inserted into the ply of the longlines or droppers, b) short lengths of string under 10 cm in length containing many sporophytes taken directly from the laboratory are inserted into the lay of the droppers or longlines or c) when seeded at low densities the string on which they were settled can be directly wrapped around longlines and allowed to grow.

Growth of kelps is highly seasonal especially in high latitude temperate areas (Kain, 1989). Kelps grow fastest during late winter to early summer. During this time both light and nutrients are plentiful. Growth of seaweeds in winter is limited by the lack of light in high latitudes. However, this period of low light is important in the development of kelps as they can store the plentiful nutrients to be used when light increases in spring. In summer nutrient concentration plummets as phytoplankton respond the increased light and out compete macroalgae for nutrients. At this time kelp growth is limited by nutrients and slows. For some species nutrient limitation during summer may be partially overcome by fertilisation or possibly by growing plants near nutrient sources such as sewer outfalls (Connolly and Drew 1984) and fish farms (Sanderson, 2006; Dworjanyn, in prep). For some kelps this seasonal growth pattern controlled by day length rather than nutrients per se (Gomez and Luning, 2001). Growth is further compromised in summer by the increased occurrence of fouling organisms and the tendency of kelps to shed a large amount of older distal tissue. This highly seasonal growth of temperate seaweeds may be one of the constraining factors that reduce the profitability of seaweed

culture in general and their use as a consistent source of feedstock for conversion fuel specifically.

The highly predictable and seasonal lifecycle of kelps in temperate regions may present an opportunity for the cultivation of seaweeds for biofuels. It is not a coincidence that much of the cultivation of seaweeds is done in countries where labour costs are low; growing kelp is labour intensive. The most labour and capital intensive aspects of growing seaweeds is arguably producing seed and deploying this seed into the field. There is potential that much of this cost can be ameliorated by relying on natural seed fall in the field. Empty longlines placed in the field during late summer/autumn naturally acquire a settlement of kelps (Dworjanyn, pers. obs.). This flora is unlikely to be mono-specific but this may not present a problem as, apart from polyphenolic content, inter-specific variation in chemical content of brown seaweeds seems not to have a large effect on bioconversion efficiency (Horn et al., 2000). In fact growing a diverse flora may result in increase yields as they are more efficient in utilising nutrients and light.

5. FEASIBILITY STUDY

5.1 Introduction

In this section we attempt a synthesis of the information given above on seaweed growth, culture and harvesting with the best available information on possible methane yields as demonstrated in a) commercial scale AD systems (with non-seaweed feedstocks) and b) data from research or pilot scale systems actually digesting seaweeds. We then try to project the extrapolated data into a locally relevant context and to give a comparison with other renewable energy generation schemes. Firstly we describe, in some detail, the current state of the art in AD in the UK through three case studies (two of which are in Scotland). It should be noted at the onset, however, that these case studies have all evolved primarily as waste management schemes, the feedstock being a substrate for which disposal is problematic, rather than using an energy crop grown and produced specifically for AD.

5.2 Case Studies

5.2.1 The South Shropshire Biogas facility

Biocycle South Shropshire is a not-for-dividend company running an AD project demonstrating the diversion of biodegradable municipal waste away from landfill. In a good example of a community orientated project the unit, built and operated by Greenfinch Ltd for South Shropshire District Council, was funded by DEFRA and Advantage West Midlands. Municipal food waste is collected from homes in the area and is delivered to the AD plant.

Participating households collect their food-waste in biodegradable corn starch bags, stored in a 20 l bin, which is emptied weekly. The lorry collecting the food waste is weighed on the weigh-bridge before entering the reception-hall; the external door is then closed before the food bags are tipped out, to minimise the smell reaching the close neighbouring businesses. The lorry then has its wheels washed before leaving the plant as the food waste contains meat and animal by-products. The food is tipped into a shredder

which reduces the particle size to less than 12 mm. A conveyor belt then carries the shredded waste to the conditioning tank where it is mixed with some previously digested liquid to produce a pumpable material. This 'soup' is pumped through macerators to further reduce the particle size before it is fed into the 900 m³ digester at regular intervals. As the resultant digestate could potentially contain microbial pathogens originating from animal by-products, the digested material is pasteurised to 70°C before storage or leaving the plant (Figs 5.1, 5.2). The digestate is separated through a rotating drum filter to produce liquid and solid fractions. The liquor is spread on local agricultural land using a conventional slurry-spreader, while the solid digestate will be used as a soil conditioner or as in-fill for landscaping.

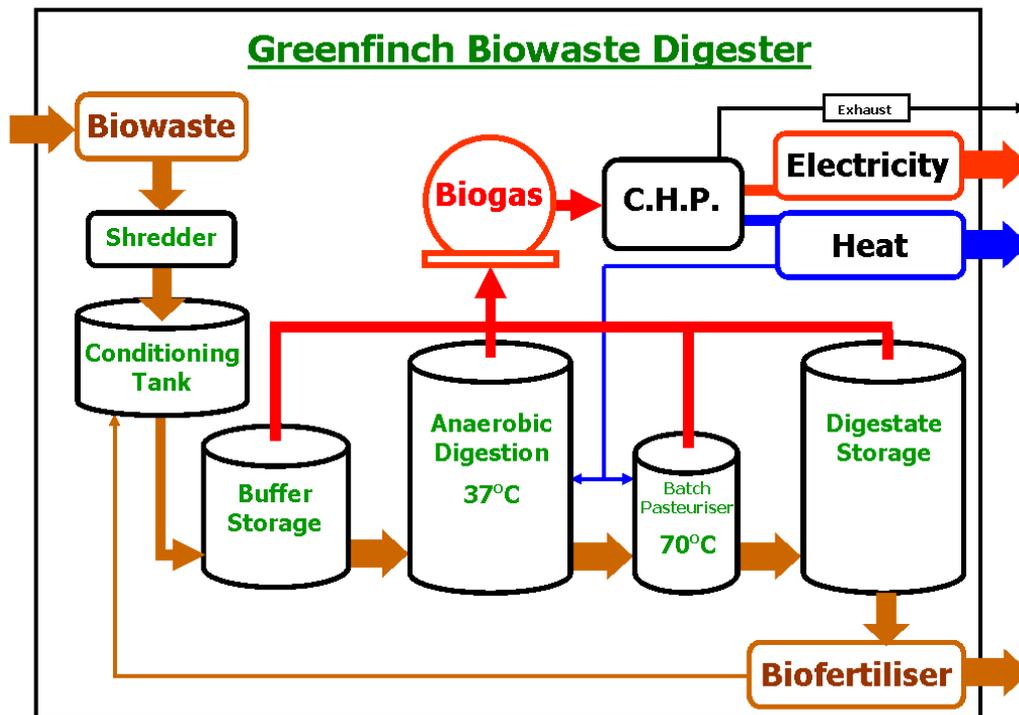


Fig 5.1 Schematic of the Biogas South Shropshire plant (courtesy of Greenfinch Ltd.)



