THIRD GENERATION BIOFUELS
IMPLICATIONS FOR WOOD- DERIVED FUELS

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Third Generation Biofuels – Implications for Wood-Derived Fuels

Executive Summary
Third-generation biofuels research and development is largely focused on algae as a raw material. Early research demonstrated that energy yields from a given surface area are far greater from algae than from plants currently used in producing biofuels. The great potential of algae is, however, clouded by a number of technical and economic hurdles which must be overcome before algae contributes in any significant way to providing energy for transportation. Among these are reduction of nutrient requirements in cultivation and energy requirements in processing. For the near to mid-term, at least, algae-derived biofuels are unlikely to pose competitive risks to the emerging second-generation cellulose-based biofuels industry.

Introduction
In 2017, Dovetail published a report on second generation biofuels1, in which we summarized the growth of second generation biofuel facilities around the world and discussed initiatives designed to stimulate further development. Therein we only briefly made reference to third generation biofuels.

In this report we discuss the essential differences between first, second, and third generation biofuels, examine progress toward development of third generation fuels, and consider potential impacts of new generation biofuel development on future prospects for lignocellulosic biomass-to-liquid fuels production. We also briefly explore what are referred to as fourth generation biofuels.

First to Fourth Generation Biofuels

First Generation Biofuels
First generation biofuels are produced from food crops such as corn and sugarcane, and soybeans and rapeseed. Ethanol produced from corn starch, and biodiesel, as currently sold commercially throughout the United States, are examples of first generation biofuels.

Stimulated by interest in developing low carbon alternatives to fossil fuels, as well as creating rural employment and domestic sources of energy, a number of U.S. states require a minimum ethanol mix in fuels in order to provide a certain market. However, because of low fossil fuel prices in recent years, first generation biofuel producers continue to require subsidies in order to operate. In addition, the industry faces continuing criticism centered on high groundwater use, extensive fertilizer and pesticide use on croplands, and potential competition with food production. Criticism is also often focused on low net energy gain in fuels production, although considerable improvement in that regard has been realized in recent years.

Regarding the food/energy issue, it is important to recognize that the ethanol production process also yields distillers grains2 as a by-product, the principal use of which is as a high-protein livestock feed. Given this, and because almost all corn used for ethanol production in North America is feed corn which would otherwise be used for livestock feed, the food/feed issue is not

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2 Distillers grains are a co-product of the ethanol production process that are rich in protein, fat, minerals and vitamins. These grains serve as a low cost alternative feed ingredient for livestock and poultry.
as direct, nor as severe, as some continue to suggest. As to net energy gain in processing, considerable improvement has been realized in recent years. The current energy balance\(^3\) falls in the range of 2.1-4.0:1 when production energy is properly allocated between ethanol and by-products (1.5-2.3 when energy used in producing distillers grains is not considered in analysis). The energy balance for first generation ethanol production was initially calculated at 1.28:1.\(^3\)

Despite the criticism of first generation biofuels, in 2016, the U.S. produced an estimated 16 billion gallons (61 billion liters) of ethanol, and 1.56 billion gallons (5.9 billion liters) of biodiesel. Ethanol production alone was equivalent to 381 million barrels of crude oil, or 10.3% of U.S. crude oil imports. In 2015, ethanol production was estimated to draw 36% of U.S. corn production away from other uses, and to account for about a quarter of U.S. harvested cropland.

**Second Generation Biofuels**

Second generation biofuels are produced from non-food lignocellulosic materials such as wood, agricultural crop residues (e.g. corn stalks, bagasse), forest harvest residues, municipal solid waste, and dedicated biomass energy crops such as switchgrass. Waste vegetable oil is also being used as raw material. The end products can be ethanol, biodiesel, aviation fuel, or any one of a wide array of industrial biochemicals. Because production of such fuels is more technically challenging than for first generation biofuels, requiring complex biochemical or thermochemical processing, it has taken decades to bring second generation biofuels to commercialization. Commercial-scale plants began operation only recently (2014-2017), and quantities produced remain relatively small.

