Energy-efficient and scalable harvesting and lipid extraction processes must be developed in order for the algal biofuels and bioproducts industry to thrive. The major challenge for harvesting is the handling of large volumes of cultivation water to concentrate low amounts of biomass. For lipid extraction, the major energy and cost drivers are associated with disrupting the algae cell wall and drying the biomass before solvent extraction of the lipids. Here we review the research and development conducted by the Harvesting and Extraction Team during the 3-year National Alliance for Advanced Biofuels and Bioproducts (NAABB) algal consortium project. The harvesting and extraction team investigated five harvesting and three wet extraction technologies at lab bench scale for effectiveness, and conducted a techno-economic study to evaluate their costs and energy efficiency compared to available baseline technologies. Based on this study, three harvesting technologies were selected for further study at larger scale. The selected harvesting technologies: electrocoagulation, membrane filtration, and ultrasonic harvesting, were evaluated in a field study at minimum scale of 100 L/h. None of the extraction technologies were determined to be ready for scale-up; therefore, an emerging extraction technology (wet solvent extraction) was selected from industry to provide scale-up data and capabilities to produce lipid and lipid-extracted materials for the NAABB program. One specialized extraction/adsorption technology was developed that showed promise for recovering high value co-products from lipid extracts. Overall, the NAABB Harvesting and Extraction Team improved the readiness level of several innovative, energy efficient technologies to integrate with algae production processes and captured valuable lessons learned about scale-up challenges.

1. Introduction

1.1. Preface

Harvesting algae and extracting the lipids are significant cost drivers in the biofuel production process [1–6]. Therefore, the goal of the Harvesting and Extraction task within the National Alliance for Biofuels and Bioproducts (NAABB) was to develop low-energy, low-cost harvesting and extraction technologies that could feed lipids into highly efficient fuel-conversion processes [7].

At the outset of the project, the NAABB leadership team determined that the harvesting and extraction technologies developed in this task must have:

- Low capital expense (CAPEX) and operating expense (OPEX)
- Ease of operation and low maintenance requirements

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**Harvesting & Extraction Task Framework**

- **Dewatering Technologies**
  - Chemical flocculation
  - Electrocoagulation
  - Membrane filtration
  - Ultrasonic focusing

- **Harvesting**
  - 1st Pond Harvest 10x

- **Concentration**
  - 2nd Dewatering 10-20x

- **Extraction**
  - Cell disruption/lipid extraction
  - Crude lipid extract
  - FFA/FAME
  - LEA

- **Wet Extraction Technologies**
  - Amphiphilic solvent process
  - Ultrasonic process
  - Cavitation/separation
  - Mesoporous extraction FFA
  - Wet solvent extraction (Valcor Toff/Processing)

- **Lipid & LEA feedstocks for Conversion & Co-products Tasks**

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- **Ease of integration with cultivation facilities to limit pumping and power requirements**
- **Compatibility with a broad range of algal species**
- **Ability to recycle water**
- **Low environmental impact, i.e., low or no hazardous chemical or solvent use**
- **Minimum energy requirements that reduce the carbon footprint**
- **Downstream compatibility, e.g., nothing be added that negatively affects later processing or quality.**
- **Feasibility of affordable scale-up and good performance at large scale**

A significant technical challenge for harvesting algae is that algal cells make up only about 0.1% of the total culture volume in a typical outdoor pond. Photobioreactors (PBRs) can produce higher density cultures, but still have < 1% cell densities. This highly dilute system presents the challenge of needing to collect a very small fraction of the total volume for downstream processing. As expected, there are significant energy (and therefore cost) penalties for pumping such large volumes of water. Centrifugation is the industry state of the art for harvesting algae for the production of high-value products. Therefore, our team aimed to develop methods for harvesting algae that reduce the energy penalty of this step, leading to significant reductions in costs and taking the industry closer to cost-competitive values for a gallon of algae-based oil. We hypothesized that the exploration of a portfolio of innovative methods would provide a path forward for cost-effective algae harvesting. Some methods employed off-the-shelf technology, while at least one method was largely conceptual at the start of the project. In each case, the team demonstrated that algae harvesting could be achieved with these technologies at costs that we projected to be significantly below the baseline case of traditional centrifugation.

Once the algae are harvested, there are two main pathways available for making a fuel or a bioproduct from the concentrated algae [8]. A conventional pathway is to extract and separate the oil from the cells. This process typically entails drying the algae, treating it with solvent, removing the liquid fraction from the remaining biomass leaving behind lipid extracted algae (LEA), and distilling the solvent from the oil. This crude oil is then sent for conversion to fuel, and the LEA can be used as a co-product. In NAABB, the focus of the Harvesting and Extraction Team was on the lipid extraction pathway, and LEA was evaluated as an animal feed co-product by the Co-Products Team. In another pathway, the harvested, whole wet algae can be directly converted to oil via a hydrothermal liquefaction (HTL) process [9]. The resulting oil can then be upgraded to a fuel. The HTL pathway was studied in the NAABB Fuel Conversion Team [7].

There are a number of challenges associated with the lipid-extraction step in the algal biofuels value chain. First, in order for the solvent to effectively remove the oil, the algae must be very dry, and drying is a costly and energy-intensive process. Simple air-drying may be incomplete and may result in spoilage of the algae, which may damage the quality of the products. Second, any cell debris (for example, with high N or S content) or solvent that carries through to the conversion process may affect the quality of the resulting fuel or co-products. Thus, an additional objective of this team was to explore effective and inexpensive wet extraction technologies. Again, a portfolio of innovative lipid extraction technologies was assessed, resulting in an improved understanding of the extraction requirements.

Much of the research reported here was initially described in the NAABB Final Report [7]. It is reviewed here with the benefit of additional time to fully analyze the data and publish more detailed descriptions of the experimental work.

### 1.2. Approach

The National Alliance for Advanced Biofuels and Bioproducts (NAABB) Harvesting and Extraction Team comprised physicists, engineers, chemists, and biologists from national laboratories, universities, and industry, who had strong track records of developing novel technologies. Our approach focused on minimizing the energy consumption of each technology, while maximizing the yield of product (as shown in Fig. 1).

In this project, harvesting was defined broadly as a 10–20 × de-watering/cell concentration process that may include one or more steps. Likewise, extraction was broadly defined to include cell disruption and recovery of lipids and lipid-extracted biomass from the de-watered, cell-concentrated feedstock in one or more steps. In order to do this, the Harvesting and Extraction Team began the NAABB program effort evaluating five harvesting technologies and four lipid extraction technologies. The initial goal was to develop proofs of concept and...
scale-up of the technologies leading to a down-selection process and then to move forward with technologies based on a feasibility study. Multiple harvesting technologies were investigated to find the most energy-efficient, low-maintenance, environmentally friendly alternative. Engineering approaches that were investigated included the following:

- Electrocoagulation or electrolytic aggregation, which uses a commercial unit (used in wastewater treatment) to apply a charge to algae cells, forcing them to aggregate and sediment [12-15]
- Cross-flow membrane filtration, using novel metallic membrane sheets with pore structures and surface properties engineered for algal harvesting [16]
- Ultrasonic focusing, in which a standing acoustic wave is applied in a flow-through system to gently aggregate algae cells and concentrate them out of the cultivation water [17,18].

