Using AspenPlus Resources to Model Biodiesel Production Applicable for a Senior Capstone Design Project

Casey Kick[a], Dr. Andrew Kline[a], Harold Hladky[a], and Dr. Betsy Aller[b]

[a]Department of Chemical and Paper Engineering
[a]Department of Industrial and Manufacturing Engineering

Western Michigan University, Kalamazoo, Michigan 49008

Email: casey.f.kick@wmich.edu

ABSTRACT

Biodiesel is the desired product from the transesterfication of vegetable oils in the presence of an alkaline catalyst and contains the essential triglycerides in a methanol solvent. The transesterfication reaction produces two products: glycerol and fatty acid methyl esters (FAME). While the FAME product can be refined and purified into the biodiesel fuel, the secondary product glycerol from the transesterfication reaction is used commonly for soap production. Other methods for producing biodiesel have been known to include crude blending, microemulsion stabilization, and pyrolysis, but transesterfication is still the most common method used in industry.

Today, due to the cost of production of biodiesel, over 50% of the plants producing biodiesel fuel have shut down from the original 87 plants that were operating in the United States as of 2006. The major setbacks facing biodiesel production are the costs of refining the biodiesel, the production capacity, and competition for the triglyceride raw materials with the food and feedstock industries. These production factors can't compete with the lower costs of petroleum refining and the availability of petroleum fuels. The key for reducing the cost for biodiesel production for countries without substantial oil wells starts with improved modeling and optimization of the biodiesel process.

In the optimization of the biodiesel process, modeling the transesterfication reaction and purification of the biodiesel has been done, but with crude estimations and non-apparent altercations to ASPEN's thermodynamic property evaluation system. Modeling of biodiesel through alkali catalyzed transesterfication was done using ASPEN Plus® v2006 software (Developed by Aspen Technology Inc., Cambridge, Massachusetts, USA). To ensure complete transesterfication, a molar feed ratio of 6:1 moles of methanol to triolein is needed for the feed stream to the reactor. This biodiesel plant utilizes a continuous reactor designed in ASPEN Plus® that operates at 60°C and 58 psia to meet the desired transesterfication kinetics with a 95% conversion of the trolein feed oil. To enhance the transesterfication reaction kinetics in the reactor, NaOH catalyst is supplied to the reactor in an amount specified as 0.8 wt% of the total mass flow of triolein in the feed. To prevent saponification in subsequent plant processes, fresh water is fed to wash the glycerol from the biodiesel product in the first decantation stage. Fresh water feed is maintained as 14 wt% of the decanter's feed stream. To maintain the purity of the glycerol for commercial sale as a byproduct, the NaOH catalyst was neutralized with an acid, H_3PO_4.

In a Capstone Senior Design Project, seniors are expected to apply their knowledge of engineering fundamentals, kinetics, thermodynamics, and design towards tackling an industry problem. This paper will explore methods to build a biodiesel flow sheet and estimate thermodynamic properties of the triglycerides, fatty methyl esters, and intermediates for improved ASPEN Plus® modeling, applicable to a senior capstone design project. Presented in this paper is a walkthrough for a student to set up a base case biodiesel production simulation in ASPEN Plus®, which will allow the student to devote more time towards optimizing the process and less time struggling with the rigors to setup the initial base case.

