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Daniel A. Feinberg

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Solar Energy Research Institute
A Division of Midwest Research Institute

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PREFACE

The Solar Fuels Research Division of the Solar Energy Research Institute, under the Aquatic Species Program, is carrying out a broad range of research activities to develop microalgae as a potential source of renewable liquid fuels. This study examines a variety of microalgal species with representative chemical compositions, ranking each for its potential as a renewable source of ethanol, methane, and lipid-derived fuels such as synthetic diesel fuel (methyl ester). This assessment is based solely on chemical composition and does not take into account the yield factor. The work was performed as a follow-up to "Fuel from Microalgae Lipid Products," by D. Feinberg and A. Hill, which was published in April 1984 as SERI/TP-231-2348.

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SUMMARY

Objective

To examine various species of microalgae with representative chemical compositions and to evaluate a variety of renewable liquid (and gaseous) fuel options.

Discussion

Each of the three biochemical fractions of microalgae (lipids, carbohydrates, and proteins) can be converted into fuels. Lipids have the highest energy content of the three. The lipids of some species are hydrocarbons, similar to those found in petroleum, while those of other species resemble seed oils, which can be converted to a synthetic diesel fuel (ester fuel) by the process known as transesterification. Carbohydratees are commonly converted to ethanol by fermentation. Alternatively, all three fractions can be converted to methane gas by anaerobic digestion. A total of eleven different cases (nine different species) are examined in this report, including four species identified as high-lipid producers, three high-carbohydrate producers, three high-protein producers, and one high-glycerol producer.

Based on the chemical compositions reported for the various species, an estimate is first made of the gross energy content available from a unit mass of each species. Then, options are considered that convert each fraction into the desired products. For example, the entire mass might be converted to methane, the carbohydrate fermented to ethanol, the lipid converted to ester fuel, or any combintaion of these.

Conclusions

Among the high-lipid producing species, Botryococcus braunii is unique in that it can produce hydrocarbons at 40% or higher of its total lipids. Most of these hydrocarbons are benzene-extractable, aromatic-type compounds, which might be directly usable as liquid fuel. A critical research question is whether sufficiently high growth rates could be achieved to permit economically competitive fuel production from this organism. Another high-lipid producer, Nannochloropsis salina, has shown the ability to produce up to 34% of its total lipid as fatty acids, which can in turn be esterified to produce ester fuel. Calculations indicate that 53.1% of the total energy content of this organism can be converted into liquid fuel. It is clear from a chemical composition standpoint that lipid producers offer the most potential for renewable production of high-energy liquid fuel.

All three of the high-carbohydrate producing species examined offer potential as renewable sources of ethanol. The diatom Cyclotella cryptica, with a reported 67% carbohydrate content, and Chlamydomonas sp., with 59% carbohydrates, would produce exclusively ethanol, converting approximately 30% of their total energy contents into a single liquid fuel. Dunaliella salina, on the other hand, contains approximately 3% fatty acid and 1% hydrocarbon as well as 55.5% carbohydrate; up to 47% of its total energy can therefore be converted to liquid fuels.

Although liquid fuels, especially hydrocarbons, are more valuable due to their ease of storage and handling (especially for the vast transportation fuel markets), all the species examined offer great potential as sources for the production of methane via anaerobic digestion. Due to the inherently lower energy requirements and higher conversions for this process, energy utilization efficiencies range from about 68% (for high-protein producers) to 75% (for high-lipid producers). The high-protein producing species, as well as another strain of D. salina that produces about 28% glycerol, might have an economic advantage due to their coproduction of higher valued products. Detailed examinations of algal productivity data, as well as economic studies, are not required to further quantify the potential of these organisms as renewable fuel producers.

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SECTION 1.0

INTRODUCTION

Photosynthetic organisms such as microalgae "fix" atmospheric carbon into the energy-storage components of their cell mass; i.e. protein, carbohydrate, and lipid. Under the limitations of current technology, algae can convert up to 15% of the photosynthetically available solar radiation (PAR), or roughly 6% of the total incident radiation, into new cell mass [1].

The conversion of solar energy into renewable liquid fuels and other products could become economically competitive with petroleum if research progress continues. The historical emphasis on high-energy lipids as the primary fuel products from microalgae was based on some species' ability to accumulate large quantities of these compounds, especially under stressful growth conditions [2]. The objective of this report is to examine the chemical makeup of a variety of algal species under different growth conditions and the conversion processes possible for each class of compounds (i.e., lipids, carbohydrates, and proteins). Based on the results of this analysis, some projections are made about the optimum fuel product conversion route(s) for several representative species.

As part of the Solar Energy Research Institute (SERI)/United States Department of Energy (DOE) Aquatic Species Program's major study of fuel products from microalgae, this report provides an important link between cultivation and harvesting of a variety of algal species and conversion of specific biochemical fractions into the desired products.

The recent work of Tornabene et al. and Ben-Amotz in characterizing different algae with respect to chemical composition, especially possible for each class of compounds (i.e., lipids, carbohydrates, and proteins). Based on the results of this analysis, some projections are made about the optimum fuel product conversion route(s) for several representative species.

As part of the Solar Energy Research Institute (SERI)/United States Department of Energy (DOE) Aquatic Species Program's major study of fuel products from microalgae, this report provides an important link between cultivation and harvesting of a variety of algal species and conversion of specific biochemical fractions into the desired products.

The recent work of Tornabene et al. and Ben-Amotz in characterizing different algae with respect to chemical composition, especially the lipid fractions, has been extremely valuable. Their reports [3, 4, 5] discuss in detail materials and methods for these characterizations. Other sources of biochemical data may be found in Burlew [2]. The first step is to examine the total chemical composition and gross energy content of several representative species. The next level of consideration is to examine the crude lipid and carbohydrate components, followed by any subfractions for which data are available; e.g., the neutral lipid fraction extracted by hexane or the benzene-soluble fraction containing aromatics and carotenoids.

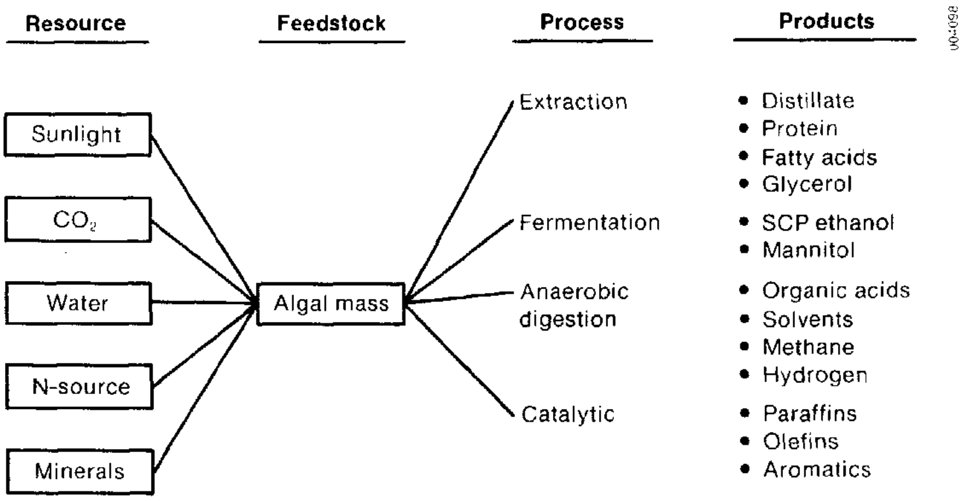

Figure 1-1. Microalgal Production and Products

It is beyond the scope of this report to consider all the potential conversion processes in detail with respect to process design and economics; however, a few process routes are considered, and each specie is evaluated to determine whether it might be a suitable feedstock. The process options considered are aerobic and anaerobic fermentation for carbohydrates, anaerobic fermentation only for proteins, and extraction and conversion processes in general and transesterification in particular for lipids. Figure 1-1 shows schematically how different conversion processes could produce a variety of fuel products from a microalgal feedstock.

