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Techno-Economic and Sensitivity Analysis of Biodiesel Production Using Co-Solvent

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Abstract

Three different continuous homogeneous alkali-catalyzed, heterogeneous alkali-catalyzed and supercritical methanolysis processes with adding tetrahydrofuran as a co-solvent to produce biodiesel from virgin vegetable oil were designed and simulated. An economic assessment was also performed based on the results of the process simulations. Technical assessment of the proposed processes showed that the homogeneous and heterogeneous alkali-catalyzed processes were the simplest with the least amount of process equipment, while for the supercritical methanolysis process; it was more complex with larger sizes of transesterification and separation units. The homogeneous alkali-catalyzed process using tetrahydrofuran was found to have the lowest total capital cost (\$2.32 million), the highest aftertax rate of return (513%) and the payback period (0.19 year). However, total manufacturing cost and aftertax net profit, the heterogeneous alkali-catalyzed process using tetrahydrofuran had the lowest operating cost (\$82.20 million) and the highest aftertax net profit (\$18.20 million). The homogeneous alkali-catalyzed process I is not only technically feasible but also economically viable. Results from the sensitivity analyses indicated that methanol recovery percent, biodiesel purification tower vacuum pressure, price of feedstock oil, price of methanol, price of biodiesel and price of glycerin by-product were the factors that most significantly affected the economic feasibility of biodiesel production.

Key words:

Biodiesel, Transesterification, Process simulation, Economic assessment, Statistical analysis

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1. Introduction

Currently, the three main resources of global energy are oil, coal and natural gas. These non-renewable fuels supply 90% of the world's energy needs. Petroleum oil provides 40% of the energy needs. The ever-growing human population and the rise of manufacturing and transport have resulted in rising energy demand all over the world. Fossil fuel consumption is 10^5 times higher than nature can produce, according to recent estimates. With internationally confirmed oil reserves estimated to be equivalent to 1,3 trillion barrels of oil, it is probable that crude oil will be exhausted in the next 50 years. [1]. **Figure 1** demonstrates Global direct primary energy consumption from 1800 to 2019 by fuel type[2].

In addition to the energy crisis, fossil fuels for energy generation had a significant negative impact on the environment. Carbon dioxide levels have been increasing at an accelerated rate over the past couple of decades [3]. The total amount of CO₂ emissions related to the burning of fossil fuels has reached about 26 billion tons. The statistical data shows that CO₂ concentration in the atmosphere is about 380 ppm, compared to 280 ppm before the industrial revolution. The total global CO₂ emissions in 2030 will be 1.6 times higher than in 2004[4].

Due to the depletion of world oil reserves and the high environmental impact, alternative resources for petroleum-based fuel, such as diesel fuel, are of interest. Due to the closer properties, bio-resource biodiesel fuel (fatty acid methyl ester) is considered to be the best candidate for diesel fuel replacement in diesel engines.[5].

The technique of transesterification of vegetable oil has been in use for more than one hundred years, although this technique has been primarily used to extract glycerin (aka glycerol) from vegetable oils. The by-products of this type of technique were methyl esters, now known as biodiesel. The history of biodiesel is more political and economical than technological. Resource depletion has continually been a concern with regard to petroleum, and farmers have constantly sought new markets for their products. Therefore, work has continued on using vegetable oils as fuel.

In the early 1980s, the usage of vegetable oils as an alternative renewable fuel was proposed to compete with petroleum. The benefits of vegetable oils as diesel fuel are its portability, availability, renewability, better heat content (approximately 88% of No. 2 petroleum diesel fuel), lower sulfur content, lower aromatic content, and biodegradability. The high energy consumption issues of the 1970s renewed interest in biodiesel, however commercial production did not begin till the late 1990s[6].

The market for biodiesel is relatively small but has been growing over the past 5 years. It currently accounts for approximately 2.1% of the 60-billion-gallon annual diesel market[7]. There are two main factors driving the biodiesel market; the feedstock price and the fossil fuel price[8]. European Union has actually been and will most probably stay the key production and consumption region for biodiesel till 2020[9].

For the Egyptian market, the yearly production for fossil diesel equals to 153,600 bbl/day in 2015; which isn't enough to overcome the yearly consumption (278,200 bbl/day in 2015) [10]. This leads to the growth of biodiesel market in Egypt as an alternative to overcome this shortage.