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1. Introduction

In today's world, many of the commonly used products and energy needs are being met with the use of petrochemical resources, namely derived components of crude oil. As the demand for energy and petroleum derived products has grown, so have the costs to supply the increasing demand. The current crude oil consumption in the United States in the past two years has averaged about 19 million barrels per day. When this crude oil is processed, about 24% of the refined crude product is diesel fuel that is commonly used as heating/fuel oil in trucks, boats, industrial machinery, and large scale furnaces. As it stands, the highway consumption for diesel fuel is about 141 million gallons per day, which is about 6% lower than the record high in 2007 due to improvements to the fuel economy standards set forth for diesel engines. [1] The underlying issue with crude oil is our dependence on importing the crude from foreign countries. Although our dependence on foreign oil is at a record low, where currently the crude oil imported makes up 45% of the crude oil demand in the U.S., there is still a great need to utilize and develop renewable, clean burning fuels.[2] As stated previously, diesel fuel consumption only represents a quarter of the crude oil products being consumed. However, given the high increase in fuel price from 2009, as shown in Figure 1, and price uncertainty of crude oil, there is a strong need for the advancement and optimization of production of biofuels to decrease the country's dependence on petroleum-based energy.
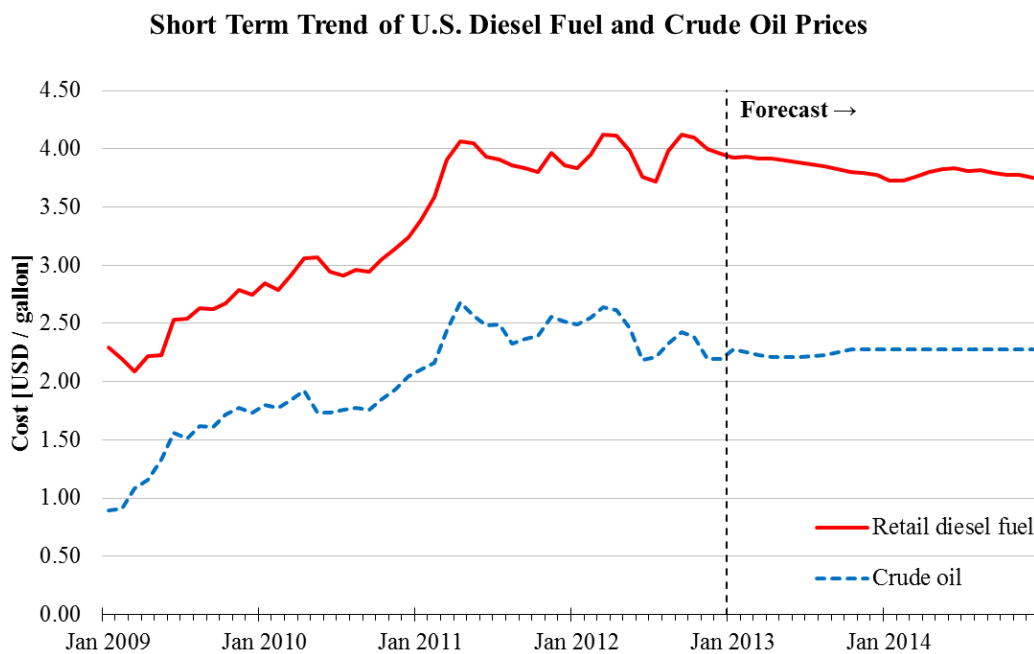
Short Term Trend of U.S. Diesel Fuel and Crude Oil Prices

Figure 1: Short-term trend of diesel fuel and crude oil prices[1]

The concept of using an alternative fuels and alternative diesel engine fuels is not a new direction. Research in this area has been continuously carried out over the past century. However, since petroleum based crude fuels were relatively inexpensive compared to the commercial cost to design engines and processes to synthesize alternative fuels, modern day

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engines were designed specifically to burn petroleum fuels. With the costs of petroleum fuels on the rise, the opportunity to revisit alternatives to petroleum fuels is increasing. From an environmental perspective, biodiesel fuels burn 75% cleaner than regular petroleum based diesel. A pure biodiesel fuel when burned generates 93% fewer hydrocarbons, gives off 50% fewer carbon monoxide emissions, produces 30% less particulate matter (ash), and creates 80% fewer cancer-causing polycyclic aromatic hydrocarbons (PAH). Furthermore, burning biodiesel fuels does not produce any sulfur-based gases because there are no sulfur based compounds in the biodiesel chemistry. Additionally, biodiesel can be synthesized from a variety of different feedstock fatty oils.

Today, more than 95% of the feedstock used in the production of biodiesel comes from virgin vegetable oils, since these oils are extracted from various types of seeds grown across the Midwest and the properties of the biodiesel fuel produced from these seeds makes it a much more suitable diesel fuel substitute.[3] The choice of feedstock is typically dependent on the free fatty acid (FFA) content within the feedstock. The disadvantage of utilizing virgin oils in the commercial industrial process is the high and variable cost of the feedstock, as the seeds and oils are also used competitively in the farming, food, and culinary industries. To make industrial biodiesel production more economically viable, these virgin oils can be replaced with lower quality oils, such as animal fats (Poultry, Fish Oil, Pork Grease, Tallow) and used cooking oils.[4-6] These oils are often lower in cost, but present a challenge due to excess water, impurities, and higher amounts of free fatty acids (FFA) presiding in the feedstock.

On the industrial scale, the presence of excess FFA in the feedstock during the transesterfication reaction can lead to higher soap formation, or saponification, increasing the cost and washing necessary to separate the biodiesel during the purification stages. Additional water present in the feedstock can contribute hydroxide ions to the triglyceride molecules, thereby causing a competitive reaction with the biodiesel transesterfication reaction which will promote the formation of soap. When excess amounts of soap forms, the triglyceride reactant necessary for transesterfication is consumed, but also the biodiesel molecule becomes emulsified. During emulsification, the biodiesel molecule's solubility in the glycerol layer increases, making it very difficult to separate during decantation and washing stages, which then reduce the biodiesel product yield.