In general, second generation biofuels result in greater displacement of fossil fuels than do first generation fuels, and emissions of carbon dioxide equivalents are lower as well. One assessment\(^5\) shows that production of second generation ethanol yields 4.4-6.6 energy units for every energy unit in. Another more recent analysis of the net energy balance in producing a range of second generation biofuels\(^6\) found ratios of energy in to energy produced of 1.32:1 to 3.76:1, and net reduction in CO\(_2\) -equivalent generation compared to fossil fuels of about 80%.

While the raw materials for production of second generation biofuels are from non-food sources, food/fuel concerns largely become a non-issue. However, to the extent that dedicated fiber crops are used as a source of raw material, the potential for competition with food crops will continue. While fiber crops can be grown on marginal farm land, higher yields are obtainable on better sites, posing difficult land use decisions for farmers. Issues related to use of pesticides and fertilizers are also linked with dedicated fiber crops such as switchgrass.

**Third Generation Biofuels**

Third-generation biofuels, which at this point exist for the most part in research laboratories, early-stage development facilities, and a few small-scale enterprises, are produced from algae.\(^7\) The term *algae* encompasses a diverse group of organisms that includes microalgae, macroalgae (seaweed), and cyanobacteria (formerly known as blue-green algae).\(^8\)

\(^3\) Gallagher et al. (2016)  
\(^5\) Sims et al. (2008)  
\(^6\) Zaimas et al. (2017)  
\(^7\) Maity et al. (2014)  
\(^8\) USDOE (2016)
There are more than 72,000 different species of algae\(^9\), and possibly as many as 800,000\(^{10}\), which occur either in the form of microalgae or seaweeds. The vast majority occur in fresh, waste, or salt-water. Algae are of interest because they grow rapidly, have harvesting cycles of days rather than months or years, develop under minimal nutrient conditions (although very high nutrient levels are required to support the magnitude of growth needed for economical production), and can thrive in wastewater. Though able to grow naturally in a variety of environments, growth rates can be markedly increased through enhancement of growing conditions, such as through control of temperature, acidity, and enrichment of nutrient levels. The potential for production of natural oils from algae is far greater on an area basis than that obtainable from crops such as soybeans or canola. Algae was previously considered as a raw material for second generation fuels until it was determined that a much higher energy yield was obtainable than from other second generation biofuel feedstocks.\(^{11}\) This recognition spurred intense interest in this group of organisms. Algal oils can be used to produce a variety of products, ranging from ethanol, butanol, biodiesel, jet fuel, syngas, bio-oil, a wide array of chemical feedstocks, and fertilizer.\(^{12}\) Hydrogen is another product option.\(^{13}\) Algal biomass can also be combusted directly to produce electricity.

Fourth Generation Biofuels

The fourth generation biofuels are variously described as those which would involve:

- metabolic engineering of plants and algae to achieve high biomass yield, improved feedstock quality, and high CO\(_2\) fixation.\(^{14}\)
- direct conversion of solar energy into fuel using designer microorganisms via application of emerging synthetic biology technologies as enabling pathways.\(^{15}\)

Biofuel Generations Summarized

In summary, various generations of biofuels are defined as follows\(^{16}\)\(^\_17\):  

1. First generation biofuels are directly related to a biomass that is generally edible by humans.

2. Second generation biofuels are defined as fuels produced from a wide array of different feedstock, ranging from lignocellulosic feedstocks to municipal solid wastes.

3. Third generation biofuels are, at this point, related to algal biomass but could, to a certain extent, be linked to utilization of CO\(_2\) as feedstock.

4. Fourth generation biofuels are envisioned as sustainable fuels, derived from engineered biological materials, to achieve high levels of energy efficiency and environmental performance.

\(^9\) Guiry (2012)  
\(^{10}\) Maity et al. (2014)  
\(^{11}\) Christian (2014)  
\(^{12}\) USDOE (2016)  
\(^{13}\) Dragone et al. (2010)  
\(^{14}\) Joshi and Nookaraju (2012)  
\(^{15}\) Aro (2016)  
\(^{16}\) Lee and Lavole (2013)  
\(^{17}\) Oregon State University (n.d.)
Unsurpassed Energy Yield Potential with Third Generation Biofuels

Algae is of interest as a source of bioenergy largely due to the energy production capacity per surface area. Described as biological solar panels that fix CO₂ from the atmosphere, and which are usually aquatic, the efficiency of photosynthesis is reported to be 3-8% for various species, compared to terrestrial crops estimated to have a photosynthetic efficiency of about 0.5%. Some algal species are considered to be among the fastest growing plants in the world.¹⁸

A theoretical production limit for microalgal oil has been estimated at about 37,000 gallons/acre/year (346,000 liters/ha/yr) of raw oil for an ideally situated location at the equator (Quinn and Davis 2015). Substantially lower oil yields from algae have been estimated for commercial production in the U.S. Nonetheless, predicted yields are far above those currently realized from agricultural crops (Table 1).

