Topic Paper #12

Macroalgae (Seaweeds)

On August 1, 2012, The National Petroleum Council (NPC) in approving its report, *Advancing Technology for America's Transportation Future*, also approved the making available of certain materials used in the study process, including detailed, specific subject matter papers prepared or used by the study's Task Groups and/or Subgroups. These Topic Papers were working documents that were part of the analyses that led to development of the summary results presented in the report's Executive Summary and Chapters.

These Topic Papers represent the views and conclusions of the authors. The National Petroleum Council has not endorsed or approved the statements and conclusions contained in these documents, but approved the publication of these materials as part of the study process.

The NPC believes that these papers will be of interest to the readers of the report and will help them better understand the results. These materials are being made available in the interest of transparency.

New Fuels: Macroalgae

Future Transportation Fuels Study, National Petroleum Council

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What are Macroalgae?

Macroalgae, or seaweeds, are multicellular, macroscopic, marine algae, defined as non-vascular plants. Compared to microalgae, whose production is estimated at no more than 20,000 tons (dry weight matter) per annum, global production of seaweeds exceeds a million tons, and their biomass sells for almost ten-fold less than that of microalgae. Less than 10% of global seaweed production is from the harvest of natural stands. The remainder is cultivated in near-shore plantations, over 80% being produced in China, with the Philippines and Japan being additional major production centers (Bruton et al., 2009). Seaweeds are cultivated near-shore at shallow depth, where the seaweeds can attach to bottom substrates (natural or artificial; seaweeds cannot grow in sandy bottoms), or, at greater depth, where underwater ropes strung out in long lines anchor seaweed to the bottom, typically in areas protected from direct storm surges. Specific cultivation techniques depend on locality and seaweed species.

Compared to microalgae, macroalgae typically have a higher carbohydrate, and lower protein and lipid contents. Carbohydrate percentages in macroalgae can range up to 80% organic matter (ash-free dry weight), though 60% organic matter with contents of about 20% protein and 15% lipids are more typical. Literature reports on composition vary considerably based on methods of analysis, growth conditions, and species studied, not to mention generally uncertain, or even lack of, corrections for ash and water content.

Macroalgae can be divided into three general types: red, brown, and green. Red algae (for example *Gelidum, Palmaria, Poryphyra*) capture light mainly with the reddish protein pigments "phycoerythrins", giving them their reddish color. Some species have been found to live down to 200 meters depth, where light is extremely weak, and which is deeper than any other algal species. Green algae (*Ulva, Codium*) have chlorophyll as the main light absorbing pigments and are typically found in intertidal, shallow water zones. Brown algae (*Laminaria, Fucus, Sargassum*) have a dominant carotenoid, fucoxanthin, as their main pigment for capturing photons. The brown, as the red, algae, can grow deeper than green algae because their pigments are more efficient in absorbing the wavelengths of light not filtered out by the water column. Both red and brown macroalgae, also contain chlorophyll, but mainly in the reaction centers of the photosynthetic apparatus, where photosynthetic water splitting takes place.

Although a few macroalgae are free-floating (e.g. *Sargassum*), most grow attached to some substrate, whether rocks near-shore or on artificial surfaces such as oil derricks. Many macroalgae have very complex sex lives and lifecycles, often with motile spores produced in large quantities that then must find some surface to which to attach.

Previous research on macroalgae biofuels production

The interest in macroalgae for biofuel lies in their high carbohydrate (e.g. polysaccharide) content. Macroalgae were first proposed as a possible source of energy by Howard Wilcox in the late 1960s, who presciently considered their production not only as a solution to the energy crisis but also for global warming (Wilcox, 1975). Much research was carried out by the US during the 1970's and early 1980's to develop open ocean macroalgae farms to produce a substitute for natural gas, an energy source then considered in the USS to be approaching depletion. The Marine Biomass Program, supported between 1979 and 1985 with over $50 million by the U.S. Dept. of Energy (about twice the budget of the 1980- 1996 U.S. DOE microalgae Aquatic Species Program) had as its ultimate objective to replace the entire U.S.