Large scale batch production of biodiesel initially took off at the turn of the century. However, due to the cost of production of biodiesel, over 50% of the plants producing biodiesel fuel have shut down from the original 87 plants that were operating in the United States as of 2006, as shown in Figure 2.[7] The major setbacks facing biodiesel production are the costs of refining the biodiesel, the production capacity, and competition for the triglyceride raw materials with the food and feedstock industries. Furthermore, achieving the compliance standards set forth by regulatory agencies such as EN 14214:2003 or ASTM 6751-07 for purification of biodiesel requires that the biodiesel product purity be 99.7% FAME.[8] Achieving this level of purity and proper viscosity for the diesel engine increases the costs for plant design and operations in a biodiesel facility. Specifically, the largest costs a biodiesel plant will encounter are the utility costs associated in the washing and separation equipment. The necessity for these high purification standards prevents a biodiesel fuel from causing significant engine damage;

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should the biodiesel blend contain any methanol, glycerol, unconverted triglycerides, monoglycerides, or any other undesirable impurity. The costs associated to achieve these production standards and acquire the necessary feedstock cannot economically compete with the lower costs of petroleum refining and the availability of petroleum fuels. The key for reducing the cost for biodiesel production for countries without substantial oil wells starts with improved modeling and optimization of the biodiesel process.
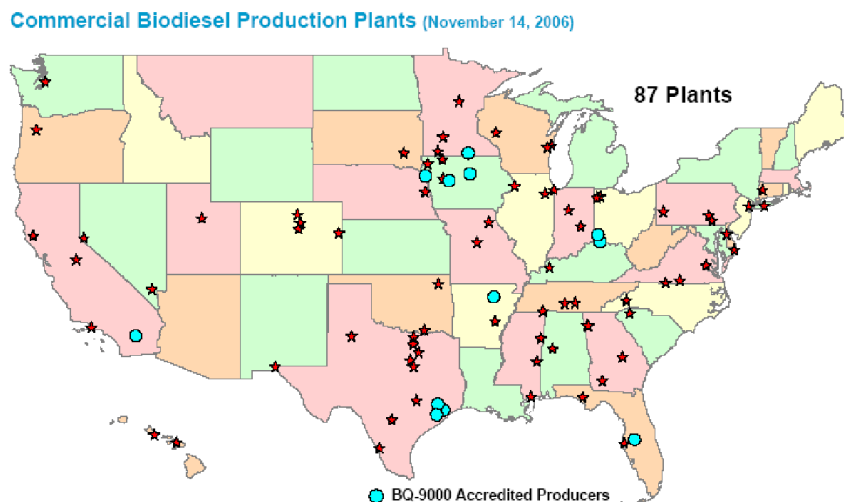

Figure 2: 2006 Reported Survey of Commercial Biodiesel Production Facilities [7]

Biodiesel fuels have become of growing interest to research and development companies seeking to reduce the costs of production and wide scale commercialization of biodiesel. It is because of the growing interest in searching for alternatives to petroleum based fuels that capital investment into small scale biodiesel production facilities are starting to take off. To reduce the costs of large scale production of biodiesel, optimizations to the processes and investigations into alternative processes for biodiesel production are best modeled using a Computer Aided Modeling Software Suite, such as ASPEN® Plus. Understanding how to model the complex reactions and separations occurring in the Biodiesel Process with ASPEN® Plus by limiting their assumptions and approximations allows for a group of seniors working on their Capstone Design Project to truly succeed.

The objective of this study is to provide a more descriptive overview from less descriptive to non-existent documentation explaining how to model biodiesel production on the industrial scale using homogeneous alkali catalyzed transesterfication. Formulating biodiesel production into a Capstone Design gives students interested in pursuing education within the alternative energy field experience with a useful tool that can be helpful in plant design, optimization, and costing elements critical for planning the development of a new modern day biodiesel production plant, without having the students experience errors in design from the overwhelming rigors of inadequate assumptions and complex equations. Providing a detailed layout for a basic biodiesel production plant with discussions to walkthrough common issues that arise in estimating unknown thermodynamic properties and/or reaction kinetics during the simulation creation form the foundation of this paper.

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2. Background

The term "Biodiesel" describes the renewable diesel fuel that is a mixture of fatty acid methyl esters (FAME), which are normally the products from the transesterfication of vegetable oils with methanol in the presence of a homogeneous alkaline catalyst, such as NaOH or KOH. Transesterfication is a common reaction where the ester of the fatty acid (COOR) reacts with an alcohol to form a new ester, which becomes bonded with the functional group from the alcohol, and a new alcohol, bonded with the functional group from the original ester. In essence, the transesterfication reaction allows the valuable ester groups to be broken off the long parent chain of a fatty acid, making the esters more available for a combustion reaction. Homogeneous alkali catalyzed transesterfication is the most widely used method for biodiesel production as it requires lower operating temperatures and much shorter retention times for the reaction to achieve maximum conversion. Compared with acid catalyst the reaction rate is 4000 times faster and requires only a molar ratio of 6:1 moles of alcohol to mole of soybean oil.[9] Between the choice of alkali catalyst considered for the transesterfication reaction, the most frequently used catalyst is methanol due to its low cost and high availability. Acid catalyzed transesterfication of the triglycerides does not create the potential for saponification (soap formation) as an alkali catalyst would. However, in the acid catalyzed heterogeneous transesterfication, higher concentrations of the catalyst lead to a higher reaction temperature and molar feed ratio of alcohol to triglyceride, which slow the speed of the transesterfication reaction. Ultimately, production from acid catalyzed heterogeneous transesterfication produces a lower yield of biodiesel product compared to alkali catalyzed transesterfication.