The objectives of this study consist of a techno-economic analysis of different biodiesel production pathways with adding tetrahydrofuran as a co-solvent through two parts. The first one is to develop different catalytic and non-catalytic transesterification continuous process flow sheets to produce biodiesel using virgin vegetable oil and to evaluate their technical benefits and limitations. The second is to carry out an economic assessment of these processes, to determine their economic feasibilities and to identify those factors having the greatest impact on the economics of biodiesel production using statistical analysis.

2. Methodology

The simulation and design calculations for different biodiesel production processes with THF as a co-solvent were performed along with the economic calculations; followed by sensitivity analyses to check the parameters affecting these processes.

2.1. Process Simulation Procedure

To evaluate the commercial feasibilities of the proposed procedures, complete process simulations have been first completed. In spite of a few predicted variations between process simulation results and real process operation, most current simulation software can offer reliable data on process operation due to their comprehensive thermodynamic packages, large component libraries and advanced calculation techniques. The process simulation software, Aspen HYSYS V8.4 developed by AspenTech Inc., was used in this thesis.

The steps for process simulation involve defining chemical components, choosing a thermodynamic model, determining plant capacity, selecting proper operating units and providing input conditions (flow rate, temperature, pressure, and other conditions).

To set up a process flowsheet and carry out a steady-state simulation, the first step was to define the chemical components and the thermodynamic model to be employed. The system consisted mainly of triglyceride, methanol, methyl ester, glycerol, tetrahydrofuran and catalyst. Information on most of these species is available in the HYSYS component library and is not further discussed here. Vegetable oil is a mixture of different triglycerides containing various fatty acids. Since oleic acid is the most common monoenoic fatty acid in plants and animals [11], triolein ($C_{57}H_{104}O_6$), containing three oleic acid chains, was chosen as the representative triglyceride in the HYSYS simulation. Accordingly, methyl oleate ($C_{19}H_{36}O_2$) was taken as the resulting biodiesel product and its properties have been available within the HYSYS component library. For those components not found within the library, like phosphoric acid and potassium phosphate, they were defined by using “the Hypo manager” tool in HYSYS. For phosphoric acid, its molecular weight is 98 g/mol. Its normal boiling point and density were defined as 406.9 °C and 1857 kg/m³, respectively [12]. Finally, HYSYS was used to estimate the other physical properties, such as critical temperature, pressure and volume.

Because of the presence of highly polar component, methanol, both the Universal Quasi-Chemical (UNIQUAC) and Non-Random Two Liquid (NRTL) thermodynamic/activity models were recommended to estimate the activity coefficients of the components in a liquid phase [13]. Detailed descriptions of these models were provided by Gess [14]. The NRTL model was used in this study.

Once the chemical components and the thermodynamic model were defined, the next step was to develop a process flowsheet by choosing operating units and define the input conditions, such as composition, flowrate, temperature, pressure, etc. In order to have an equal basis for comparison, each process was designed for the same plant capacity. Thus, in the current process design, a plant with 100,000 tons/year biodiesel was simulated.

2.2. Process Design for the Selected Processes

As mentioned before, the biodiesel production through transesterification includes many processes. In this study, three transesterification processes were selected according to:

- Homogenous alkali-catalyzed process was selected as the most studied and conventional process.
- Heterogeneous alkali-catalyzed process was selected as the correspondence process to compare between it and the homogenous process.
- Supercritical methanolysis process was selected for its promising conversion results and shorter reaction times.

The three different continuous processes that were designed and simulated are summarized in **Table 1**. **Figures (2, 3 & 4)** shows the process flowsheets for the three processes, while **Table 2** shows the process parameters chosen to simulate in HYSYS; and a detailed process description follows.

2.2.1. Transesterification

Fresh methanol (stream Methanol), recycled methanol (stream 201B) and co-solvent (stream THF) were mixed before entering into reactor R-100; with addition to virgin vegetable oil (stream Oil) and KOH catalyst in Process I or CaO catalyst in Process II. In R-100, 91%, 97% & 98.5% of oil was converted to biodiesel according to the experimental results for Process I, II & III respectively; and glycerol was produced as a by-product. Outlet stream from the reactor was introduced to methanol recovery distillation tower T-100 after being used to heat the inlet oil stream. For Process II, the outlet stream from R-100 was introduced to catalyst removal separator (solid/liquid) before entering T-100 due to the need to remove solid catalyst before proceeding.