Multiple lipid extraction techniques were considered based on their potential to eliminate the need for drying the algae and reduce or eliminate the need for solvents. These included:

- Amphiphilic solvents used in a system designed to force algal biomass to move from hydrophilic water phase to a hydrophobic solvent phase and assisted by a pressurized homogenization technique to rupture the algae cells in the process [19-21]
- Ultrasound cavitation and streaming to lyse the algae cells and release the lipid [18]
- Mesoporous nanomaterials for selective sequestration of (high-value) free fatty acids (FFAs) in either aqueous media of viable algal cultures or in organic solvent solutions after oil extraction from the algae culture. Once sequestration of the FFAs in the pores of the material is complete, the algal oil can be processed for fuel conversion and the FFAs can be further processed for co-products [22].

2. Technical accomplishments

2.1. Down-selection

The down-selection process was based on an evaluation of the five algae harvesting and three lipid extraction technologies noted above, developed and studied within the NAABB program during the first 18 months of the program. Each project submitted a data set to the NAABB Sustainability Team for a formal evaluation, which focused on understanding energy balance, mass balance, operation costs, and parasitic energy losses (PEL) of each technology as it was envisioned in a test pilot-scale system. The process evaluated a set of minimum criteria for the implementation and development of each harvesting and extraction technology for a 100 L/h culture or 1 L/h concentrated scale process, respectively.

For the down-selection evaluation, each project submitted a process flow diagram (PFD) of its technology that provided information on:

1. All major process equipment, including process vessels and pumps
2. All energy and mass-flow streams
3. Comprehensive energy and mass-balance information for all streams leading in and out of the major process equipment
4. A full account of the fate of chemicals, water, metal ions, and other materials in the system
5. Energy input reported in kWh.

A set of standardized assumptions was developed and used to construct the values provided in each project PFD:

1. Algal water feeding to the harvester:
   a. Feed rate of 1 L/h;
   b. Algal content of 1 kg (dry weight)/1000 L algal water;
   c. Lipid content of 0.5 kg lipid/kg dry weight algae.
2. Algal water feeding to the extractor (i.e., for systems not including a harvester):
   a. Feed rate of 1 L/h concentrated algal water;
   b. Algal content of 90 kg (dry weight)/1000 L of concentrated algal water; and
   c. Lipid content in algae of 0.5 kg lipid/kg dry weight algae.

No assumption was made regarding the ash content in the solids feeding to the harvester and extractor.

Based on the evaluation, compared to the baseline technologies, three of the harvesting technologies showed superior performance on the criteria: electrolytic, membrane filtration, and ultrasonic harvesting. The results for this evaluation are shown in Table 1.

Consequently, these three harvesting technologies were selected for scale-up. The mesoporous nanomaterials sequestration method was also selected for continuation because of the unique contribution of this method to the total economic feasibility of algal biofuels production for high-value product extraction, despite the current significantly higher cost.

The selected technologies were considered to present the best chance for NAABB to make significant impacts in the field and were
supported by a vision and state of technology representing a high reduction in operational expenses (OPEX) and minimized parasitic energy losses (PEL) when compared to the baseline technologies.

None of the extraction technologies were selected to move forward to a field test as they did not show a path to lower energy and lower cost extraction than available by industry. NAABB brought in an industry partner (Valicor) to apply its wet solvent extraction process for toll processing of lipids and lipid extracted algae (LEA) to consortium members.

It is important to recognize the technologies that were not selected for development past the 18-month decision point in this project. With further maturation, or in a different application context with additional or different criteria applied, the technologies that we did not pursue beyond the 18-month decision point may yet prove to be valuable technologies for the algal biofuel and bioproduct industry. More detailed descriptions of these technologies are provided in the NAABB Final Report [7].

2.2. Harvesting technologies and harvesting field tests

The three selected harvesting technologies successfully underwent field tests with a target of 100–1000 L/h processing during the third year of the NAABB program. The field tests served to:

- Demonstrate the feasibility of the technology at the target scale;
- Identify technical gaps needing further research and development, particularly with efficient operation of the scaled-up devices; and
- Introduce potentially game-changing harvesting technologies to industry.

2.2.1. Electrolytic methods

There are three established electrolytic methods: electrocoagulation, electroflocination, and electroflocculation. Electrically driven methods of harvesting are attractive because they are energy efficient, safe, and cost effective. Electrocoagulation uses reactive metallic electrodes to produce positively charged ions that induce coagulation of the negatively charged microalgae cells. This results in the algae cells being removed from the solution through settling. As more electricity flows through the solution, more metal is dissolved to form ions. Aragon et al. [23] previously examined this method and determined that it was superior to chemical flocculation because of lower cost, a shorter time needed for separation, and a lower probability that the microalgae would be contaminated with metallic hydroxides. Low current strengths were needed to achieve effective coagulation. A direct relationship was determined between the power input and the microalgae removal rate.

Electroflocculation uses an inactive metal cathode and a reactive metal anode to create hydrogen bubbles from the electrolysis of water as well as releasing a metal ion from the anode. The ion attracts the negatively charged algae to create flocs and the hydrogen bubbles cling to the flocs, which are then carried to the surface where they can be removed by conventional skimming methods. Alfafara et al. [24] conducted a study on removing microalgae using this method where it was determined that increasing the electrical power increased the rate of removal and decreased the time required to remove the algae from solution.

Electroflocculation utilizes an inert anode and cathode and moves negatively charged algal cells to the positively charged anode. Once the cells reach the anode, the negative charge is dropped from the microalgae and the microalgae form flocs without any metal ions. Poelman et al. [25] conducted a study on electrolytic flocculation of microalgae where it was determined that 80–95% of the microalgae solution could be removed from a 100 L vessel in 35 min.

Each of these methods has the potential for scale-up. Electrocoagulation is commercially available in the wastewater treatment industry. Preliminary testing did not demonstrate any advantage of electroflocculation over electrocoagulation; both flocs contained metal ions and the sediment from electrocoagulation was more easily recovered and was more concentrated. Thus electroflocculation was not evaluated in further studies for this project. Electroflocculation utilizes the same equipment as electrocoagulation with only a change in electrode material. Prior research has demonstrated that the processes are effective when used to harvest or dewater microalgae. A series of electrolytic tests on electrocoagulation and electroflocculation of algae (N. oculata) were performed in a 400 mL glass beaker serving as the lab-scale electrolysis unit as shown in Fig. 2. A commercial bench-scale power supply provided a direct current charge to the electrodes at a measured voltage and current. Various electrode materials were evaluated with aluminum, iron, and chromium showing the most potential to effectively achieve electrocoagulation [14]. Additional tests were performed using stainless steel electrodes to attempt to achieve electroflocculation. While these tests were successful, control technologies for current density were not sufficient to maintain a consistent electroflocculation process [12], especially with electrode material that, while more resistant to electrolytic forces, was not inert to them and would release ions under high current densities. Therefore, all subsequent research was concentrated on electrocoagulation.