natural gas supply with 25,000 square miles of floating open-ocean farms. The farms would be fertilized via a large pipe by upwelling deep (~300 m) water with wave actuated pumps. The concept was to cultivate the giant kelp *Macrocystis pyrifera*, which was thought to have very high productivity, and for which already extensive experience in harvesting wild stands with specially built ships off the San Diego coast existed. In World War I over a million tons of giant kelp were harvested there and fermented with bacteria to produce acetone, a critical ingredient in munitions for the British Navy (Neushel, for the production of by converted by bacterial . The harvested biomass was to be anaerobically digested to produce biogas. However, the great difficulties of working in the open ocean, even with near-shore simulations of the production systems, and the instability of cultivation of giant kelp, among other problems, resulted in the program not achieving any significant results in open ocean cultivation (Huesemann et al. 2010). Nevertheless, a great deal of basic information on kelp physiology, growth rates, composition, productivity and conversion to methane was developed by this program (Bird and Benson, 1987; Chynoweth 2002). But the main reason this effort was abandoned by the early 1980s, was the change in political leadership in the U.S., as well as the finding of large new resources of natural gas in the U.S., following natural gas price deregulation.

Potential of macroalgae for biofuels

Macroalgae are again being considered as a biofuel feedstock for similar reasons as thirty years ago: because they are thought to have very high biomass yields (though still this remains to be established) and, perhaps most importantly, because they don't compete with agricultural crops for land, water resources, and, potentially, fertilizers. Herein we neglect the land-based cultivation of seaweeds, which suffers from several inherent problems, mainly the very high water exchange and/or mixing required for high productivity cultivation, in addition to CO2 supplementation. However, land-based cultivation is already a commercial process for some seaweed species, and may be of interest for biofuels production in some locations, though undoubtedly their greatest potential is in open ocean cultivation. Compared to microalgae, macroalgae have a major advantage: their macroscopic nature allows for ready and low cost harvesting. Against these advantages must be placed the difficulties of working in the sea, even near-shore, which imposes significant costs and risks, as already experienced by the earlier U.S. Marine Biomass Program. The three most commonly mentioned fuels that could be derived from macroalgae are methane, ethanol, and butanol.

The interest in macroalgae for biofuels was recently re-initiated, mainly in Japan, Korea and Europe, but at a relatively low level of funding initially. In Japan, Tokyo Gas studied the production of biogas from seaweed that was collected from biomass naturally deposited on beaches after storms and high tides (Huesemann et al., 2010). However, several factors - the small amounts and sporadic nature of such harvests, the sand and dirt collected along with such biomass, and the transportation costs - make such schemes impractical. Thus most attention has focused on off-shore cultivation of local seaweeds, with a popular candidate species being *Laminaria japonica*, the most common seaweed currently used for food and chemical production, and already considered thirty years ago for such applications (Tseng 1981; Chynoweth 2002). In Ireland, *Laminairia* ssp and *Ulva* ssp, are being considered because of their relatively high carbohydrate content (Bruton et al. 2009). *Ulva* can be readily digested to methane gas and seem to lack epiphytes, e.g. microalgae growing on the surface of the seaweed leaves, which can interfere with their production (Chynoweth 2002). Other species also evaluated for fuel production in the 1980s, include *Gracilaria tikvahiae* (a red algae species), notable for its high yields in on-shore cultivation tests (Hanisak 1987).

Another interesting macroalga is *Sargassum*, notable because it is one of the few species that is found free floating in the open ocean (Chynoweth 2002). The possibility of growing Sargassum in the open ocean is intriguing, but there is presently no reasonably plausible approach to its mass cultivation. Their cultivation was already discussed over forty years ago, and the concept proposed (but not published) was to release propagules of Sargassum into a marine current, near an upwelling zone, and then harvest the plants downstream, after a few weeks of growing in the ocean current. Of course, this intriguing concept is at this point entirely hypothetical.

Because of limited suitable near-shore areas, many already being used extensively for commercial macroalgae cultivation, the key concept for cultivation of macroalgae for biofuels remains, as before, some type of open ocean cultivation technology. However, the design of such systems also remains, as before, mainly hypothetical, with no design apparent at present that could be scaled-up or deployed beyond a near-shore environment. An earlier analysis for the U.S. Biomass Program of such systems pointed out the many inherent essentially insurmountable engineering difficulties of such concepts (Ashare et al., 1978). In what follows we thus must per-force assume that an open ocean cultivation technology will eventually prove to be technically and economically feasible, and that the macroalgae productivities will be high enough to justify such efforts. The remaining issues are then harvesting and conversion to fuels.