2.2.2. Methanol recovery

In T-100, the excess methanol is being recovered from other components. Stream 201 was a pure methanol distillate, containing almost the total methanol in R-100 products stream. To keep the bottom temperature under 150 °C, vacuum distillation was used. Fresh make-up methanol (stream Methanol) was mixed with pure methanol (stream 201B) and then headed back into reactor R-100. Bottom stream 202 was sent to Biodiesel/Glycerol separator; except for Process I, it was sent first to neutralization reactor R-200 to remove excess liquid catalyst as not to affect the purity of the final products.

2.2.3. Catalyst removal

For Process I, to remove the KOH catalyst, bottom stream from T-100 was fed to neutralization reactor R-200; and phosphoric acid was added. The resulted by-product K_3PO_4 was removed in solid/liquid gravity separator. The resulted potassium phosphate may be used as a valuable byproduct (e.g., fertilizer).

For Process II, the excess CaO removed by catalyst removal separator (solid/liquid) can be used as a low quality by-product or go to regeneration to be used again in the process.

2.2.4. Biodiesel/Glycerol separation

Gravity separator V-100 was used to separate the biodiesel from the glycerol and methanol. The heavy liquid phase (aka Glycerol) was removed in the bottom stream (stream Glycerol); while the biodiesel was removed in light liquid stream and headed to biodiesel purification tower T-200. The glycerol obtained in stream Glycerol has high purity (>95% purity) which can be sold as technical grade.

2.2.5. Biodiesel purification

To obtain a final biodiesel product complying with ASTM specifications, biodiesel distillation T-200 was used. To prevent degradation of the biodiesel, T-200 was operated under vacuum to keep temperatures low enough. A partial condenser was used to separate biodiesel from water and methanol in the column overhead. Water and methanol were removed as vent gases (stream 401). Biodiesel product was obtained in stream Biodiesel as a liquid distillate;

while the unreacted oil remained at the bottom of T-200. In the reboiler, superheated high pressure steam was the heating medium.

2.3. Economic Assessment

The technical assessment is not the only aspect to assess a project; as there are different factors like economical, environmental and social factors. The economic performance is an essential aspect in assessing process viability. It tests the project's profitability, either it will lose cash; or it will earn cash. The economic overall performance of a biodiesel plant (e.g., fixed capital cost, total cost of manufacturing, and the break-even price of biodiesel) can be calculated once specific factors are identified, which include plant capacity, process technology, raw material cost and chemical costs.

The following assumptions were considered in the economic evaluation of this study:

- Operating hours was assumed to be 8000 hr/year.
- Pump efficiency was assumed to be 70%. This was used to determine the pump shaft power.
- All costs shown are in US\$. Equipment prices were updated from mid-2006 to Oct 2016 values using the Chemical Engineering Plant Cost Index (CEPCI), where $I_{\text{Mid 2006}} = 500$ and $I_{\text{Oct 2016}} = 543.4$ [18].
- All costs of raw materials, catalysts and products are given in **Table 3**.

According to the definition of capital cost estimation provided by Turton [24], the economic estimation in this study is considered as a “study estimate”. This means that a process flow diagram needed to be developed besides rough sizing of major process equipment. No further data, such as a layout plot or process piping and instrumentation diagram were considered. This study estimate had a range of accuracy ranges from +30% to -20%. Accordingly, results from this type of preliminary evaluation will not accurately reflect the final profitability of a chemical plant but can be used as an indicator for comparing between different process alternatives.

The module cost technique is a common technique used to calculate the cost of a new chemical plant. It is known as the best technique for making preliminary cost estimates; and is used in this thesis. The economic assessment was developed by the literature outlined by Turton.

2.3.1. Purchased cost of equipment and bare module cost

To calculate an estimate of the capital cost of a chemical plant, the costs related to main plant equipment have to be available. To calculate those costs, Capcost, an excel-based program developed by Turton was used in this study.