Key process parameters for electrocoagulation are current density and solution pH [26]. Current density has been shown to determine the rate and amount of electrocoagulation by controlling the rate at which ions are released from the electrodes. Vasudevan et al. [27] determined that removal efficiencies of copper ions increased with current density up to a level of 0.025 A/m². Above this level, removal efficiency was constant at 99%. Electrolytic separation studies by Holt et al. [28] demonstrated that low operating currents combined with higher voltage potentials resulted in settling; whereas, higher currents with lower voltage potential resulted in the formation of hydrogen bubbles and flotation of the floc.

Vasudevan et al. [27] considered the effects of coexisting ions on removal efficiency. Electrocoagulation of copper ions was decreased in the presence of increasing levels of carbonate (HCO₃⁻), phosphate (H₂PO₄⁻ and HPO₄²⁻), silicate, and fluoride. Carbonate and phosphate exhibited a threshold of 5 mg L⁻¹, where concentrations below this had no effect on copper removal but silicate and fluoride preferentially competed for the aluminum ions in the electrocoagulation process and decreased the removal efficiency of copper at any concentration. Consequently, ion variations in the water source would be presumed to affect the electrocoagulation process.
An analysis of ground water used for media preparation at the test location in Pecos, Texas showed levels high in calcium (18 ppm), sodium (1188 ppm), silica (SiO₂ 36 ppm), chloride (993 ppm), and sulfate (SO₄ 964 ppm). These values were accounted for when formulating media; however, the fate of any excess was not determined. It may be captured in the biomass or remain in solution in the filtrate following separation. An analysis of the precipitate following electrocoagulation in the field trial discussed below reported levels for chromium of 460 ppm, iron at 1900 ppm, and nickel at 279 ppm. Since the electrode material for this trial was stainless steel, we would expect these elements as these are the ions released from the electrodes. The impact of the ions in the ground water and introduced through the electrocoagulation process on the fuel conversion process is a potential concern and should be addressed further.

The team conducted field tests of their electrocoagulation approach using a commercial electrocoagulation Sur-Flo unit loaned from Kaselco (Fig. 3). The field tests were conducted at the Texas AgriLife Research, Pecos, Texas, facility in the summer of 2011 and 2012. The average percent of solids and biomass of the solution was calculated for each test and these values are shown in Table 2 [13].

A complete harvest of an algal batch was conducted in 2012 to demonstrate the feasibility of operating the electrocoagulation system at pilot scale over an extended period [13]. The reactor was operated at 60 Lpm and 17,244 L were treated with electrocoagulation using stainless steel electrodes. Following overnight settling in a cone-bottom tank, the sediment was further dewatered using a commercial (Alfa Laval) disc and bowl centrifuge rated at 50 Lpm. The centrifuge site glass was used to mark the change between the bottom greenish layer containing the sedimented algal cells and the lighter, brownish layer containing non-sedimented cell debris.

The incoming algae media had an ash free dry weight (AFDW) concentration of 0.1%, which was concentrated to 2.8% with electrocoagulation. The precipitated solids were 83.8% ash (16.2% biomass by difference). Following centrifugation of the precipitate, the final solids concentration was 8% and the ash concentration was 65.7% (34.3% biomass by difference). The high ash content was a concern. As noted above, an assay determined high levels of chromium, iron, and nickel in the precipitate, which would be bound to the biomass and present as ash. Following the separation of the algae, a 1000 L batch of ground water containing no algae and no additional nutrients was treated with the electrocoagulation system and significant precipitation was observed. This precipitate from the ground water may have also added to the ash concentration following electrocoagulation of the entire media volume of 17,244 L. The lower ash content in the concentrate from the centrifuge would support this hypothesis as some of the water contaminants may exist as dissolved solids and be removed from the sample by centrifugation.

The power demand using electrocoagulation was 0.003 kW L⁻¹ compared to 0.016 kW L⁻¹ using the centrifuge. A total of 17,244 L was treated in a 5-hour period using electrocoagulation resulting in a total energy consumption of 258.7 kWh. Following a 24-hour settlement period, the precipitate of 3785 L was centrifuged for 4.25 h resulting in a total energy consumption of 257.4 kWh. Therefore, the total energy consumed was 516 kWh to harvest one pond of algae. At an electricity cost of $0.08 kWh⁻¹, this represents a cost of $41.28 to harvest. If this batch was harvested with the centrifuge alone, which was the baseline process, it would take an estimated 16 h and result in an estimated cost of $350 for electricity.

Electrocoagulation may serve as a primary dewatering step with a secondary step needed to reach the final desired moisture content. Electrocoagulation removed 78% by volume of the liquid prior to secondary dewatering. The reduced volume to be processed in the secondary phase consequently reduced costs. There is a caveat that the impact of the increased ash content and the presence of specific ions may interfere with downstream processes and must be accounted for in the overall process design.

2.2.2. Membrane technology

Membrane microfiltration and ultrafiltration technologies are widely used in industry, such as wastewater treatment (at the low-value end) and protein concentration (at the high-value end). Reverse osmosis membranes are used for seawater desalination at very large scales. Polymeric membranes are dominant membrane products for these applications, while ceramic and metal membranes only account for a small fraction of the market. Although a variety of membrane-based filtration approaches are available, application of membranes to algae harvesting and dewatering was relatively new at the time of this study. More recent articles have reviewed the emerging use of membrane processes for harvesting and dewatering algae [29,30].

Although there are many commercially available filtration technologies (for example, from Pall Corporation, Port Washington NY) further research and development of membrane technology is needed to address the barriers for practical application of membranes to algae harvesting. The first barrier is the need to significantly enhance filtration flux. Since the algae content in the culture solution is low, the membrane has to be highly permeable to water. For a given culture production rate, the membrane area required decreases proportionally

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**Fig. 3.** Kaselco Sur-Flo electrocoagulation reactor tested.