Harvesting and Processing to Fuels

As already mentioned, near-shore cultivation of seaweeds has been developed into a major industry in many countries, in particular China. The algae are harvested, typically by hand, and loaded into barges. Mechanical harvesting has also been developed, in particular to harvest natural stands of the giant kelp off California, for which, as noted above, specially designed ships were built almost a hundred years ago and are still used today. Macroalgae can be harvested by raking from a boat or using mechanical methods such as drag rakes, winchers, dredges, or Scoubidous which are boats with rotating hooks to bring in seaweed (Bruton et al. 2009). For offshore farms, mechanically harvesting would be used, and the seaweed loaded on barges and transported to an on-shore holding facility (Brehany 1983).

Processing of seaweed requires the removal of debris, e.g. any dirt or sand, washing off excess salt, and reducing the water content to the extent feasible. For ethanol and butanol fermentations, the macroalgae cell wall polysaccharides must first be broken down through microbiological, enzymatic, chemical or/and thermal processing. Although macroalgae do not contain lignin nor, generally, cellulose, the polysaccharides, both structural and storage, must be broken down by such means to become accessible to the yeast or bacteria involved in the ethanol, butanol fermentations. Polysaccharide breakdown and fermentations would require development of specialized micro-organisms, but this should be readily amenable to modern biotechnological technologies.

For example, Horn et al. (2000), in Norway, reported on testing several bacteria and yeast to ferment *Laminaria hyperborea* (a brown macroalgae) to ethanol, finding that the yeast *Pichia angophorae* could convert both laminaran and mannitol into ethanol. Adams et al. (2009), using *Saccharina latissima* (a brown macroalgae, which, as its name implies, is quite high in sugars), showed that the one hour pretreatment at pH 2 and 65 ˚C used by Horn et al. (2000) was not required to produce ethanol from this alga. Optimal pretreatment conditions to release monosaccharides and thus increase ethanol yields have been studied in Korea by Jeong and Park (2010) and Wi et al., 2009).

In the USA, the major current effort on macroalgae for biofuels is by a partnership of a small California company, Bio Architecture Lab (BAL) with Dupont Corp., in a $6 million project funded by the US DOE (under the ARPA-E program), to develop a low cost butanol fermentation program. It is not clear if BAL intends to produce the macroalgae for this project in the USA; it has started a production project in Chile. BAL uses synthetic biology to develop microbial pathways and enzymes for converting macroalgae into fuels. BAL has also partnered with Statoil of Norway to develop technology for the conversion of Norwegian seaweed into ethanol. BAL is responsible for the conversion to ethanol technology, and Statoil for the development of the seaweed cultivation process, for *Saccharina latissima*, already mentioned above (Statoil 2009a). One of the plantings of *Saccharina latissima* will be outside Tjeldbergodden methanol plant in Norway which has favorable water temperature in addition to CO_2 and NO accessibility (Statoil 2009b).

Anaerobic digestion does not require any particular pre-treatment or bacterial selection, though a high S content in seawater and seaweeds will required scrubbing of the biogas. Compared to the challenges of cultivating macroalge for biofuels, the conversion processes do not present major challenges.

Biotechnology of Seaweeds

As already noted, much more research and development is needed before macroalgae could become a practical biofuel feedstock, in particular the design of the cultivation systems that can actually operate off-shore and the productivity of the macroalgae. This will require selection and genetic improvements of macroalgae species for such applications. Genetic improvements of many commercially grown macroalgae have already been achieved with conventional breeding techniques and the applications of advanced biotechnology techniques has been initiated (Cheney et al., 2003; Roesjadi et al., 2008),. For examples, the genomes of the red alga *Porphyra purpurea* and of the brown algae *Ecotocarpus siliculosisus* are being sequenced by the US DOE Joint Genome Institute in California, and Génoscope – Centre National de Séquençage in France, respectively, and the genetic transformation of macroalgae has also been started in several species (Huesemann et al. 2010).

Current World-wide Projects in Macroalgae Biofuels Production

The past two or three years have seen a major upswing in the interest in open ocean cultivation of seaweeds for biofuels. This is driven perhaps more by the recognition of the limitations of land-based biofuel systems, both of higher plants and microalgae, than any particular appearl of macroalgae, other than the promise of essentially unlimited area, water and CO2. A few examples of recent projects initiated in this space are:

- In Japan, the Ocean Sunrise Project will investigate the farming of *Sargassum fulvellum* and its conversion to ethanol production in unused maritime areas around Japan (Aizawa et al. 2007).. Organic compounds, salt, and ash leftover from processing would be used for cattle feed and fertilizer. This project also plans to adapt farming technology used for *Laminaria* and *Undaria pinnatifida* in coastal zones to offshore areas, with rope cultures configured as a trawl net. Water bag transport and storage systems for the harvested biomass are being proposed. Clearly these concepts are hypothetical.