SECTION 2.0

APPROACH

Based on the reported algal composition, a gross energy content is calculated. "Typical" algal proteins are assumed to contain 23.86 MJ/kg (10,260 Btu/lb); carbohydrates 15.92 MJ/kg (6840 Btu/lb); lipids 38.93 MJ/kg (16,740 Btu/lb); and glycerol 18.05 MJ/kg (7760 Btu/lb) [2].

In today's conventional ethanol fermentation, yeasts such as *Saccharomyces cerevisiae* can convert up to 95% of the "available" carbohydrate, i.e., glucose, into a 1:1 (weight) ratio of ethanol and carbon dioxide. The main requirement here is to estimate the available carbohydrate. Algal carbohydrates typically are complex mixtures of mono-, poly-, and oligosaccharides, with pentoses and hexoses having been identified [2]. A reasonable approach is to assume that about two-thirds of the carbohydrate can be hydrolyzed to fermentable hexose monomer with the remainder essentially all pentose; i.e., not fermentable under current commercial practice. A combined hydrolysis-fermentation yield of 80% is assumed for this carbohydrate fraction, which is much less homogeneous but more accessible to hydrolysis than, say, lignocellulose. These assumptions result in a net alcohol production of 0.329 L/kg (0.04 gal/lb) and a total energy content of 7.74 MJ/kg (3330 Btu/lb) of total carbohydrate. Figure 2-1 shows the ethanol yield and energy production as functions of the carbohydrate content. A fermentation by-product, carbon dioxide (approximately 39 L/L or 5.2 ft^3/gal of ethanol), is also produced.

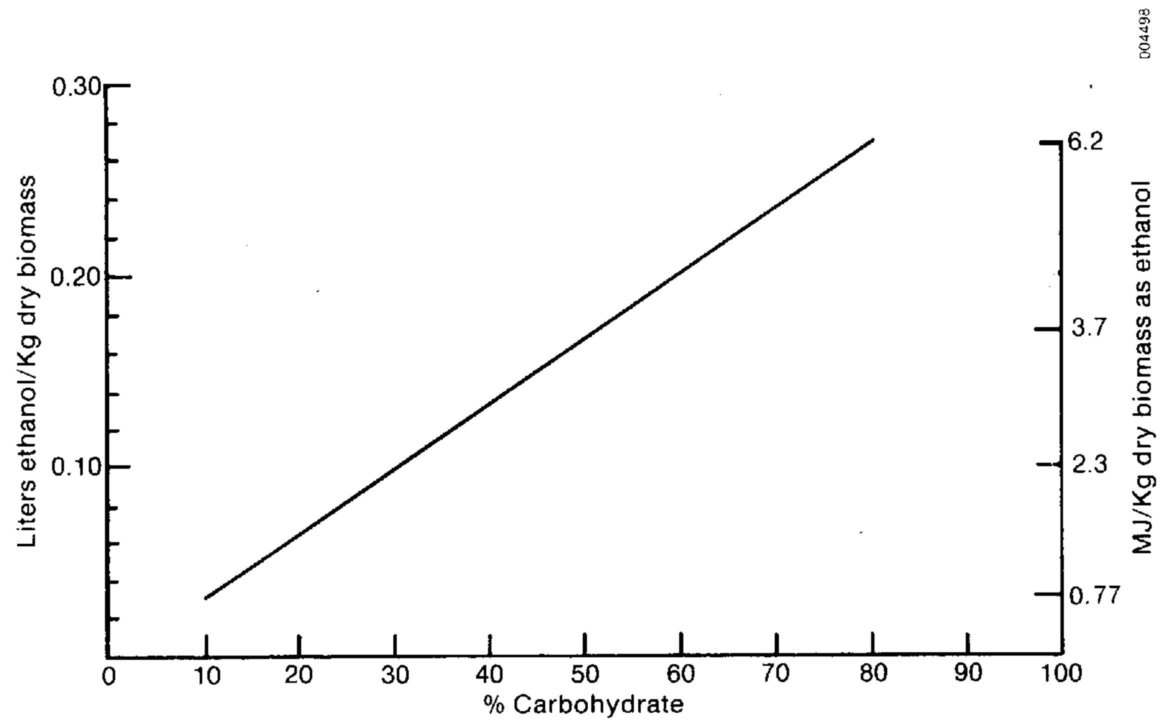

Figure 2-1. Ethanol Yield from Microalgae Biomass

This screening study examines two lipid utilization routes: transesterification (conversion of triacylglycerols to monoesters of either methanol or ethanol) and a "simple" extraction of hydrocarbons. Based on data from Tornabene et al. [3], the hydrocarbon extraction calculations assume that the neutral lipids directly usable as fuel would be equal to the hexane extract plus one-half the benzene extract. In fact, the hydrocarbons of many species, at 28+ carbons, may require cracking or other processing to insure their suitability. These fractions could be recovered with processing losses of only 2%, yielding 1.15 L of hydrocarbon liquids per kg of lipid (0.65 gal/lb). Based on the energy content being equal to diesel fuel at 39 MJ/L (129,500 Btu/gal), 44.96 MJ (19,370 Btu) of energy per kg (lb) of lipid in the form of hydrocarbon could be recovered (Figure 2-2).

Transesterification, which is discussed in more detail elsewhere [6], produces a mixture of fatty acid esters, which have been shown to be suitable substitutes for diesel fuel. The assumed conversion of 95% of the triglycerides to fatty esters is routinely achieved in commercial processes. The critical parameter is the fraction of total lipids available for conversion; i.e., the triglyceride/fatty acid fraction. This fraction is estimated at 89% of the chloroform extract (exclusively triglyceride, converted to fatty acids) plus 65% of the methanol extract (phospholipids converted to fatty acids) [7]. Alternatively, in some cases the triglyceride/fatty acid contents have been reported directly. The ester fuel produced has an energy content of 35 MJ/L (116,200 Btu/gal) or about 10% below that of diesel fuel [8]. These assumptions result in an ester fuel production of 1.25 L/kg (0.73 gal/lb) and an energy content of 43.8 MJ/kg (18,850 Btu/lb) of triglyceride (Figure 2-2).