**Table 2**

<table>
<thead>
<tr>
<th>Test</th>
<th>Number of plates in the reactor</th>
<th>Electrode</th>
<th>Average % solids in the sediment</th>
<th>% Ash in the solids</th>
<th>% Biomass in the solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>SS</td>
<td>2.8%</td>
<td>84.4%</td>
<td>15.6%</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>Al</td>
<td>2.9%</td>
<td>80.1%</td>
<td>19.9%</td>
</tr>
<tr>
<td>3</td>
<td>07/11</td>
<td>SS/Al</td>
<td>3.0%</td>
<td>79.6%</td>
<td>20.4%</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>Al</td>
<td>2.4%</td>
<td>79.9%</td>
<td>20.1%</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>SS</td>
<td>2.2%</td>
<td>81.8%</td>
<td>18.2%</td>
</tr>
<tr>
<td>6</td>
<td>07/11</td>
<td>SS/Al</td>
<td>1.9%</td>
<td>74.0%</td>
<td>26.0%</td>
</tr>
</tbody>
</table>

Table Notes: SS = Stainless Steel; Al = Aluminum. The percent biomass was determined by difference.
with increasing flux. At the start of this project, we conducted a preliminary process analysis and found that a very large membrane surface area and footprint would be needed for a commercial-scale algae cultivation system if the algae filtration flux is similar to that currently achieved for wastewater treatment, which may become cost-prohibitive. Another barrier is membrane stability. Membrane fouling, particularly biological fouling, is a problem in current wastewater treatment processes. Algae cultures are rich in biologically active species, lipids, carbohydrates, and proteins. Potential chemical- and bio-fouling of membrane processes for algal harvesting is a serious concern, of which little is known.

Polymeric membranes used for wastewater treatment are natural candidates for algae filtration applications; however, fouling remains a major issue [31]. A variety of commercially available micro- and ultrafiltration flat sheet membranes made of fluoro-polymeric materials were compared for filtration of \textit{Chlorella pyrenoidosa} FACHB-9 algae cells, and similar performance was found in their ability to concentrate algae [32]. Another study suggests that algal organic matter in \textit{Chlorella zeolina} algae culture tends to rapidly plug the pores of hollow-fiber polyvinylchloride (PVC) ultrafiltration membranes (50 kDa Molecular Weight Cut-Off). [33].

Ceramic and metallic inorganic membranes are viewed as having better biofouling resistance and higher water flux than polymeric-based membranes. For this reason, these inorganic-based membranes have received a considerable amount of research interest for the past two decades, although without widespread adoption by industry. The high cost per unit of surface area and low surface-area packing are the main drawbacks. In sharp contrast to fruitful exploration of new membrane materials with applications, research publications on development of new membrane products have been limited. Recently, developments of ceramic monolithic membrane modules of small channel sizes (~1 mm) [34,35] and capillary inorganic membrane tubes [36] have been reported. These product concepts show promising progress toward increasing the surface area packing density of inorganic membranes more closely to that of polymeric hollow-fiber membranes.

Therefore, based on the expected anti-fouling characteristics of metallic membranes, and leveraging advances in membrane fabrication, we elected to focus our work under the NAABB project on development of thin, flat-metal-sheet membranes. Our approach was to make porous metal-sheet membranes fabricated with a surface area packing density equal or comparable to flat-sheet polymeric membranes. For this type of membrane product design, manufacturing and engineering capabilities developed in the polymeric-membrane field may be utilized. A variety of metals are made as foams or screens commercially [37], which include aluminum, copper, zinc, nickel, silicon, Inconel, silver, and gold. These structures typically have pore sizes from tens to hundreds of micrometers, which are too large to be effective for microalgal filtration. In addition, the metal foam is mechanically too weak to be used as thin sheets (< 300 μm). Therefore, we considered the desirable properties of a metallic microfiltration membrane sheet to be [1] light, highly permeable, mechanically strong, and flexible; [2] chemically stable and resistant to solvent attack; and [3] thermally stable, enabling membrane processing and/or separation operation at elevated temperatures.

Research and development of membrane harvesting for algae can be approached through evaluating the performance of current membrane products for algae filtration, modifying current filtration module and/or process designs, and innovation of new membrane and process ideas. We believed that the current membrane producers were better positioned than we were to evaluate their products for new applications. Therefore, in this project we focused on innovations of new membrane materials and products. While commercial membrane materials were evaluated briefly to fill the knowledge gap, our focus was on the development of novel ceramic-modified thin (~50 μm thick) porous metal sheet membranes (Fig. 4) for microalgal harvesting applications. The thin metal sheet of uniform pore structures at submicrometer level throughout the thickness is adequately strong and flexible to be self-supported and molded. The pore size and surface chemistry of this metal sheet can be modified by coating with ceramic particles.

For the scale-up membrane filtration field test, we developed a thin porous Ni alloy metal sheet membrane (Fig. 4d). A cross-flow membrane module (Fig. 5) was assembled from 18 12 cm × 12 cm membrane sheets on a mobile unit that was tested at the Texas AgriLife Research, Pecos, Texas, facility during the winter of 2012 and early 2013 using \textit{N. salina}. NAABB also worked with Pall, Inc., to test one of their commercial hollow-fiber unit membranes as a baseline, commercially available technology.

Fig. 6 shows variations of operation parameters with time in one representative batch filtration run. The algae from a storage tank was pumped through the membrane module and returned to the tank, while a clear solution was withdrawn from the permeate side of the membrane module under vacuum. The permeate flow direction was perpendicular to the feed flow. Since the liquid velocity inside the feed channel in these runs was fairly low (0.27 m/s) relative to typical cross-flow filtration operation, the liquid feed was aerated by introduction of air pulses to mitigate accumulation of filtration cake layers on the membrane surface. As a result, the module inlet pressure fluctuated over a wide range, while the outlet pressure stayed near atmospheric pressure. The permeate flow fluctuated accordingly. However, the flux gradually decreased with time. The post-examination of the membrane sheet showed no or little deposition of the algae species on the exterior surface of the Ni alloy membrane sheet as expected. The gradual decline of the flux with time was likely due to adsorption of soluble polymers in the culture inside the membrane pores. As a result, the membrane module was cleaned every day during the field tests. A few common chemical cleaning agents were evaluated and found no more effective than physical cleaning by back-flushing. More effective membrane cleaning methods need to be developed for industrial operation. For comparison, the flux of the present module was about two to three times that of the flux obtained with a commercial polyvinyl alcohol (PVA) membrane plate (SINAP Membrane Tech. Co., Ltd., Shanghai, China), which was designed as a bioreactor membrane for wastewater treatment application.

The energy consumption and cost of the membrane technology projected for the commercial scale operation are listed in Table 3. We noted that the energy consumption predominantly resulted from the generation of a pressure gradient across the membrane, mainly due to the membrane properties. For a given pressure gradient, the harvesting cost would proportionally decrease with increasing membrane permeability. The energy consumption and cost for dewatering the concentrated sludge was insignificant relative to the cross-flow filtration cost. Thus, concentration of the algae culture should be the main focus for significant reduction to the energy consumption and cost. Overall, the membrane process is an efficient means of harvesting with energy consumption comprising only a small percentage of the algae fuel value. The numbers in Table 3 were calculated based on an algae content of 0.04 wt% in the culture. The energy consumption and cost will likely be reduced by increasing the algae content in the culture.

