Optimal Design of an Algae Oil Transesterification Process

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Abstract
An optimization strategy for designing processes to convert algae oils to biodiesel is introduced. In this brief paper, just a typical oil sample is used, grown experimentally using Nannochloropsis salina algae in salt water by Solix and transesterified using the Catilin solid T-300 acid catalyst. NIST thermophysical property data in ASPEN PLUS and literature data were used to estimate the properties of the chemical species. Approximate group contribution methods were used to estimate missing properties.

A transesterification process was synthesized and simulated using ASPEN PLUS. For the transesterification reactor design, three reversible reactions were assumed. Because kinetic data were unavailable, pre-exponential factors and activation energies for the transesterification of palm oil were used, adjusted using residence-time data from Catilin for transesterification of an algal oil1. A USER2 FORTRAN subroutine was written to solve the CSTR mass balances.

The process was heat integrated to reduce energy consumption. Next, the Aspen Process Economic Evaluator was used to estimate equipment sizes and purchase and installation costs. In this brief paper, just the results for a single case study are presented. In a full manuscript, the optimization strategy for selecting the best algal oil is presented.

Keywords: Biodiesel, Nannochloropsis salina, Transesterification

1. Introduction

1.1 Background
Because of their compatibility with conventional combustion engines, biofuels are being considered as replacements for petroleum-based, liquid transportation fuels. Originally, beef tallow, plant-derived oils, and waste oils, were transesterified to biodiesel; however, in recent years, various strains of algae have been explored as sources of oil because algae grow in much higher density, using land and water that are unfit for terrestrial plant cultivation.

Because salt water is significantly cheaper and more plentiful than fresh water, the Nannochloropsis salina strain of algae, which is cultivated in salt water, is an excellent candidate for the production of biodiesel. This strain yields oil levels in excess of 50% (on a dry basis3), using mixotrophic conditions1.

After the algae are grown, they can either be transesterified directly under supercritical conditions, or the oil can be extracted from the cells and converted at milder conditions using an acidic or basic catalyst; we have chosen the latter approach for this initial study. During the extraction, the triglycerides are separated from an algae-sludge using a standard hexane extraction procedure, yielding relatively pure triglycerides and a byproduct of residual algae biomass.
1.2 Transesterification Kinetics

One kinetic model for converting triglycerides to biodiesel is the three-reaction mechanism in Figure 1. In each reaction step, a fatty-acid group, attached to the glycerol backbone, is reacted with methanol to form a fatty-acid, methyl ester (FAME). First, the triglycerides are converted to diglycerides, which become monoglycerides, finally yielding glycerin.

![Transesterification Kinetics](image)

Figure 1. Transesterification Kinetics

This kinetic model is based upon the bench-scale Catilin process, which uses their proprietary T-300 solid-metal, acid catalyst for the conversion of triglyceride to FAME. We are using kinetic data for palm oil (with modified activation energies to match Catilin-reported conversions for the transesterification of algae oil) to size the reactors.

1.3 Species Data

The thermophysical property data for triglycerides and their derivatives within ASPEN PLUS were extremely limited. ASPEN’s databanks were supplemented with information from the NIST databank, which is interfaced with ASPEN PLUS for easy data-sharing; however, many important properties remained absent for key chemical species. Therefore, an extensive literature search was performed to obtain the missing properties.

Three sources were used for the Antoine equation parameters for the triglyceride and FAME molecules; these data were nonexistent for the monoglycerides and diglycerides. Unsaturated bonds were assumed not to affect the Antoine constants or boiling points. When Antoine constants could not be found or regressed, boiling-point data were used. When there was a disparity between two sources, the more recent source was used.

A similar search was conducted for density data, returning five sources. Because ASPEN PLUS only accepts the density data at 60°C, whenever possible, the density was adjusted using linear interpolation. If an adjustment was not possible, and the data were at temperatures within 20°C of 60°C, the density was assumed constant over this range.

When pure component data were unavailable, they were estimated by ASPEN PLUS using the JOBACK group-contribution method. Liquid-Liquid interaction parameters were calculated using the UNIFAC-LL group-contribution method, and
vapor-liquid interaction parameters were calculated using the traditional UNIFAC group-contribution method.

2. Process Analysis

2.1. Process Description

A process flowsheet based upon the Catilin bench-scale process is shown in Figure 2. Eventually, alternative syntheses will be considered. Algal-extracted triglycerides are mixed with excess methanol (7 mol methanol/mol triglycerides – containing catalyst pellets), heated, and sent to a CSTR, where they are converted to the FAME product and glycerol byproduct. The effluent is filtered to remove the catalyst (which is recycled to the reactor) before being sent to a decanter. The decanter separates the FAME (light phase) and glycerol (heavy phase) by gravity; methanol distributes itself between the two phases.

The light phase is sent to a second CSTR for further conversion. Its effluent is subjected to the same separation techniques, and is then sent to a distillation column, where the FAME (biodiesel) is recovered from methanol. The glycerol effluents from the decanters are combined and sent to a distillation column, where nearly-pure glycerol is recovered from methanol. The methanol effluents are recycled.

The major material inputs and outputs from the process are shown in Table 1. Due to space limitations, stream data (temperatures, compositions, heat capacities, etc.) computed by ASPEN PLUS must be obtained from the authors. Note that 39,993 kg/hr is 0.003% of the biodiesel consumed daily in the United States in 2010.