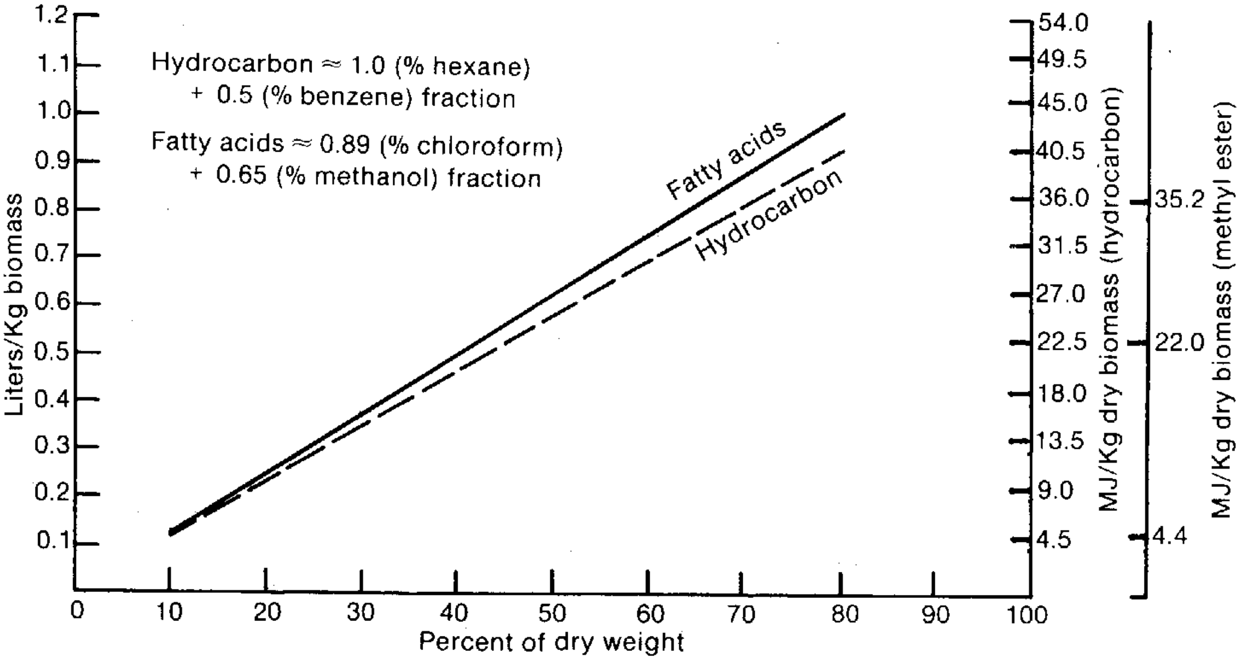

Figure 2-2. Hydrocarbon/Methyl Ester Yield from Microalgae Biomass

Anaerobic digestion is the most flexible process in terms of available feedstocks. Basically, the entire organic weight, which was not used by one of the previously mentioned processes, is digested. The theoretical methane production rates [9] are 0.49 m^3 of methane per kg of protein converted, 0.37 m^3 per kg of carbohydrate, and 1.04 m^3 per kg of lipid, and it is assumed that 80% of the volatile solids are converted to products (80% COD removal). The gaseous product is assumed to contain the typical biogas composition of 60% methane and 40% carbon dioxide. With an energy content of 37.2 MJ/m^3 (1000 Btu/ft^3) of methane, energy production per kilogram of volatile solids converted is 30.95 MJ/kg (9960 Btu/lb) lipid, 14.58 MJ/kg (4740 Btu/lb) protein, and 11.01 MJ/kg (3600 Btu/lb) carbohydrate (and glycerol). This information is shown graphically in Figure 2-3.

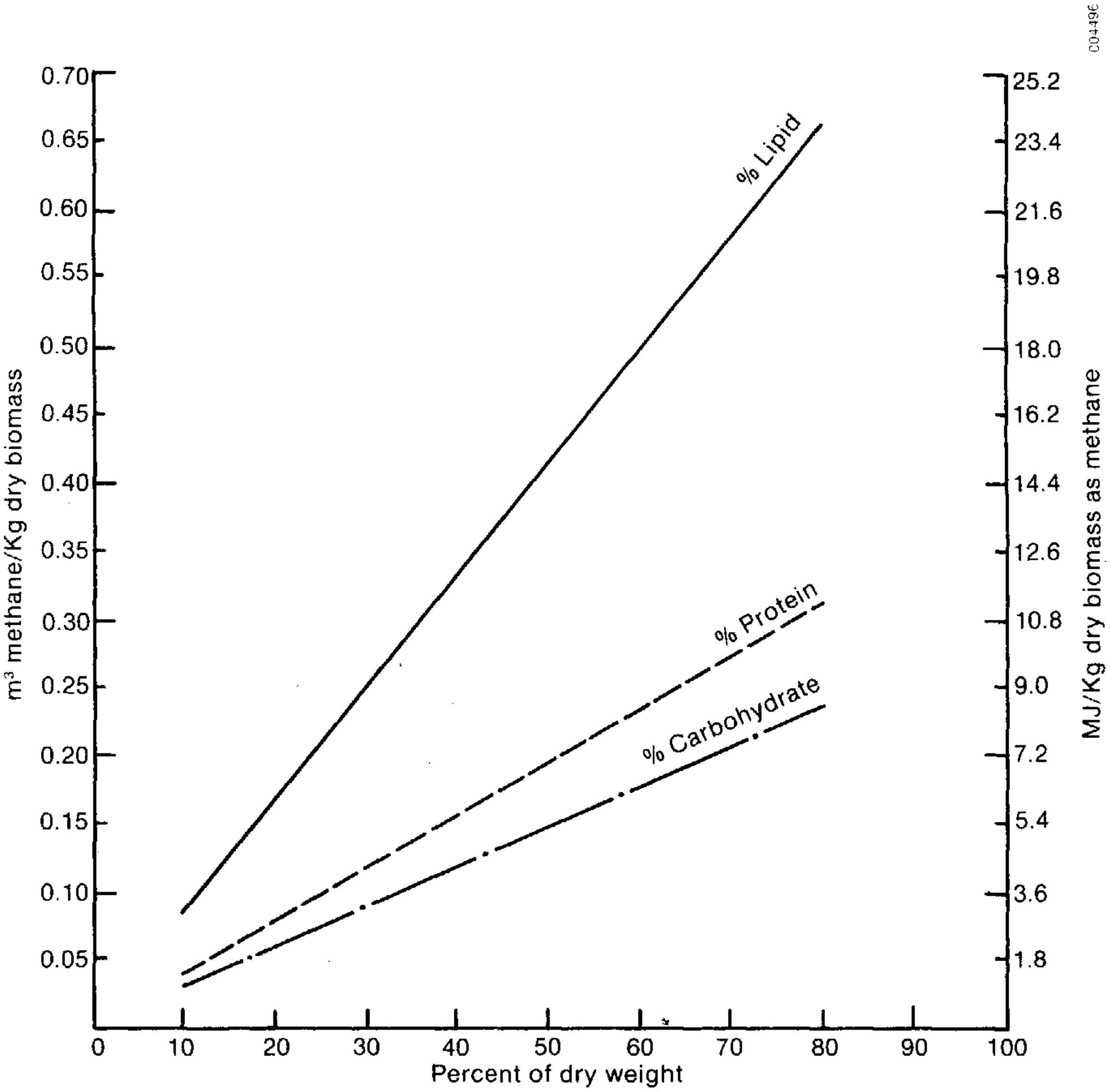

Figure 2-3. Methane Yield from Microalgal Biomass

SECTION 3.0

FUEL OPTIONS AS DETERMINED BY CHEMICAL COMPOSITION

Table 3-1 summarizes the chemical composition of representative algal species grown under a variety of nutrient and salinity conditions. The different species are grouped according to the primary products: lipids, carbohydrates, protein, and glycerol. The glycerol fraction could either be digested for gas or recovered as a by-product. For each species the amount of energy that can be converted to fuels and the fraction of the gross energy content are calculated in the following ways:

- Methane only: anaerobic digestion of the entire (ash-free) cell mass, including glycerol
- Methane-glycerol: anaerobic digestion of the cell mass, excluding glycerol
- Ester-methane: digestion of the protein and carbohydrate fractions only, with the lipids being converted to ester fuel and hydrocarbon
- Ethanol-methane: digestion of the protein and lipid fractions, with the carbohydrate being converted to ethanol
- Ester-ethanol-methane: digestion of the protein fraction only, with ester fuel, hydrocarbon, and ethanol production.

These are identified in Tables 3-2 through 3-12 as Options 1 through 5, respectively. All energy values are reported in MJ/kg ash-free dry weight (multiply by 430 to convert to Btu/lb).

3-1. Botryococcus braunii

B. braunii, a slow-growing organism, is interesting because it accumulates a large fraction of its biomass as hydrocarbon/lipid. Table 3-1 (Example 1) shows that under nitrogen-deficient growth conditions in fresh water, this organism accumulates lipids at 54.2% of ash-free dry weight. A sizeable protein-carbohydrate fraction, about 34%, is also present. More than 53% of the total lipid content is benzene extractable and consists of aromatic hydrocarbons, which could be directly usable as fuels. Another 14.9% of total lipids are hexane-extractable, straight-chain alkanes (saturated hydrocarbons) primarily in the 30-32 carbon range. Coupled with this extremely high hydrocarbon content is a low fatty acid content estimated at 7.8% of the total lipid. Examination of this fraction shows more than 55% to be saturated and singly unsaturated, indicating an ester fuel product relatively stable toward autooxidation during storage.

There is little question that this lipid content would be high enough to use the organism as a conversion feedstock if it could be grown at sufficiently high rates (Table 3-2). In general, the options that convert lipids to liquid fuels would be preferred, since more of the cell's energy is then recovered in the premium liquid form. An overall energy utilization rate of 75% can be achieved by anaerobic digestion of the lipid and protein fractions, and either

Table 3-1. Chemical Composition of Various Microalgae

Example	Name	Stress	Main Product^a	Protein^a	Carbo-hydrate^a	Lipid^a	Glycerol^a	Hexane Fraction^b	Benzene Fraction^b	Chloroform Fraction^b	Methanol Fraction^b	Fatty Acid^b	Reference
1	Botryococcus	+++	Hydrocarbon	0.206	0.143	0.542	0.001	0.149	0.527	0.034	0.074	0.078	3
2	Ankistrodesmus	+	Lipid	0.151	0.193	0.426	0.000	0.000	0.033	0.135	0.121	0.199	3
3	Isochrysis	+++	Lipid	0.233	0.205	0.26	0.001	0.022	0.284	0.180	0.253	0.325	3
4	Nannochloropsis	+	Lipid	0.23	0.07	0.54	0.000	0.040	0.402	0.355	0.043	0.344	5
5	D. salina	++	Glycerol	0.125	0.555	0.092	0.047	0.001	0.248	0.206	0.228	0.331	3
6	Chlamydomonas	-	Carbohydrate	0.17	0.59	0.23	0.000	0.000	0.000	0.000	0.144	0.094	5
7	Cyclotella cryptica	+	Carbohydrate	0.13	0.67	0.180	0.000	0.000	0.000	0.000	0.000	0.000	10
8	Spirulina platensis	-	Protein	0.50	0.088	0.166	0.000	0.020	0.034	0.014	0.366	0.250	3
9	Chlorella (Thomas)	-	Protein	0.469	0.097	0.207	0.000	0.001	0.006	0.017	0.221	0.159	4
10	Nannochloropsis	-	Protein	0.558	0.156	0.286	0.000	0.020	0.050	0.050	0.330	0.259	4
11	D. salina	++	Glycerol	0.359	0.125	0.185	0.277	0.002	0.021	0.282	0.136	0.339	3

Legend:

- No stress
+ Nitrogen stress
++ Osmotic stress
+++ Nitrogen and osmotic stress
[a] Fraction of ash-free dry weight.
[b] Fraction of total lipid.

digestion or fermentation of the carbohydrate. Conversion of the lipids to liquid fuels (ester fuel and hydrocarbon) would recover 42% of the gross energy content in liquid form; fermentation would contribute another 5%, for a liquid fuel utilization rate of 47% and an overall utilization rate of 58%.

One of the key issues to be addressed by those wishing to cultivate this organism for fuel production would be: what are the limitations on the direct use of the hexane and benzene fractions as fuels? The predominance of saturated hydrocarbons with 30-32 carbons mentioned earlier may be too long for diesel fuel and possibly even for heavy fuel oils. An additional processing step might be required for conversion of part (or all) of the lipid fraction into usable liquid fuels. With this arguement the most critical question is whether a high enough growth rate can be maintained to enable these fuel options to be economically pursued.

3-2. Ankistrodesmus falcatus

The next high lipid-producing species considered is Ankistrodesmus falcatus, grown in nitrogen-deficient media. As shown in Table 3-1, more than 42% of the ash-free dry weight is lipid, with another 34% consisting of carbohydrate and protein. Unknown components represent a substantial 23%. The hexane fraction is negligible and the benzene extract constitutes only 3.3% of total lipids. The chloroform (13.5%) and methanol (12.1%) are also small, resulting in a total fatty acid content of 19.9% of total lipids. Maximum overall fuel utilizations of approximately 75% are again achieved by anaerobic digestion, with or without fermentation. Conversion of triglycerides into ester fuel (without ethanol fermentation) produces both an overall energy utilzation rate (58.3%) and a liquid fuel utilization (17.3%) much lower than Botryococcus; inclusion of fermentation further reduces overall utilization to 34.9% but increases liquid fuel utilization to 25.5% (Table 3-3). These calculations show that high lipid content alone may not be indicative of a promising algal species if the right kind of lipids is not prevalent.

3-3. Isochrysis sp.

Example 3 shows the composition of an Isochrysis cultured under moderately saline (0.5 M NaCl), nitrogen-deficient conditions. Although the lipid content is a moderate 26%, this organism is included among the high-lipid producers; lipid contents as high as 45% have been reported recently. Protein (23%) and carbohydrate (21%) are both substantial components. The hexane fraction represents 2.2% of total lipids, the benzene fraction 28.4%, the chloroform fraction 18%, and the methanol fraction 25.3% (total fatty acids 32.5%). Tornabene has tentatively identified the major constituent of the benzene fraction as an oxygenated cyclic C-37 isoprenoid chain, which could be significant either for fuels or by-products. Table 3-4 shows that the total energy content under these conditions is 18.9 MJ/kg, considerably lower than the previous species. However, both the overall and liquid utilization efficiencies compare well with those of Botryococcus: the highest overall utilization is found in the methane-only option at 72.3%, with the highest liquid fuel utilization found in the ester-ethanol-methane option with 40.3%. The overall utilization rate of 58.2% is slightly higher than the corresponding utilization rate for Botryococcus.