Fig 5.2 The South Shropshire Biogas digester a) building and tanks b) delivery lorry c) waste food in biodegradable bags d) first hopper / shredder e) 900m³ digester and smaller pasteurisation tank f) gas holder g) plant room h) CHP engine i) dried digestate

The biogas is used to power the on-site CHP engine which at 85% efficiency delivers 32% of its energy as electricity at a constant output of 200kW_e , and 53% as heat, therefore 330kW_{th} . The electrical output of 200kW is estimated to be sufficient to power 80 homes. The CHP unit runs off biogas directly, the biogas containing 60% methane, 40% carbon dioxide, and some trace elements such as hydrogen sulphide.

A proportion of the heat is used on-site to heat the digester and pasteurisation tank. The biogas is also used to mix the digester contents by bubbling it up through the tanks. As the AD is by definition a sealed unit, and with a few simple precautions to minimise smells from the deliveries, the level of odour is low, and it is perfectly acceptable to situate this type of process alongside manufacturing businesses in a small industrial estate, for example. The collection, handling and running of the AD plant has resulted in the creation of 3 new jobs in Greenfinch's growing workforce.

5.2.2 The Western Isles Council, Anaerobic Digester / Municipal Waste Treatment Centre, Isle of Lewis

Remote and sparsely populated rural areas of mainland Scotland and the Scottish islands share some of the challenges of both energy supply and waste management. The Western Isles provide a good example; while around one half of the islands' 28,000 population is concentrated in and around Stornoway on the Isle of Lewis, the remainder are spread over 3,000 sq km of rugged and windswept terrain, on a group of islands stretching over 230 km from end to end. The mainland of Scotland is 55 km away at its closest point. However, although the EU Landfill Directive and the Scottish recycling targets apply equally here as they do throughout the rest of Scotland, the logistics of waste collection, recycling, treatment and disposal are relatively more difficult.

Neither anaerobic digestion nor composting alone were seen as an adequate solution on their own to this waste management issue and the Western Isles has therefore attempted to find a solution that allows it to be almost totally independent in the way that it treats and disposes of its waste, whilst meeting the fundamental driver to satisfactorily meet the landfill-diversion targets allocated by the Scottish Government (Recycling and Waste World, 2007).

Earth Tech UK, in conjunction with its technology partners Linde, a Germany company specialising in AD and HotRot, a Norfolk based company using New Zealand technology, have come together and developed a £9.8 million waste treatment facility. The project was managed from inception to delivery by Uisdean Fraser, now a Director with Synergie Scotland in Inverness.

The system is designed to treat 20,000 t of household waste annually. It has an AD capacity for 8,500 t of source separated bio-waste (kitchen waste, paper/card and garden waste) combined with In-Vessel Composting (IVC) process for the treatment of the organic fraction of the residual waste (4,000 t pa) (Fig. 5.3). The plant produces 'green' electricity as well as high-grade compost. Both processes are fed via a common front-end reception and pre-treatment stage, which will feed the AD for two hours per day, and the IVC for

the remaining six hours of the working day. It is the AD part of the plant that is of most relevance to this review; the organic waste is crushed and screened before it is fed into the digester chamber. The retention period is not less than 25 days and the digester operates in the thermophilic range ($\geq 57^{\circ}\text{C}$). The digestate passes through a two-stage de-watering process firstly in a screw-press and then in a decanter centrifuge before the material then goes for maturation. Ultimately the digestate is to be used as a high grade soil improver and the liquor as a liquid fertiliser. The bio-gas produced is first filtered and cooled before it is passed through a de-sulphurisation unit. It is stored in a 400 m³ double membrane external gas holder and is used to power a 290 kW CHP engine. A portion of the heat is used on site in the process and administration block and there are further plans to use the excess heat in a local hydroponics scheme. The scheme provides the islands with self-sufficiency in waste management and significant employment opportunity (approximately 30 jobs to date, in collection, sorting and plant operation, U. Fraser pers. comm.). In addition there is the potential for long term improvement of crop growing capacity through soil improvement and therefore a significant contribution towards more sustainable practices in the Western Isles. Furthermore, and while not part of the core scope of supply, the plant has been designed in such a way as to be able in future to receive and digest fish waste, one of the largest commercial waste streams on the Western Isles, and one which currently is being exported off the islands for treatment and ultimate disposal.

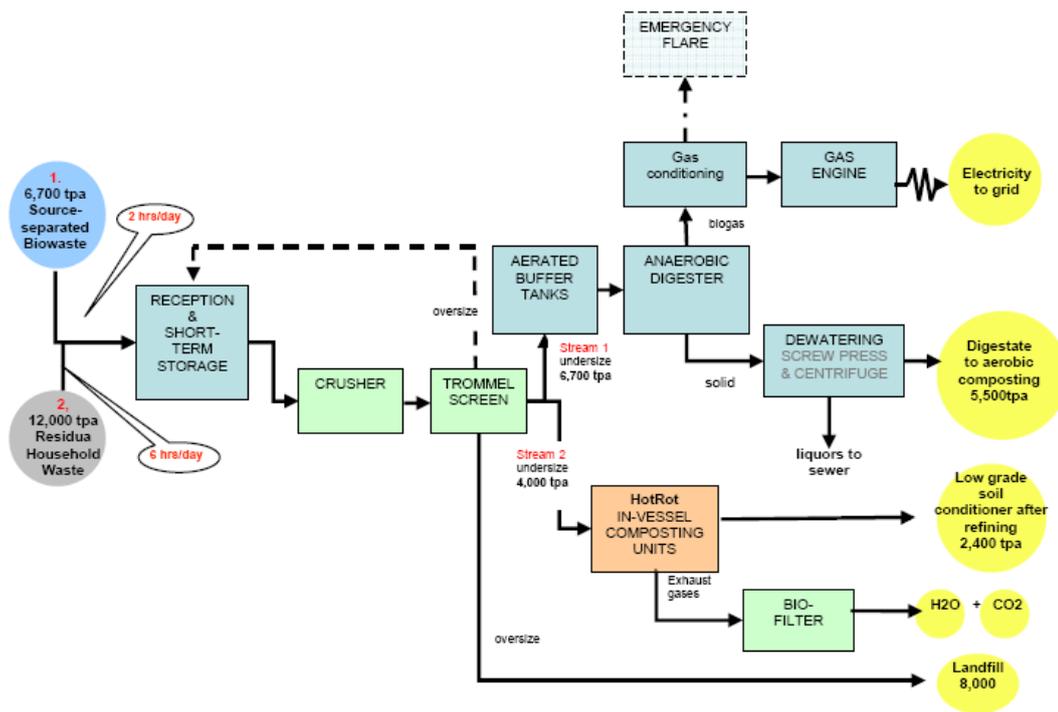


Fig 5.3 Process flow diagram for the biological treatment process (Courtesy of Uisdean Fraser, Synergie Scotland)

This is the first commercial-scale waste treatment facility in the UK to generate renewable electricity by the dry anaerobic digestion of source-separated kitchen and other organic waste. Notably there has been a complete absence of any adverse public reaction to the new plant, something that is almost unheard of for this type of development. The facility, when fully commissioned, will allow the Western Isles to fully meet its waste management and environmental needs, exceeding landfill diversion targets to such an extent that the council will be able to generate revenues by trading its surplus allowances under the landfill allowance trading scheme (LATS). It is also an overall net producer of electricity from renewable sources.