In summary, the thin porous Ni sheet membrane showed 100% higher flux (or permeance) than common polymeric (e.g., polyethersulfone, PVA) microfiltration and ultrafiltration membrane products under comparable conditions. The scale-up feasibility of the new membrane sheet from the laboratory bench test unit to a cross-flow membrane module for field tests was shown. A customized, mobile membrane-testing skid was built to conduct further field tests in the future. The feasibility to achieve a 44 to 66 times concentration factor for \textit{Chlorella} sp. DOE1412 was shown through field tests at the Pecos, Texas, facility.

2.2.3. Ultrasound technology

The use of ultrasonic fields to harvest and disrupt algae cells to extract lipids and proteins from algae and recover the water has been
Our approach uses ultrasonic-focusing technology and minimal electrical energy to concentrate the algae cells and to disrupt the cells for separation into lipids and lipid-extracted biomass. The lipids, or oils, can be refined into biofuel, the remaining biomass used for animal feedstock or other valuable coproduct, and the water recycled. Our ultimate concept is to conduct all three operations in one integrated system and reduce the overall costs of harvesting and extraction by several orders of magnitude. The system would be portable and used at the site of algae cultivation to reduce transportation costs.

The use of ultrasonic fields to harvest and extract lipids from algae has several advantages over conventional methods. Like membrane-based methods, no chemicals are used to concentrate the algae; therefore, there are no downstream effects on the conversion products or coproducts. The ultrasonic extraction process is a “wet” extraction process, with no drying needed before cell lysis and lipid extraction. No solvents are used for extraction, therefore eliminating hazardous chemicals and the need to remove them from the downstream processes. Using ultrasound to concentrate cells and to extract and separate lipids from algae allows the water to be recycled and reused at each step. The process is environmentally benign and a study of energy efficiency indicated that the ultrasonic process is projected to be more cost effective than conventional methods.

In the first year of this project, we conducted laboratory-scale experiments to investigate the feasibility of using ultrasonic fields to concentrate and disrupt the algae cells and to separate the lipids from the rest of the biomaterials and water. Different ultrasonic treatment regimes were used: a high-frequency regime (1–2 MHz) to harvest the...
algae (Fig. 7) and a low-frequency regime (< 1 MHz) to disrupt the algae cells by cavitation and streaming. A high-frequency regime similar to the harvesting treatment was also used to separate algal oil from water.

Characteristics of the algae, lipids, and proteins were analyzed after treatment with acoustic fields, and were used to establish conditions for operation and optimal performance. In Year 2 we continued to gather performance data on the effect of ultrasonic fields on harvesting, cell disruption, and oil separation. These data were used in an economic analysis to establish the efficiency of the ultrasonic technology at the liter scale [17].

After 18 months, a technoeconomic analysis of harvesting and extraction technologies was performed and the ultrasonic harvesting portion of the process was selected for scale-up to pilot scale. Fig. 8 shows the process flow diagram (PFD) of the ultrasonic harvesting process; Table 4 shows the corresponding mass and energy balance information for two species of algae. The electrical costs shown in Table 4 (based on laboratory-scale studies) are equivalent to 4.3 ¢/gal and 1.1 ¢/gal of lipid for *N. salina* and *Auxenochlorella protothecoides*, respectively. These electrical costs compare to 62–200 ¢/gal of lipid when centrifugation is used at the same feed rate and to achieve the same level of dewatering.

In Year 3, we built a pilot-scale harvester and tested it in a field study. The scaled-up ultrasonic harvester unit was designed for maximum flow rates of 45–225 L/h using 9 modules (Fig. 9). The scaled-up device was assembled in a shed outside a laboratory area in Los Alamos, New Mexico, and tested in 46 batch and flow-through experiments during September/October 2012 using 1000 L of *Nannochloropsis oculata* feedstock provided by Solix Biosystems from their Coyote Gulch facility. The initial algae concentration was approximately 1.75 g/L AFDW. Up to 18× concentration of algae was seen and we routinely observed visual confirmation of algae concentration above the feedstock concentration (Fig. 10).

Over a several-hour trial, we found considerable variability in the harvester performance (Fig. 11). The removal rates were always higher

Table 3

<table>
<thead>
<tr>
<th>Cross-flow filtration (first stage harvesting, 1°)</th>
<th>Dewatering (second stage concentration, 2°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration factor</td>
<td>100</td>
</tr>
<tr>
<td>Concentrated algae, solid wt%</td>
<td>4.0%</td>
</tr>
<tr>
<td>Membrane permeability, L/m²/h/bar</td>
<td>200</td>
</tr>
<tr>
<td>Electricity consumption, kWh/kg (product)</td>
<td>0.103</td>
</tr>
<tr>
<td>Energy consumption, % of algae fuel value</td>
<td>4.94%</td>
</tr>
<tr>
<td>Membrane area required, m²</td>
<td>43,313</td>
</tr>
<tr>
<td>Membrane cost, $/MT (product)</td>
<td>$48.34</td>
</tr>
<tr>
<td>Electricity cost, $/MT (product)</td>
<td>$10.32</td>
</tr>
<tr>
<td>Total cost, $/MT</td>
<td>$58.66</td>
</tr>
</tbody>
</table>

The values in the table are based on an algal pond culture solution of 0.04 wt% and a trans-membrane pressure gradient (TMP) of 0.9 bar.

1° harvesting of the algae pond.

2° second stage dewatering of the concentrated sludge from the 1° stage.

a Assumed electrical efficiency of pumps is 60%.
b Product is net weight algae biomass recovered on an AFDW basis.
c Assumed factor of 3.32 for conversion between the electrical and thermal energy. Thermal energy is the caloric value of the algae biomass recovered vs. the electrical energy used. Assume the algae thermal energy content of 25 MJ/kg.

d Assumed membrane operation time of 16,000 h (two years) and membrane cost of $50/m².
e Assumed electricity cost of $0.1/kWh.
with the “power on” (dynamic flow-through tests) relative to the “power off” (static batch tests), and ranged from around 15 to 52%.
However, the removal rates measured in the flow experiments (typically single module experiments at flow rates of 5 L/h) quickly dropped to lower than the short-time (1 min) removal rates that were routinely measured in no-flow experiments. Future development of the ultrasonic harvester will focus on improvement in process control and harvester design to achieve consistent high performance.

3. Harvesting conclusions

Continued refinement and expanded demonstration of the innovative NAABB harvesting technologies at scale would serve to reduce the financial risk to industry, thereby encouraging the acceptance and transfer of these technologies to commercial use. However, further development is needed to achieve high and affordable performance at large scales and maintain high performance over long durations of operation.

A wide variety of real-life microalgal feedstocks need to be tested in each device in order to better understand how broadly each approach can be applied. Additionally, the quality of the feedstock input (e.g., ash content) and its effect on harvesting performance and downstream processes needs to be determined.

