PLANT DESIGN PROJECT: Biodiesel Production Using Acid-Catalyzed Transesterification of Yellow Grease

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10 years, the chemical industry, federal and state agencies, and the chemistry and chemical engineering profession have been increasingly invariant and family and family and family and family and family and family and fam and state agencies, and the chemistry and chemical engineering profession have been increasingly investing intellectual, technical, and financial resources on the research, development, and application of chemicals and fuels generated from renewable raw materials and sustainable processes. The main goal of the involved parties is to develop energy-efficient and cost-effective processes that prevent pollution and decrease our dependency on foreign oil. The number of papers describing sustainable processes and renewable fuels that have appeared in the publications and conferences of the American Chemical Society (ACS) and American Institute of Chemical Engineers (AIChE) have increased significantly over the last five years. The 2005 57th AIChE Institute Lecture was titled "Energy Supply Challenges and Opportunities." The ACS dedicated one issue of *Environmental Science and Technology,* **the society's main publication on environmental research, to sustainable** processes.^[1] Presently, that journal includes a section on sus**tainable technologies in every issue. Additionally, numerous papers were presented at the 2005 Annual AIChE Meeting (Cincinnati) on biorefineries, sustainable technologies, and renewable fuels.**

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The main contributing factor to the chemical engineering and chemistry professions' focus on efforts to promote the development of sustainable technologies and the production of renewable alternative fuels such as ethanol, biodiesel, and hydrogen has been the commitment of resources by the U.S. Environmental Protection Agency (USEPA), the U.S. Department of Agriculture (USDA), the National Science Foundation (NSF), and the U.S. Department of Energy (USDOE). One way to develop creative new production processes for renewable chemicals is to educate future chemists and chemical engineers on the design, advantages, disadvantages, and economics of current production techniques.

The last core course in the chemical engineering curriculum at most universities in the United States is capstone design. In this course, students have the opportunity to practice, for the last time in an academic environment, the design and economic evaluation of industrial chemical plants. To our knowledge, most chemical engineering capstone design projects focus on the use of petroleum-based raw materials for producing specialty and commodity chemicals. To broaden the students' perspective on the potential contributions of chemical engineering to areas such as new energy sources, global warming, and environmental sustainability, they should be introduced to the conversion of plants, natural oils, microorganisms, and other types of biomass into alternative energy sources and value-added products. The capstone course represents an excellent opportunity to assign projects in which students synthesize and analyze renewable-chemicals production facilities. The objective of this paper is to describe a project entitled "Design of a Biodiesel Production Facility Using Acid-Catalyzed Transesterification of Yellow Grease," assigned to the capstone design course at Mississippi State University (MSU). Research on biodiesel is conducted by the class instructor's research group. Thus, the design problem

Biodiesel is an alternative renewable fuel derived from vegetable oils or animal fats, which conforms to ASTM D6751 specifications for use in diesel engines.[2J Biodiesel utilization has increased significantly over the last 10 years, mainly due to environmental benefits and government efforts to reduce dependence on foreign oil. The use of biodiesel reduces emissions of CO₂, CO, SO₂, and particulates from operating diesel engines. Under a newly established sustainable energy policy by the U.S. Department of the Interior, over 20 national parks operate boats, trucks, heating systems, electricity generators, and other fuel related systems on 100 percent biodiesel and/or biodiesel/petroleum diesel blends. Blends of 20 percent biodiesel with petroleum diesel require no engine modifications. Furthermore, biodiesel/petroleum diesel blends have demonstrated lubricity enhancements over the newly required low sulfur petroleum diesel. Numerous school districts, transit authorities, public utility companies, and recycling companies have also successfully used biodiesel. Recently, the U.S. military has begun to procure biodiesel for use in on-base vehicles. These numerous experiences with the use of biodiesel have clearly shown the environmental and high performance characteristics of this alternative fuel.

