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Review

Review: A chance for Korea to advance algal-biodiesel technology

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ABSTRACT

In order to reduce the effects of greenhouse gas (GHG) emissions, the South Korean government has announced a special platform of technologies as part of an effort to minimize global climate change. To further this effort, the Korean government has pledged to increase low-carbon and carbon neutral resources for energy to replace fossil fuels and to decrease levels of carbon dioxide. Renewable and recycled energy, which constituted 2.3% of Korea's total energy resources in 2006, will be required to reach 5% in 2011 and 9% in 2030.

Biodiesel, which is currently only 1% of diesel oil consumed in South Korea, will be required to be 3% in 2012. The measures are designed to reduce the use of fossil fuels and to increase environment-friendly alternative energy. Korea emitted 591 million tons of carbon dioxide in 2005, which is a 98.7% increase from 1990. The nation is the world's sixth largest emitter of carbon dioxide and the fastest growing emitter among members of the Organization of Economic Cooperation and Development countries.

It is important that under the new Korean initiative, pilot scale studies evolve practices to produce algae-based biodiesel and obtain optimal harvest of such aquatic algae with anthropogenic CO_2. Work should be initiated to establish a multilateral network, taking into consideration institutional infrastructure, scientific capabilities, and cost effectiveness.

Contents

1. Introduction

Global biofuel production has tripled from 4.8 billion gallons in 2000 to about 16 billion in 2007, but still accounts for less than 3% of the global transportation fuel supply, according to US Department of Agriculture report [1]. Concerns about energy security, climate change, and soaring oil prices have driven policymakers and scientists to develop alternative energy sources that would allow them to break their dependence on foreign oil. Specifically, the added demand for corn and soybean as energy sources drove prices of the crops to near-record highs on the world market. These crops are commonly used to feed livestock as well,

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so meat and poultry prices also jumped [2]. To resolve the problems, it is essential that we should find new sources of biomass for alternative energy.

Algae's potential as a feedstock is dramatically growing in the biofuel market. Microalgae (to distinguish it from such macroalgae species as seaweed) have many desirable attributes as energy producers [3–5]:

- algae is the most promising non-food source of biofuels,
- algae has a simple cellular structure,
- a lipid-rich composition (40–80% in dry weight),
- a rapid reproduction rate,
- algae can grow in salt water and harsh conditions,
- algae thrive on carbon dioxide from gas- and coal-fired power plants,
- algae biofuel contains no sulfur, is non-toxic and highly biodegradable.

Algal biodiesel could easily supply several "quads" (quadrillion BTU: It is about equal to the amount of energy in 45 million tons of coal, or 1 trillion cubic feet of natural gas, or 170 million barrels of crude oil) of biodiesel—substantially more than existing oilseed crops could provide. Microalgae systems use far less water than traditional oilseed crops. Land is hardly a limitation. Two hundred thousand hectares (less than 0.1% of climatically suitable land areas in the U.S.) could produce one quad of fuel [6]. Thus, though the technology faces many R&D hurdles before it can be practicable, it is clear that resource limitations are not an argument against the technology.

2. Algal chemical composition

Algae are made up of eukaryotic cells. These are cells with nuclei and organelles. All algae have plastids, the bodies with chlorophyll that carry out photosynthesis. But the various strains of algae have different combinations of chlorophyll molecules. Some have only Chlorophyll A, some A and B, while other strains, A and C [7].

Algae biomass contains three main components: proteins, carbohydrates, and natural oil. The chemical compositions of various microalgae are shown in Table 1. While the percentages vary with the type of algae, there are algae types that are comprised of up to 40% of their overall mass by fatty acids [8,9]. It is this fatty acid (oil) that can be extracted and converted into biodiesel.

The interest in algal oil is not new, though the widespread interest in making biodiesel form algal oil is more recent. Algae oil has been produced and used for the cosmetic industry; primarily from macroalgae (larger size algae) such as oarleaf seaweed [3,10]. However, most current research on oil extraction from algae is focused on microalgae.