During the transesterfication reaction to produce FAME, a secondary byproduct, glycerol, is also produced. While the FAME product can be refined and purified into the biodiesel fuel, the secondary product glycerol from the transesterfication reaction is used commonly for soap production. According to the reaction scheme in Figure 3, the triglyceride, which is the primary component of vegetable oil, contains three fatty acid chains esterified to a glycerol molecule. In the presence of an alcohol and a catalyst to speed up transesterfication, the fatty acids are released at the ester bond from the glycerol molecule. These three fatty acids then combine with three methyl groups to form the fatty acid methyl esters. The free hydroxide ions then join to create the glycerol byproduct. Other byproducts that can be formed in lieu of glycerol from the transesterfication reaction can be monoglycerides and triglycerides. However, the selectivity of the reaction and the rate at which the biodiesel reaction is operated tends to favor the production of glycerol and FAME as the primary products.

Extensive research into the kinetics and yield of the transesterfication reaction have been performed on the laboratory scale by Freedman et al (1986), Noureddini et al (1997), Darnoko et al (2000), and Vicente et al (2007). The conditions for the transesterfication reaction have been summarized by these authors works to occur at 60ºC, under atmospheric operating conditions, with the 6:1 molar feed ratio of methanol to triglyceride, for the period of approximately 90 minutes to achieve a 93-98% conversion of the triglycerides into the FAME and glycerol products. [10-13] Once the transesterfication reaction is complete, a series of complex washing and separation stages are necessary to purify the biodiesel (FAME) product and separate it from the glycerol byproduct.
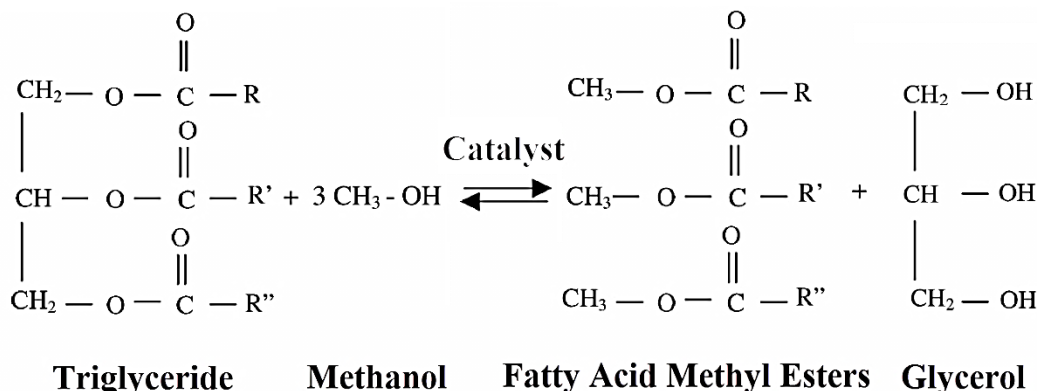
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\begin{array}{c}
\text{O} \\
\parallel \\
CH_2 - O - C - R \\
\mid \quad\quad O \\
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CH - O - C - R' \quad + \quad 3\,CH_3\text{-}OH \\
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CH_2 - O - C - R''
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Triglyceride   Methanol   Fatty Acid Methyl Esters   Glycerol

Figure 3: Transesterfication of trigylcerides ("R" fatty oils) with methanol under an alkali catalyst to form FAME (biodiesel) and glycerol

3.   Process Design Considerations

3.1 Overview of Alkali Catalyzed Transesterfication

The production and purification of biodiesel through alkali catalyzed transesterfication is a standard process, with a few modifications to the order of the washing and separation stages varying from plant to plant. Figure 4 below details the sequence of processes and separations required for biodiesel production. Production through alkali catalyzed transesterfication first begins with raw material transport and handling. On one end, methanol (MEOH) and NaOH catalyst (CATALYST) are mixed together in a stirred mixing tank, M101. The mixture of methanol and catalyst is then pressurized to 58 psia and combined with a recycle stream of methanol (Stream 7A), which is fed into the transesterfication reactor (R-TRANS). The triolein (TRIOL) is also fed to this reactor after the oil is pressurized and heated to 58psia and 60ºC, which are desired operating conditions for the transesterfication reaction.

Transesterfication of the triolein with methanol under a NaOH catalyst proceeds according to the reaction scheme detailed in Figure 5. The products of this reaction are the Oleic Acid Methyl Ester (Biodiesel) and Glycerol. The products in Stream 9 are then fed to a simple distillation column where the unreacted methanol is separated from the product stream and recycled back into the feed stream through Stream 7A. These products at 127 ºC in Stream 9B are then cooled in a heat exchanger to 60ºC for the water washing decantation stage (T-WASH). The water-washing process uses water to collect the glycerol into solution, thus aiding in the separation of biodiesel from the water-glycerol mixture. The biodiesel product leaving T-WASH in Stream 11 is then processed in another process decantation unit (DECAN1) to remove any lingering water from the biodiesel product before final purification. The remaining triolein (R-TRIOL), methanol (MEOHW), and biodiesel (FAME) are separated to purity in another distillation column, T-FAME. The final biodiesel product is purified to 99.8% purity in the T-FAME distillation column.