5.2.3 The Meikle Laught, Ayrshire, on-farm cow slurry biodigester

This case study is presented as an example of a highly automated and self-contained unit operating with a lower energy feedstock, and which as a consequence is used to provide only heat and is not producing surplus electricity for sale. In fact a dairy-farm based digester working at capacity has a parasitic energy requirement with an equivalent energy value of generally less than 10% of total methane production (J. Gasgoine, Greenfinch, pers. comm.). The Meikle Laught farm, near Saltcoats in Ayrshire has a herd of approximately 110 dairy Ayrshire cows. The soils of the region tend to be heavy and not particularly permeable and consequently raw slurry applications can result in run-off to the local receiving waters, including the designated bathing beaches of Saltcoats. It was this type of agricultural run-off which was the suspected source of the high numbers of faecal-indicator bacteria found in, and hence down-grading the quality of, the local bathing waters. In 2004, the Scottish Executive therefore selected seven farms in the region and offered to install on-farm AD systems in a scheme whereby the AD plant will actually be owned and maintained by the Scottish Government for five years after which the farmers will have the opportunity to buy the system at its current market value. Greenfinch Ltd, who designed and installed the systems, also have the contract to maintain them over the five year period. The installation of the bio-digesters had a positive impact on the quality of the local bathing waters in a similar project (Sandyhills beach on the Solway).

The 110 Meikle Laught cows produce around 10t of slurry (approximately 6% dry matter content) per day. In the summer months when the cows graze on pasture the slurry is only collected during the morning and evening hours when they are in the dairy; in the winter however the cows are indoors all the time, housed over slatted flooring, beneath which the slurry collects in tanks before it is pumped to the holding tank (800 m³). Therefore, prior to the installation of the AD, there was only storage for around 80 days before it became necessary, regardless of the weather and soil conditions at the time, to spread the raw slurry on the land.

Now however, the slurry is pumped as required from the storage tank to the 80 m³ feeder tank, and then into the 200 m³ digester. The digester is fed, mixed, heated and the gas collected in an entirely automated and computer controlled system housed in a cabin between the feeder and digester tanks (Fig 5. 4). The pump which feeds the digester has an in-line macerator which reduces the slurry solids to 10 mm. The pump runs for approximately 1 minute every hour, feeding approximately 0.5 t of slurry to the digester in each pumping interval. The gas from the digester is collected in a gas holder which is simply constructed from two fibreglass tanks, the upper one inverted and floating on the lower, and buoyed up by the gas it contains (Fig 5.4e). The digester contents are mixed by bubbling biogas from the gas holder back through the digester, the digester is also fitted with a safety gas-vent and a condensation trap. The biogas also powers a gas-boiler, which both heats the digester and provides the hot water needs of the household and dairy. The cabin also contains the gas boilers, pumps and heat exchangers which warm the slurry in the digester to 37°C. The control panel illustrates the degree of automation and the level of information provided for the operator by this computer controlled system. The average total cost of the AD system installation across the programme was £240,000 (J. Gasgoine, Greenfinch pers.comm.).

The gas output (quality and volume) depends on the quality of the slurry going into the system and this varies according to season, and the fodder the cows are receiving. The slurry tanks also receive the washing water from the dairy and certain percentage of rain water as the feed tank and slurry store are open to the elements (Fig 5.4). The slurry has a total solid (TS) content typically around 6% (the figure achieved after a sample is dried to a constant dry weight at approximately 100°C). On this basis a 250 m³ slurry digester, receiving 10 t of slurry every 24hrs and operating at 39°C would be expected to deliver in the region of 8 m³ of biogas (at a total methane content of 60-65%) per hour. The system is designed to have a 20 day retention time, to maximise the reduction of the faecal-indicator bacteria in the digester. The digestate is stored in a 1000 m³ capacity tank and can be spread by a conventional slurry-spreader. The digestate, which is thinner than raw slurry,

is absorbed into the ground more rapidly. There is an additional benefit in that the nutrients of the digestate are more readily plant-available than those in raw slurry. The farmer can hence have an additional saving on the costs of chemical fertilisers. Running on cow slurry alone, this scale of digester is not generating sufficient quantities of biogas to produce electricity, and at present powers only gas boilers for hot water supplies. Therefore there are electrical energy costs associated with running this plant which functions primarily as a waste disposal system.

However, in AD technology at present more attention is being given to co-digestion or the use of a mixture of feedstocks, combined to provide the optimum 'diet' for the digester's gas output. This requires analysis of the feed stock so that the C:N ratio can be appropriately balanced. The Greenfinch advisor is suggesting that the farmers add a small quantity of glycerol to their digesters. Low-grade glycerol is a by-product of biodiesel production and the addition of as little as 4% can double the gas output of a cow slurry digester. Research from German farms suggests that up to 10% by volume allows for the highest efficiency.



Figure 5.4 Meikle Laught on-farm biodigester a) 200m³ digester tank, plant cabin and conditioning tank b) raw slurry in conditioning tank c) digestate d) plant in cabin, showing control panel, gas boiler and heat exchangers e) digestate storage tank, gas skids and gas store

5.3 Analysis

5.3.1 Data comparison

Data on methane yields from feedstocks are often described as the output of methane in $\text{m}^3 \text{kg}^{-1}$ of VS where VS (volatile solids) are expressed as a percentage of the TS (total solids), and the VS is the weight of organic matter minus any inert matter in the sample (also termed the ash-free dry weight).

Chynoweth et al., (1987) describes the production of methane from *Laminaria saccharina* in these terms and illustrates how the TS content varied from 9.9 to 24.6% and that methane yield appeared to be affected by whether the plants were in low, ambient or high light regimes as well as by whether or not they received artificial fertilisers. The average methane yield over all the conditions reported here ($0.27 \text{ m}^3 \text{ kg}^{-1}$) (Table 5.1) compares with the figure of $0.22 \text{ m}^3 \text{ kg}^{-1}$ re-calculated from the semi-commercial scale trials on the same species of seaweed (assuming a TS of 10% of the initial wet weight) as reported from Matsui et al., (2007) (Table 5.2).