3. Liquid solar energy

Although "diesel" is part of its name, pure biodiesel does not contain any petroleum-based diesel, also called "petrodiesel" [11]. Instead, biodiesel is created from newer organic matter. It can be made from virtually any vegetable oil, including soy, corn, rapeseed (canola), peanut or sunflower—as well as from recycled cooking oil, animal fats or even algae. Biodiesel has been called "liquid solar energy" because its energy content is derived from plants that capture solar energy during photosynthesis. The plants grown to produce biodiesel consume carbon dioxide (CO_2), so they naturally balance most of the CO_2 released when the fuel is combusted, offsetting a major contributing factor to global warming [12].

Using vegetable oil for fuel is not a new idea. When Rudolf Diesel invented the original diesel engine in the 1890s, he designed it to run on a wide range of fuels—including vegetable oils [13]. But beginning in the early 1900s, diesel engines were adapted to burn mainly petrodiesel, a cheaper fuel. During the energy crisis of the 1970s, researchers began to reconsider vegetable oil fuels and found a simple method for turning vegetable oil into a usable diesel fuel. This process, called "transesterification" was developed in the late 1970s and early 1980s [14]. It involves blending vegetable oil with alcohol, and adding a catalyst that will initiate the reaction that forms biodiesel.

4. Conventional process of biodiesel production

Commercial experience with biodiesel has been very promising [15]. Biodiesel performs as well as petroleum diesel, while reducing emissions of particulate matter, CO, hydrocarbons and SOx. Emissions of NOx are, however, higher for biodiesel in many engines. Biodiesel virtually eliminates the notorious black soot emissions associated with diesel engines. Total particulate matter emissions are also much lower [16–18]. Other environmental benefits of biodiesel include the fact that it is highly biodegradable and that it appears to reduce emissions of air toxics and carcinogens (relative to

Table 1
Biochemical composition of algae expressed on a dry matter basis [8].

Strain	Protein	Carbohydrates	Lipid	Nucleic acid
Scenedesmus obliquus	50–56	10–17	12–14	3–6
Scenedesmus quadricauda	47	–	1.9	–
Scenedesmus dimorphus	8–18	21–52	16–40	–
Chlamydomonas rheinhardii	48	17	21	–
Chlorella vulgaris	51–58	12–17	14–22	4–5
Chlorella pyrenoidosa	57	26	2	–
Spirogyra sp.	6–20	33–64	11–21	–
Dunaliella bioculata	49	4	8	–
Dunaliella salina	57	32	6	–
Euglena gracilis	39–61	14–18	14–20	–
Prymnesium parvum	28–45	25–33	22–39	1–2
Tetraselmis maculata	52	15	3	–
Porphyridium cruentum	28–39	40–57	9–14	–
Spirulina platensis	46–63	8–14	4–9	2–5
Spirulina maxima	60–71	13–16	6–7	3–4.5
Synechoccus sp.	63	15	11	5
Anabaena cylindrica	43–56	25–30	4–7	–

Note: Algal-oil is very high in unsaturated fatty acids. Some UFA's found in different algal-species include: Arachidonic acid (AA), Eicospentaenoic acid (EPA), Docasahexaenoic acid (DHA), Gamma-linolenic acid (GLA) Linoleic acid (LA).

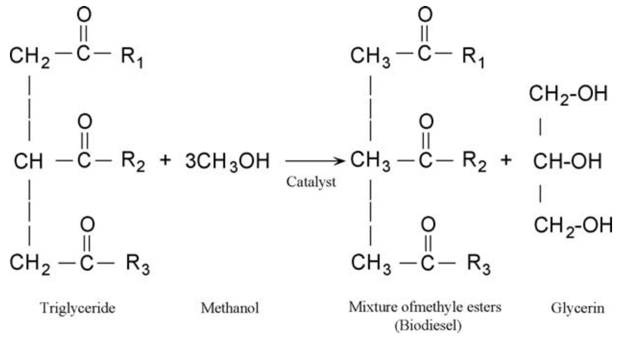

Fig. 1. The transesterification process [3].