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Figure 4: Process Flow Diagram of Homogeneous Alkali Catalyzed Transesterfication

Figure 5: Transesterfication of triolein into methyl oleate (FAME) biodiesel product and glycerol

The byproduct glycerol in Stream 10B leaving the T-WASH unit is combined with waste water leaving DECAN1 in a mixer M-104 and is sent to a neutralization tank R-NEUT to neutralize the alkali catalyst, NaOH. This prevents further saponification reactions with the glycerol and water, preventing soap and foaming in the plant so that the purity of the glycerol is maintained. During the neutralization reaction, an acid is added to the catalyst to from a salt precipitate, which will be separated out in the process decanter, DECAN2. Finally, the water used to wash the glycerol from the biodiesel will be separated in the Distillation column

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T-GLYCOL to purify the glycerol byproduct to 100% purity. With this overview in mind, the following subsections will describe the parameters and details instrumental in developing a biodiesel simulation in ASPEN Plus®.

3.1.1   Choice of the Feedstock

Soybean oil typically consists of 22-31% oleic acid and 49-53% linoleic acid, along with many other various acid derivatives. Within soybean oil, the majority of the triglycerides present are represented in the oleic acid form. However, ASPEN Plus's database does not have thermodynamic or physical property data available for oleic acid. The best substitute to represent the oleic acid form is to use the thermodynamic properties associated with trioleic acid, or triolein. Since triolein is composed of three oleic acid chains, it presents the best substitute for simulation purposes. Also, the thermodynamic characteristics for triolein can represent the thermodynamic properties for triglyceride linoleic and oleic acid, since linoleic and oleic acid share very similar boiling points. Using this substitute, triolein represents the triglyceride molecules in the soy oil that are made up of the oleic, linoleic, and other various acids in the simulation, which makes the ASPEN® Plus simulation valid for other feedstock alternatives that may have different ratios of these triglycerides. Since trolein is used as the feedstock, the FAME product for biodiesel is then oleic acid methyl ester, or methyl oleate, as previously shown in Figure 5.

3.1.2   Process Parameters

The kinetics and selectivity for the transesterfication reaction were all obtained from experimentally reported data from the literature.[14] For the model, a continuous reactor was designed in ASPEN Plus® to operate at 60ºC and 58 psia. The conversion of triolein to methyl oleate was specified as a 95% conversion. The feed stream of oil to the reactor was preheated to 60ºC, and fed at rate of 1084.16 kg/hr to the reactor. To maintain the proper molar ratio, the fresh methanol (Stream 7) was combined in a mixer (M103) with recycled methanol (Stream 7A) such that 6 moles of methanol were being fed to the reactor for every one mole of triolein. The total combined flow of methanol being fed to the reactor in Stream 8A was 213.36 kg/hr. The NaOH catalyst used for this transesterfication reaction was added and mixed with the fresh methanol (Stream MEOH) in a mixer (M101) in a quantity representing 0.8wt% of the total mass flow of triolein entering the reactor. The FAME, glycerol, and unreacted feedstock is next fed to the first separation operation in the methanol vacuum distillation tower T-MEOH.

3.1.3   Methanol Separation

A rigorous distillation column was used in ASPEN Plus® to model the vacuum separation of excess methanol from the FAME and glycerol products. The operating parameter for this column was 2.9 psia, with 5 theoretical trays for separation and an operating reflux ratio of 2. The high reflux ratio (L/D) ensures that for every 1 mole of distillate (D) produced (Stream 9T), two moles from the splitting point (L) are returned and recycled back in the column T-MEOH. This reflux ratio is high enough to insure a higher purity of methanol in the distillate

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(Stream 9T), but low enough such that the operating costs for the column are not too outrageous. The main purpose for running the column under vacuum conditions is to ensure that the separation process does not degrade the FAME and glycerol products due to high temperatures. Operating the column in vacuum keeps the column re-boiler operating below 150ºC.[14] Should there be any degradation of the FAME or glycerol products, the two will also be more difficult to separate in subsequent separation operations. The recovery of methanol in Stream 9T was specified to be 94% of the total methanol in Stream 9. The recovered methanol from T-MEOH is then recycled and mixed with fresh methanol to be used as feedstock for the transesterfication reaction once again. Concentrated FAME and glycerol in Stream 9B then move onto a preheater and then proceed to the water washing stage.

