# AQUATIC BIOMASS RESOURCES AND CARBON DIOXIDE TRAPPING

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Abstract—Intensively managed microalgal production facilities are capable of fixing several-fold more carbon dioxide per unit area than trees or crops. Although  $CO_2$  is still released when fuels derived from algal biomass are burned, integration of microalgal farms for flue gas capture approximately doubles the amount of energy produced per unit of  $CO_2$  released. Materials derived from microalgal biomass also can be used for other long-term uses, serving to sequester  $CO_2$ . Flue gas has the potential to provide sufficient quantities of  $CO_2$  for such large-scale microalgae farms. Viewing microalgae farms as a means to reduce the effects of a greenhouse gas (carbon dioxide,  $CO_2$ ) changes the view of the economics of the process. Instead of requiring that microalgae-derived fuel be cost competitive with fossil fuels, the process economics must be compared with those of other technologies proposed to deal with the problem of  $CO_2$  pollution. However, development of alternative, environmentally safer energy production technologies will benefit society whether or not global climate change actually occurs. Microalgal biomass production has great potential to contribute to world energy supplies, and to control  $CO_2$  emissions as the demand for energy increases. This technology makes productive use of arid and semi-arid lands and highly saline water, resources that are not suitable for agriculture and other biomass technologies.

Keywords-Global climate change, greenhouse gas, microalgae, biomass.

#### 1. BACKGROUND

Recently, concern has increased about the threat of global climate change. Projected consequences include a rise in the sea level, the transformation of much of the southeastern United States into arid land, and the shift of the corn belt from the United States to Canada.<sup>1-3</sup> These changes may result from increased trapping of heat by a greenhouse effect as various gases accumulate in the atmosphere. These gases are generated by a variety of current practices including chlorofluorocarbon use, deforestation, and vegetation decay, but the most important source is accumulation of CO<sub>2</sub> from burning of fossil fuels in boilers, furnaces, and automobile engines.<sup>1</sup> In the United States, 35% of CO<sub>2</sub> emissions in 1985 were produced by electric utilities, mostly from coal burning. CO<sub>2</sub> emissions from electric utilities are predicted to rise from 0.43 petagrams of carbon per year (Pg C year<sup>-1</sup>, 1 Pg C =  $10^{15}$  g C) in 1985 to 0.77 Pg C year<sup>-1</sup> in 2010, which is 44% of predicted total U.S. emission.<sup>4</sup> Coal burning contributes the most CO<sub>2</sub> per unit of energy released, followed by petroleum, then natural gas. In view of the potentially significant environmental consequences, the development of methods for reducing  $CO_2$  accumulation in the atmosphere is a research and policy priority.

#### 2. THERMODYNAMIC CONSIDERATIONS FOR CO<sub>2</sub> CAPTURE

Because of the mounting concerns about global climate change, the Environmental Protection Agency (EPA) is considering a number of measures to reduce the accumulation of greenhouse gases. One of the recommended actions would impose emissions fees on fossil fuels such as coal, natural gas, and oil so that their price reflects the risk of climate change. The cost of trapping and concentrating CO<sub>2</sub> is projected to increase the cost of electricity by 75–150%.<sup>4</sup> Because such fees would sharply alter the economic viability of fossil fuel use, it is desirable to find ways to remove CO<sub>2</sub> from flue gas, which will reduce emissions substantially.

In general, a chemical reaction is needed to fix the carbon over the long term. Such a reaction could proceed by the following stoichiometry:

$$CO_2(g) + Reactant$$

 $\rightarrow$  Fixed Carbon Product. (1)

The free energy change of this reaction at constant temperature,  $\Delta G$ , can be calculated from the fundamental thermodynamic relationship:

$$\Delta G = \Delta H - T \Delta S, \qquad (2)$$

in which  $\Delta H$  is the enthalpy change for the reaction, T is the temperature, and  $\Delta S$  is the entropy change. Now, to provide an economically viable  $CO_2$  storage reservoir, the fixed carbon product in eqn. (1) should be a liquid or a solid. Thus, the entropy change in eqn. (2) is likely to be negative, resulting in a positive contribution of  $T\Delta S$  to the free energy. However, for the reaction to proceed spontaneously,  $\Delta G$  must be negative, implying that  $\Delta H$  must have a negative value (i.e. reaction (1) must be exothermic) that is greater in absolute magnitude than  $T\Delta S$ .