Table 5.1 Data from Chynoweth et al., 1987. Composition of *L. saccharina* and *Macrocystis pyrifera*.

Light conditions	Fertiliser applied	TS (as % of wet weight)	VS (as % of TS)	Methane yield $\text{m}^3 \text{ kg}^{-1}$
<i>Laminaria saccharina</i>				
Ambient	Yes	16.6	78.6	0.26
High	No	23.5	82.5	0.29
High	Yes	24.6	83	0.29
Low	No	18.9	75.6	0.24
Low	Yes	20.6	76.2	0.26
Ambient	Yes	10.4	61.8	0.26
Ambient	No	9.9	60.4	0.30
<i>Macrocystis pyrifera</i>				
Ambient	No	12.6	60.2	0.43

Table 5.2 Comparative data on methanisation of macroalgae

Species	Source	Available information		Methane yield m ³ kg ⁻¹ VS added
<i>Laminaria saccharina</i>	Chynoweth et al., 1987. (lab. scale)	TS (as % of wet weight) 9.9	VS (as % of TS) 60.4	0.30
<i>Macrocystis pyrifera</i>		12.6	60.2	0.43
<i>Gracilaria tikvahiae</i> clones	Bird et al., 1990 (small lab. scale)			0.28 – 0.40
<i>L. digitata</i>	Morand et al., 1991 (pilot scale)	30 m ³ digester fed 1-1.5 t day ⁻¹ , producing 29.8m ³ methane over final 21 days		0.5 (close to theoretical yield therefore some doubt over accuracy)
Following 3 examples as cited in Morand et al., 1991				
<i>L. saccharina</i>	Troiano et al., 1976;	Digester volume 50l, 37°C Completely mixed		0.22 / 0.20
<i>L. saccharina</i>	Asinari et al., 1981 ;	Digester volume 2l, 35°C Completely mixed		0.25
<i>L. saccharina</i>	Hanssen et al, 1987	Digester volume 8l, 37°C Completely mixed		0.23
<i>L. saccharina</i>	Matsui et al., 2007 (pilot scale)	TS 1-5% <u>after</u> addition of diluting water. 1 t wet weight added day ⁻¹ to 30m ³ methane fermenter, 22m ³ day ⁻¹ over 150 days (15 – 25 day HRT)		0.22 calculated from an estimated 10% TS pre –dilution, and value of 22m ³ CH ₄ t ⁻¹ wet weight

5.3.2 Costs of seaweed culture

Currently the South Shropshire Biogas plant charges the local council for every load of organic waste delivered. If the proposed seaweed fuelled AD facility was to operate as a stand alone commercial enterprise, it would have to purchase its feedstock from the growers and this cost should be factored into the economic assessment.

Sanderson (2006) estimated the costs of setting up a one ha seaweed farm, based on a detailed breakdown of the costs per 40 m longline (surface barrel-floats, headline, anchor rope, stainless steel swivels, thimbles for splicing, shackles and mooring blocks) of £2382.49, depreciated over 5 years, together with approximations of other annual costs. Following on from these assumptions he estimated the one ha plot would have to yield worth 130 t wet weight, worth £500 t⁻¹ to break even. While clearly many of his estimated costs will be affected by economies of scale, presumably advantageously, it is worth noting the RCEP (2004a) report priced cultured energy crops (willow, miscanthus and wood pellets or chips) suited for energy generation via combustion at £40-80 t⁻¹ (oven dried) and forestry and agricultural residues priced at £15 t⁻¹ (oven dried). What is required now are accurate costs of the production of seaweed biomass on a large scale and a comparative study on the relative costs per unit of energy (methane) recovered from supplying the AD facility with a similar amount of dry matter from a marine and a terrestrial crop.

While the data from a wide range of studies (Tables 5.1, 5.2) indicate the methane yield from macroalgal feedstocks is relatively well established, the costs of production of macroalgae from large scale cultures in a UK context has not been evaluated. Table 5.3 gives a preliminary comparison of terrestrial and marine feedstocks based on such figures that are available but also assuming the costs of *L. saccharina* production on a commercial scale would be similar to those for fodder beet.

Table 5.3 Comparative data on energy output from different feedstocks compiled by Lucy Lewis, Greenfinch Ltd; *Laminaria saccharina* values derived from Chynoweth et al. (1987), values in lightly shaded sections are estimates and will vary with growing conditions. Values in the darkly shaded areas are based on the unsupported assumption that the cost of *L. saccharina* production* will be equivalent to that of the most expensive terrestrial crop used in the comparison.

	Maize	Ryegrass	Fodder Beet	<i>Laminaria saccharina</i>	Units
Crop Yield	45	56	86	150	tonnes/ha/year
% Dry Matter	30	20	17	10	%DM
%Oven dried matter (ODM)	95	88	90	75	%ODM
Methane Yield	370	340	410	270	m ³ CH ₄ /tonne ODM
% Methane	55	55	55	60	%CH ₄
Cost of Crop Production	720	800	1,000	1,000*	£/ha/year
Tonnes ODM	12.8	9.9	13.2	11.3	Tonnes ODM/ha/year
Methane Production	4,745	3,351	5,423	3,038	m ³ CH ₄ /ha/year
Methane Production	105	60	63	20	m ³ CH ₄ /tonne Crop
Biogas Production	8,628	6,093	9,860	5,063	m ³ Biogas/ha/year
Biogas Production	192	109	114	34	m ³ Biogas/tonne Crop
Electrical Output	1.7	1.2	2.0	1.1	kWe/ha
Electrical Output	15,058	10,634	17,209	9,639	kWh/ha
Cost of Crop Production	16	14	12	7	£/tonne
Cost of Crop Production	56	81	76	89	£/tonne ODM
Cost of Methane from Crops	15	24	18	33	pence/m ³ CH ₄
Engine Efficiency	85.0	85.0	85.0	85.0	%
Electrical Efficiency	32.0	32.0	32.0	32.0	%
Thermal Efficiency	53.0	53.0	53.0	53.0	%
Average House consumes	4000.0	4000.0	4000.0	4000.0	kWhr/yr
Number of hectares/house	0.3	0.4	0.2	0.4	

5.3.3 Nutrient availability for seaweed culture

Data from research at SAMS (Sanderson, 2006; Dworjanyn, unpublished) indicates that at certain times of year seaweeds grow best when they are in proximity to sources of additional nutrients, for example, salmon farms. To achieve maximum yields it would therefore be necessary to site seaweed farms close to nutrient sources or in areas of high primary productivity. Additional nutrients enter the sea from acid rain and rivers enriched with (treated) urban sewage, farmyard waste and drainage from fertilised soils. In the north and west of Scotland, fish farms are the most important source of extra nutrients in lochs and voes (Black et al., 2001).