3.1.4   Water Washing of FAME and Glycerol

Water washing the bottoms products (Stream 9B) from the T-MEOH column is quite common in industry to separate the FAME from the glycerol byproduct, NaOH catalyst, and excess methanol. Water washing also presents a major expense to the production plant, because significant amounts of water are required to remove any soap that may have developed from possible saponification during the transesterfication reaction. Unfortunately complete separation of FAME from the glycerol, methanol, and NaOH is impossible, but according to industrial practice referenced in the literature by Dorado et al, water washing is fed to the separator in a quantity equivalent to about 14% of the total feed stream (Stream 10) to be washed. For this separation unit T-WASH, water was fed to the separator at a flow rate of approximately 165 kg/min, or about 44 gallons per minute.[15] Washing was operated with four theoretical stages for separation with wash water available at 25ºC. The unit T-WASH was able to remove all the glycerol from the FAME product in Stream 10T, providing a stream containing 94 wt% FAME, 5.3 wt% Triolein, and the balance water and methanol. The wash water used from the separation system, captured the glycerol in stream 10B, providing a stream composition containing 38.3 wt% glycerol, 57.7 wt% water, and the balance methanol and NaOH. The majority of the catalyst used from the transesterfication reaction is then sent to a neutralization tank, R-NEUT, to neutralize the NaOH catalyst remaining in the glycerol.

3.1.5   Neutralization of the Catalyst

The use of a neutralization tank in the final stages of purification is to prevent any saponification reactions and maintain the purity of the glycerol byproduct for sale. Neutralization is carried out in R-NEUT, where 6.58 kg/hr of catalyst is being supplied in Stream 14. To neutralize the catalyst, pure H_3PO_4 is fed to the tank to form a salt precipitate, Na_3PO_4, which will gravity settle in the reutilization tank and be sold as a possible fertilizing agent. Once the catalyst has been effectively removed, the water, glycerol, and methanol components are sent to a final glycerol purification stage, T-GLYCOL.

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3.1.6   Glycerol Purification

The final purification stage for the glycerol byproduct occurs in separation unit, T-GLYCOL. Before separation, the glycerol, water, and methanol solution is preheated to 102ºC to assist in the water and methanol separation from the glycerol. Preheating the solution prior to the separation tank reduces the energy needed to separate the mixture. All of the water and methanol are separated from the glycerol from the top distillate stream in Stream MEOHW2. The bottoms product from the separation column contains pure glycerol, which can be sold as a value added byproduct. The T-GLYCOL column was operated with 5 theoretical stages and under vacuum conditions to achieve this 100% separation of glycerol and methanol/water components.

3.1.7   FAME Purification

The FAME Product after water washing is the product of interest for sale as biodiesel. However, after washing and decantation in DECAN1, the residual water and methanol has left the FAME product only 94 wt% pure. To achieve compliance standards of 99.7wt% purity set forth by government regulatory committees, a final vacuum distillation column, T-FAME, is used operating with 5 theoretical stages and a reflux ratio again of 2, to achieve a 99.8% purity of the FAME product in Stream FAME. The condenser on the vacuum distillation column, T-FAME, is operated as a partial condenser, meaning that only a fraction of the vapor generated in the column condenses. This allows for the methanol and water components to remain in the vapor phase, and allows for the FAME product to condense to the liquid phase. This ideally makes it easier to extract the biodiesel from the T-FAME column. The FAME product has a higher boiling point (associated with its higher molecular weight), and therefore will condense before the methanol and water components (having boiling points at lower temperatures).

4.   Development of the Process Simulation

4.1 Basis of Calculation

The modeling of a homogeneous alkali catalyzed transesterfication process for the production of methyl oleate as the FAME biofuel from triolein was modeled according to a plant production capacity of 1000 kg/hr of biodiesel product from Stream FAME. Using this as a basis of production, the biodiesel production plant was created in ASPEN® Plus v2006 using the process description above. The results of the simulation are presented in the following tables. Table 1 presents the key feedstock and product streams entering and leaving the biodiesel plant. Table 2 then presents the individual process streams in between each major unit operation from the transesterfication reactor to the final glycerol and FAME distillation columns. The final process flow diagram for the biodiesel production plant is presented below in Figure 5, with labeled streams to accompany the data presented in Tables 1 and 2.

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Table 1: Primary Feedstock and Products for Homogeneous Alkali Catalyzed Transesterfication

STREAM ID	CATALYST	MEOH	TRIOL	MEOHW	FAME	RTRIOL	MEOHW2	GLYCEROL
Mass Flow kg/hr								
MEOH	0.00	116.95	0.00	0.02	0.00	0.00	5.66	0.00
GLYCEROL	0.00	0.00	0.00	0.00	0.00	0.00	9.66	96.71
TRIOLEIN	0.00	0.00	1084.16	0.00	2.01	56.84	0.00	0.00
METHYL OLEATE	0.00	0.00	0.00	4.04	1000.52	25.87	0.00	0.00
NAOH	8.67	0.00	0.00	0.00	0.00	2.97	0.00	0.00
WATER	0.00	0.00	0.00	4.10	0.00	0.00	171.65	0.00
H3PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SALT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass Frac								
MEOH	0.000	1.000	0.000	0.003	0.000	0.000	0.030	0.000
GLYCEROL	0.000	0.000	0.000	0.000	0.000	0.000	0.052	1.000
TRIOLEIN	0.000	0.000	1.000	0.000	0.002	0.663	0.000	0.000
METHYL OLEATE	0.000	0.000	0.000	0.495	0.998	0.302	0.000	0.000
NAOH	1.000	0.000	0.000	0.000	0.000	0.035	0.000	0.000
WATER	0.000	0.000	0.000	0.502	0.000	0.000	0.918	0.000
H3PO4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
SALT	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Flow kg/hr	8.67	116.95	1084.16	8.17	1002.53	85.68	186.98	96.71
Total Flow m^3/hr	0.01	0.15	1.19	86.91	1.15	0.19	0.19	0.09
Temperature [C]	25.0	25.0	25.0	178.2	178.2	305.2	47.2	239.8
Pressure [psia]	14.5	14.5	14.5	1.5	1.5	2.9	1.5	2.9