Table 3-2. Fuel Production Options for Botryococcus braunii

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	GEC[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	21.365	0.000	0.000	0.000	21.365	28.308	0.755	0.000	0.000
2	21.354	0.000	0.000	0.000	21.354	28.290	0.755	0.000	0.000
3	4.579	1.861	10.053	0.000	16.493	28.290	0.583	11.914	0.421
4	19.779	0.000	0.000	1.402	21.181	28.290	0.749	1.402	0.050
5	3.004	1.861	10.053	1.402	16.321	28.290	0.577	13.317	0.471

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

Table 3-3. Fuel Production Options for Ankistrodesmus falcatus

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	G.E.C.[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	17.512	0.000	0.000	0.000	17.512	23.258	0.753	0.000	0.000
2	17.512	0.000	0.000	0.000	17.512	23.258	0.753	0.000	0.000
3	4.327	3.712	0.316	0.000	8.355	23.258	0.359	4.028	0.173
4	15.387	0.000	0.000	1.893	17.280	23.258	0.743	1.893	0.081
5	2.202	3.712	0.316	1.893	8.123	23.258	0.349	5.921	0.255

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

3-4. Nannochloropsis salina (high lipid)

This organism when cultured in nitrogen-deficient seawater by Ben-Amotz developed high levels of total lipids (54%). In particular the benzene (40.2%) and chloroform (35.5%) fractions were high [5]. Fatty acids are estimated at 34.4% of total lipids. A substantial carbohydrate fraction (23%) is also present. The gross energy content at 27.6 MJ/kg is only slightly lower than that of Botryococcus. Once again, the anaerobic digestion options recover 75% of the gross energy content, with the ester-ethanol option having both a very good overall utilization rate (62.3%) and a moderate liquid fuel utilization rate (53.1%) (Table 3-5). The ester-ethanol-methane option could produce a greater amount of energy than could Botryococcus (18.0 vs. 16.3 MJ/kg).

3-5. Dunaliella salina (high carbohydrate)

When subjected to both osmotic stress and nitrogen deficiency, Dunaliella salina produced large quantities of carbohydrate. Listed as Example 5, this organism accumulated 55.5% of ash-free dry weight as carbohydrate. Both protein and carbohydrate were present at approximately 10%, and glycerol (4.7%) was also present, which will be discussed later (Example 11). The large carbohydrate content and small lipid content contribute to the gross energy content being considerably lower than the lipid-producers (16.2 MJ/kg, including glycerol). The energy utilization rates (Table 3-6) are also somewhat lower, especially in the methane options; less lipid and more carbohydrate to be digested means a lower net energy production. Liquid fuel utilization in the ester-ethanol-methane option for this organism (47.4%) is comparable to the lipid producers; the difference is that 74% of the liquid fuel energy comes from ethanol. The methane-ethanol option, with an overall utilization rate of 65.7% and a liquid fuel utilization rate of 35.4%, might also be acceptable as a lower-cost alternative that still offers moderate liquid fuel production.

3-6. Chlamydomonas sp.

This organism was cultured by Ben-Amotz in seawater with no environmental stresses and is characterized by a high carbohydrate content (59%) (Example 6). Lipid (23%) and protein (17%) contents were moderate, resulting in a gross energy content (22.4 MJ/kg) that compares favorably with the lipid producers (Table 3-7). The ethanol-methane option has a high overall utilization (68.7%) and a moderate liquid fuel utilization (25.8%), while the ester-ethanol-methane option has the lowest overall utilization (41.1%) and a liquid fuel utilization (30%) that does not compare favorably with other species. The overall utilization of 71.9% in the methane-only option is good, however.

3-7. Cyclotella Cryptica

This diatom, grown by Werner [10] in nitrogen-deficient media, produced exceptional carbohydrate content (67%). Lipid content is a moderate 18% (Example 7), which contributes to a gross energy content of 20.77 MJ/kg. No

Table 3-4. Fuel Production Options for *Isochrysis sp.*

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	GEC[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	13.713	0.000	0.000	0.000	13.713	18.961	0.723	0.000	0.000
2	13.702	0.000	0.000	0.000	13.702	18.943	0.723	0.000	0.000
3	5.655	3.700	1.917	0.000	11.272	18.943	0.595	5.617	0.297
4	11.445	0.000	0.000	2.010	13.455	18.943	0.710	2.010	0.106
5	3.398	3.700	1.917	2.010	11.025	18.943	0.582	7.627	0.403

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

Table 3-5. Fuel Production Options for *Nannochloropsis salina* (high lipid)

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	GEC[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	20.838	0.000	0.000	0.000	20.838	27.624	0.754	0.000	0.000
2	20.838	0.000	0.000	0.000	20.838	27.624	0.754	0.000	0.000
3	4.125	8.139	5.852	0.000	18.116	27.624	0.656	13.991	0.506
4	20.067	0.000	0.000	0.686	20.754	27.624	0.751	.686	0.025
5	3.354	8.139	5.852	0.686	18.032	27.624	0.653	14.678	0.531

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

Table 3-6. Fuel Production Options for Dunaliella salina (high carbohydrate)

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	GEC[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	11.299	0.000	0.000	0.000	11.299	16.242	0.696	0.000	0.000
2	10.781	0.000	0.000	0.000	10.781	15.394	0.700	0.000	0.000
3	7.934	1.337	0.517	0.000	9.788	15.394	0.636	1.854	0.120
4	4.670	0.000	0.000	5.443	10.113	15.394	0.657	5.443	0.354
5	1.823	1.337	0.517	5.443	9.120	15.394	0.592	7.297	0.474

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

Table 3-7. Fuel Production Options for Chlamydomonas sp.

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	GEC[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	16.094	0.000	0.000	0.000	16.094	22.397	0.719	0.000	0.000
2	16.094	0.000	0.000	0.000	16.094	22.397	0.719	0.000	0.000
3	8.976	0.944	0.000	0.000	9.919	22.397	0.443	0.944	0.042
4	9.598	0.000	0.000	5.786	15.384	22.397	0.687	5.786	0.258
5	2.479	0.944	0.000	5.786	9.209	22.397	0.411	6.730	0.300

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

data is available on lipid subfractions, so digestion is essentially the only lipid utilization option considered. As Table 3-8 shows, the overall energy utilization rate is 71.5% in the methane-only option, and drops only to 67.6% in the ethanol-methane option. Liquid fuel utilization efficiency is 31.6%, which is close to that of D. salina (Example 5) for this option. Each of the three representative carbohydrate-producing species has a particular characteristic to recommend it: Dunaliella has the highest liquid fuel utilization rate (35.4% in the ester-ethanol-methane option); Chlamydomonas has the highest gross energy content (22.4 MJ/kg), resulting in the highest energy production values (up to 16.1 MJ/kg); and Cyclotella has extremely high carbohydrate content, resulting in the highest ethanol production (6.6 MJ/kg ash-free dry weight).