In spite of the fact that Mississippi ranks 4th and 16th nationally in yellow grease generation and soybean production (main biodiesel feedstocks), there are no biodiesel production facilities in the state. The Swalm Engineering Design Group at MSU was asked by the Alternative Energy Company to perform a preliminary design of a 2,240 lb/hr biodiesel production facility using acid-catalyzed transesterification of yellow grease, and to evaluate the process economics. In order to perform sensitivity analysis of process variables, the company requires a simulation of the whole process using ChemCad. The company has acquired land adjacent to a fertilizer manufacturing company in Yazoo City, Miss., at the cost of \$1,000,000 as the plant site. The design is to be based on a project life of 20 years. The major equipment, however, is to be depreciated in accordance with applicable IRS regulations. In your final design report, you are requested to provide estimations of the annual return on investment as well as the rate of discounted cash flow taking into account the most recent laws and regulations on corporate taxes. Design basis and specifications, available utilities, and other information will be provided in further communications.

Some of the comments in the students' course evaluations were ... , "What I like most about this course was the fact that the project was broken into separate portions over the whole semester," and "I loved the layout of the class "

also represented an excellent opportunity to integrate research and education. As part of the course, invited speakers and the course instructor presented seminars on ethics, job interview preparation, entrepreneurship, and the social and environmental implications of reducing our dependency on petroleum. A workshop on ChemCad (chemical process simulation software) was offered to students and faculty by the software creators.

PROJECT DESCRIPTION

The statement of the problem submitted to the students on the first day of class is presented in Figure 1. The class was divided into five groups and each group had four members selected by the instructor. The same project was assigned to all groups. The open-ended nature of the problem statement led to five different design configurations.

The design project was divided into three progress reports (memorandums) and one final report. Several activities and rules were established to maximize participation of all students:

(A) Progress reports and the final report were accompanied by an oral defense. The student in charge of presenting the oral defense was selected at the time of the presentation. Each member of a design group was questioned extensively during each progress report presentation.

(B) Written peer evaluations were required after each progress and final report. The evaluation forms were similar to those suggested by Fogler.^[3]

C) A panel of industry and academic members judged and selected the best final presentation. The presence of industry representatives was additional encouragement for all the students to prepare for the presentation. The instructor selected the best report. The group or groups with the best presentation and final report received plaques and cash awards.

PROGRESS REPORTS

Division of the design project into progress reports had two objectives. The first objective was to evaluate an inductive approach to the teaching of plant design. This approach consists of the presentation of a general problem or concept, followed by closer focus on details and the solution of component small problems. This method is applied by the chemical industry and during academic and industrial research and development activities and it is an approach suggested by chemical engineering educators. [4, 5l

The second objective was to facilitate the organization of the project and enhance students' time-management skills. Some of the comments in the students' course evaluations were related to the second objective. For example, "What I like most about this course was the fact that the project was broken into separate portions over the whole semester," and "I loved the layout of the class-progress reports and the final presentation." The tasks conducted for each progress report were as follows:

Progress Report 1: *Literature survey, calculation of gross profits, block diagram preparation, overall mass balance calculations, and input of yellow grease components into the ChemCad database.*

Progress Report 2: *Preparation of process-flow diagram and simulation of the transesterification reactor and methanol recovery system.*

Progress Report 3: *Simulation of all the biodiesel purification steps: neutralization, solids removal, glycerol recovery, and biodiesel and glycerol purification.*

PROJECT SOLUTION

Yellow grease is the fat generated during animal rendering activities. It is mainly composed of oleic, palmitic, and stearic fatty acids attached to glycerol,^[6] and contains a relatively high percentage of free fatty acids (15%). Zhang (2000) used triolein (triacylglycerol) as a test compound to represent yellow grease during a Hysys simulation of a biodiesel production facility.[7l The acid-catalyzed transesterification of this compound using methanol as the alcohol results in methyl oleate and glycerol. Zhang (2000) assumed that biodiesel could be represented by methyl oleate.^[7] To generate a mixture of transesterification products with similar biodiesel chemical and physical properties, the students were encouraged to use several triacylglycerols and oleic acid (free fatty acid) as representative of yellow grease for the ChemCad simulation of the biodiesel production facility. Figure 2 presents the reactions of acid-catalyzed transesterification of the selected triacylglycerols and oleic acid. The acid-