Table 1  
Oil Yield of Different Feedstocks for Biodiesel  

<table>
<thead>
<tr>
<th>Crop</th>
<th>Oil Yield (gallons/acre/year)</th>
<th>Oil Yield (liters/ha/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybeans</td>
<td>48.0</td>
<td>449</td>
</tr>
<tr>
<td>Camelina</td>
<td>59.8</td>
<td>559</td>
</tr>
<tr>
<td>Sunflowers</td>
<td>101.9</td>
<td>953</td>
</tr>
<tr>
<td>Jatropha</td>
<td>201.7</td>
<td>1,887</td>
</tr>
<tr>
<td>Palm oil</td>
<td>634.0</td>
<td>5,930</td>
</tr>
<tr>
<td>Algae</td>
<td>1,500-5,000</td>
<td>14,031-46,770</td>
</tr>
</tbody>
</table>

Source: USDOE (2016)

Actual yields thus far have been considerably lower. For instance, in 2014 Algenol Biotech, a biotechnology company that manufactures multiple types of algae from molecular to commercial scale, reported an actual yield of 8,000 gallons of biofuel per acre (75,120 l/ha) from blue-green algae grown in an environment of salt water and carbon dioxide.¹⁹

While the energy production capability of naturally occurring algae is substantial, the potential for genetic modification to increase growth rates, improve stress tolerance, boost nutrient uptake, and/or control production of specific chemical constituents is viewed as vast.²⁰ Considerable research is focused on understanding the genetic makeup of various species of algae and identifying genes that control particular traits. Other research is targeted on identification of algal species with the highest capacity for fuel production (generally linked to lipids production).

As earlier indicated, a number of energy products can be produced from algae. Also obtainable, either as primary products or co-products of energy production, are a wide array of chemicals, industrial enzymes, surfactants, nutritional supplements, cosmetics, pharmaceuticals, plastics, animal feed, and fertilizers. In this regard, third generation biofuels are similar to second generation fuels.

An important factor in determining production potential is land availability, since production of algae in either open or closed systems would require relatively large areas for implementation. When high yield potential is considered in the context of alternative production systems, land

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¹⁸ Alaswad et al. (2015)  
¹⁹ Markham (2014)  
²⁰ US DOE (2016)
area requirements are nonetheless quite large. As recently reported by the US Department of Energy, even at levels of photoautotrophic microalgae biomass and oil productivity that would stretch the limits of an aggressive R&D program, approximately 5.5% of the land area of the continental US would be required to generate about half of 2010 U.S. petroleum imports for transportation through open pond production. Another estimate indicated that about 10% of the surface area of the continental US and Hawaii would be required to totally displace fossil fuels assuming production using photobioreactors.

**Cultivation of Algae**

In comparison to agricultural crops, which are typically harvested once or twice a year, or to woody biomass which might be available from a given site once a decade or less often, microalgae grow so quickly that they can be harvested in cycles of one to several days. In some cases continuous harvesting may be possible.\(^{21}\)

Algae can be categorized as follows, based on their ability to grow under various conditions (USDOE 2016):

- **Photoautotrophic** – wherein algae utilize light to grow. Most algae fall within this category, and include microalgae and cyanobacteria.
- **Mixotrophic** – wherein the algae may utilize either light or a carbon source to enable growth. Microalgae and cyanobacteria also fall within this category.
- **Heterotrophic** – wherein algae grow without light, using carbon sugars as a source of energy.