3-8. Spirulina platensis

Spirulina sp. has been cultivated for commercial protein production. Cultivated by Tornabene et al. in an unstressed environment [3], the organism produced 50% of its cell weight as protein (Example 8), with a moderate (16.6%) lipid content, of which 5.4% was in the hexane and benzene fractions and 38% in the chloroform and methanol fractions (fatty acids estimated at 25%). With the slightly higher energy content of protein versus carbohydrate, a gross energy content of 19.8 MJ/kg of dry biomass is calculated (Table 3-9). As discussed earlier, the only method considered here for using the protein fraction for fuel production is anaerobic digestion. Examination of all the fuel-producing options shows the methane-only option to have the highest overall utilization rate (67.7%), with both ester-producing options (with and without ethanol production) having overall utilization rates at approximately 52% and liquid fuel utilization rates at 10%-15%.

3-9. Chlorella sp.

Example 9 of Table 3-1 shows a Chlorella that was isolated from desert saline waters [4]. It was high in protein (45.9%), moderate in lipid (20.7%), and low in carbohydrate (9.7%). Neutral lipids totaled only 2.3% of total lipids, and fatty acids were estimated at 15.9%. Gross energy content was calculated at 20.8 MJ/kg (Table 3-10), and energy utilization ranged from 51.8% for the ester-ethanol-methane option (with a liquid fuel utilization rate of 11.7%) to 68.8% for the methane-only option.

3-10. Nannochloropsis salina (high protein)

This organism has been shown to be a potential high-lipid producer when subjected to environmental stress (Example 4); however, Nannochloropsis produces high protein content in the absence of stresses (Example 10). With a protein content of 55.8%, lipid content of 28.6%, and a carbohydrate content of 15.6%, Nannochloropsis has a gross energy content of 26.9 MJ/kg, the highest of the protein-producing species (Table 3-11). The methane-only option has an energy utilization rate of 69.5%, and both ester-methane options (with and without fermentation) have overall utilization rates of approximately 50% and liquid

Table 3-8. Fuel Production Options for <u>Cyclotella cryptica</u>

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	GEC[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	14.844	0.000	0.000	0.000	14.844	20.769	0.715	0.000	0.000
2	14.844	0.000	0.000	0.000	14.844	20.769	0.715	0.000	0.000
3	9.273	0.000	0.000	0.000	9.273	20.769	0.446	0.000	0.000
4	7.467	0.000	0.000	6.571	14.037	20.769	0.676	6.571	0.316
5	1.896	0.000	0.000	6.571	8.466	20.769	0.408	6.571	0.316

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

Table 3-9. Fuel Production Options for <u>Spirulina platensis</u>

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	GEC[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	13.398	0.000	0.000	0.000	13.398	19.792	0.677	0.000	0.000
2	13.398	0.000	0.000	0.000	13.398	19.792	0.677	0.000	0.000
3	8.260	1.822	0.276	0.000	10.358	19.792	0.523	2.098	0.106
4	12.429	0.000	0.000	0.863	13.292	19.792	0.672	0.863	0.044
5	7.291	1.822	0.276	0.863	10.252	19.792	0.518	2.961	0.150

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

Table 3-10. Fuel Production Options for <u>Chlorella</u> (Thomas)

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	GEC[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	14.314	0.000	0.000	0.000	14.314	20.792	0.688	0.000	0.000
2	14.314	0.000	0.000	0.000	14.314	20.792	0.688	0.000	0.000
3	7.907	1.441	0.037	0.000	9.385	20.792	0.451	1.478	0.071
4	13.246	0.000	0.000	0.951	14.197	20.792	0.683	0.951	0.046
5	6.839	1.441	0.037	0.951	9.268	20.792	0.446	2.429	0.117

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

Table 3-11. Fuel Production Options for <u>Nannochloropsis salina</u> (high protein)

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	GEC[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	18.707	0.000	0.000	0.000	18.707	26.930	0.695	0.000	0.000
2	18.707	0.000	0.000	0.000	18.707	26.930	0.695	0.000	0.000
3	9.855	3.247	0.579	0.000	13.680	26.930	0.508	3.825	0.142
4	16.989	0.000	0.000	1.530	18.519	26.930	0.688	1.530	0.057
5	8.137	3.247	0.579	1.530	13.492	26.930	0.501	5.355	0.199

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

fuel utilization rates of 15%-20%. All of these results are highest of the protein producers examined. The ester fuel (3.25 MJ/kg) and total lipid (3.83 MJ/kg) components of the net energy output are both quite high for what are essentially secondary products.

3-11. Dunaliella salina (high glycerol)

Example 11 in Table 3-1 shows the composition of D. salina grown in a salt-stressed environment. Instead of principally carbohydrate as in optimal culture conditions (Example 5), the organism now produces a substantial quantity (27.7%) of glycerol. The major product by weight is protein (35%), with lesser amounts of lipid (18.5%) and carbohydrate (12.5%). Without going into great detail, a few important properties of glycerol should be noted. Glycerol is a commodity chemical (approximately 175,000 tons/yr) used in the food processing, cosmetic, and pharmaceutical industries, among others. A clear, high-boiling, viscous liquid, it is a member of the "generally regarded as safe" list, which makes its use common in the above applications. Another important property is that it is primarily a natural product; petroleum-based glycerol has always been more expensive than natural glycerol produced as a by-product of soap manufacture. It is thought that the ability of this organism to accumulate large quantities of glycerol could be put to economic advantage. This assertion would need to be tested in some detail by analysis that is beyond the present scope.

Table 3-12 summarizes the energy recovery potential from this organism. Of the gross energy content of 22.8 MJ/kg, 5 MJ or 22% is due to the glycerol content. Extraction of the glycerol for use of its potential by-product value actually increases the overall utilization efficiency from 67.6% in the methane-only option (which includes digestion of the glycerol to methane) to 69.5% in the methane-glycerol option. Without the fuel value of the glycerol, the gross energy content is a somewhat low 17.8 MJ/kg, but overall utilization rates are approximately 53% in the ester fuel-methane and ester-methane-ethanol options. Liquid fuel utilization ranges from 16% without fermentation to 23% with it. A final note of emphasis should be added concerning the potential economic benefit of glycerol as a by-product.

Table 3-12. Fuel Production Options for Dunaliella salina (high-glycerol)

Option	Methane MJ/kg	Ester MJ/kg	Hydrocarbon MJ/kg	Ethanol MJ/kg	Total Recovered MJ/kg	GEC[a] MJ/kg	Utilization Fraction[b]	Liquid Fuel MJ/kg	Liquid Utilization Fraction[c]
1	15.387	0.000	0.000	0.000	15.387	22.756	0.676	0.000	0.000
2	12.337	0.000	0.000	0.000	12.337	17.757	0.695	0.000	0.000
3	6.611	2.752	0.104	0.000	9.467	17.757	0.533	2.856	0.161
4	10.961	0.000	0.000	1.226	12.187	17.757	0.686	1.226	0.069
5	5.235	2.752	0.104	1.226	9.317	17.757	0.525	4.082	0.230

[a] Gross energy content, calculated as described in text.