In addition to providing an exothermic reaction with  $CO_2$ , the reactant in eqn. (1) should be abundant and low in cost to be economically attractive. The lowest cost solid reactant is lime (calcium oxide), ranked sixth in chemical production in the United States in 1990 at more than 13 Teragrams (Tg) per year.<sup>5</sup> Lime would react with carbon dioxide according to the reaction

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s).$$
 (3)

This reaction has an enthalpy change of -178kilojoules (kJ) mole<sup>-1</sup> and a free energy change of  $-130 \text{ kJ} \text{ mol}^{-1}$  of CO<sub>2</sub>. Although these properties would appear to make lime desirable for CO<sub>2</sub> removal, more than 4 t (metric) of lime are required per ton of coal burned. Even at the low price of about \$44  $t^{-1}$  for lime, the cost is an additional \$176 t<sup>-1</sup> of coal. This represents more than a 400% increase in coal utilization costs for just the lime, not taking capital and operating costs into account. In addition, more than 2.7 Pg of lime would be needed each year at current coal utilization levels, neglecting recovery of CO<sub>2</sub> from natural gas and oil-fired plants. Ultimately, the use of lime is not sensible because lime is produced by direct firing of calcium carbonate in kilns, and more CO<sub>2</sub> is released in lime manufacture than can be captured from flue gas.

One might be tempted to use other natural products such as sodium carbonate that are produced in abundance (sodium carbonate is ranked eleventh in production quantity in the United States<sup>5</sup>) but do not require  $CO_2$  removal

during manufacture. In this case, the reaction stoichiometry is

However, now more than 8 t of sodium carbonate are required per ton of coal burned, which at current prices of about  $176 t^{-1}$  contribute more than  $1400 t^{-1}$  of coal used for the chemical reactant alone. The higher cost of sodium carbonate compared to lime is compounded by the greater molecular weight of sodium carbonate, with the result that the cost per mole required for reaction (4) is excessive. Furthermore, the requirement for sodium carbonate to just fix the CO<sub>2</sub> from coal-fired plants exceeds current production by several orders of magnitude.

Based on these considerations, it becomes apparent that we must find a cheaper reactant for  $CO_2$  than lime or sodium carbonate. Because lime and sodium carbonate are among the lowest cost and most abundant chemicals produced, the obvious candidate is water. Water also has a lower molecular weight and is a logical choice because it was produced along with  $CO_2$  during combustion. One possibility is to fix  $CO_2$  by formation of carbohydrates according to the reaction

$$CO_2(g) + H_2O(l) \rightarrow CH_2O(s) + O_2(g),$$
 (5)

in which the oxygen consumed during combustion is regenerated. This reaction is of course the same as that of photosynthesis. Careful examination of this reaction or other similar reactions of the class that fix  $CO_2$  with water reveals that they are simply the reverse of combustion reactions. Furthermore, because the heat of combustion of gaseous CO<sub>2</sub>, liquid water, and gaseous oxygen is each defined as zero, the heat of reaction is simply equal to the negative of the heat of combustion of the carbon-fixing product. Thus, reactions such as (5) must be endothermic, and by eqn. (2) and the expectation that  $\Delta S$  will be negative, we would anticipate that  $\Delta G$  will be positive. If the free energy change is positive, reaction (5) and probably other reactions that employ liquid water to fix  $CO_2$ , cannot occur spontaneously.