Differences in various forms of algae and their growth requirements allow different approaches to cultivation. Systems currently being evaluated include:

- **Open ponds** – Can be used for production of microalgae and cyanobacteria. Open ponds represent a low capital cost solution, the efficiency of which is limited by an inability to maintain optimum conditions for growth. These systems also are exposed to risk of contamination from other organisms which can compromise system operation, and are subject to evaporation losses that can markedly impact water consumption.
- **Open off-shore or coastal facilities** – This kind of system is appropriate for production of macroalgae (seaweed).
- **Closed-loop systems** – These systems are enclosed, allowing greater control of growth conditions than with open ponds. Closure also permits enhancement of atmospheric carbon dioxide levels, and opens possibilities to direct linkage to industrial emissions of this gas. These systems typically admit light, so again are appropriate for cultivation of microalgae and cyanobacteria.

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\(^{21}\) Dragone et al. (2010)
Photobioreactors – Bioreactors are sophisticated closed systems which allow total optimization of growth conditions, including temperature and nutrient levels. These can be designed to accommodate virtually any kind of algae, but require high investment costs and are also the most expensive to operate.

Algae are also sometimes cultivated in wastewater treatment facilities. In this kind of environment, the cost of supplying nutrients to augment algal growth is reduced, and in addition algal treatment of wastewater is more efficient and less expensive than conventional tertiary treatment. A limitation to this practice is that wastewater sometimes contains toxic substances which negatively affect algal growth.22

Because some forms of algae, including microalgae, are able to fix CO₂ efficiently from different sources, including the atmosphere, industrial exhaust gases, and soluble carbonate salts, closed-loop systems and bioreactors are sometimes linked to sources of industrial exhaust gases for the dual purpose of mitigating emissions and enhancing algal growth. Industrial exhaust gases such as flue gas contains up to 15 % CO₂ (as compared to 0.36% in the atmosphere), providing a CO₂-rich source for microalgal cultivation.23 In some cases photobioreactors have been installed at mines and power plant facilities to capture greenhouse emissions and also to produce microalgal biomass for on-site biofuel production.24

Conversion of Algae to Biofuels

Options for processing of algae to energy products include (1) conversion of whole algal biomass, (2) extraction of metabolites (i.e. oils, fatty acids, steroids, carotenoids, polysaccharides, halogenated compounds, polyketides), or (3) collection and processing of direct algal secretions. Third-generation initiatives are currently heavily concentrated on option (2), whereas fourth generation biofuels initiatives tend to focus on option (3).

Steps in Production of Biofuels from Algae

When extraction technologies are employed in the conversion of algae to liquid fuels, steps in processing include harvesting, dewatering, extraction, and processing to energy products and co-products. The cell structure of algae is broken down by solvents or sound waves to extract lipids, carbohydrates, and proteins, followed by chemical, biochemical, or thermochemical processes for conversion of algal oil to biofuels (Figure 2).

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22 Alaswad et al. (2015)
23 Dragone et al. (2010)
24 Maity et al. (2014)
Current Outlook for Third Generation Biofuels

Ongoing R&D

A substantial research effort has been dedicated to development of algae as a source of biofuels since the mid-1980s, with early work dating back to the late 1950s. Beginning in the 1980s, efforts were made to foster public/private partnerships for R&D initiatives and large-scale infrastructure projects. Algal biofuels research was given a considerable boost in the U.S. in 2007 with passage of the Energy Independence and Security Act; this provided funding and coordinated leadership of fuels biotechnology research and development.

Today, a number of consortia of government laboratories, universities, and industries are working to address the full scope of issues associated with commercialization of algal energy. These include identification of the most promising algal species, breeding and genetic modification, cultivation, harvesting, dewatering, extraction, fundamental and technical aspects of fuels production systems, identification of co-product potential, economics, and

Source: USDOE (2016)
environmental factors. In short, all aspects of fuels and co-product production from algae are under investigation.

Factors Favoring Further Algal Fuels Development

As explained by Dragone et al.,\textsuperscript{25} the utilization of microalgae for biofuels production offers a number of advantages over use of higher plants:

- they synthesize and accumulate large quantities of neutral lipids and grow at high rates;
- they are capable of year-round production, potentially increasing oil yield per surface area far above the yield of the best oilseed crops;
- they need less water than terrestrial crops, therefore reducing freshwater demand;
- microalgae cultivation does not require application of herbicides or pesticides;
- microalgae cultivation can utilize CO\textsubscript{2} from flue gases emitted from fossil fuel-fired power plants and other sources, thereby reducing industrial emissions of a major greenhouse gas;
- microalgae can be used to facilitate wastewater treatment (e.g. agricultural run-off, concentrated animal feed operations, and industrial and municipal wastewaters) while at the same time producing raw materials for biofuels and other products;
- combined with their ability to grow under harsh conditions and their reduced needs for nutrients, microalgae can be cultivated in saline/brackish water/coastal seawater on non-arable land without competing with conventional agriculture.