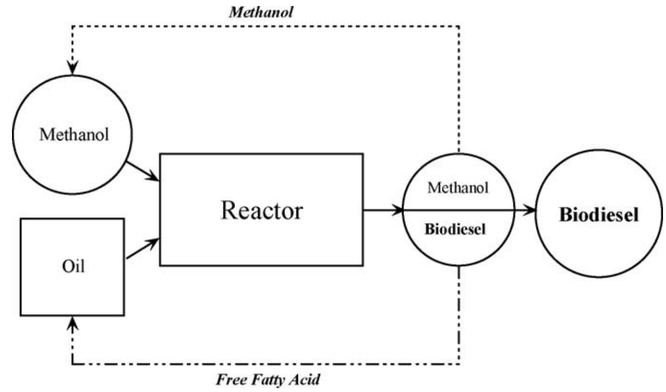

Fig. 3. The Mcgyan process for biodiesel production [23].

petroleum diesel) [19]. A proper discussion of biodiesel would require much more space than can be accommodated here. Suffice it to say that, given many of its environmental benefits and the emerging success of the fuel in Europe, biodiesel is a very promising fuel product.

The process for making biodiesel is relatively simple and can be extremely low-technology (Fig. 1). Biodiesel is produced by chemically reacting a fat or oil with an alcohol, in the presence of a catalyst (Fig. 2). The product of the reaction is a mixture of methyl esters, which are known as biodiesel, and glycerol, which is a high value co-product. The process is known as transesterification, as shown in Fig. 1, where R_1, R_2, and R_3 are long hydrocarbon chains, sometimes called fatty acid chains. There are only five chains that are common in most vegetable oils and animal fats (others are present in small amounts). The relative amounts of the five methyl esters determine the physical properties of the fuel, including the cetane number (CN), cold flow, and oxidative stability. Biodiesel can be used neat and when used as a pure fuel it is known as B100. However, it is often blended with petroleum-based diesel fuel and when this is done the blend is designated "BXX" where XX is the percentage of biodiesel in the blend. For example, B20 is a blend of 20% biodiesel and 80% petroleum diesel [22].

While virtually all commercial biodiesel producers use an alkali-catalyzed process for the transesterification process, other approaches have been proposed including acid catalysis [20] and enzymes [21]. The use of acid catalysts has been found to be useful for pretreating high free fatty acid feedstocks but the reaction rates for converting triglycerides to methyl esters are very slow. Enzymes have shown good tolerance for the free fatty acid level of the feedstock but the enzymes are expensive and unable to provide the degree of reaction completion required to meet the ASTM fuel specification [1]. Immobilization of the enzyme and use of multiple enzymes in sequence may provide future opportunities in this area [21].

5. New process of biodiesel production

Researchers at Augsburg College and SarTec Corporation have *developed* and are commercializing a new continuous transesterification process for the production of biodiesel. The "Mcgyan Process" – so termed based on the names of the inventors (Dr. McNeff, Dr. Arlin Gyberg of Augsburg College and Dr. Bingwen Yan.) – can use a wide variety of feedstocks, does not consume the