Even if we can drive reaction (5) thermally, the overall heat of reaction for this endothermic transformation is  $+469 \text{ kJ mol}^{-1}$  of CO<sub>2</sub>, while the energy released when coal is burned is approximately  $485 \text{ kJ mol}^{-1}$  of carbon produced. Thus, very little net energy would be gained with the coupled system, assuming the reactions could be conducted without inefficiencies. If thermal losses are considered, more heat would be required to capture CO<sub>2</sub> than could be recovered during coal burning. In addition, the free energy change for reaction (5) is about +481 kJ mol<sup>-1</sup> of CO<sub>2</sub> reacted, indicating that the reaction will not proceed spontaneously as written. Alternatively, if the reactions could be driven electrochemically, a minimum of 481 kJ would be required to capture a mole of CO<sub>2</sub>, bid

but because electricity is produced at about a 40% efficiency from coal, approximately 1200 kJ of heat would have to be produced to capture a mole of  $CO_2$ . This would require the release of about 2.5 mol of  $CO_2$  to capture 1 mol, a definite losing proposition.

One could envision using photovoltaic cells or equivalent nonfossil-fuelled devices to generate electricity to drive a reaction such as (5), but several problems are evident. First, remember that the coal plant that is emitting  $CO_2$  would use 485 kJ of heat to produce 192 kJ of electrical energy and release 1 mol of  $CO_2$  in the process. Capture of the mole of CO<sub>2</sub> would require that at least 481 kJ of photovoltaic or other outside source of electricity be used for reaction (5). Thus, a total of 962 kJ of energy would be applied to the overall electrical generation and carbon recovery process, 481 kJ of which is electricity, to make 192 kJ of electricity. Regardless of the price of the outside source of electricity, the only sensible alternatives are to (1) pay the fine for  $CO_2$  release or (2) use the other source of electricity to replace the need to burn fossil fuels in the first place. The former is not a solution to global warming; the latter is not viable for relieving CO<sub>2</sub> emissions from fossil-fuelled plants.

With all these negative aspects of  $CO_2$  recovery, it would be tempting to conclude that the situation is hopeless. However, several points can be gained from these considerations. First, a very inexpensive chemical such as water or air is needed to fix the carbon. Second, the product formed should be a solid or liquid, preferably with a long stable lifetime. Third, water is desirable as a "reactant" because it has a low molecular weight, resulting in a low cost per mole. Fourth, a reaction such as (5) is desirable because it effectively reverses combustion, regenerating oxygen while fixing  $CO_2$  with water, its coproduct from combustion. Finally, an alternate reaction to (5) must be found that requires far less energy per mole of  $CO_2$  fixed, or an energy source other than heat or electricity with low cost potential must be used to drive the transformation.

With respect to the last of these points, one possibility is photon energy from the sun. Although man has yet to figure out a way to chemically fix carbon with low energy requirements and high yields, plants routinely carry out reaction (5) to fix large amounts of  $CO_2$  with water by a series of low temperature reactions through photosynthesis (capture of  $CO_2$  in biomass).

#### 3. BIOMASS METHODS FOR CO<sub>2</sub> CAPTURE: FORESTRY

technologies provide attractive Biomass alternatives to chemical means of reducing CO<sub>2</sub> emissions. One such biomass technology, which has been proposed to trap  $CO_2$ , is large-scale reforestation. Although forestry-based biomass is part of the biomass solution, it cannot be used in all areas. For a typical rapidly-growing plant such as might be grown in a cellulosic biomass plantation, more than 550 kg of water must be withdrawn from the soil for every kilogram of  $CO_2$  fixed.<sup>6</sup> This water needs to be high-quality soil moisture from rainfall or irrigation water. This requirement for large quantities of fresh water eliminates many of the arid undeveloped areas of the world from consideration.