Despite the apparent advantages, there are a number of challenges that must be overcome before algae can become a significant contributor to energy supplies.

Challenges to Commercialization

One of the biggest challenges to algae-derived biofuels commercialization is development of extraction systems that consume less energy than contained in the algal products. In this regard, high energy needs associated with both handling and drying algal biomass, as well as separating out desirable products are problematic.\textsuperscript{26} Economic and technical hurdles are posed by scale-up issues for systems in which growth of microalgae requires light, CO\textsubscript{2}, water, abundant nutrients and essential inorganic elements, and in which temperature regime needs to be tightly controlled. Moreover, in order to reduce costs, production must rely on freely available sunlight, despite daily and seasonal variations in natural light intensities.\textsuperscript{27}

Other than the issue of economics, a number of other problems must be addressed if algal biofuels are to come into the mainstream. These include:

- Nutrients, including phosphorous, must be supplied in substantial quantities because of the additional need in the growing medium for metal ions (iron, manganese, zinc, copper, cobalt, molybdenum) with which phosphates can react, making them less available to growing algae.\textsuperscript{28}

\textsuperscript{25} Dragone et al. (2010)
\textsuperscript{26} USDOE (2016)
\textsuperscript{27} Alam et al. (2015)
\textsuperscript{28} Dragone et al. (2010)
• Even when grown in wastewater, algae require large amounts of water, nitrogen, and phosphorous to grow. The fertilizer required to harvest a high yield of algae can produce more greenhouse gas emissions than are saved by using an algae-based biofuel.\textsuperscript{29}

• Under large commercial scale industrial build-up of algal biofuels, the quantity of nutrients required nationally could begin to approach the same order of magnitude as large-scale agriculture. Likely increases in national nitrogen and phosphorus nutrient consumption are estimated to range from 1.4 to 4, and 1.3 to 2.9 times, respectively, for the production of 5 to 21 billion gallons annually of algal biofuel.\textsuperscript{30}

• Even if marginal land is used, perceived conflict of food and feed production versus fuel could pose challenges for an algal biofuels operation.\textsuperscript{31}

• Large volumes of water are required for industrial scale, presenting a major problem for countries like Canada where the temperature is below freezing during a significant part of the year. The high water content is also a problem when lipids have to be extracted from the algal biomass, which requires dewatering, via either centrifugation or filtration before extracting lipids.\textsuperscript{32}

**Potential Impact on Cellulose-Based Biofuels Industry**

In view of the huge difference in oil yield per unit of surface area between terrestrial crops and algae it would not be illogical to conclude that algal-based energy will eventually dominate the biofuels market. However, given what at present are enormous technical, economic, and environmental problems that must be solved before commercialization can occur, it is unlikely that algal biofuels will reach commercialization for at least several decades, and perhaps longer. Consequently, to the extent that biofuels remain part of the transportation energy mix (with growth of electric vehicles a significant wild card in the transportation energy picture), first and second generation biofuels will likely continue to play a role in vehicle and air transport energy markets for the foreseeable future.

**The Bottom Line**

The state of technology for producing algal biofuels is advancing on a number of fronts as a result of cooperative efforts and significant investment on the part of the public and private sectors. However, substantial hurdles remain to be overcome before algae can substantially contribute to societal energy needs. Additional research in both fundamental and applied arenas, as well as concerted development effort, will be needed if major deployment of affordable, scalable, and sustainable algae-based biofuels is to be realized. For the near- to mid-term, at least, algae-derived biofuels are unlikely to pose competitive risks to the emerging second-generation cellulose-based biofuels industry.

\textsuperscript{29} Christian (2014)  
\textsuperscript{30} USDOE (2016)  
\textsuperscript{31} USDOE (2016)  
\textsuperscript{32} Lee and Lavole (2013)
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