Notwithstanding these uncertainties and room for improvement, incorporation of NAABB’s innovative, energy-efficient harvesting technologies into algal biofuel production processes are expected to ultimately lower the cost of algal biofuels and lower the carbon footprint of algal biofuels production. This conclusion was supported by analyses conducted by the NAABB Sustainability Team on the greenhouse gas emissions of each of the three harvesting approaches evaluated by the NAABB Harvesting and Extraction Team [7].

Table 4
Mass and energy balance for the ultrasonic harvester process. Flow stream locations 1 through 5 are shown in Fig. 8. Results are based on laboratory-scale experiments with N. salina and A. protothecoides. The electrical costs are equivalent to 4.3 ¢/gal and 1.1 ¢/gal of lipid for N. salina and A. protothecoides, respectively.

<table>
<thead>
<tr>
<th>Flow stream</th>
<th>Description</th>
<th>Units</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Flow</td>
<td>L/h</td>
<td>100</td>
<td>10</td>
<td>90</td>
<td>1</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>kg/h</td>
<td>99.91</td>
<td>9.93</td>
<td>89.98</td>
<td>0.93</td>
<td>8.998</td>
<td></td>
</tr>
<tr>
<td>Biomassa</td>
<td>kg/h</td>
<td>0.1</td>
<td>0.0784</td>
<td>0.0216</td>
<td>0.07624</td>
<td>0.00216</td>
<td></td>
</tr>
<tr>
<td>Lipid</td>
<td>kg/h</td>
<td>0.05</td>
<td>0.0392</td>
<td>0.0108</td>
<td>0.03812</td>
<td>0.00108</td>
<td></td>
</tr>
</tbody>
</table>

Electrical energy system

<table>
<thead>
<tr>
<th>Algal species</th>
<th>Units</th>
<th>E1&lt;sup&gt;a&lt;/sup&gt;</th>
<th>E2&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Total electrical usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>N. salina</td>
<td>kWh/m³</td>
<td>0.0541</td>
<td>0.0541</td>
<td>0.108</td>
</tr>
<tr>
<td>C. protothecoides</td>
<td>kWh/m³</td>
<td>0.0143</td>
<td>0.0143</td>
<td>0.0286</td>
</tr>
</tbody>
</table>

<sup>a</sup> Microalgae, including all intracellular material such as lipids, protein, DNA, and carbohydrates.

<sup>b</sup> NOTE: These energy values were based on early assessments and are not representative of the current state of ultrasonic technology. Basis for N. salina: Circa 80% of biomass at 15 mL/min flow and 0.292 W true power input. Energy estimate also incorporated an assumed increase in energy efficiency from 15% to 90%. Energy requirements for A. protothecoides were estimated by factoring in the square of the algae cell diameter ratio (3.6 μm/7 μm). Electrical cost contributions to lipid product were calculated assuming a lipid density of 0.9 kg/L and electricity costs of $0.08/kWh.
4. Extraction technologies

4.1. Wet algal-biomass lipid extraction and LEA fractionation

Valicor (formerly Solution Recovery Services, or SRS) is a world leader in the recovery and separation of products from industrial process fluids. Valicor formed a wholly owned spin-off, Valicor Renewables, which developed AlgaFrac™, a patent-pending process as a result of five years of R & D [40,41]. This separation and fractionation technology is capable of recovering and purifying three basic algal biomass fractions suitable for downstream processing to value-added fuels and bioproducts. The three target fractions are a lipid fraction containing glycerides (for downstream fuels and lipid nutraceuticals), a solid residual biomass fraction with proteins (feed and food applications), and an aqueous fraction (soluble sugars and recyclable nutrients).

Whereas more traditional processes require algal cell drying and cell lysis, the AlgaFrac process is a wet extraction platform. Input algae biomass of 10–20% solids content can be rapidly processed into lipids, residual biomass, and aqueous streams (Fig. 12). Valicor Renewables’ wet extraction platform is cost- and energy-effective, recovering over 80% of the net available energy [42].

Within NAABB scope, the AlgaFrac process was used to accomplish two goals. First it provided needed data for technoeconomic analysis of wet extraction technology. Second, it provided extraction services for processing algal biomass to produce lipids and LEA fractions as feedstock for the Conversion and Co-products tasks. The second goal was accomplished through toll processing of wet algal-biomass extraction by Valicor to provide material for downstream efforts. To this end, Valicor conducted a series of bench-scale extraction tests to optimize oil yields for various algae strains and harvests. Findings from bench-scale fractionation were used to define optimal conditions for toll processing of large quantities of algae. Valicor processed NAABB-generated algal biomass in its pilot plant to produce requisite quantities of oil and LEA fractions. Valicor also dried the LEA when necessary in its pilot plant for distribution to NAABB team members. The oil and LEA fractions were

![Fig. 9. Side view of two scaled modules attached to a customized cart containing a total of 12 modules (i.e., two different designs of 9 and 3 modules). Feed into both sides of the distributor tube can be seen on the module on the right. There is a tray between the modules that collects processed (dilute) algal water from the rear of the modules and the concentrate is removed and collected from the bottoms of the modules.](image)

![Fig. 10. Visual comparison of the dilute feedstock (left tube) and concentrated product (right tube) following ultrasound harvesting.](image)

![Fig. 11. Algae (N. oculata) removal rates measured in the field at a feed rate of 5 L/h in a scaled-up ultrasonic harvester module. One unit is equivalent to 1.75 g of biomass, which was contained in 1 L of feed. Removal rate is the product of the concentrated stream flow rate (circa 0.5 L/h) and its concentration in units per liter. The “no power” data represent removal rates obtained without any concentration effect from the harvester. These values drifted from 0.5 units/h as the concentrate stream flow rate varied. The “power” values represent the average removal rate measured over a 5- or 10-minute period when the power was applied. Removal rates are shown over time periods where the true power input was periodically increased, as indicated by the different colored regions.](image)

![Fig. 12. Schematic of Valicor’s AlgaFrac™ process.](image)
supplied to downstream partners for their tasks.

The Valicor AlgaFrac process was successfully applied to various NAABB algae species to produce large quantities of oil and LEA—both dry LEA with dissolved sugars, etc. and dry LEA after dewatering. The species processed were *Nannochloropsis* sp., *N. salina*, *N. oculata*, *Desmid* sp., and *Chlorella* sp. These algae strains were extracted at the bench and pilot scale. Fig. 13 shows oil extracted with the Valicor Renewables process, and Fig. 14 illustrates a typical analysis of oil samples. Good mass balance closure and consistent oil yields were obtained, thereby indicating robustness of the Valicor Renewables process. Two examples of typical mass balance results are shown in Figs. 15 and 16.

An important part of the AlgaFrac process is a conditioning step. The role of the “conditioning step” (high temperature acid treatment) in the Valicor process is two-fold:

1. To partially lyse the cell walls causing porosity that allows ingress of the chosen solvent (hexane) and permits efficient extraction of the lipids within, and
2. To hydrolyze the polar lipids into lyso-lipids (diglycerides), which have higher solubility in hexane, enhancing extraction efficiency.

