Processing Algae and Other Biomass to Form Biopolymer By-products

Using Teledyne ISCO Syringe Pumps

Rusty Sutterlin, Ph.D
University of Alabama, Tuscaloosa, AL, 35487 USA

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Syringe Pump Application Note
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Abstract

The present investigation pertains to the processing of biomass with an aqueous mixture with and without the presence of a catalyst to form cleaved biopolymer byproducts. These byproducts can consist of cleaved proteins, lipids, lignin, and polysaccharides to form smaller oligomers or monomers that may or may not be derivatized.

Background

Over the past three decades interest in the reduction of air pollution, and in the development of domestic energy sources, has triggered research in many countries on the development of non-petroleum fuels for internal combustion engines. For compression ignition (diesel) engines, it has been shown that the simple alcohol esters of fatty acids (biodiesel) are acceptable alternative diesel fuels. Biodiesel has a higher oxygen content than petroleum diesel, and therefore reduces emissions of particulate matter, hydrocarbons, and carbon monoxide, while also reducing sulfur emissions due to a low sulfur content. Initial efforts at the production, testing, and use of biodiesel employed refined edible vegetable oils (e.g. soybean oil, canola oil), used cooking oils (e.g. spent fryer oils) and animal fats (e.g. beef tallow) as feedstocks for fuel synthesis.

For spark ignition (gasoline) engines, ethanol, produced by fermentation of simple sugars generated from corn starch, can be blended with petroleum gasoline to substitute petroleum content with renewable content fuel, reduce dependence on foreign oil, reduce carbon dioxide emissions, and improve octane in the blended fuel. Since both ethanol and biodiesel are made from agricultural materials, which are produced via photosynthetic carbon fixation (i.e. by plants and by animals that consume plants), the combustion of biodiesel and ethanol does not contribute to net atmospheric carbon levels.

The production of ethanol for fuel use is well established and the growth in this industry over the past two decades has been significant. Fermentation is an (obviously) old process going back literally thousands of years to early wine and beer making. The basic techniques remain the same, however. In the modern ethanol production process highly efficient enzymes and yeasts have been developed to provide for more efficient conversion of the fermentable materials. Further, the process technology associated with fuel grade ethanol production has also advanced over the years, e.g. energy recovery, so that current technology has a high degree of efficiency.

The feedstocks used for current biodiesel production are conventional commodity materials; thus, they have other established markets which basically set the minimum commodity prices. As a result, the bulk of the biodiesel production cost relates to the feedstock cost. While there are a number of established process technologies in the biodiesel industry, as a result of this high feedstock cost factor (i.e. 75% to 80%), there is a surprisingly small difference between the overall operational costs of the various processes.

The primary feedstocks for current commercial ethanol production are corn (primarily in the United States) and sugar (especially in Brazil). As in the biodiesel case, these materials are “conventional” agricultural commodities and have historically had various markets associated with them, e.g. food sources and the like. It is also apparent that since these are commodity products, there are various non-fuel market pressures that dictate price. As such, for ethanol production, as in the case of biodiesel, the feedstock represents the vast majority of the operating cost (i.e. as much as 80%).

For both the biodiesel and ethanol fuel markets and for the large-scale expansion of the renewable fuels industries, it is apparent that development of a potentially large scale, lower cost feedstock source would be advantageous. Recently, significant advances have been made in carbon dioxide sequestering technology using various species of algae to provide photosynthetic carbon fixation. This technology has tremendous value when applied to industrial sources of carbon dioxide, such as: coal fired power generation, natural gas fired power generation, petroleum fired power generation, industrial gas generation, cement manufacturing, industrial fermentation, and various additional industries that are significant emitters of carbon dioxide. The algae resulting from the photosynthetic carbon fixation represents an opportunity for the production of transportation fuels as well as various value added chemical products. In a designed pond or “farming” system, the volume of algae produced per acre is estimated at between 100,000 pounds to 600,000 pounds per year on a dry basis, and is substantially greater in terms of oil and fermentable material content than the volume of soybeans or corn produced per acre at 2,500 pounds to 10,000 lbs per year. The volume of algae produced allows for a far greater production density versus corn or soybeans, with a relatively small geographic footprint. In addition, the algae selected comprise free fatty acids (FFA), triglycerides, polysaccharides, cellulose,

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hemicellulose and/or lignocellulose. However, the economical processing of the selected algae provides significant challenges for conventional biofuel processing techniques.