Land may be equally limiting. For instance, one scenario proposes the development of largescale forestry with storage of trees at the bottom of the ocean;<sup>7</sup> this concept is based on the fact that trees can absorb 0.7–0.9 kg C m<sup>-2</sup> year<sup>-1</sup>. However, to absorb 2.72 Pg of carbon annually (the amount of carbon that is accumulating in the atmosphere), 3 million km<sup>2</sup> of trees would need to be grown, a land area roughly equal to that of Zaire.8 Futhermore, reforestation must continue at a rate sufficient to offset the predicted increase in fossil fuel consumption. In addition, although there are areas of the world (48 million km<sup>2</sup>) that are underutilized most of these are arid or semi-arid,<sup>9</sup> and thus unsuitable for significant reforestation. Furthermore, 24 million km<sup>2</sup> of that total are unsuitable to even support human life, and 0.5 million km<sup>2</sup> have been damaged by salt accumulation.<sup>10</sup> Further complicating the picture, a conservative estimate suggests that 100,000 km<sup>2</sup> of tropical rainforest per year are lost chiefly to uses (e.g. rangeland or degraded land) that are vastly less

productive.<sup>11</sup> In addition, 60,000 km<sup>2</sup> per year are subject to irreversible desertification, and an additional 200,000 km<sup>2</sup> per year are rendered unusable.<sup>11</sup> Similarly, in the United States alone, more than half of the 650,000 km<sup>2</sup> of rangeland managed by the Bureau of Land Management was rated as being in only "fair" condition in 1988, meaning that valuable forage plants had been replaced by less desirable plants or by bare ground.<sup>12</sup> An additional 17% was classified as being in "poor" condition, having been stripped of much of its topsoil and vegetation. The 200,000 km<sup>2</sup> of land in "poor" of "bad" condition were damaged primarily by overgrazing.<sup>9</sup>

Substantially increasing the productivity of these nonproductive poor or bad lands is often impossible because water is either unavailable for irrigation or too saline to be used for crop plants or trees. Thus, the prospects are poor for conventional agriculture or forestry in these areas. Where sufficient water exists to support forestry, the increases in productivity over existing uses as rangeland or cropland would be only about 2-fold.<sup>13</sup>

Basically, we can conclude that globally, the fight to stop deforestation is being lost on a large scale, and that the deforested land has much lower productivities, adding to the already large area of arid and semi-arid lands. In addition, it will be difficult to compensate for this nonproductive land with existing conventional land plants. This will become increasingly important within U.S. borders as global climate change proceeds.<sup>2</sup>

#### 4. BIOMASS METHODS FOR CO, CAPTURE: AQUATIC BIOMASS ON DESERT LANDS

Of the plants, algae are the most productive  $CO_2$  users and can fix greater amounts of  $CO_2$ per land area than higher plants (e.g. trees and sugar cane). Plant leaves exist in an aerial environment and are subject to large evaporative moisture losses, which directly inhibit the process of photosynthesis (CO<sub>2</sub> uptake). Microalgae in mass culture are not subject to such photosynthetic inhibition because the water content of the culture can be controlled by proper engineering. This difference is the basis for the several-fold higher CO<sub>2</sub> absorption capacity of microalgae compared to plants. Furthermore, CO<sub>2</sub> can be trapped effectively in algae ponds without covers, while higher plants would require expensive canopies to contain the CO<sub>2</sub> for efficient plant growth. Of course,

although photons are "free" in principle, significant costs may be involved to provide a controlled system for  $CO_2$  fixation. The need is to improve the technology to the point that the cost of the integrated process is low.<sup>14</sup> Nonetheless, for any reasonable system, net energy production is still possible while efficient carbon dioxide capture is assured.