Valicor developed this process in order to deliver an oil that can be readily hydro-treated to diesel and jet fuel. The noble metal hydro-treating catalysts, typically platinum, are poisoned by many hetero-atoms such as nitrogen and phosphorus. The level of phosphorus in the oil is particularly critical since phosphorus is a stoichiometric poison for platinum catalysts; thus a viable process for extracting algal oil must deliver the oil with ultra-low levels of phosphorus. Since autotrophic microalgae are rich in phospholipids this presents a major problem.

To exemplify the problem and the solution offered by their process, Valicor studied a *Nannochloropsis oculata* strain. First, a sample of the biomass was extracted (TLE or total lipid extraction) using the Bligh-Dyer method [43]. As shown in Table 5, over 60% of the lipids extracted were polar lipids and of these 2/3 (over 40% of the total) were phospholipids. A second sample of the same algae harvest was then extracted applying the Valicor process using hexane as solvent. The resulting HPLC spectrum of the resulting oil is shown in Fig. 17 where it is compared with the oil extracted with the TLE (Bligh-Dyer) process. It can be seen that the polar lipids (glycolipids and phospholipids) were, to a very high degree, hydrolyzed to lysolipids (diglycerides) by the conditioning step of the Valicor process. In this process the heteroatoms are expelled into a separate aqueous phase, which can be used as fertilizer or recycled as nutrients for the next algae batch.

Elemental analyses of the oil extracted by the Valicor process exhibited very low levels of phosphorus (< 4 ppm) making it suitable for hydrotreating. Further optimization or lower pH conditions/higher temperature in the conditioning step would be expected to further lower the phosphorus levels by completing the hydrolysis.

4.2. Selective sequestration of high-value biomolecules by mesoporous nanoparticles

Acquiring all possible value out of microalgal oil is imperative to make it an economically viable feedstock for biofuel. Current technologies utilize food-based oils as the feedstock for base catalyzed conversion of triacylglycerides (TAGs) to fatty acid methyl esters (FAMEs, or biodiesel). These feedstocks are ideal because they contain > 99% TAGs. However, microalgal oil contains a greater variety of lipid and hydrocarbon molecules, some of which are considered high-value or value-added. As such, these biomolecules would contribute to the economics of the microalgal biorefinery if they could be separated from fuel precursors and distributed to the optimal industry (i.e., the industry that gives the naturally produced molecule of interest the greatest value). Current separation and purification techniques for naturally produced lipids, hydrocarbons, and organic acids are challenging and energy-intensive, with extraction and distillation the most common techniques, using organic solvents or supercritical fluids.

A high-surface-area, porous-silica–based nanoparticle material for the selective sequestration and removal of these high-value and value-added molecules from microalgal oil was developed [22]. Synthesized and characterized nanomaterials that independently target free fatty acids (FFAs), polyunsaturated free fatty acids (PUFAs), tocopherol (vitamin E), and microalgal cells from growth media as a magnetic dewatering technology are illustrated in Fig. 18. Pores with an average diameter of 10 nm were found to be optimal to capture FFAs when compared to nanomaterials with smaller pore sizes of 3 and 5 nms [22]. Decorating the pore surface with primary amine functional groups selectively targeted FFAs, restricting other molecules normally found in microalgal oil from entering the pores and adsorbing to these porous nanomaterials. This is shown in Table 6 where we compared the results of biomolecule uptake by primary amine functionalized nanomaterials to unfunctionalized nanomaterials both with an average pore size of 10 nm. All the FFA was sequestered by both nanomaterials along with much of the other types of biomolecules (triglyceride, terpene, and sterol). However, when the surface of the nanomaterial was modified with primary amine groups, the sequestration of biomolecules other than FFAs was decreased significantly. By rinsing these nanomaterials with organic solvents, the FFAs were desorbed leaving a solution of highly pure, naturally produced FFAs [44]. Acids have been shown to desorb from porous nanomaterials by pH adjustments to the solvents. By mixing aqueous solvents with methanol the pH is increased and FFA is desorbed from the surface of the porous nanomaterials [44]. The FFA can also be desorbed by electrophoretic separation of the acid after being sequestered, forming a fatty acid methyl ester, which no longer would be electrostatically bound to the porous nanomaterials. This approach was also used as a direct method to quantify the sequestration amount via GC.

Following this discovery, the purified FFAs were analyzed to determine if targeting and removing the high-value FFAs (Omega-3/-6) is possible by adjusting some of the properties of the sequestration materials. We also determined that smaller pore sizes capture PUFAs selectively while limiting the diffusion of saturated and monounsaturated FFAs into the pores. This observation can be attributed to the folding of these organic acids in the microalgal oil. Because all double bonds in the...
naturally produced fatty acids are cis, PUFAs will fold into tighter arrangements making the size of Omega-3/-6 the smallest among the different saturations. In more recent work [45] we determined that by controlling the size of the mesopores on the nanomaterial, the smaller pores were selective for high-value free fatty acids (polyunsaturated), while larger pore nanomaterials were not selective for polyunsaturated, monounsaturated or saturated FFAs.

Tocopherol is naturally produced by many microalgae strains in concentrations up to 5 wt% lipids. Naturally produced tocopherol has considerable advantages over industrially synthesized tocopherol.

**Fig. 14.** Typical analysis of oil samples extracted using the Valicor process.

**Fig. 15.** Example mass balance of extraction process using *Nannochloropsis* sp. obtained from Pecos, Texas.
including higher nutritional value (up to half the stereochemistry configurations of the non-natural tocopherol have no biological activity). Furthermore, obtaining these nutrients from natural sources avoids use of finite petroleum resources.

By functionalizing the pore surface with a unique organic moiety that reacts noncovalently with functionality on the tocopherol molecules we were able to synthesize and characterize a sequestration nanomaterial that selectively targeted vitamin E. In unpublished work, we investigated the uptake and sequestration of tocopherol in pentfluorophenyl functionalized porous nanomaterials. Initial experiments showed > 70% of the tocopherol in a simulated microalgal oil solution was sequestered while only capturing 15% of the FFAs and 4% terpenes from the same solution. Through a wet impregnation synthesis with iron salt on the nanomaterials and subsequent thermal treatment, we produced magnetic porous nanomaterials. We used this magnetic nanomaterial to sequester tocopherol and separate the nanomaterials from the solution. We thereby demonstrated, for the first time, that separation of these magnetic, high-surface-area porous nanomaterials can be made possible by including magnetic functionality in the synthesis.

These nanotechnologies not only offer a new method to target and remove molecules of interest from the alphabet soup of molecules that are produced by microalgae, but will likely open the minds of researchers toward other applications for these materials. The relative ease and speed with which these materials can be specifically functionalized along with their biocompatibility and nontoxic nature make them ideal platforms for exploration in biorefinery and biofuel applications. Nevertheless, there is much work to be completed on techno-economic analyses, life cycle assessments, and long term durability before the synthesis of these materials can be scaled up for industrial use.