[b] Total recovered/GEC

[c] Liquid fuel/GEC

SECTION 4.0

DISCUSSION

It is clear even from this limited-scope review that a number of microalgae represent potential sources of renewable energy. Many of the significant compounds found in a barrel of crude oil may also be found in or be produced from algal lipids. Biochemical characterizations have indicated a wide range of potential products from microalgae, this slate being dependent on the particular strain of algae and the conditions under which that strain was grown. What needs to be immediately addressed is whether the product slate of a particular species can be maintained (or even achieved) in outdoor mass culture for production of large quantities of renewable fuel products.

The petroleum industry over a period of decades has developed a series of flexible downstream processing options that produce maximum amounts of gasoline during certain seasons of the year (or certain economic conditions) or fuel oils at other times. The achievement of a similar state of affairs with microalgae, though a long way off, does appear feasible. If the kind of compositional variability observed in many species when culture conditions change is the rule rather than the exception, then that kind of flexibility will be a necessity. When lipids or carbohydrates predominate, they would be economically recovered; when not, anaerobic digestion offers an alternative way to produce energy. A culture system where algal composition is continuously monitored for this kind of variation, followed by changes to the production schemes and the product slates, is easy to imagine.

SECTION 5.0

CONCLUSIONS

Many of the species considered here have potential to become superior biomass feedstocks. Figure 5-1 shows the high lipid-producing organisms. Botryococcus braunii with its high hydrocarbon production (10.1 MJ/kg) and Nannochloropsis salina with high ester fuel production (8.1 MJ/kg) are the most promising. Ankistrodesmus and Isochrysis appear less promising based on these

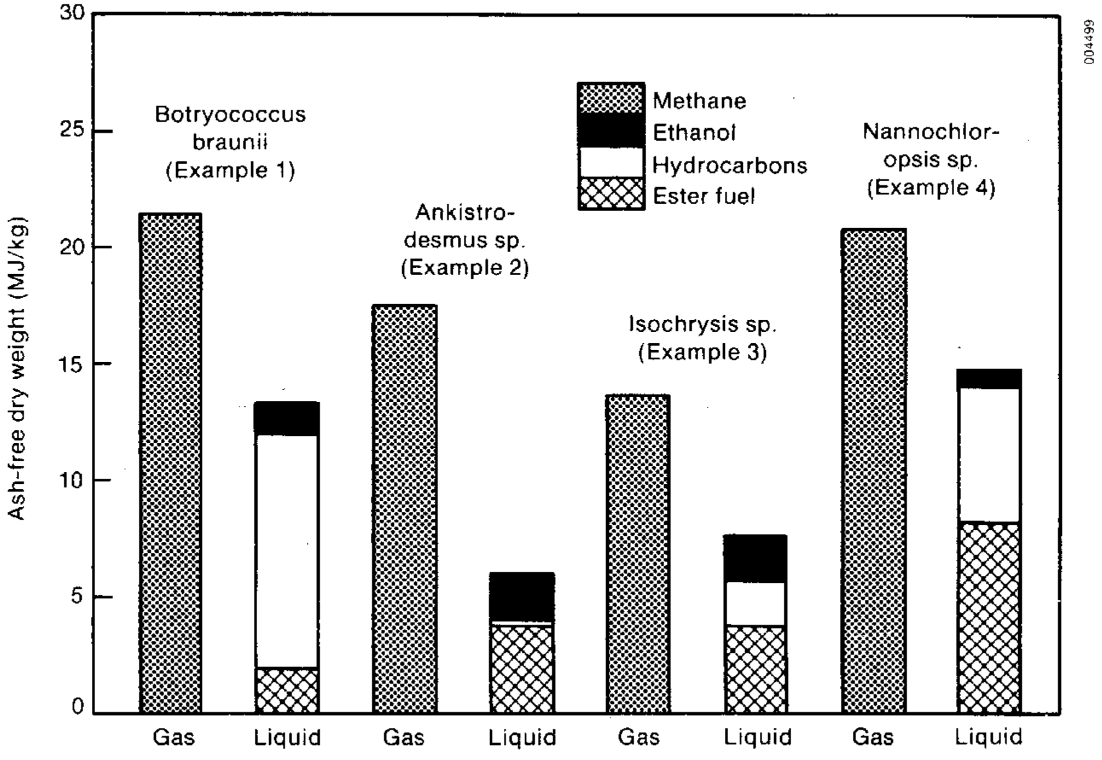

Figure 5-1. Gas vs. Fuel Production from Representative High-Lipid Producers

data, but continued research could result in improvements to productivity, lipid content, or other factors. The results of this analysis seem to favor neutral lipids, whose energy is recoverable with minimal processing losses. Further analysis is required to determine which species could be economically produced, then where the economic trade-offs lie between anaerobic digestion and the liquid fuel options such as transesterification.

Figure 5-2 summarizes the results for the carbohydrate producers. Data for Dunaliella salina are shown for the high-carbohydrate and high-glycerol producing strains. The former has the lowest gross energy content and overall