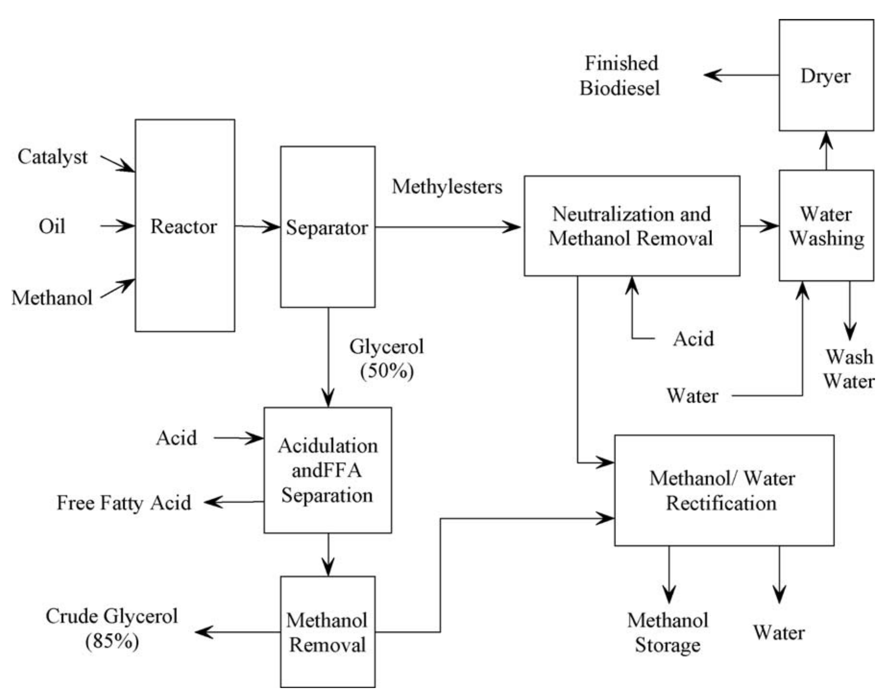

Fig. 2. Process flow schematic for biodiesel production [3].

catalyst, reduces the reaction time from hours to seconds, and uses no water or dangerous chemicals (Fig. 3).

An alcohol and a lipid (vegetable oil or tallow) are combined by high pressure pumps into a lipid stream that is passed through a continuous fixed-bed reactor filled with a sulfated metal oxide catalyst at elevated temperature and pressure. The reactor performs transesterification and esterification reactions simultaneously.

The output contains excess alcohol and biodiesel fuel. The fuel is then distilled to recover the excess alcohol and other co-products, and the biodiesel is polished to remove residual free fatty acids, which can be recovered and put back into the input side of the system. Benefits of the Mcgyan process, according to the inventors, are [23]:

- Flexible feedstock; animal or plant sources of lipids can be used. Current waste products can be turned into fuel.
- No use of strong acids or bases in the process.
- Fast reaction times (seconds).
- Cheap feedstocks such as waste grease and animal tallow as well as a variety of plant oils can be converted to biodiesel.
- The metal oxide-based catalyst is a contained in a fixed bed reactor thereby eliminating the need to continuously add catalyst to the reaction mixture and reducing waste.
- Side reactions of free fatty acids are eliminated, reducing unwanted soap production.
- Insensitive to free fatty acid and water content of the feedstocks.
- The catalyst does not poison over time.

A patent is now pending on the Mcgyan process. Ever Cat Fuels Corporation is a new company currently producing 50,000 gallons of biodiesel per year using the Mcgyan process. Its production capacity will increase to 3 million gallons per year when a new plant begins operation in Isanti, MN later this year [24]. Ever Cat Fuels hopes to sell the technology and equipment globally.

6. Culture technology

The concept of microalgae biomass production for conversion to fuels (biogas) was first suggested in the early 1950s [25]. Shortly thereafter, Golueke et al. at the University of California–Berkeley demonstrated, at the laboratory scale, the concept of using microalgae as a substrate for anaerobic digestion, and the reuse of the digester effluent as a source of nutrients [26,27].

There are two common methods to grow algae. The first uses a series of storage tanks linked by transparent tubes that rest on support structures. Algae and water are pumped through the pipes to ensure maximum exposure to sunlight. CO_2 is piped into the tanks. Algae hold great promise as a possible source of biodiesel because they grow rapidly, are rich in lipids and can be cultivated in ponds of seawater, reducing the need for fertile land and fresh water [4,5]. Many companies are seeking ways to produce algal oil on a commercial scale, but they face significant hurdles. There is little risk of contamination of the algae as they are grown in a closed environment resembling laboratory conditions. Productivity per hectare is also high so the equipment takes up less land than open systems. However, the equipment is expensive – several kilometers of tubes are necessary to produce commercial amounts of oil – as are maintenance costs to keep it clean and working. The alternative method pumps water around a continuous loop of a man-made, open-air channel to expose the algae to sunlight. The raceways at existing open pond algae farms hold about as much water as a municipal swimming pool [28]. Such open ponds are cheaper than closed systems, but they have their drawbacks too: light only reaches the algae near the surface, water easily evaporates and the temperature is harder to control [3]. The risk of contamination is also greater than in closed systems. Predators such as small shrimp-like organisms that eat algae can enter open ponds, carried by wind or spread by waterfowl.