![Figure 2. Modified Catilin Transesterification Process](image)

<table>
<thead>
<tr>
<th>Stream</th>
<th>Triglyceride Inlet</th>
<th>Methanol Inlet</th>
<th>FAME Outlet</th>
<th>Glycerol Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate (kg/hr)</td>
<td>39,735</td>
<td>4,623</td>
<td>39,993</td>
<td>4,364</td>
</tr>
</tbody>
</table>
2.2. Heat Integration

The heat capacities were averaged between the source and target temperatures for each stream, and then assumed constant. A pinch-analysis spreadsheet, produced by ICHME, was used to determine the minimum utility targets. Stream matching was done using methods described in the literature\textsuperscript{13}. Although the glycerol and FAME product streams were a source of heat for the “cold” streams, they were not cooled to room temperature (77°F); therefore, cooling water was not used to cool them.

The resulting system has 14 heat exchangers, including the condensers and reboilers for the two distillation columns: yielding hot and cold utility requirements of 2,450 KW and 1,820 KW, respectively.

2.3. Process Economics

Using Aspen’s Economic Process Evaluator (AEPE), cost estimates for the transesterification process were computed. The total depreciable capital was estimated to be approximately 9 million USD. The key results are in Tables 1 and 2. The auxiliary costs include the costs of concrete and setting, structural steel, instrumentation, piping, insulation, electrical wiring, and paint.

Table 2. Costing Results for Process Equipment.

<table>
<thead>
<tr>
<th>Equipment</th>
<th># of items</th>
<th>Purchase Cost</th>
<th>Auxiliary Cost</th>
<th>Installation</th>
<th>Total Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centrifugal Pumps</td>
<td>5</td>
<td>$22,700</td>
<td>$93,400</td>
<td>$67,200</td>
<td>$183,300</td>
</tr>
<tr>
<td>Decanters</td>
<td>2</td>
<td>$46,300</td>
<td>$213,500</td>
<td>$63,900</td>
<td>$323,700</td>
</tr>
<tr>
<td>Distillation Towers</td>
<td>2</td>
<td>$95,200</td>
<td>$286,000</td>
<td>$112,200</td>
<td>$493,400</td>
</tr>
<tr>
<td>Heat Exchangers</td>
<td>14</td>
<td>$192,700</td>
<td>$670,100</td>
<td>$327,500</td>
<td>$1,190,300</td>
</tr>
<tr>
<td>Pressure Vessels</td>
<td>2</td>
<td>$46,300</td>
<td>$213,500</td>
<td>$63,900</td>
<td>$323,700</td>
</tr>
<tr>
<td>Reactors</td>
<td>2</td>
<td>$178,200</td>
<td>$509,900</td>
<td>$103,500</td>
<td>$791,600</td>
</tr>
<tr>
<td><strong>Total Cost of Equipment</strong></td>
<td></td>
<td><strong>581,400</strong></td>
<td><strong>1,986,400</strong></td>
<td><strong>738,200</strong></td>
<td><strong>3,306,000</strong></td>
</tr>
</tbody>
</table>

Table 3. Costing Results for Yearly Recurring Costs.

<table>
<thead>
<tr>
<th>Utilities per year</th>
<th>Labor Costs per Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling Water</td>
<td>Operating Labor</td>
</tr>
<tr>
<td>Electricity</td>
<td>Maintenance</td>
</tr>
<tr>
<td>Heating Oil</td>
<td>Supervision</td>
</tr>
<tr>
<td><strong>Total Utilities</strong></td>
<td><strong>Total Cost of Labor</strong></td>
</tr>
<tr>
<td>$760,200</td>
<td>$621,300</td>
</tr>
</tbody>
</table>

Shell-and-tube heat exchangers, with surface areas estimated using overall heat-transfer coefficients of 730.87 kcal/hr-m²-K (default in ASPEN PLUS), were used. The CSTR’s were 95 m³ (using a 1-hr residence time provided by Catilin). No costs for the T-300 catalyst were available. Also, the filter costs were neglected.

Cooling water (at 90°F, heated to 120°F) and heating oil were provided by a nearby utilities plant. Costs were $0.075/1000gal and $1.50/gal, respectively. A heating value of 146,100 kJ/gal was used to determine the amount of oil needed\textsuperscript{14}.

The hourly labor costs for operators and supervisors were estimated at $20/hr and $35/hr, respectively, with 330 operating days per year.

In terms of product and raw material costs, the diesel price ($1.90/gal) was set at the wholesale price in 2009\textsuperscript{15}, and the price of methanol ($1.16/gal) was extrapolated from a graph provided for 2008 and 2009\textsuperscript{16}. The glycerol by-product is assumed to yield no profit; it is recycled to the cultivation process as feed for the mixotrophic algae. At
an investor’s rate of return (IRR) of 20%, a triglyceride purchase price of $1.78/gal was estimated, very close to the diesel wholesale price, $1.90/gal. Clearly, to obtain diesel, this transesterification process adds a small increment to the cost of triglyceride oil.

3. Conclusion

In this brief paper, a strategy for designing transesterification processes is presented. In a full manuscript, the strategy is applied to select the best algal oil for production of biodiesel. The design optimization is based upon data for the transesterification of various algae strains using the Catilin T-300 acid catalyst. A combination of the ASPEN PLUS database, the NIST database, and an extensive literature search was used to obtain data to rigorously estimate thermophysical and transport data of the triglycerides and fatty-acid methyl esters (FAMEs). Herein, results for just a typical process are illustrated, prior to optimization. This process was heat integrated to reduce its utilities cost. Lastly, a profitability analysis shows that this transesterification process, using the T-300 catalyst, doesn't add significant capital or utilities costs.

References

4. W. Yuan, A.C. Hansen, Q. Zhang, 2005, Vapor pressure and normal boiling point predictions for pure methyl esters and biodiesel fuels, Fuel, 84, 943-950