Microalgae farming can increase the productivity of desert land almost 70-fold to a level<sup>15</sup> more than twice that of a typical tropical rainforest.<sup>13</sup> We estimate that microalgae farming with specially designed photobioreactor technology can increase the productivity of desert land 160-fold ( $6 \times$  that of a tropical rainforest). Furthermore, in contrast to the limited available arable land for forestry, there is much desert land available globally for microalgae farming. Microalgae require only 140-200 kg of water per kg of carbon fixed (based on average pond evaporation rates<sup>14</sup>), and this water can be low-quality, highly saline water. Thus, the biophysical and thermodynamic constraints favor microalgae, particularly in arid and semi-arid regions of the United States.

Examination of the availability of land, water, and CO<sub>2</sub> resources required for microalgal production has revealed that significant resources are available in Arizona and New Mexico, and large-scale microalgae farms could have a major impact on CO<sub>2</sub> emissions from power plants in these two states.<sup>16</sup> Futhermore, most of the resources in these two states coincide with or are within a moderate distance (80-160 km) of existing fossil-fuel power plants, and the total emissions from these two states (50 Tg of  $CO_2$  per year) could be absorbed by farms covering 0.25% of their area.<sup>16</sup> It is expected that similar studies of other locations in the United States or other countries would identify a wide range of sites at which algal technology could capture  $CO_2$  and provide a resource for valuable products.

One criticism of biomass energy systems is the amount of land and water they require. Microalgae are unique among photosynthetic plants in that they can achieve extremely high productivities at salinities as high as twice that of seawater,<sup>17-19</sup> and thus use low-quality (saline) water that is unusable for agriculture or urban uses. Thus, microalgae energy farming, with its focus on use of arid and semi-arid land and highly saline groundwater or seawater, utilizes resources not easily used by other biomass technologies or conventional agriculture.<sup>20,21</sup> Large-scale aquatic plant farming is not a new concept. The average rice crop requires 100 days of irrigation (ponding), and 2 crops per year are not uncommon.<sup>22</sup> Worldwide, more than 1.4 million km<sup>2</sup> of rice were harvested in 1985, including more than 10,000 km<sup>2</sup> in the United States.<sup>23</sup> Thus, microalgae should be viewed as simply a new crop for aquatic species farming with higher potential productivity on waste land and with otherwise unusable water resources. As such, it deserves consideration as one of the technologies that can contribute to the reduction in net global CO<sub>2</sub> emissions.

#### 5. PRODUCTS FROM MICROALGAE

Products derived from microalgae include extraction products such as hydrocarbons, fatty acids, glycerol, protein, pigments, and polysaccharides; bioconversion products such as alcohols, organic acids, and methane; and catalytic conversion products such as paraffins, olefins, and aromatics. Work at NREL has focused on the potential of microalgae to provide an alternative, renewable energy resource. Fuels obtainable from microalgae include ethanol, triglyceride-based diesel fuel, ester fuel. methane, and gasoline. The unique ability of microalgae to accumulate up to 60% of their cellular organic mass as lipid, as well as the higher fuel value of lipids vs. other cellular components, has led us to concentrate our efforts on the production of lipid-based fuels.

One issue to be addressed in the growth of microalgae for production of fuels or chemicals is the requirement for  $CO_2$ . As the major raw material of photosynthesis, CO<sub>2</sub> is the major feedstock for microalgal production. In addition, CO<sub>2</sub> supply has been identified as the largest single contributor to the cost of liquid fuels derived from microalgae.14 Microalgae farms sufficient to produce 50 Tg of biomass would require approximately 160 Tg of  $CO_2$ annually. If one assumes an annual average yield of at least  $30 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  for intensive microalgae farming and 270 operating days per year, more than  $25 \text{ kg C} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$  are required.  $CO_2$  levels in the atmosphere (0.033%) are not sufficient to support such high microalgae productivities. Thus, a concentrated supply of  $CO_2$  is essential if high yields are to be obtained, and flue gas from fossil-fuel power plants is an excellent potential source of CO<sub>2</sub>.<sup>24</sup>

The following equation illustrates the stoichiometry for production of a triglyceride composed of polyunsaturated, 18-carbon fatty acids with an energy content of 39.5 megajoules  $(MJ) kg^{-1}$ :

57 
$$\text{CO}_2 + 31 \text{ H}_2\text{O} \rightarrow \text{C}_{57}\text{H}_{62}\text{O}_6 + 69.5 \text{ O}_2.$$

One can calculate that the production of such a triglyceride requires approximately 3.0 kg of  $CO_2$  per kg of triglyceride produced. This large requirement for  $CO_2$  makes lipid-producing microalgae particularly useful for trapping  $CO_2$ .