Sanderson (2006) estimated the amount of nitrogen a one ha plot of *L. saccharina* would remove, at harvest, assuming a range of possible nitrogen content of dry *L. saccharina* from 1 -3 %, a varying yield for the one ha plot from 40 – 260 wet t ha⁻¹ and the dry: wet weight ratio as 1:9. The one ha plot was assumed to be made up of 40, 100 m longlines with vertical droppers attached. The nitrogen removal is expressed as a percentage of that derived from the production of 500 t of salmon over a two year production cycle and a food conversion ratio of 1.2: 1. So there is an assumption that 23 t dissolved nitrogen (46 g soluble N in every 1200g feed) are lost to the environment and are 'plant available' per production cycle, and that there are two crops of *L. saccharina* in this time frame (Black, 2001).

At the range of values most likely to be encountered (shaded values, Table 5.4). The one ha plot would remove 1.4 – 5.3 % of the nitrogen resulting from the 500 t salmon farm operation. The 500t unit represents approximately 0.36 % of the annual Scottish production of salmon of 137,000t (projected production, FRS, 2006). To remove all of the additional nitrogen resulting from this level of production, would require between 19,571 and 7,820 ha of seaweed culture. Assuming an average value of 3.5 % nitrogen in the seaweed at a production level of 180 t ha⁻¹ wet weight would require 14,412 ha (144 km²) of seaweed production.

Table 5.4 Percentage of salmon farm derived nitrogen (N) theoretically removed by harvest *L. saccharina* assuming the production of 500 t salmon results in the loss of 23 t of N to the receiving waters over a 2 year production cycle. *L. saccharina* yields range from 40 – 260 t ha⁻¹ and N values from range 1 – 3%. The shaded area indicates actual % N values measured for *L. saccharina* during the course of the study. (Sanderson, 2006).

	% N in harvested <i>Laminaria saccharina</i> plants (dry weight and wet: dry weight ratio 1:9)				
Yield t ha ⁻¹ wet weight	1	1.5	2	2.5	3
40	0.4	0.6	0.8	1.0	1.2
60	0.6	0.9	1.2	1.4	1.7
100	1.0	1.4	1.9	2.4	2.9
140	1.4	2.0	2.7	3.4	4.1
180	1.7	2.6	3.5	4.3	5.2
220	2.1	3.2	4.3	5.3	6.4
260	2.5	3.8	5.0	6.3	7.5

In areas outwith the Scottish highland and islands it might be possible to link in-shore seaweed cultivation to areas identified by the Scottish Government as Nitrate Vulnerable Zones (NVZs), where higher levels of nitrate rich runoff from agricultural land reach receiving waters. In accordance with the requirements of the European Commission's Nitrates Directive 91/676/EEC, four areas of Scotland were designated as NVZs in 2002-03: Moray, Aberdeenshire, Banff and Buchan; Strathmore and Fife; Lothian and Borders and Lower Nithsdale (Scottish Government, 2007).

6. RESEARCH RECOMMENDATIONS

The previous sections of this report have attempted to re-introduce the concept of marine biomass as a biofuel, to illustrate the extent of the literature already existing on this subject and to emphasise that it is probably as good a feedstock for AD/methane production as many terrestrial plants and some anthropogenic, or terrestrial agricultural wastes. The further research recommendations can be categorised as those relating to 1) obtaining the seaweed biomass 2) then optimising the methane (or other energy carrying) output from that biomass 3) the economic aspects of installing the infrastructure required to farm at sea, to process the biomass and the socio-economics of large scale seaweed farms. As many of the factors in the first of these two categories will influence the last one, the emphasis in this report is on issues surrounding obtaining the biomass and optimising the methane output. The recommendations for each category are listed in order of priority but recommendation 1 below is considered prerequisite for the others

1. As a starting point for introducing the concept of marine energy crops there is a recommendation for establishing a government/industry forum, where representatives from all parts of a potential marine biomass energy supply chain (academics, farmers, transporters, generators, construction companies, local councils, central government policy makers and end users) could identify problems, share solutions and make recommendations. The first task of such a Marine Biomass/Biogas forum would be to tightly define the prime purpose for a marine biomass/biogas industry, and to prioritise its aims in terms of providing:
 - a) a carbon neutral energy source
 - b) a source heat, power or fuel for remote communities
 - c) a means of generating or diversifying employment in economically fragile areas
 - d) providing economic return on investment

The forum would then be able to direct future research. However, care should be taken to ensure research activities are not restrained by local political activities. A strategic and long term view on sustainable and intelligent exploitation of a natural resource should be formed by sector leaders, with input from a public forum.

6.1 Obtaining the seaweed biomass.

Utilising marine as opposed to terrestrial biomass for methane energy production circumvents the growing problems surrounding switching agricultural land from food to fuel production. In addition, the production of marine biomass will not be limited by freshwater supplies, another of the contentious issues behind increasing terrestrial biofuel production. If these seaweeds are to be cultured in huge quantities, as required for bioenergy, rather than harvested from the wild, the cultures might conceivably influence the marine environment on a scale as yet unknown. Licensing large seaweeds farms within the strictures of today's legislation would be challenging and support for the production of marine biomass on any scale will require political will. Therefore a massive change is required in what we perceive to be an acceptable use of our marine resources. There is the potential for conflict with other user groups. However, cynically, one might forecast that rapid alterations to our lifestyles and amenities, forced by a shortage of hydrocarbon fuels, will be one of the main drivers in rapidly altering our perceptions as to what is an acceptable degree of use of the marine environment for farming.

Some regard the seas as the last unexploited resource, however this is far from the case as even a casual appraisal of any marine ecosystem report will advise (RCEP, 2004b; Clover, 2004). The large scale culture of seaweeds may prove to be a relatively environmentally inert practice, or even to be beneficial in terms of the sequestering of carbon, providing habitat for fish, increasing biodiversity and extracting nutrients of anthropogenic, agricultural or aquacultural origin from the marine environment. There are hydrographic considerations as to where such farms should be sited; an area of relatively

strong tidal exchange is desirable, bringing a constant supply of nutrients to the plants. The farm should not impede water exchange to onshore areas. The effect of the farmed seaweeds reducing the level of light penetration and their competing with phytoplankton for nutrients should be considered.

Kelp forests typically have high biodiversity; acting as nursery grounds or providing habitat for a large number of species. If a wild harvest were to be contemplated then this would have to be developed with strict controls in place to ensure that even, for example, the five year rotational harvesting plan as used by the Norwegians, would not affect the wider kelp community. The sensitivity of different locations to harvesting, and data set in a Scottish context, are poor or lacking.