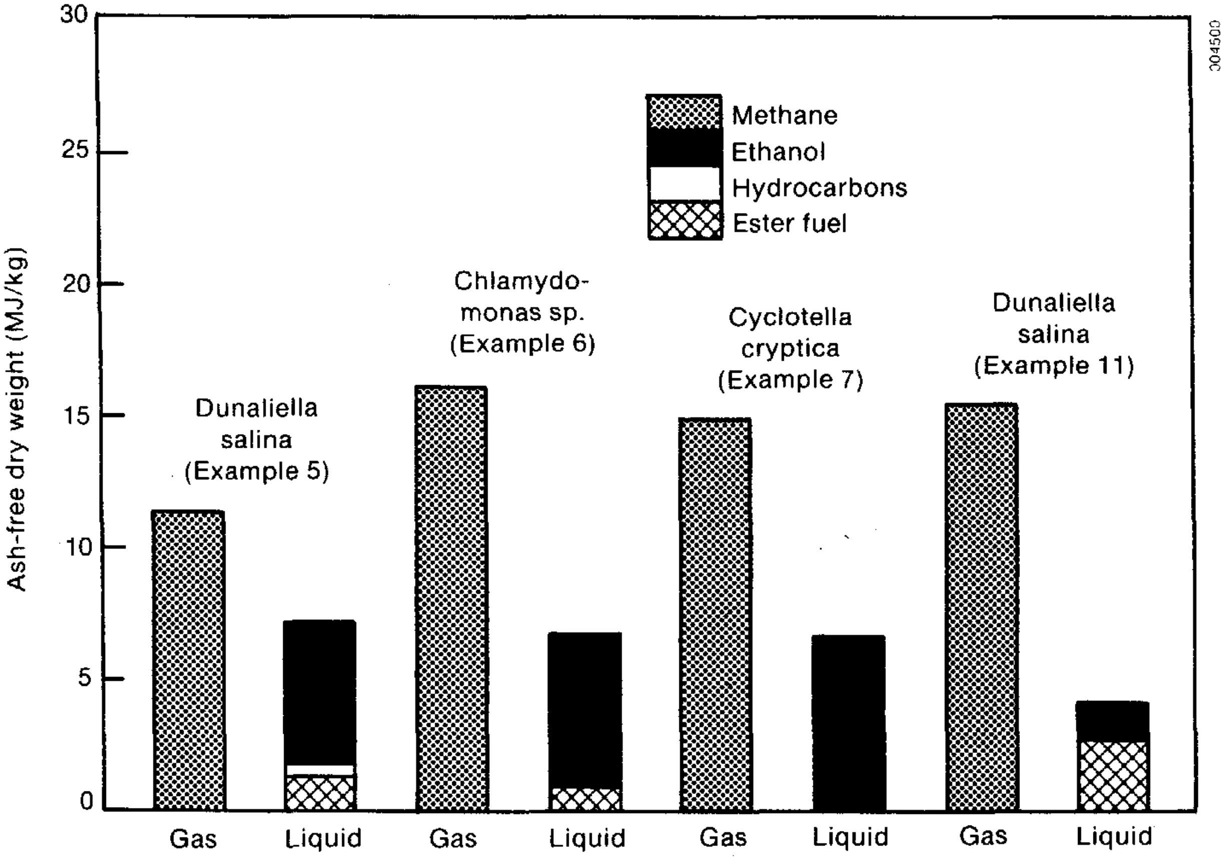

Figure 5-2. Gas vs. Liquid Fuel Production from Representative High-Carbohydrate Producers

energy utilization but the highest liquid fuel production and utilization data due to its relatively high proportion of fatty acids. The diatom Cyclotella cryptica has the highest ethanol production and highest carbohydrate content, and Chlamydomonas, with the highest lipid content, has the highest gross energy content and highest overall utilization efficiency. It should be recalled that the standard set of assumptions made about carbohydrates leads each species equally from carbohydrate to ethanol; characterizations of each species' carbohydrates are required to differentiate them.

Figure 5-3 shows graphically the energy data for the high protein-producing species. Nannochloropsis salina, with the highest lipid content; achieves the

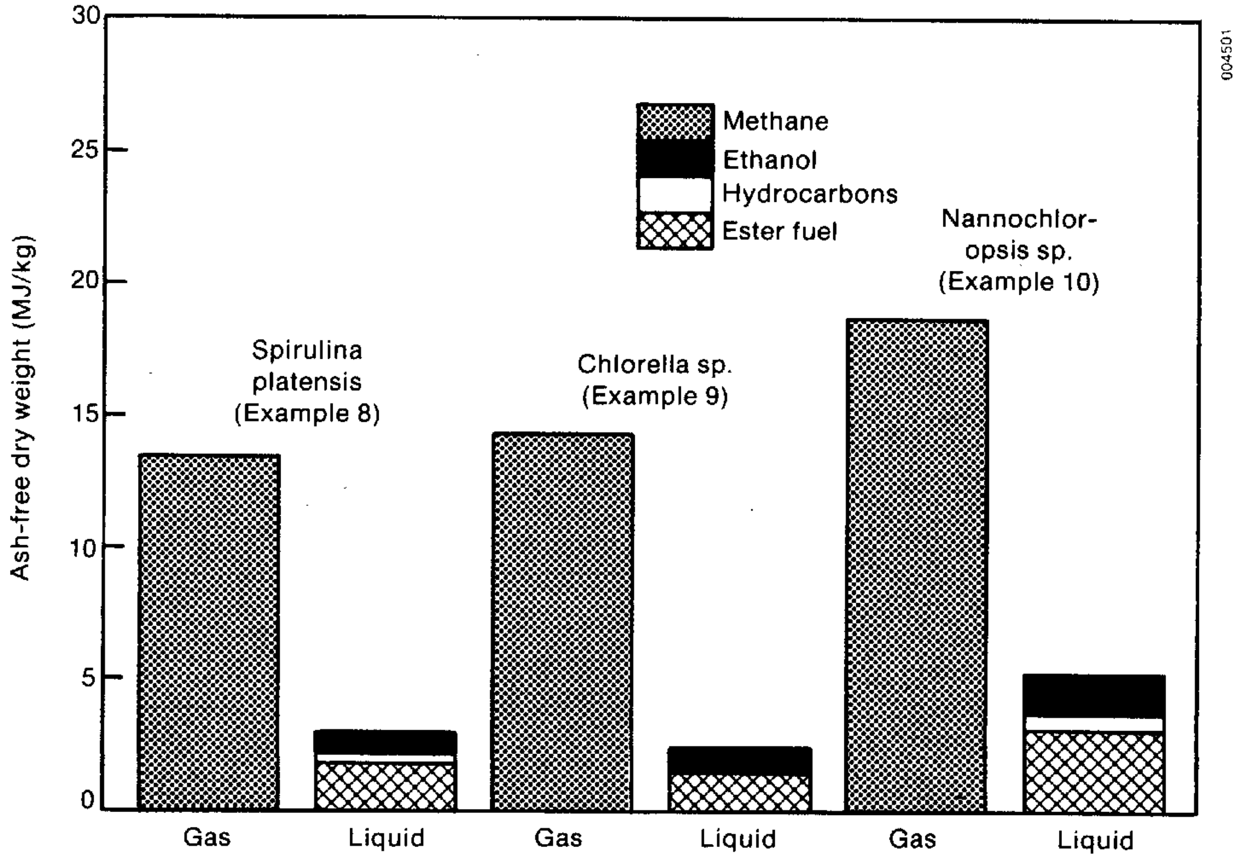

Figure 5-3. Gas vs. Liquid Fuel Production from Representative High-Protein Producers

highest gross energy content and the highest individual production values for all the products examined (methane, ester fuel, hydrocarbons, and ethanol). This organism also has the highest overall utilization efficiencies in its methane-only option. *Spirulina platensis* has higher overall utilization efficiencies in integrated liquid-gaseous fuel processing options, while the *Chlorella* strain examined here shows slightly less promise than the others.

A few quick points should be made in summary. The only cases we have seen where lipid conversion routes are clearly the best choice are in the cases of extremely high lipid content coupled with very high fractions of either neutral lipids or fatty acids. Species with more moderate lipid content await the results of more detailed examination of the processing options, e.g., transesterification. Similarly, more detailed process design information will be required for comparison of fermentation with anaerobic digestion with regard to the carbohydrate fraction. It is also clear that the actual process conversion efficiencies that can be achieved will be critical to the economic success of the fuel production schemes.

SECTION 6.0

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16. Abstract (Limit: 200 words)

Representative species of microalgae are examined with respect to their reported chemical compositions. Each species is analyzed under a variety of culture conditions, with the objective being to characterize an optimum mixture of fuel products (e.g., methane, ethanol, methylester) which should be produced by the particular species. Historically the emphasis has been on the entire algal cell mass. Using the reported chemical composition for the representative species under specific sets of growth conditions, some conclusions can be drawn about the preferred fuel product conversion routes that could be employed.

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a. Descriptors Algae ; Chlamydomonas ; Chlorella ; Fuels ; Unicellular Algae

b. Identifiers/Open-Ended Terms Botryococcus Braunii ; Ankistrodesmus Falcatus ; Isochrysis ; Nannochloropsis Salina ; Dunaliella Salina ; Cyclotella Cryptica ; Spirulina Platensis ; Nannochloropsis Salina

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