Microalgal mass cultivation has been an object of research for more than 40 years. A great deal of progress has been made in mass culture of algae since this early work, but a great deal of research still needs to be done. Yields in the early days were often in the range of  $1-5 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ ; today,  $15-25 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  are not uncommon,<sup>25</sup> and short-term yields as high as  $50 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  have been obtained.<sup>26</sup>

technological developments Additional would seem to be necessary to make a fuelsfrom-microalgae technology economically feasible. These developments are the focus of the technology assessment of Neenan et al.,<sup>14</sup> which demonstrates that gasoline and diesel fuels could be produced from microalgae at prices that will be competitive with conventional fuels. This assessment considered the potential fuel products from microalgae, the environmental and resource constraints, and the biological and engineering aspects of the technology. Specific research goals were identified, which are restated and updated as follows:

Environmental and resource constraints. Because  $CO_2$  is the largest single contributor to the cost of fuel from microalgae, improvement in the separation of  $CO_2$  from flue gas or minimization of flue gas processing requirements should be emphasized.

**Biology and engineering**. The technology assessment identified biological issues as the most critical research needs. Improvements in biological productivity and lipid content are necessary to make microalgal fuels economically feasible. Under laboratory conditions, productivities have been achieved that come very close to identified targets; these results must be extended to large-scale, outdoor cultures.

**Fuel products**. This analysis identified gasoline and ester fuels as the most promising products from microalgal biomass. Extraction and conversion research, as well as detailed information regarding the fuel characteristics of microalgal lipids, were identified as research priorities. With current technology, the cost of fuel from microalgae is estimated at  $\$1.331^{-1}$ , of which almost 30% is for CO<sub>2</sub>. If the research goals identified above can be met, Neenan *et al.*<sup>14</sup> concluded that fuels from microalgae could be produced for  $\$0.421^{-1}$  by the first decade of the next century. However, if concerns about global climate change result in the levy of fines for release of CO<sub>2</sub>, the cost of this vital algal nutrient could become zero or negative (paid to use it), and costs for algal fuel could drop to the range of  $\$0.251^{-1}$ .

#### 6. GLOBAL CLIMATE CHANGE—MICROALGAE AND FOSSIL FUEL EMISSIONS

By converting microalgae into a fuel product that displaces fossil fuels, an algae farm cuts approximately in half the greenhouse-enhancing CO<sub>2</sub> emissions per gigajoule (GJ) delivered from the power plant. Depending on the composition of the algae and the amount of CO<sub>2</sub> emitted per GJ of energy released from coal, the integration of microalgal mass culture technology with coal-fired power plant could reduce the  $CO_2$ emitted per GJ from 86-97 kg to 39-49 kg CO<sub>2</sub>. These numbers compare to the 54 kg  $CO_2$  GJ<sup>-1</sup> from natural gas, and the 69 kg  $CO_2$  GJ<sup>-1</sup> from oil. Significant reductions would also be realized from gas-fired plants, which have cleaner flue gas, and would require less pre-processing of flue gas prior to injection into ponds. If commodity chemicals instead of fuels are produced from algae, the net CO<sub>2</sub> released could be reduced even further.