7. Production chanllenges

The huge amount of water needed for large-scale production in both systems poses another challenge. The water holding algae must be refreshed each day and taken out of light to kill any predators or weeds. That involves pumping it out of the production system and back in again. "It's like any agricultural system, but at very high intensity," says Ian Archibald, a scientist with Shell Global Solutions International B.V. The smallest practical size for an algal biodiesel plant is 1000 ha, which pumps about 1 billion liters of salt water a day [6]. This is about twice the amount of fresh water used for agricultural irrigation. Researchers expect to reduce the amount of salt water needed to produce oil from algae.

Harvesting algae and extracting oil present other technical and cost hurdles [29,30]. The dominant algal species found in a pond could range from small unicellular to large colonial or filamentous species, harvesting of the algae for biomass conversion would require a universally applicable harvesting technology, such as centrifugation or chemical flocculation, to enable the recovery of any algal type [31]. However, these processes are very expensive. Both methods are expensive when applied in large-scale commercial production. Researchers are seeking the best of a variety of approaches.

There are also competing methods to extract the lipids and treatments to make biodiesel. Common methods to extract oil from algae involve pressing it out of dried algae or adding chemicals to remove the oil [1,20]. However, vegetable oil must be treated before it can be used as a fuel. A diesel engine can run on vegetable oil but gummy deposits will form in the motor and the fuel will go solid at low temperatures. The standard treatment to make oil from land crops more palatable for engines can also be applied to algae. A chemical reaction breaks their carbon chains and adding methanol yields oil that can be blended with petrodiesel. The treated algal oil can be used in diesel blends of up to 10% [32]. An alternative method, hydrotreatment, uses hydrogen instead of methanol and catalysts to speed up the chemical reaction. This approach yields a fuel that is identical to fossil fuel, but it is complex and more expensive as it is costly to produce hydrogen and catalysts.

8. Seeking an efficient strain

There are more than 100,000 known strains of microalgae in the world [3]. The search for the best one for biofuel production is still under way. A Shell research program involving several universities is looking for the strain with a winning combination of high oil content and a rapid growth rate. Algae reproduce by dividing their cells. Usually algae with high oil contents grow relatively slowly. For example, algae containing 80% oil will only divide once every 10 days, whereas algae containing 30% oil may divide three times daily [8]. Moreover, strains capable of producing large amounts of lipids tend to do so when they are starved of nutrients. But starvation also slows growth. Some researchers hope to genetically modify algae to produce more oil. Others have taken a different approach and produced yellow algae that allow light to penetrate further into ponds, promoting more uniform growth. Recent history serves as a cautionary tale to rapid commercialization of algae-based biofuel on a large scale. The 1970s oil crises prompted several government-funded studies into algal fuel in France, Germany, Japan and the United States, among others, in a bid to increase energy security [3,33,34]. But the technology was expensive and development costs were too high. The U.S. Department of

Energy's Aquatic Species Program, for example, built two 1000-square-metre open pond systems and found that algae were only economically viable as a biofuel at oil prices of more than $60 a barrel [1]. The Clinton administration ended the program 11 years ago after spending about $25 million as low oil prices of the day made it unattractive economically. In Japan the Research for Innovative Technology of the Earth program extensively studied uses for microalgae. The program concentrated on closed systems to grow algae but it was stopped after an investment of more than $100 million as the technology was seen as unfeasible [3]. New approaches combine the best of both of these worlds. Today's all-time high oil prices and advances in biochemical science and technology have breathed new life into researching the green slime. Whether algae-based fuels will thrive depends on whether the technological and commercial hurdles can be overcome. If they can, algae – one of the world's oldest organisms – may prove a boon to the transport needs of the future.

