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In situ Microalgal Biomass Processing for Biodiesel Production

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Background

Among the simple microorganisms on our planet are microalgae which have adopted broadly to marine and terrestrial environments. Most strains of microalgae utilize CO_2 as the carbon source and undergo photosynthesis under sunlight to grow biomass. Under certain conditions, some microalgae can accumulate high levels of lipids in their cells, ranging from 15% to 70% of their body weight [1]. Such algal lipids can be a good feedstock for biodiesel production. The potential yield of algal lipids per acre is in the range of 1,000–6,500 gal per acre per year [2], which is much higher than that of conventional oilseed crops (e.g., 45–55 gal for soybean and 70–150 gal for canola). Algal lipids contain free fatty acids (FFA) and triglycerides that are similar to those in seed oils, although the actual fatty acid profiles vary widely, depending on the strains, level of maturity of the microalgal biomass at harvest, etc. Since the 1990s, massive efforts have been made in microalgal biology, microalgal strain development, and cultivation technologies to maximize microalgal lipid productivity (e.g., [3]). Conventionally, after cultivation, microalgae are harvested, dewatered/dried before the algal lipids are extracted and converted to biodiesel (Fig.1). Realizing these processes for practical applications can be very cumbersome and challenging. This is the time that process engineering plays an important role.

In situ Processing

To obtain lipids after microalgae are harvested and the cells are ruptured, organic solvent extraction is typically used. The lipid/solvent mixture needs to be separated from the cell debris typically by filtration. The lipid/solvent mixture then undergoes a vaporization process to vaporize the solvent off the mixture, recapture it via condensation, and then purify it via fractionation before reuse. Therefore, high operating and energy costs are obvious. In recent years, a one-step, *in situ* microalgae processing has been studied by many researchers.

The *in situ* microalgae processing involves reacting an alcohol, commonly methanol, with the microalgal lipids in microalgal biomass directly into fatty acid methyl esters (FAME or biodiesel) without extracting the lipids first. There are generally two categories of *in situ* microalgae processing, namely, with or without the application of a catalyst. To conduct the *in situ* microalgae processing, the operating conditions are different from those of conventional oil (or triglycerides) to FAME process. Generally, elevated operating temperatures and application of catalysts are necessary to overcome the barriers of the microalgal biomass structure in order to have a reasonable conversion rate/productivity. The operating temperature is generally in the range of 60-100°C, and base/acid catalysts, such as KOH or sulfuric acid, are commonly used. Base catalysts typically perform better than acid catalysts in terms of conversion rate. (e.g., [4-6]). Application of a homogeneous base or acid catalyst typically requires a post-reaction treatment to remove the residual catalyst from the FAME product. It is obvious that if no catalysts are used, the post-reaction treatment can be simpler.

To avoid using catalyst, a higher operating temperature (and a high pressure) is required. When methanol is used as the reacting alcohol, the temperature ranges from 180-250°C to even higher. Under this high temperature, methanol is at or near its supercritical point, i.e., 240°C & 8.1 MPa (465°F & 1,170 psi). It is also referred to as supercritical methanol (SCM) processing. In addition to supercritical methanol, supercritical ethanol can also be used, and maybe more preferred due to its lower critical pressure at its critical point (241°C & 6.1 MPa) [7].

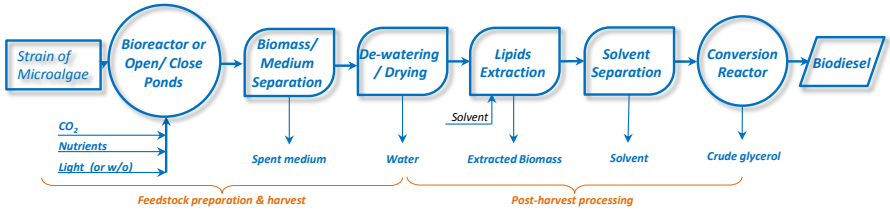

Figure 1 Illustration of conventional microalgal lipids to biodiesel process.

SCM processing of microalgae has many advantages. In SCM processing, lipid extraction and trans-esterification of lipids occur simultaneously. At the supercritical state, methanol behaves as a strong solvent which greatly enhances the lipid extraction. Meanwhile, methanol at high temperatures is

very chemically active and readily reacts with the extracted lipids (or even the lipids *in vivo*) to yield FAME without the presence of a catalyst. In addition, SCM can process wet microalgal biomass directly without drying it beforehand [7, 8]. These make the SCM process even more attractive because drying microalgae before lipid extraction is one of the most burdensome and energy consuming process.

Microalgal lipids are well known for containing high FFA content [1]. In SCM, FFA can be easily converted to FAME while in conventional processing high FFA feedstock needs to be pre-treated or undergone a two-step conversion process. Another commonly encountered dilemma in processing seed oils is the presence of phospholipids, which is cumbersome in traditional processes because it interferes with the transesterification of triglycerides and therefore has to be pre-treated/de-gummed. In SCM, phospholipids can also be converted to FAME without much difficulties [9].

Work at University of Idaho

Research has been conducted at the University of Idaho on *in situ* transesterification since 2012. The goal was to explore a one-step processing technology to process microalgae in sub-/super-critical methanol. The effects of process parameters, including operating temperature, reaction time, and methanol molar ratio on the process efficiency were studied through a factorial experimental design. *Schizochytrium limacinum* (containing approx. 55%wt lipids) was used as the model microalga.

Experimental results showed that satisfactory product yields and selectivities can be attained at either lower operating temperature (210°C; sub-critical methanol) and longer reaction time (120 min), or higher operating temperature (250-290°C; SCM) and short reaction time (30 min or less). The optimal operating conditions are dependent on the optimization targets such as the unit FAME productivity (at short reaction time but high operating temperature), or best product purity in the product mixture (at lower operating temperature and relatively long reaction time). The final decision should be made ultimately by optimizing the system based on the overall capital/operational costs.

For example, 68.7% product yield was reached after 60 min at 210°C with a 35% FAME selectivity. If a higher temperature of 250°C was maintained for 30 min, the FAME selectivity was 46.8% with a product yield of 68.6%. For details on this work, readers are suggested to refer to the publication by the authors [10].

Perspective

Although technologies of microalgae as the feedstock for biofuel production have advanced greatly in the past two decades, issues still remain, such as the nutrient requirements and nutrient cycling for microalgae

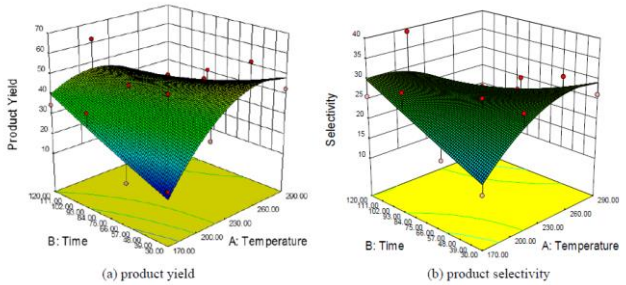

Figure 2 Surface response analysis of the product yield and selectivity of microalgal esters via in situ transesterification with sRatio 1:75.

cultivation [11] and heterogeneous elements (such as nitrogen and sulfur) removal from algal lipids/biofuels [12]. Challenges are still ahead in practically applying the *in situ* transesterification of microalgal lipids as one of the technologies for algal biodiesel production, especially from a process engineering point of view, such as the realization of continuous-flow processing and the purification of product mixture.

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