## 7. IMPACT OF FLUE GAS COMPONENTS ON MICROALGAE GROWTH

Earlier cost analyses of microalgal biomass production proposed the use of flue gas as a source of  $CO_2$  for microalgae. Although ponds are currently being operated with pure  $CO_2$ injection, to date, very little actual data have been obtained regarding the direct use of processed or unprocessed flue gas on microalgal growth. The Electric Power Research Institute sponsored a project designed to test flue gas as a carbon source for microalgae, but the data obtained in this study were very limited.<sup>27</sup> Mitsubishi is currently working on a project to scrub  $CO_2$  from flue gas using microalgal ponds.<sup>28</sup>

Flue gas obtained from coal combustion contains a large number of trace contaminants that may affect microalgal growth, in addition to oxides of nitrogen and sulfur. We have done some preliminary calculations to answer the following questions. (1) Can the nitrogen in flue gas contribute significantly to the nitrogen requirement of algae? (2) Will the water vapor in flue gas contribute to the water requirement of algal ponds? (3) If all incoming sulfur is converted to acid, what effect will this have on the pH of the culture? (4) If all incoming sulfur is neutralized to salts, what effect will this have on the salinity of the culture? (5) Will the waste heat from the power plant have a significant effect on the temperature of the ponds? We have based these calculations on a constant amount of  $CO_2$ , because the  $CO_2$  emitted from combustion of different fuels varies considerably.

### 7.1. Nitrogen

The purpose of this calculation was to determine the maximum possible contribution of nitrogen from flue gas. We assumed that the algae contained 25% protein, 16% of which is nitrogen.<sup>29</sup> Assuming 10 kg of nitrogen oxides emitted per ton of coal combusted,<sup>30</sup> we calculate that this nitrogen will contribute only 6.1% of the nitrogen required for algal yields of  $50 \text{ g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ . Similarly, oil combustion could supply 6.5% of the algal nitrogen requirement, and natural gas combustion could supply 4.7% of the nitrogen needed.<sup>30</sup> These numbers are potential maxima, and do not reflect the poor solubility of oxides of nitrogen in water.

## 7.2. Water

For these calculations, we assumed that all hydrogen in the fuel would be converted to water during combustion, and that all water in the fuel would end up as water vapor in the flue gas. Coal contains approximately 10% moisture and 5% hydrogen,<sup>31</sup> and combustion of this fuel would contribute only 0.4% of the daily water requirement of a microalgae pond. Oil, with 0% moisture and 12.5% hydrogen,<sup>32</sup> could contribute 0.7% of the daily water requirement. Natural gas, with 1% moisture and 24.5% hydrogen,<sup>33</sup> could contribute 1.5% of the daily water requirement. The total amount of water available from flue gas is very small, but it is fresh water, and will reduce slightly the requirement for blowdown water.

## 7.3. Acidity

Bituminous coal combustion yields 37.5 kgSO<sub>2</sub> t<sup>-1.34</sup> If all the sulfur is converted to H<sub>2</sub>SO<sub>4</sub>, 57.5 kg of acid could be obtained per ton of coal burned. The addition of this acid to the standing water in an algal pond would lower the pH of an unbuffered system to 3.5. Oil combustion yields 25 kg  $SO_2^{-1}$ ,<sup>34</sup> and could lower the pH to 3.75. Natural gas combustion releases very small quantities of  $SO_2$ , and would result in a pond pH of 7.0. These calculations are independent of the pH-lowering effects of CO<sub>2</sub>, and do not take into account the alkalinity of the ponds. These numbers are also calculated as potential maximum contributions to acidity. Flue gas desulphurisation would drastically reduce the sulfur content of the flue gas. In addition, it may be possible to offset pH changes caused by sulfur by adding lime to the ponds, instead of treating the flue gas with lime prior to its use in algal ponds.

#### 7.4. Salinity

If the sulphur introduced into the ponds as  $SO_2$  from flue gas is neutralized to form sodium sulfate, it would contribute to the salinity of the pond rather than the acidity. Using the  $SO_2$  figures from above, we have calculated that flue gas would add no more than 0.0225 parts per thousand per day salinity to the ponds. This figure is insignificant when compared to the salinity of the water in the pond.