- In Indonesia, the Korea Institute of Technology (KIIT) and partners will develop seaweed cultivation to provide biomass for ethanol production, leasing 25,000 hectares of coastal waters for this project. Indonesia coastal areas have large natural seaweed stands unlike Korea, and Korea will supply the conversion technology and most funding. Similarly, a project under the South Korea National Energy Ministry plans to create a 35,000-hectare offshore seaweed forest for producing ethanol from macroalgae.

- In Brazil, the State of Rio Grande do Norte Agricultural Research Company (EMPARN) is developing large-scale production techniques for fuel from seaweed.
- In Japan, Tohoku University and Tohoku Electric Power Company claim to have discovered a natural yeast for the conversion of macroalgae into ethanol. Their conversion rate after two weeks was 200 mL of ethanol from 1 kg macroalgae.
- At the University of Maine, there is a project on the life cycle assessment of macroalgae for biofuel and the study of the conversion of Algefiber® from *Eucheuma spinosum* (red algae) into carboxylic acids to be converted into alcohol fuels.
- In India, the Central Salt and Marine Chemicals Research Institute (CSMCRI) has produced ethanol from the species *Kappaphycus alvareziii* (red algae).
- In Denmark, scientists are trying to apply similar ethanol conversion technology from Horn et al (2000) to the green algae *Ulva lactuca* which is abundant in their area (Huesemann et al. 2010).
- Yoon et al. (2010) of the Korea Institute of Industrial Technology recently reported on the saccharification and conversion of *Gelidium amansii* (red algae) into ethanol. The group selected this species because of its wide variety and growth rate. Also, red seaweed has no lignin and its galactan and glucan content can be processed into monosugars of glucose and galactose that can be readily converted to bioethanol (Yoon et al. 2010).
- Sustained commercial cultivation of algae has only successfully been done with *Laminaria japonica* in China which showed yields of about 25 t/ha (Bruton et al. 2009).
- For offshore farming, German scientists investigated an offshore ring system for *Laminaria saccharina* (Buck and Buchholz 2004). The design is for food production but can also be

used for fuel. First macroalgae sporophytes are grown in the lab to a suitable length, and then they are places in the ring structure. The ring structure has been found to be stable in offshore farming. However any scale-up

- The Sustainable Fuels from Marine Biomass project (BioMara) in the UK and Ireland, plans to investigate the economics and feasibility of using macroalgae for methane and ethanol production.

Challenges

The major challenge facing fuel production from macroalgae is the technical feasibility of off-shore cultivation and the economics of even near-shore production processes. Certainly millions of tons of seaweed are being produced commercially, and near-shore areas are available in some countries for such systems. However, production costs are too high for biofuels production by a factor of perhaps up to five-fold (Aresta et al. 2003). Macroalgae cultivation currently requires a great deal of manual labor, which is excessive even for many low-wage countries. The greatest challenge, however, is to move from near-shore areas to open ocean waters (Chynoweth 2005). and the technical feasibility to expand cultivation to such environments, even for conventional, high value, seaweed products, must be at this point considered at best a long-term goal. For example only, in designing offshore aquaculture systems, the drift and drag of the nets, ropes, and/or lines used presents daunting problems. Developing macroalgae farms in conjunction with off shore wind farms could provide anchorage to prevent drifting (Bruton et al. 2009), but these would still be relatively near-shore, and limited in scale. Another fundamental limitation for such offshore farm concepts is the supply of needed nutrients. Compared to the cultivation challenges in off-shore environments (e.g. too deep to anchor the conventional macroalgae line or rope systems), the challenges of harvesting and processing macroalgae biomass to biofuels must be considered rather modest, and present relatively minor challenges. However, the very large potential for such systems, should they be developed, would justify continued long-term research and development, possibly over several decades.

Key Findings

Despite over 30 years of research and development, macroalgae for fuels is still in the very early, even conceptual, stages of research and development. There are now many new entrants into this field, from around the world, and significant funding is starting to flow into this area. However, the challenges are also daunting, in particularly if the cultivation systems are to be extended into deeper, less protected areas of the ocean, where anchoring is not possible. Even for near-shore systems, the current costs of macroalgae production are excessive, and major breakthroughs may be more difficult as this is already a well-established technology. Nevertheless, even if visions of enormous floating macroalgae farms are not realized, or realizeable, macroalgae have the potential of becoming a significant world-wide crop that could contribute not just to fuels but also to food and feed production, justifying continued R&D.

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