$C_{57}H_{104}O_6 + 3CH_3OH \xrightarrow{H_2SO_4} 3C_{19}H_{36}O_2 + C_3H_8O_3$		
Triolein	Methyl Oleate Glycerol	
$C_{51}H_{98}O_6 + 3CH_3OH \xrightarrow{H_2SO_4} 3C_{17}H_34O_2 + C_3H_8O_3$		
Tripalmitin	Methyl Palmitate Glycerol	
$C_{57}H_{34}O_2 + 3CH_3OH \xrightarrow{H_2SO_4} 3C_{19}H_{38}O_2 + C_3H_8O_3$		
Tristearin	Methyl Stearate Glycerol	
$C_{18}H_{34}O_2 + CH_3OH \xrightarrow{H_2SO_4} C_{19}H_{36}O_2 + H_2O$		
Oleic acid	MethylOleate	

Figure **2.** *Acid-catalyzed transesteriftcation reaction for producing fatty acid methyl esters (FAME).*

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catalyzed transesterification of the proposed components of yellow grease results in a mixture of methyl esters of oleic, palmitic, and stearic fatty acids. This mixture contains more than 90% of the methyl esters found in commercial biodiesel from yellow grease. Phase behavior of triglyceride- and alcohol-rich phases was ignored for simplicity. Students recognized that they were making this simplification.

The complete process flow diagram (PFD) and stream table are presented in Figure 3 (a and b) as well as in Table 1. Both were prepared using the ChemCad process

simulation software licensed by Chemstation in Houston. Some of the physical and chemical properties of the yellow grease-assumed components were determined using the UNI-FAC Group Contribution method in ChemCad. Other basic properties, such as boiling point and melting point, were input manually into the simulator.

The first main unit operation of the PFD is the transesterification reaction system (R200). To determine reactor volumes, it was assumed that the reactors were half full and the reactions followed first-order kinetics. Reactor volume meeting

the conversion requirement (97% the initial triglycerides) was minimized by including two equal-size reactors in series. The first and second reactors achieve an overall 83% and 97% conversion, respectively. The volume of each reactor was 200 ft^3 and the material of construction selected was 316 stainless steel. The reactions were performed at 80 °C and 400 kPa. The reactor influents were 3.35 lbmol/hr, 3.93 lbmol/hr, 170.42 lbmol/hr yellow grease, sulfuric acid, and methanol. The reactors were simulated in Chem Cad using the equilibrium reactor. This reactor gives the user the capability to simulate multiple reactions.

return excess, umeacted methanol to the reactor to save raw material costs. The major challenge in simulating the methanol recovery tower is to return as much methanol as possible to the reactor, thus minimizing water in the recycle stream. Conversion of triglycerides into biodiesel drops dramatically if the reactants contain between 0.5% and 5% water. The simulation was conducted using the ChemCad tower module. The column was operated using atmospheric pressure for the overhead stream and a bottom pump-out pressure of 110 kPa. The smallest number of theoretical stages that could be obtained while keeping the water-weight percent of the reactor feed below 0.10% was 13 with a feed stage of seven. This resulted in a water concentration 0.064% by weight in *Chemical Engineering Education*

The purpose of the methanol recovery system (T210) is to *220*

the feed to the reactor. The distillation column recycles 99 .9% by weight of the methanol in the reactor effluent.

The remaining portion of the process after the methanol recovery system consists of separation and purification steps to obtain purified biodiesel, glycerol, and yellow grease recycle streams. The effluent of the surge tank (V-220) is pumped into the bottom stage of the liquid-liquid extractor (T-300). Water cascades down the column after being fed into the top stage. The wash water extracts the entrained glycerol while the biodiesel and umeacted yellow grease exit the top of the column. The ChemCad simulation of T-300 resulted in four theoretical stages for complete separation of biodiesel from glycerol. The students conducted a sensitivity analysis using ChemCad to determine the effect of reboiler operating temperature of the biodiesel distillation column and wash-water flow into the liquid-liquid extractor on cost and biodiesel purity, respectively. Figure 4 shows the effect of wash-water flow on biodiesel purity. It can be observed that water flows in excess of 500 lb/hr have a negligible effect on biodiesel purity. This type of analysis is essential to determine optimum plant operating conditions to meet biodiesel quality.