#### 7.5. Heat

The addition of waste heat from a power plant to a microalgal pond has been postulated to be a problem in the summer and a boon in the winter, but calculations as to the magnitude of the input have not been published. We based our calculations on a power plant efficiency of 38%, and used 90% of the 24 h average minimum and maximum solar inputs for the desert southwest<sup>35</sup> to calculate the magnitude of waste heat compared to solar radiation. The microalgal pond was sized to the coal-fired plant by assuming 100% capture of CO<sub>2</sub> and a yield of  $50 \text{ g} \cdot \text{m}^{-2} \text{day}^{-1}$ . We found that the heat input from a 1380  $MW_{\theta}$  coal plant was on the order of 200 Wh $\cdot$ m<sup>-2</sup>·day<sup>-1</sup>, while the input of heat from solar radiation ranged from 3400 to 9000 Wh $\cdot$ m<sup>-2</sup> $\cdot$ day<sup>-1</sup>. Therefore, the heat input from the power plant on a sunny, summer day is less than 3% of the input from solar radiation.

Heat losses were assumed to occur via convection, radiation, and evaporation. A heat differential of 5°C was used for the convection and radiation calculations, and an evaporation rate of  $0.0035 \text{ m} \cdot \text{day}^{-1}$  was assumed.<sup>14</sup> Using

these assumptions, total potential heat losses were calculated to be in the range of  $3700-6400 \text{ Wh} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ .

#### 8. CONCLUSIONS

Algae can produce a number of chemical products derived from CO<sub>2</sub> through photosynthesis. For example, certain microalgae are capable of accumulating up to 60% of their cellular organic mass as intracellular lipids, thereby increasing their heat of combustion and their fuel value. These lipids can be readily converted to gasoline and diesel fuel. Although  $CO_2$  is still released when algal fuels are burned, integration of algal fuel farms for flue gas capture approximately doubles the amount of energy produced per mole of CO<sub>2</sub> released. Alternatively, a number of other chemical products could be derived from algae that would fix carbon for extended periods, and even mineral products can be formed that fix carbon in the long-term geological cycle.

Flue gas has the potential to provide sufficient quantities of CO<sub>2</sub> for large-scale microalgae farms. Two analyses of costs for aquatic biomass systems<sup>36,37</sup> both assumed direct use of flue gas. Cost calculations did not include gas scrubbing, although both studies mention that this might be necessary. Neenan and coworkers<sup>14</sup> assumed concentration of CO<sub>2</sub> from flue gas, and included this cost in their analysis. Our preliminary calculations indicate that flue gas will have very little impact on the nitrogen requirement, water requirement, salinity, or temperature of algal ponds. Flue gas has the potential to have a significant impact on the acidicity of the ponds if large quantities of sulfur are introduced. It may be possible to neutralize this acidity in the ponds themselves, rather than by treating the flue gas. Stricter government standards regarding emissions of sulfur dioxide may make this a moot point as sulfur may be removed upstream. Insufficient data exist about the effect of flue gas on microalgal growth. Further work investigating the use of flue gas for algal culture is necessary.

Viewing microalgae farms as a means to reduce the effects of a serious pollutant (CO<sub>2</sub>) changes the view of the economics of the process. Instead of requiring that microalgae-derived fuel be cost competitive with fossil fuels, the process economics must be compared with those of other technologies proposed to deal with the problem of CO<sub>2</sub> pollution. However, development of alternative, environmentally safer energy production technologies will benefit society whether or not global climate change actually occurs.<sup>1,7</sup> Fuels from microalgae have great potential to contribute to world energy supplies, and to control  $CO_2$  emissions as the demand for energy increases. This technology makes productive use of arid and semi-arid lands and highly saline water, resources that are not suitable for agriculture and other biomass technologies. If fuels from microalgae are to be economically justifiable, improvements in biological productivity and product yield must be realized.

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