9. Microalgae and sequestration of CO_2

CO_2 is recognized as the most important (at least in quantity) of the atmospheric pollutants that contribute to the "greenhouse effect," a term coined by the French mathematician Fourier in the mid-1800s to describe the trapping of heat in the Earth's atmosphere by gases capable of absorbing radiation [1,12,35]. While there is still much debate on the effects of increased CO_2 levels on global climate, many scientists agree that the projected increases could have a profound effect on the environment [3,36]. Most of the anthropogenic emissions of carbon dioxide result from the combustion of fossil fuels for energy production. It is the increased demand for energy, particularly in the developing world, which underlies the projected increase in CO_2 emissions. Meeting this demand without huge increases in CO_2 emissions requires more than merely increasing the efficiency of energy production. Carbon sequestration – capturing and storing carbon emitted from the global energy system – could be a major tool for reducing atmospheric CO_2 emissions from fossil fuel usage.

The costs of removing CO_2 from a conventional coal-fired power plant with flue gas desulphurization were estimated to be in the range of $35–$264 per ton of CO_2 [3,36]. The cost of power was projected to increase by anywhere from 25 to 130 mills/kWh. The goal of the DOE is to reduce the cost of carbon sequestration to below $10 per ton of avoided net cost. As shown in Fig. 4, CO_2 (from the fossil fuel combustion system) and nutrients are added to a photobioreactor. Microalgae photosynthetically convert the CO_2 into compounds of high commercial value or mineralized carbon for sequestration.

The advantages of the proposed process include the following [36]:

- High purity CO_2 gas is not required for algae culture. It is possible that flue gas containing 2–5% CO_2 can be fed directly to the photobioreactor. This will simplify CO_2 separation from flue gas significantly.
- Some combustion products such as NOx or SOx can be effectively used as nutrients for microalgae. This could simplify flue gas scrubbing for the combustion system.
- Microalgae culturing yields high value commercial products that could offset the capital and the operation costs of the process. Products of the proposed process are: (a) mineralized carbon for stable sequestration; and (b) compounds of high commercial value. By selecting appropriate algae species, either one or both can be produced.
- The proposed process is a renewable cycle with minimal negative impacts on environment.

10. Economic importance

Compared to biofuels from agricultural crops, the amount of land required would be minimal. Trials in ideal conditions show that fast-growing micro-algae can yield 1800–2000 gallons/(acre - year) of oil—compare this with 50 gallons for soyabeans, 130 gallons for rapeseed and ~650 gallons for palm oil. It can grow on fresh or brackish water on marginal land so that it does not compete with areas for agricultural cultivation. As Sean Milmo points out in his article in Oils and Fats International [37]; oil from algae on 20–40 M acres of marginal land would replace the entire US supply of imported oil, leaving 450 M acres of fertile soil in the country entirely for food production. Biomass can also be harvested from marine algae blooms and algae can even be cultivated in sewage and water treatment plants.

However, most estimates of algal fuel productivity estimate that with current production technologies algal diesel can be manufactured for, at best, $4.54 per gallon using high density photobioreactors. In order to compete economically with petroleum diesel costs – and not accounting for any potential subsidy scheme, which is a likely possibility – requires the reduction of these costs to near $1.81 per gallon relative to 2006 fuel prices. These cost reduction figures take into account the fact that materials input and refining of fuels (in this case the algae vegetable oil) account for roughly 71% of total at pump fuel cost [38]. Algal biodiesel becomes even more plausible given the potential for GHG regulation in the near future. Since for every ton of algal biomass produced, approximately 1.83 tons of carbon dioxide are fixed while petroleum diesel carries a massive negative