Crop	Oil Yield (L/ha)
Corn	172
Soybean	446
Canola	1,190
Jatropha	1,892
Coconut	2,689
Palm	5,950
Algae	136,900

A significant degree of pretreatment of the algae sludge is required to prepare the material for the more traditional solvent extraction methods to recover the contained oil. This front-end pretreatment would need to be combined with multi-stage esterification (for free fatty acid esterification) and transesterification (for triglyceride conversion), and a completely separate process would be required for acid hydrolysis of the lipid depleted algae pulp to produce monosaccharides, disaccharides, trisaccharides or polysaccharides for production of ethanol by fermentation. This series of processing steps would add significant cost to the resulting materials to be produced from algae. Therefore, there is a need for further development of simplified processing routes for the production of fatty acid alkyl esters (i.e. FAME), amino acids, peptides, monosaccharides, disaccharides, trisaccharides or polysaccharides in a simplified, direct process.

In addition to algae, the current growth in biofuel production from food commodities is generating a substantial increase in co-products such as corn distillers grains, sorghum distillers grains, and rice bran meal. These co-products have underutilized value from the cellulosic content (45-55% by mass) and oil content (7-22% by mass), which represent an opportunity to increase the supply of biofuels to market by simply increasing the processing efficiency of current methods.

Again, the interest in cellulosic feeds such as algae for ethanol has increased considerably over the past several years; however, some of the same issues apply to other sources. For example, distillers grains have cellulosic content as well as contained oil values, both of which could be useful for conversion to biofuels. With cellulosic feeds typical approaches include enzyme treatment followed by yeasts, which convert the cellulosic materials to sugars and subsequent alcohol but have little effect on any contained oil content. Thus, there remains a significant need in the art to develop a simple and efficient method for the production of biofuels and ethanol from renewable energy sources.

Summary of the Investigation

Prior to the present investigation, the conversion of biomass into biofuel and ethanol was a time-consuming and multi-step procedure that was both economically inefficient and wasteful. Additionally, conventional methods are inhibited by the presence of water. By way of this investigation, there is now a fast, single-step, and efficient method for the conversion of biomass into biofuel and sugars to produce ethanol that can be performed in the presence of water. This method includes a feedstock that is hydrolyzed or derivatized in a reactor in the presence of an optional acid catalyst, and optionally in the presence of water in a pressurized reactor to yield the desired products.

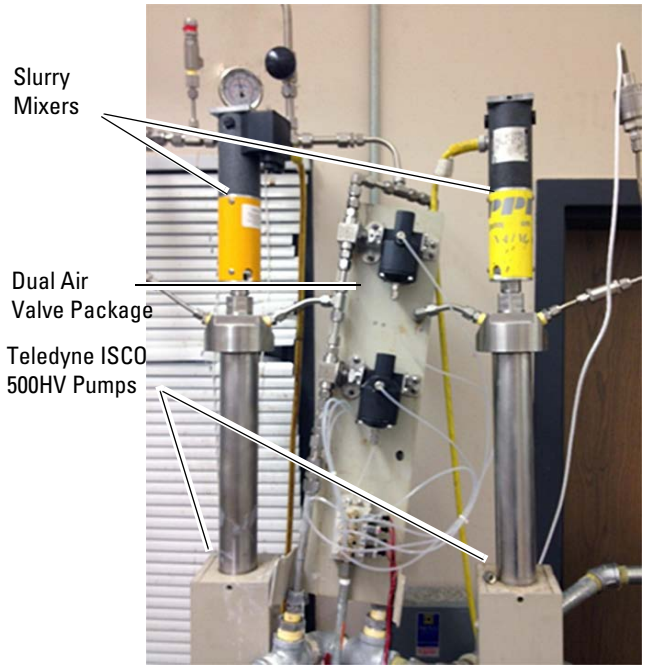
The feedstock for this process can be, for example, algae (e.g., fresh or salt water algae, prokaryotic algae), or other oil-containing material that may also contain potentially fermentable cellulosic material (e.g., polysaccharides, cellulose, hemicellulose, and lignocellulose), protein, or both. The oils of the feed stock can include phospholipids, FFAs, monoglycerides, diglycerides, triglycerides, or a combination thereof. The feedstock can also be a combination of different oil-containing materials. The feedstock can be unextracted, meaning it has not been purified to remove certain components (e.g., water, cellulosic material, proteins, or mixtures thereof). For example, the feedstock can contain phospholipids, FFAs, glycerides, cellulosic material, and proteins. The feedstock can also be purified (e.g., a soapstock or crude vegetable oil). The feedstock can contain husks, shells, or other non-feedstock materials grown by the feedstock source. Materials containing both oil and cellulosic components lead to attractive renewable fuel alternatives. Prior to reaction, the feedstock can be dried or wet.