The west coast of Scotland is the part of the UK most obviously suited to large scale aquatic farming; its heavily indented coastline and relatively clean waters mean that it is already home to 95% of the UK's aquaculture both by value and volume. However, the creation of other large offshore infrastructure, such as wind farms, and the continuing research effort into developing offshore aquaculture methods (Buck and Buchholz, 2004) may allow for the culture of large expanses of seaweeds, out of sight from the shore and of those who might consider them aesthetically unpleasing.

There are no major biological problems to overcome with regard to seaweed culture, it being well established at a commercial scale in many countries and progressing already on a research scale in Scotland. Past pilot aquaculture projects have shown that the smaller the trial farm is, the greater the likelihood of making scaling mistakes when data are extrapolated upwards for costing commercial operations. The estimated costs generated by Sanderson (2006) are almost certainly over estimates, and could be considerably lower given economies of scale. There is certainly the opportunity to avail of technology transfer from countries where seaweeds are cultured on a massive scale, for example, China. As there is a major difference in the costs of labour between the UK and China, further mechanisation of the culture methods would be vital to help alleviate labour costs in the UK. There may be suitable technologies in

the mussel industry for handling and harvesting longlines that could be adopted.

The potential tonnages obtainable from each method (culture versus wild harvest), within strict environmental boundaries, should be ascertained. Hard data should be collected from trial farms and trial harvest plots in Scotland.

2. There is a research requirement for a semi-commercial scale farm, to allow the development and streamlining of technologies for the grow-out phase and to provide realistic data on infrastructural and operational costs as well as to return biological data on yield, biomass quality, and nutrient up-take. Any trial plot should be relatively large, probably several hectares, and there should be replicate plots experiencing different environmental conditions and stresses. The design, costing, construction and operation of a trial farm should be done in close cooperation with experienced aquaculturists, drawing from existing seaweed industries of China and from industries in this country with related technologies, such as the long line mussel industry. The plot would allow the ground-truthing of data required for research requirement 3, below. Hydrographic data for the potential locations would be advantageous for site selection. A selection of species should be cultured to assess their suitability, robustness and performance in a larger scale farming scenario. The optimisation of farm size in economic terms must be balanced against the potential environmental cost (depletion of nutrients, shading, altering hydrography, etc.).
3. A survey of the larger and accessible kelp beds identified in Section 4 should be conducted to assess their current status. Small scale trials should be initiated to determine re-growth rates and productivity, and to allow estimation of the quantity that might be sustainably harvested from well managed beds and of the best times to harvest. Comparisons should be made of harvested and untouched beds.

4. A full Environmental Impact Assessment (EIA) is required of the effect of large scale seaweed aquaculture versus seaweed harvesting, based on data collected in Scotland and drawing on the ecosystem data from China (culture) and Norway (harvesting). The environmental impact of collecting storm cast kelps from beaches should also be considered.
5. A provisional estimate should be made as to the hectareage theoretically available for seaweed culture, given the physical restrictions for farm-site selection including hydrography, bathymetry and degree of exposure.
6. A key objective for marine biomass energy must be improvements in crop yield. There is undoubtedly potential for improving biomass yields through selective breeding of seaweeds or genetic manipulation, and research should be initiated with this intention. Plant breeding could lead to better seaweed morphologies and superior growth rates at higher plant densities. Opposition to the sea-based culture of selected strains of native macroalgae should be resisted, and a parallel made with the development through selective breeding of other aquatic and terrestrial crops to improve yields, etc. Clearly the use of GM strains would be more controversial.
7. A further and urgent research requirement concerns the continuity of supply; to maximise output the AD system must run continually which means it must be fed daily. Preliminary data generated at SAMS suggests that the seaweed harvest is primarily an annual (summer) event with the possibility for a second, smaller, autumn harvest. To guarantee continuity of supply techniques to permit multiple harvests, the storage of biomass, supplementation of biomass from wild harvest (perhaps over winter / spring) or the use of other feedstocks are required.
8. The potential for producing large volumes of seaweeds in continuous tank or open pond-based culture systems, where aerated tumbling

cultures are fed nutrients (nitrogenous-rich waste from agriculture or sewage sludge mixed with seawater) should be assessed but through a series of smaller scale trials. The culture tanks should be insulated, heated and illuminated. A weekly harvest could be fed directly to an adjacent digester. Heat generated from the methane output of the AD system could be used to heat the culture tanks. To minimise the energy needs for aerating, lighting and heating the cultures, the systems should be constructed to avail of other renewable energy sources (wind and solar). Such systems may not be economically viable unless the production of high value by-products i.e. vitamins, plant hormones, pharma/nutraceuticals are facilitated by the more controllable systems.

6.2 Maximising methane yields

Each of the topics in sections 3.2.1 – 3.2.10 translates directly into an identifiable research need for maximising the efficiency of the AD process, in addition to a number of others identified throughout the course of the review, these are summarised below.

9. Chynoweth et al. (1987) report on Anaerobic Biogasification Potential (ABP) assay to determine the suitability of biomass for biogasification (Figure 6.1). It is proposed that this evaluation should be performed on each identified candidate species from Scotland. The process begins with a simple ABP assay of test feedstocks under ideal conditions. Low conversion efficiencies may lead to an evaluation of the effects of various pre-treatment techniques or screening for the presence of inhibitors in the feed; poor results in the screening tests may lead to the decision to terminate work with that feedstock. High conversion efficiencies would support the continuation of research to bench or process development stages.
10. The assessment of pre-treatments, to maximise methane yields, are required such as a) mechanical treatment (simple chopping, crushing or ultrasonic grinding) b) enzymatic c) heating d) spontaneous pre-

treatments such as natural hydrolysis. Pre-treatment is also the stage at which value-added compounds may be extracted before sending the processed material to energy generation.

11. Biomass composition: seaweeds with high ash content have lower volatile solids (VS) content. Methane production has been positively correlated with mannitol content in *Macrocystis pyrifera* and further research is required to understand the relationship between nutrient supply and nutrient content of other species. Biomass composition within species is also known to vary considerably depending on growth and time of harvest; levels of light and the addition of fertilisers to seaweeds in culture may also affect their biodegradability and methane yields. There is a research requirement to explore ways of maximising levels of storage polysaccharides (mannitol and laminarian) from seaweeds cultivated in Scotland. It is necessary to monitor levels over a season, across geographic locations and plant life history stage, to correlate this with nutrient levels, time of harvest, harvest method and handling techniques.