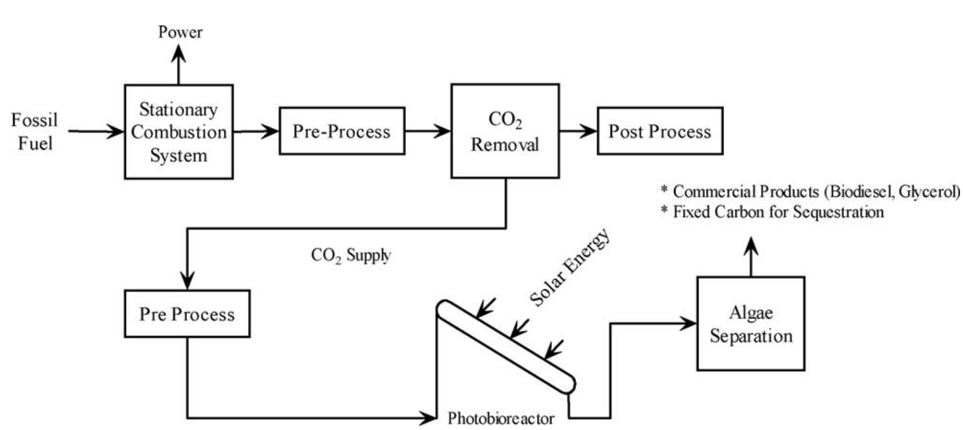

Fig. 4. Recovery and sequestration of CO_2 from stationary combustion systems by photosynthesis of microalgae [36].

Table 2
Leading the algae-based fuel industry, laboratories, and universities in the US [39].

Company	Bioreactor or pond?	Research affiliation	Status	Funding
GS Clean Tech www.gs-cleantech.com	Bioreactor	Ohio State University	Pilot Project	Subsidiary of Green Shift Corp. & Veridium Corp., Public company.
GreenFuel Technologies www.greenfuelonline.com	Bioreactor	Massachusetts Institute of Technology	Finished R&D, finalizing specs	$22 million in venture capital from Draper Fisher Jurvetson, Polaris, Axis Partner.
PetroAlgae www.petroalgae.com	Bioreactor	Arizona State University	R&D	Subsidiary of XL Tech Group Inc.
Solix Biofuels www.solixbiofuels.com	Bioreactor	University of Colorado	R&D, looking into Fischer Tropes processing	$500,000 University of Colorado.
LiveFuel www.livefuels.com	Pond	NREL, Sandia National Laboratory	R&D	Private funded by Morgenthaler family.
Infinifuel www.infinifuel.com	Pond	University of Nevada at Reno and the Desert Research Institute	R&D; Final construction phase of geothermal biodiesel processing plant	Private investors.
Algae Biofuels www.petrosuninc.com	Pond	Undisclosed	Final stage of field testing	Subsidiary of PeteroSun Drilling Inc., Public Company.
Energy Farms www.tgoiltech.com	Pond	Nanoforcetechnologies	R&D	Subsidiary of TransGlobal Oil Corp., Public Company.

Note: This list was prepared with input from Dr. David Brune, Newman Endowed Chair of Natural Resources Engineering at the Dept. of Agricultural and Biological Engineering at Clemson University and a visiting professor at the University of Hawaii.

balance, the competitiveness of algae diesel increases as GHG externalities are taken into account.

Given certain research objectives these cost reductions are achievable in the near future. The National Renewable Energy Laboratory (NREL) outlines many such research objects including: increasing photosynthetic efficiency of algae species for high lipid production, control of mechanisms of algae biofocculation, understanding the effects of non-steady-state operating conditions, and methods of species selection and control [3].

11. Future perspectives

Algae have great potential as a sustainable feedstock for production of diesel-types with very low-carbon dioxide emissions. Nonetheless, there are currently serious drawbacks, and it would be harmful to overestimate the greenness of this up and coming technology. Today, algae can be grown in ponds and bioreactors in just a few days, and oil can be extracted directly from the harvested algae. Success in microalgae culture achieved in the US is providing momentum in many other countries in the region. Table 2 shows that some companies have just finished R&D on expansion of production areas through location of new farming sites [36]. While some companies (Solazyme, GreenFuel Technologies, Solix, and Livefuels) have perfected culture techniques, other companies are looking for new areas for exploitation and are focusing on the protection of existing stocks from over harvesting through proper management practices.

Research on algae-based fuel is still in the beginning stages, and any large-scale use of algae for biofuel would require massive investments in production facilities. That would take many years and large amounts of money to develop, but it might be possible if Korea were willing to commit the resources to developing this renewable fuel. Geographically, Korea, being surrounded by ocean waters on three sides, has a natural advantage for algae culture. There is a chance for Korea to advance algae-based biofuel technology. Specifically, industrialized Ulsan and Pusan, with their close proximity to the ocean, have the potential to be algal fuel hubs in Northeast Asia.

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