The crude glycerol stream from the bottom of the extractor flows to the reactor (R-500) for the neutralization of the sulfuric acid catalyst by the following reaction:

$$
H_2SO_4 + CaO \rightarrow CaSO_4 \text{ (gypsum)} + H_2O
$$

Calcium oxide (CaO) was the base choice due to low cost,

limited complications in regard to materials of construction, and low solubility of its salts formed by neutralization. A CSTR was selected to perform the transesterification reaction. The reactor was simulated in Chem Cad using the stoichiometric reactor module and assuming 100% conversion of sulfuric acid. The reactor was maintained at 80 °C. Effective mixing of solids is easily maintained by physical agitation in a CSTR. Additionally, the CSTR should prevent any excess collection of calcium sulfate in the neutralization reactor. A centrifuge (CN-510) was used to separate the gypsum from the glycerol and water. A solids effluent moisture fraction of 10% was defined for the centrifuge. It was assumed that the gypsum recovered was sold to a cement company at \$56/ton.¹

The liquid stream from the centrifuge flowed into the glycerol purification tower (T-600) to achieve a bottoms product of 99.5% by weight purity glycerol. Four theoretical stages were required to achieve the desired purity. To use high-pressure steam, the column must be operated at a reduced pressure so that the reboiler temperature is 250 °C. The final reflux ratio of 1.8 results in a reasonable reboiler duty while maintaining the desired purity of 99.5%.

The biodiesel purification column (T-400) must produce 99.6% by weight biodiesel by separating the methyl esters from the umeacted yellow grease. This column presented several challenges in simulating its operation due to the lack of experimental vapor-liquid equilibrium data for biodiesel

Figure 4. Effect of wash-water flow into the liquid-liquid extractor on the biodiesel purity exiting the distillation tower.

1 Communication with cement company.

and yellow grease. Operation of the column at atmospheric pressure required extremely high reboiler temperatures of up to 600 °C to achieve a sufficient biodiesel purity. Therefore, the column was simulated under severe vacuum with top and bottom operating pressures of 8 kPa and 20 kPa, respectively. The necessity of low vacuum for the separation of triglycerides from biodiesel also has been observed by other investigators.^[6, 7] Under these conditions, the bottom product temperature was 330 °C. The vacuum necessary for this separation can be achieved using multistage steam injectors.^[8] Dowtherm G at 357 °C was selected as the heating medium for the reboiler.

Students prepared the final report following the format suggested by Peters, et al.^[9] Capital and operating costs were determined using the Cap Cost software included in the textbook by Turton, et al.,^[10] Web sites, and communications with vendors. Several scenarios were evaluated to determine plant economics. For example, students evaluated return on investment (ROI), taking into consideration the biodiesel tax incentive (\$1.00/gal) included in the current version of the Energy Bill. ROI also was determined after increasing the operating capacity of the plant. These scenarios helped students understand the economics of scale and the current situation of the biodiesel industry in the United States, which requires government incentives to be economically feasible.^[11]

The results of the estimation of capital and total product costs are presented in Tables 2 and 3. The information in these tables was essential to determine net present value and the ROI. The prices used for raw materials costs were: yellow grease, \$0.1175/lb; methanol, \$0.6/gal; sulfuric acid, \$67/ton;

and calcium sulfate, \$56/ton. Except for the price of calcium sulfate, all the other prices were obtained from the September 2003 issue of the *Chemical Market Reporter*.^[12] The students assumed that the solid recovered during the neutralization step (calcium sulfate) was sold to a local cement company. They contacted a local cement company to obtain a calcium sulfate purchasing price. Utilities costs were the following: low-pressure steam, \$2.50/1000 lb; high-pressure steam, \$5.50/1000 lb; natural gas, \$2.70/1000 SCF; electricity, \$0.04/kWh; cooling water, \$0.05/1000 gal; wastewater treatment, \$56/1000 m³; and process water, $$0.5/1000$ gal.^[10-13]