5. Overview conclusions

The NAABB Harvesting and Extraction Team made significant progress in the development of innovative technologies for harvesting and...
extraction of algal biomass and lipids. The projects addressed several key challenges and provided preliminary answers to the potential viability of each approach. Moreover, the new technologies were demonstrated on a range of different algal species and a range of scales.

Specific accomplishments by the team provided new results to support continued technology development and commercialization of processes, for example the Valicor fractionation process. Three innovative harvesting approaches were taken from proof of concept at the laboratory scale to a larger scale with a minimum feedstock-processing rate of 100 L/h:

- The team demonstrated an electrocoagulation method for dewatering at pilot scale (5000 L/h) at the Texas AgriLife Research facility at Pecos. This method reduced the energy demand to 25% of the baseline of centrifugation and resulted in 95% recovery of the biomass [12-15].
- The team built a pilot-scale cross-flow membrane filtration system with novel membranes and improved performance over commercially available membrane materials [16,34,35].
- The team scaled up the ultrasonic harvesting technology 10-fold in comparison to the laboratory-scale device, and measured algae removal with concentrations up to 18 times the feed concentration [17,18].

All three technologies show promise as primary harvesting techniques. In addition, cross-flow filtration could be used for further dewatering to 24% solids. All show energy savings compared to the baseline technology of centrifugation and may be used in combination with each other to achieve higher concentration factors or higher throughput. Moreover, each of these harvesting technologies would be compatible with both algae processing pathways of lipid extraction and whole algae HTL. In fact, the electrocoagulation technology demonstrated here, combined with HTL of whole algae was determined by the NAABB Sustainability Team to be the most cost-efficient coupling of harvesting and conversion technologies [7]. Table 7 summarizes the results of each NAABB harvesting technology and its impact on energy reduction. Finally, the three harvesting technologies were also found to have low greenhouse gas emissions, as reported in a study conducted by the NAABB Sustainability Team [7]. By taking three innovative harvesting technologies to field trials, information about key process parameters previously not available in the public domain was generated. In each case, the field trial provided new insight into the technical challenges of scale-up and identified the gaps needing to be filled to further improve the performance of each technology.

In the lipid extraction area, NAABB demonstrated a lab-scale, selective sequester of polyunsaturated FFAs and tocopherol, value-added algae products from crude lipid extracts [22,44,45]. Using the Valicor process, which uses wet algae and thus eliminates the cost of drying from the total extraction cost, NAABB successfully demonstrated > 60 wet solvent extractions of > 40 algae strains producing crude lipid and LEA samples with mass balance data [40-42]. These samples were provided to the downstream processing teams.

The team found several important factors that affected the efficiencies of harvesting and extraction technologies. Although we demonstrated new technologies that were compatible with a variety of different algal species, the difference between species proved to be important factors to the efficiency of harvesting and extraction. Likewise, the starting concentration of the cultivation feedstock was important to the overall harvesting and lipid extraction efficiencies. There is an urgent need to collect long-term performance data of new technologies using real-world feedstocks and at larger scales. Finally, each new harvesting technology had specific engineering issues that will need to be addressed to improve performance and enable eventual implementation. For example, electrocoagulation technologies will need to reduce the introduction of metal ions into the algae as they may adversely affect the quality of the fuel product; membrane technologies suffer from clogging and fouling; and ultrasonic harvesting will need to overcome variable performance over long operating periods. For the
Table 7
Summary of NAABB harvesting technology and impact on energy reduction.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Scale</th>
<th>Concentration—initial, final, and factor</th>
<th>Energy reduction</th>
<th>Recovery</th>
<th>Energy consumption, kWh/m³culture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electro-coagulation</td>
<td>3445 L per h</td>
<td>Initial: 0.8 g/L, Final: 40 g/L, Factor: 50 x</td>
<td>Energy use was 25% (59 kWh) of that used by the centrifuge (236 kWh) under the same conditions</td>
<td>95% of biomass recovered in floc</td>
<td>Not available (N/a)</td>
</tr>
<tr>
<td>Cross-flow filtration with thin-sheet metal membrane</td>
<td>0.4 L/h</td>
<td>0.65 g/L N. salina; 45-fold concentration to 30 g/L</td>
<td>N/a</td>
<td>100%</td>
<td>0.387 @ 2.0–2.5 m/s velocity demonstrated in this lab run 0.056 @ 0.15–0.5 m/s of velocity targeted for commercial-scale unit and tested at Pecos</td>
</tr>
<tr>
<td>Ultrasonic harvesting (lab scale)</td>
<td>0.9 L/h</td>
<td>Initial: 3 g/L, Final: 27.8 g/L, Factor: 9.3</td>
<td>Baseline: 13.65 kWh/m³ for centrifugation Ultrasonic harvesting: 0.32 kWh/m³</td>
<td>92.0%</td>
<td>N/a</td>
</tr>
<tr>
<td>Ultrasonic harvesting (scale-up)</td>
<td>5 L/h feed</td>
<td>Initial: 1.75 g/L, Final (max): 10.1 g/L, Final (avg): 4.49 g/L, Factor (max): 5.7, Factor (avg): 2.57</td>
<td>Energy reduction: 97.7%</td>
<td>23.3%</td>
<td>N/a</td>
</tr>
<tr>
<td></td>
<td>Of the 23.3 L total processed in this batch run, 6 L were processed at a power setting of 10 W. 5 L/h</td>
<td>Initial: 1.75 g/L, Final (max): 12.6 g/L, Final (avg): 8.7 g/L, Factor (max): 7.2, Factor (avg): 5.0</td>
<td>Baseline: 13.65 kWh/m³ for centrifugation Ultrasonic harvesting: 2 kWh/m³</td>
<td>Energy reduction: 85.3%</td>
<td>N/a</td>
</tr>
<tr>
<td></td>
<td>Of the 23.3 L total processed in this batch run, 6.5 L were processed at a power setting of 21 W. 5 L/h</td>
<td>Initial: 1.75 g/L, Final (max): 10.9 g/L, Final (avg): 7.2 g/L, Factor (max): 6.2, Factor (avg): 4.13</td>
<td>Ultrasonic harvesting: 4.2 kWh/m³</td>
<td>Energy reduction: 69.2%</td>
<td>45.2%</td>
</tr>
<tr>
<td></td>
<td>Of the 23.3 L total processed in this batch run, 10.8 L were processed at a power setting of 30 W.</td>
<td>Energy reduction: 56%</td>
<td>Baseline: 13.65 kWh/m³ for centrifugation Ultrasonic harvesting: 6 kWh/m³</td>
<td>30.3%</td>
<td>N/a</td>
</tr>
</tbody>
</table>

foreseeable future, achieving affordable and sustainable scale-up and long-term high performance will continue to be the most serious challenge to address.

Acknowledgements

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References