Table 2: Input and Output Streams for Homogeneous Alkali Catalyzed Transesterfication

STREAM ID	3	7	7A	8A	8B	9	9B	9T	10	10B	10T	11	12A	12B	13	14	15	18
Mass Flow kg/hr																		
MEOH	116.95	116.95	87.74	204.61	0.00	93.42	6.05	87.74	6.05	5.57	0.00	0.00	0.00	0.00	0.00	0.00	5.59	5.65
GLYCEROL	0.00	0.00	0.00	0.00	0.00	106.40	106.46	0.00	106.46	106.59	0.00	0.00	0.00	0.00	0.00	0.00	106.71	105.39
TRIOLEIN	0.00	0.00	0.00	0.00	1084.16	58.39	58.07	0.00	58.07	0.00	58.12	58.12	58.12	0.00	58.12	116.24	0.00	0.00
METHYL OLEATE	0.00	0.00	0.00	0.00	0.00	1030.22	1030.73	0.00	1030.73	0.00	1030.74	1030.74	1030.43	0.00	1030.43	2061.17	0.00	0.00
NAOH	0.00	8.67	0.00	8.75	0.00	9.08	8.47	0.00	8.47	5.57	3.29	3.29	3.29	0.00	3.29	6.58	0.00	0.00
WATER	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	160.30	4.39	4.39	4.08	0.78	4.08	8.47	171.68	171.68
H3PO4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SALT	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.00	0.00	0.00
Mass Frac																		
MEOH	1.000	0.931	1.000	0.959	0.000	0.072	0.005	1.000	0.005	0.020	0.000	0.000	0.000	0.001	0.000	0.000	0.019	0.020
GLYCEROL	0.000	0.000	0.000	0.000	0.000	0.082	0.088	0.000	0.088	0.383	0.000	0.000	0.000	0.000	0.000	0.000	0.363	0.373
TRIOLEIN	0.000	0.000	0.000	0.000	1.000	0.045	0.048	0.000	0.048	0.000	0.053	0.053	0.053	0.000	0.053	0.053	0.000	0.000
METHYL OLEATE	0.000	0.000	0.000	0.000	0.000	0.794	0.852	0.000	0.852	0.000	0.940	0.940	0.940	0.000	0.940	0.940	0.000	0.000
NAOH	0.000	0.069	0.000	0.041	0.000	0.007	0.007	0.000	0.007	0.020	0.003	0.003	0.003	0.003	0.003	0.003	0.000	0.000
WATER	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.577	0.004	0.004	0.004	0.996	0.004	0.004	0.584	0.607
H3PO4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
SALT	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.034	0.000	0.000
Total Flow kg/hr	116.95	125.62	87.74	213.36	1084.16	1297.51	1209.78	87.74	1209.78	278.03	1096.53	1096.53	1095.92	0.78	1095.92	2192.45	293.97	282.72
Total Flow m^3/hr	0.15	0.15	0.11	0.27	1.19	1.45	1.34	0.11	1.34	0.26	1.25	1.25	1.25	0.00	1.25	0.29	0.27	0.28
Temperature [C]	25.0	25.0	31.2	27.2	60.0	60.0	127.3	29.0	60.0	60.0	50.0	50.0	40.0	40.0	40.0	60.0	31.2	102.4
Pressure [psia]	58.0	58.0	58.0	58.0	58.0	29.0	4.4	2.9	18.0	17.4	16.0	16.0	15.5	15.5	16.0	16.0	16.0	16.0

4.2 Thermodynamic Models used for Alkali Catalyzed Transesterfication

A few different physical property packages were used to develop the biodiesel simulation. These physical property packages allow ASPEN® Plus to calculate ideal and non-ideal Vapor-Liquid Equilibria, estimate thermodynamic properties of components, calculate precise predictions for component separations, and provide close approximations for energy

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requirements for the various unit operations employed in the simulation. The two physical property packages employed were the UNIQUAC model for performance and separation calculation around the distillation columns, and the Electrolyte NRTL model, which was used for the electrolyte equilibrium system presented in the alkali catalyst neutralization stage. The Electrolyte NRTL is a variation of the Non-Random Two Liquid (NRTL) model for estimating equilibrium separation and interaction for non-electrolyte systems. However, the Electrolyte NRTL package is capable of predicting physical interactions of binary and multicomponent electrolyte parameters over a wide range of concentrations and temperatures, making it ideal for this model. This package was already pre-installed in ASPEN® Plus v2006 used to create this simulation.