Total income was calculated by adding biodiesel, glycerol, and calcium sulfate sales. The prices used for biodiesel, glycerol, and calcium sulfate were \$2.40/gal (the price of petroleum diesel at the time was \$1.40/gal and the \$1.00/gal tax incentive was added), $\$0.72/\mathrm{lb}$, $^{[12]}$ and $\$15/\mathrm{ton}$, $^{[14]}$ respectively. The mass and volume rates are presented in Table 1. The total annual income was \$7,083,700. Subtracting the total product costs shown in Table 3 results in annual gross earnings of \$888,100. Assuming a35% tax, the after-tax profit (ATP) was \$577,200.

The after-tax cash flow (ATCF) is the sum of the ATP and depreciation. ATCF is calculated for every year of plant operation. The depreciation was calculated using straight-line depreciation with 9.5 years recovery period. Thus, depreciation and ATCF were given by:

$$
d = \frac{\text{original investment}}{9.5 \text{ years}}
$$

\n
$$
d = \frac{\$2,291,642}{9.5 \text{ years}} = \frac{\$241,226}{\text{ year}}
$$

\n
$$
ATCF = ATP + d
$$

\n
$$
ATCF = \$577,277 + 241,226 = \$818,503
$$

Only half of the depreciation was added in year 10 of operation and no depreciation was added in the final years of operation.^[10] ROI is a profitability measure defined as the ratio of profit to investment. Average profit over the 20 years of plant operation and fixed capital investment were used to calculate ROI for the biodiesel production facility. This value resulted in:

$$
ROI = \frac{\sum_{1}^{20} ATP}{20} \times 100
$$

$$
ROI = \frac{$577,277}{$2,864,552} \times 100 = 20\%
$$

This value of ROI is considered acceptable for a new product entering into an established market.^[9] The payback period is the length of time necessary for the total

¹ Communication with cement company.

return to equal the capital investment. It was calculated using the following equation:

PBP =
$$
\frac{FCI}{\frac{\sum_{1}^{20} \text{ATCF}}{20}}
$$

PPBP =
$$
\frac{$2,864,552}{$13,837,187 \mid 20} = 4.14 \text{ years}
$$

To calculateATCF, full depreciation was only added the first nine years of operation and only half of the depreciation was added for year 10. As mentioned above, no depreciation was added the final years of operation. The value of PBP obtained is also acceptable for a new product entering an established market.^[9] The students concluded that a biodiesel production facility is not economically feasible without government tax incentives. This result gave the students an understanding of the need for state and federal support for developing new industries associated with renewable energy.

Some of the results presented above were taken from the class-best final report. Student course evaluations and senior exit interviews indicated that the application of research and teaching was an exciting and motivating experience for the class. Some of the students'

comments about the project included:

- *"I liked the fact that the project was a real-life application."*
- *"I became more competent with ChemCad."*
- *"This class helped with my teamwork skills."*

Additionally the class benefited by:

- Access to the instructor's extensive literature *collection on biodiesel production technology.*
- *Excitement of working on the production of renewable Juel with clear environmental, health, and safety benefits.*
- *Discussing contemporary issues associated with the economic feasibility of a renewable Juel.*
- *Visualizing the importance of lifelong learning on the application of chemical engineering principles to contribute solutions to society s dwindling energy resources.*
- *Determining the capital and operating cost drivers of the acid-catalyzed transesterification biodiesel production process.*

CONCLUSIONS

The design project offered students the opportunity to apply chemical engineering to the transformation of a nontraditional raw material into a fuel. The students gained a new perspective on the potential contributions of chemical engineering to areas such as new energy sources, sustainability, and policy. The approach of presenting a general problem or concept, followed by a closer focus on details and the solution of component small problems using chemical process simulation, was key to the successful completion of the design problem.

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