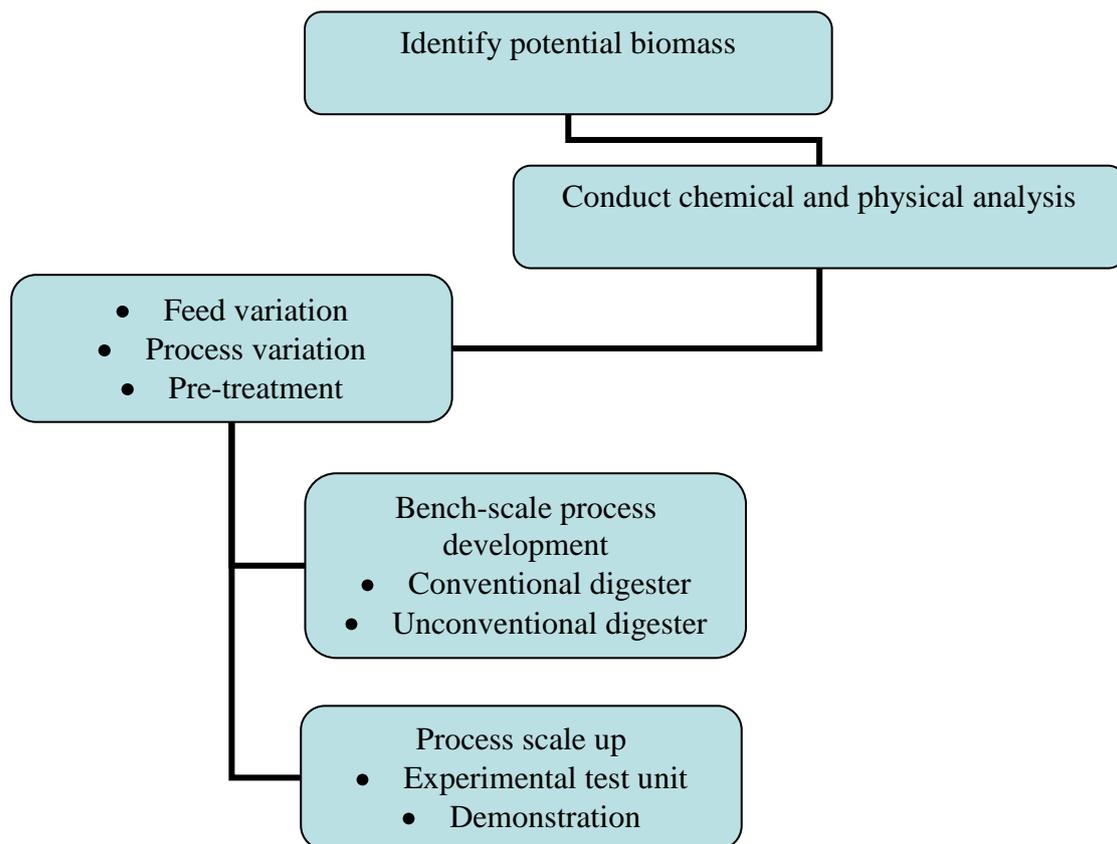


Figure 6.1 Approach for development of a process for anaerobic digestion of biomass (adapted from Chynoweth et al., 1987).

12. Toxicity: Inhibition of methanisation can result from high concentrations of substances such as phenols, heavy metals, sulphides, salts and volatile acids. The AD process for each species under trial has to be optimised in regard to each of these potential contaminants. In the seaweeds which seem the most likely candidates for the next phase of research in Scotland, phenols are a possible cause of disruption of the AD process. A series of experiments are required to assess if certain post-harvest practices reduce phenol levels and to assess where the phenols are concentrated anatomically in the plants.

13. Inoculum: The potential for enhancing gas production with an inoculum containing marine bacteria should be investigated. It may be possible

to screen for and isolate bacteria that are better able to digest specific phycocolloids and accelerate biogas production.

14. Temperature: Little or no justification for the use of thermophilic bacteria has been reported for digestion of seaweeds. However, this should be re-appraised for each of the species under consideration. The economic viability of thermophilic systems may be adverse to their widespread application, but advanced modular AD systems may make better use of heat and so temperature effects are important in the context of the proposed studies.
15. Elemental ratios: Nitrogen is the major nutrient, other than carbon sources, that is needed for AD. Chynoweth (1987) found the methanisation of *Laminaria* sp. was highest when the C/N ratios were low. However this should be characterised and optimised for all potential seaweed substrates.
16. Digester 'Diets': The impact of modifying C/N/P ratios through mixing seaweed biomass with other substrates, such as municipal sludge waste or manure has been examined with mixed results, and should be re-evaluated for the seaweeds under consideration. The ability to mix algae with other feedstocks and to understand the operation of digesters under this varying load is important. The effect of digesting mixed seaweed populations, such as those that might be acquired from natural settlement on culture ropes should also be assessed. This in essence leads to the design of specific 'diets' for a digester based on the nutritional composition of the basic feedstock. Relatively small additions of other substances (preferably wastes from another process, e.g. glycerol a by-product of the production of biodiesel) could possibly be used to great advantage in increasing methane yields. Similarly the residues from the alginate extraction industry, rich in mannitol and laminaran should be assessed as performance enhancers in modern digesters. Additional feedstock enhancers could include fish and

shellfish wastes, particularly where seaweeds are produced in integrated systems (see recommendation 25 below).

17. Reactor types: Data is required on the performance of seaweeds in modern digesters, such as those used by Greenfinch Ltd. to test a variety of wet-crops. These intermediate scale 1000l capacity digesters are equipped with gas counters and use some of the biogas produced to continuously stir the reactors. The performance of seaweeds in other reactor types should be explored, however it should be noted that centralised AD (CAD) facilities are capitally expensive and this has hindered the growth of AD technology in the British Isles. This study should focus on smaller, higher throughput systems designed for sustainable communities.
18. Use of the digestate: Early work proved that the liquid and solid residues of the red algae *Gracilaria tikvahiae* were an excellent source of nutrients for the cultivation of the seaweed itself. Further research is required on the potential to add value to the digestate of species such as *L. saccharina*. However where the digestate has been generated from a mixed feedstock, particularly one containing animal or human waste, then some forms of re-use will be prohibited.
19. Ethanol production: Novel isolates of marine bacteria should be screened for ethanol producing capability based on their ability to mitigate the effects of polyphenol-induced inhibition and their adaptability to grow and produce biofuel under the high salt concentrations inherent to seaweed biomass and its extracts. Chemical mutagenesis and the subsequent selection of mutant strains displaying improved rates and yields should be adopted.

The gut flora of seaweed-grazing sheep (from the Orkney Islands) is currently being investigated for their ethanol fermentation capability, as part of the SUPERGEN Marine Biomass project (J. Adams, Aberystwyth University, pers. comm.).