The dried algae or other feedstock is ground to reduce its particle size and is then transferred to the loading vessel, wherein the feedstock is mixed with the selected reagents to form a biomass slurry. The amount of liquid-to-biomass ratio can vary, but would typically be sufficient to allow for a slurry mixture. In order to keep the biomass suspended and agitated, the biomass slurry is pumped in a loop from the loading vessel to the high pressure pumps, where the slurry is extracted as needed, and then back to the loading vessel. One of the major challenges of conducting these experiments on a laboratory scale in a continuous reactor is the ability to pump the solid biomass in the form of a liquid slurry into the reactor in a continuous manner without pulsing. This is not a large obstacle with scaled up processes, since commercially available pumps used in the petroleum and waste treatment industry are readily available. However, in the laboratory we must run at much lower flow rates in order to study the kinetics and avoid the other constraints that such a large pump would impose on a small reactor and laboratory setting.

Our required conditions were a pump that could:

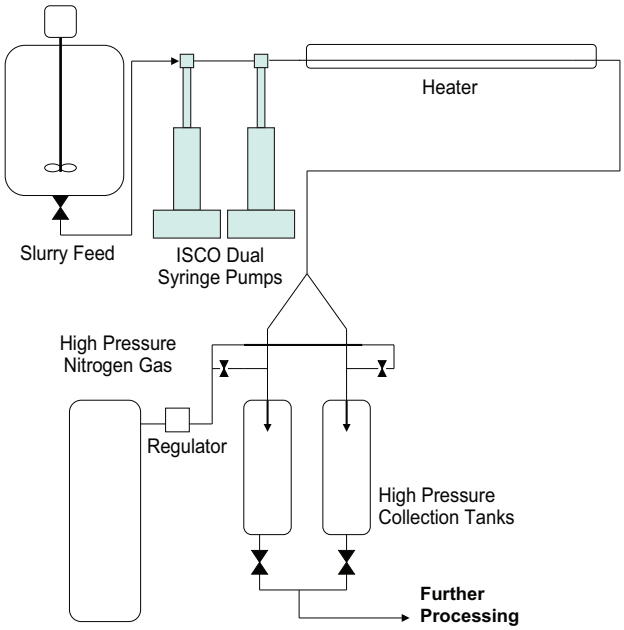
- Inject material into a pressurized system
- Be continuous without pulsing
- Have relatively low flow rates of less than 150 mL per minute
- Have tunable flow rates
- Be capable of keeping the biomass slurry in suspension without settling

To achieve these desired pump conditions, two Teledyne ISCO Syringe Pumps (Model 500HV—High Viscosity [see note]), their corresponding overhead mixers, and 3/8" Continuous Flow Air Valve Package were used.



After the biomass slurry passes through the pumps, it enters the reactor zone. The continuous pipe reactor is designed to allow sufficient residence time for the reaction to complete and is operated under a target pressure and temperature range. The pipe allows for reasonable reaction to occur with minimal vessel complexity. The reaction can be carried out for a period of between 1 and 120 minutes, depending on the selected reaction system and operating temperature.

The reaction product slurry typically consists of the algae or biomass pulp (containing cleaved cellulosic material, shortened peptides, and amino acids), crude free fatty acids and fatty acid derivatives, excess alcohol, catalyst, water and glycerin. The resulting fatty acid and fatty acid ester mixture will be in the range of 10-50wt% of the product slurry. The resulting peptides/amino acids will be in the range of 0-50wt% of the product slurry. The resulting cleaved cellulosic materials will be in the range of 0-50wt% of the product slurry. The reaction slurry is transferred to a Liquid/Solid Separation system. In this step, the liquid fraction is separated from the solids portion, and each biomass fraction is further separated and purified.



Conclusion

Algae and other biomass feedstocks are normally difficult to unbind and separate into their free biomass constituents, such as fractions consisting of protein, polysaccharides, and fats. We have shown that alternative biomass feedstocks can be reacted under well-designed conditions to facilitate the conversion of these feedstocks into their desired products of free carbohydrates, free amino acids, free fats, and shorter chain oligomers and derivatives of the aforementioned biomass constituents. One of the keys in accomplishing this task on a laboratory scale is the need of a versatile pump in order to facilitate the biomass slurry into the reactor under the desired pressures and flow rates.

Note:

The 500HV model pump, which was used during the original experiment, is discontinued. Current model A500xv is the recommended replacement for the older 500HV model.

Teledyne ISCO
P.O. Box 82531, Lincoln, Nebraska, 68501 USA
Toll-free: (800) 228-4373 • Phone: (402) 464-0231 • Fax: (402) 465-3091
E-mail: IscoInfo@teledyne.com

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Product model names have been updated in this document to reflect current pump offerings.

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