4.3 Estimation of Thermodynamic Data for Complex Components of the Feedstock

Although ASPEN® Plus is equipped with a large database of known compounds with various thermodynamic data, including a direct link into the National Institute of Science and Technology (NIST) database, the compounds oleic acid, and linoleic acid are not present. As stated before, these two components make up a large portion of the triglycerides found in the oils used as feedstock for biodiesel production. Thermodynamic properties for these two compounds can be estimated by one of three ways. One method is to choose compounds that exist in the database that have comparable molecular weights. The large assumption is that for compounds sharing similar molecular weights, their thermodynamic properties will be comparative. A second possibility is to manually enter in the thermodynamic properties using a user defined method, if the thermodynamic properties for the unlisted compounds happen to be available. However, the availability of unlisted thermodynamic properties is not always an option.

A preferable way to estimate thermodynamic properties is to draw the molecular structures using the ISIS draw patch to ASPEN® Plus v2006. The ISIS draw program will import the molecular structure into a user defined method and will estimate thermodynamic properties by using ASPEN's UNIFAC group contribution factor evaluation system. While ISIS is limited in the types of molecular configurations a compound can have, it can still provide a fairly decent prediction of an unlisted compounds thermodynamic properties.

5. Conclusions

Biodiesel is a clean burning fuel derived from the transesterfication of oils/fats to produce a fatty acid methyl ester. With all the methods used to synthesize FAME, or biodiesel, alkali catalyzed transesterfication of vegetable oils and fats is still the most common method. While many types of feedstock oils/fats can be used to synthesize biodiesel, raw materials containing a high percentage of fatty acids or water can react with the alkali catalyst to form soaps that emulsify the biodiesel product. Therefore, to reduce saponification reactions and increase the yield of the biodiesel product, water washing and acid neutralization of the catalyst is essential to prevent undesirable side reactions. From a design perspective, water washing and supplemental purification of the biodiesel product add significantly to the capital and operations cost for a plant to synthesize biodiesel. Originally, these costs made biodiesel production uneconomical

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compared to the plant costs to refine petroleum based fuels for diesel engines. But as the demand for diesel and petroleum fuels increases, a need for alternative fuels is becoming greater.

Today, biodiesel production and research is back on the rise. Small scale biodiesel production plants are growing in numbers until a large enough demand exists in the market to support larger scale production facilities, or until fossil fuel prices increase tremendously driving the need for larger scale production. To make biodiesel production more economical for large scale production, design and optimizations have to begin at the simulation scale first. While trials performed at the industry scale are not economical and not sufficient for true process optimization, a great deal of power for process design lies in utilizing simulation software, like the ASPEN® Plus suite. Understanding how to model the complex reactions and separations occurring in the Biodiesel Process with ASPEN® Plus was the key focus of this paper. The goal was to provide suggestions and walkthroughs helpful for a student working on modeling a biodiesel production process with ASPEN® Plus.

In the optimization of the biodiesel process, modeling the transesterfication reaction and purification of the biodiesel has been done, but with crude estimations and non-apparent altercations to ASPEN's thermodynamic property evaluation system. To adequately model a biodiesel production plant, four factors affect the operation of the simulation: feedstock feed ratio, reaction conversion, reaction temperature, and catalyst neutralization. To ensure complete transesterfication, a molar feed ratio of 6:1 moles of methanol to triolein was used in the feed stream to the reactor. For this model, a continuous reactor was designed in ASPEN Plus® to operate at 60°C and 58 psia. The conversion of triolein to methyl oleate was specified as a 95% conversion. To achieve the required transesterfication reaction kinetics in the reactor, the quantity of NaOH catalyst supplied to the reactor was fed in a quantity representing 0.8wt% of the total mass flow of triolein entering the reactor. To prevent saponification later in the process, fresh water was fed to the process decanter to wash glycerol from the biodiesel product. The water being supplied in the first decantation stage was fed in a quantity to about 14% of the total mass flow of the decanter's feed stream. Later, the NaOH catalyst was neutralized with an acid, H_3PO_4, to maintain the purity of the glycerol for commercial sale as a byproduct.

This type of design project is applicable to a Capstone Senior Design Project, where seniors are expected to apply their knowledge of engineering fundamentals, kinetics, thermodynamics, and design towards tackling an industry problem. In the case of biodiesel production, the question to answer is how to economically synthesize alternative fuels to limit the country's dependence on petroleum based fuels? By providing a walkthrough for a base case biodiesel production plant with descriptions on how to tackle common milestones during the initial simulation setup, students in their Senior Capstone Design Project will focus more time on optimizing the process and less time struggling to build a base case. In plant design, assisting the students with this base case allows them to build upon the work and knowledge that has already been done. Focusing on the optimization of current processes feeds innovation to design an economic plant that will handle the large scale manufacture of biofuels. This will make the widespread implementation and use of biodiesel fuels in diesel engines a closer reality.

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