6.3 Economic appraisal

It is hard to assess the economic viability without accurate figures on the culture costs of seaweed production, potential productivity and methane yield. These could, in part, be derived from scale trials (recommendations 2 and 3) combined with an assessment of cost-reduction through the economies of scale. Clearly seaweed cultivation is economically viable in parts of the world where labour costs are relatively low and where the seaweeds are destined for a relatively high value end use such as food or for the alginates industry. Further information on likely production costs in a UK context could be extrapolated from the Chinese experience, adjusting for differences in labour costs and the degree of mechanisation. Culturing seaweeds will incur costs just like the culture of any terrestrial crop, for seed supply, infrastructure (longlines), planting out, maintenance of the crop, harvesting, storage and transport. Unlike terrestrial crops, where seaweeds are cultured on a large scale, they are not treated with fertilisers, pesticides or selective herbicides. It will be necessary to review the comparative costs of marine versus terrestrial production of a biomass crop, in terms of either dry matter produced or the net value of the crop per ha, after labour and operational costs.

Aquaculture producers will not embark on energy-crop cultivation unless it provides an adequate return. For terrestrial farmers the Energy Crops Scheme (currently under review for a new programme) intended to encourage farmers and end users to work together to ensure supply and demand were satisfied. It took into account environmental and landscape issues as well as energy requirements. For example, it recognised that short rotation coppice (SRC) crops enhanced biodiversity, attracting a fauna similar to that found in woodland (RCEPa, 2004). In the 2000–2006 scheme, worth £29 million, DEFRA made grants of between £920 and £1600 ha⁻¹ available to terrestrial farmers to support the establishment of energy crops, provided the growers had a contract for the energy end-use of their crops. Grants of up to 50% were available for setting up Willow SRC groups and to help with the purchase of planting and harvesting machinery to be held in common for the

group. The EU Common Agricultural Policy provides two kinds of support, energy crops can be grown on set-aside land (without loss of its set-aside revenue) and on non-set-aside agricultural land they may receive a grant under the CAP of €45 ha⁻¹. Despite the combination of these funds, there has been a slow uptake of energy crop production in the UK, mainly due to the lack of markets for the fuel and issues over long-term investment in crops (that only yield after 5 years for example) affecting farmers' security (RCEPa, 2004).

Before marine energy crops can become commercially viable there has to be a demonstrable market demand for the seaweeds as feedstock for AD plants producing methane. Downstream of this there has to be a need for the methane to power CHP engines to help meet local heat and electricity needs or as transport fuels. In all of the examples in this report the AD plants are running on feedstocks that are wastes, the disposal of which would have incurred costs. This situation needs to change so that AD plants operate at sufficient margins that they can afford to pay for their feedstocks. Further increases in the price of fuels from non-renewable resources may affect this change. A Renewable Obligation credit for energy supplied as heat, rather than just as electricity would also help address the economic balance.

20. A full economic appraisal of seaweed culture for methane production is required. This should cover both the supply side and energy generation (AD) side. The supply side assessment should include the costs of applying for licensing, the cost of EIA's and hydrographic and primary productivity surveys, hatchery facilities to provide seeded strings; installing the long-line system including anchors, buoys and top ropes, labour, boats for deploying seeding strings and harvesting, and boat access. The sea sites would ideally be run by an existing aquaculture company with relevant experience and skilled staff. This should be contrasted with the costs of utilising agricultural land for the production of a similarly rated energy crop. The energy generation side should examine the economics of energy supply (electricity, heat and compressed methane from seaweed as biogas for transport fuels)

where the AD plant has to pay for its feedstock. The potential for the expansion of aquaculture for seaweeds and the associated downstream conversion of the biomass to methane to increase employment opportunities in maritime communities should be included in the economic assessment.

21. As part of the economic appraisal a robust and rigorous examination of the energy budget for each phase of the operation is required.

22. Carbon life-cycle analysis is required.

23. The seaweed supply and the AD side of the business should ideally run as independent and stand alone businesses, the former enhancing profit margins with higher value seaweed products. The cost of installing the AD plant could be assessed accurately once the amount of biomass to be treated daily has been determined.

24. There is a necessity to consider how both location and scale of the planned digesters affects the economic viability. An AD facility, situated close to the production areas (e.g in the Highlands and Islands) and running solely on seaweed incurs the risk of a seasonal supply (depending on the outcomes of point 7 above), and the possibility that the digester is not productive for part of the year. The alternatives are to transport in other digester feedstock, which could possibly seriously erode the carbon benefits of the operation or, site the digester close to other digestible feedstocks (likely to be outwith the Highlands and Islands) and transport the seaweeds to the digester.

If seaweeds were to be produced as part of an integrated system (now also referred to as Integrated Multitrophic Aquaculture or IMTA, Wikipedia, 2008), see also section 5.3.3, other downstream and even onshore production systems, such as growing glasshouse / polytunnel crops could be incorporated. Such systems could avail of the heat produced in a CHP system. The compost/growing medium could be produced from the liquid and

solid residues from the digester, mixed with locally abundant high carbon substrates such as bracken or wood chips. Local production and consumption of the resulting crops would further reduce carbon miles and increase revenue. After use in the polytunnels the compost could be used outside as a soil improver for the production of long cycle coppice such as Alder which can be valuable as a source of high grade charcoal. Similarly, shore-based aquaculture of high value species such as abalone or sea urchins could also use heat from the CHP and the seaweeds grown on the farm are suitable as food for these species.

25. An integrated approach to seaweed farming would assist in attaining economic viability, so seaweeds grown for biomass are simultaneously used as a means of pollution abatement, coastal protection, fertiliser production and the production of other high value raw materials, pharmaceuticals or nutraceuticals.

The socio-economic aspects of the concept need appraisal. The RCEP (2004a) report, that experience in Austria and Sweden has shown that if biomass energy is introduced sensitively and transparently that society welcomes it. However, in Scotland terrestrial wind-farm installations can face public opposition, often based on a dislike of large scale changes in the landscape. Marine conservation/management issues, such as those recently surrounding the proposals for a Marine National Park also incited some debate when put out to public consultation.

26. The development of the concept of marine energy crops should be transparent and aim to achieve stakeholder buy-in early in the process.

27. After a data gathering phase, an expert group should be convened, with local and international knowledge and capable of appraising all aspects of the concept of marine biomass as a source of biogas (perhaps as a sub-group of the forum, recommendation 1). The expert group should deliver an appraisal of the biology, culture and chemistry of the seaweeds, their conversion to methane including the economic

and socio-economic aspects. The group should provide recommendations at government level to deliver a sustainable and value added, vertically integrated industry in this previously undeveloped area of activity.

6.4 Priorities

It would be advantageous if activities were to commence in each of the three categories 6.1–6.3 simultaneously. Recommendations 1, 2, 3, 10, 11, and 20 should be given priority to allow a logical progression to the further recommendations listed in each category.

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