The program requires the user to enter data about the equipment; as an example, the capacity, operating pressure, and materials of construction. The cost data can be adjusted for inflation through adding the current value of the CEPCI. The equipment options available in the program includes evaporators and vaporizers, reactors, towers, heat exchangers, process vessels with/without internals, mixers, pumps with electric drives ...etc. The cost obtained from the program is the bare module cost (C_{BM}) for each equipment; which reflects the sum of direct and indirect costs related to the installation of the equipment.

2.3.2. Total capital investment

The total capital investment (CTCI) is split into fixed and working capital investments. The fixed capital investment (C_{FC}) is the investment required to make the plant ready for start-up; and it contains two groups: contingency and fee costs and auxiliary facilities costs.

2.3.2.1. Contingency and fee costs (CCF)

This factor is included in the evaluation of the cost as a protection against oversights and faulty information; and it can be calculated using Equation (1). Adding these costs to the bare module cost provides the total module cost (C_{TM}) as described in Equation (2).

$$C_{CF} = 0.18C_{BM} \quad (1)$$

$$C_{TM} = C_{BM} + C_{CF} \quad (2)$$

2.3.2.2. Auxiliary facilities costs (CAF)

These include costs for site development, auxiliary buildings, and off-sites and utilities; and it can be calculated using Equation (3). These terms are generally unaffected by the materials of construction or the operating pressure of the process. Adding these costs to the total module cost provides the fixed capital cost (C_{FC}) as described in Equation (4).

$$C_{AF} = 0.3C_{BM} \quad (3)$$

$$C_{FC} = C_{TM} + C_{AF} \quad (4)$$

2.3.2.3. Working capital costs (CWC)

It represents the amount of investment needed to start up the plant and financially covers the first few months of operation before start gaining revenues from the process; and it can be calculated using Equation (5). Adding these costs to the fixed capital cost provides the total capital investment (C_{TCI}) as described in Equation (6).

$$C_{WC} = 0.15C_{FC} \quad (5)$$

$$C_{TCI} = C_{FC} + C_{WC} \quad (6)$$

2.3.3. Total cost of manufacturing

The costs related to daily operation of a chemical plant must be calculated before start assessing the economic feasibility of a proposed process. Those costs are defined as total cost of manufacturing (COM) and represented in Equation (7). The COM can be categorized into three parts: direct manufacturing costs, fixed manufacturing costs and general expenses.

$$COM = DMC + FMC + GE \quad (7)$$

2.3.3.1. Direct manufacturing costs (DMC)

These costs include operating expenses that alter with production rate; and it covers the costs of raw materials, utilities, waste treatment, operating labor, direct supervisory and clerical labor, maintenance and repairs, operating supplies, laboratory charges and patents and royalties.

The prices for the used raw materials, utilities and waste treatment are included in **Table 3**; which used beside with their flowrates to calculate their yearly costs.

Operating labors costs (C_{OL}) was calculated using Equation(8) provided by Turton; where N_{OL} is the number of operators per shift; P is the number of processing steps involving the handling of particulate solids; for example, transportation and distribution, particulate size control, and particulate removal. N_{np} is the number of non particulate processing steps and includes compression, heating and cooling, mixing, and reaction.

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{NP})^{0.5} \quad (8)$$

The other costs which include direct supervisory and clerical labor, maintenance and repairs, operating supplies, laboratory charges and patents and royalties can be calculated by multiplying with a factor as stated in **Table 4**.

2.3.3.2. Fixed manufacturing costs (FMC)

These costs are independent of changes in production rate. They include plant overhead costs, property taxes and insurance and depreciation; which are accounted at constant rates even when the plant is not operating. They can be calculated by multiplying with a factor as stated in **Table 5**.

2.3.3.3. General expenses (GE)

These costs represent an overhead burden that is required to execute business functions. They include management, sales, and research functions. They can be calculated by multiplying with a factor as stated in **Table 6**.

2.3.4. Profitability analysis

There are three bases used for the evaluation of profitability: time, cash and interest rate. The time criterion and interest rate criterion are being used in this study to evaluate the profitability. But, before start evaluating, the annual net profit (A_{NP}) must be calculated.

2.3.4.1. Annual net profit (ANP) and income tax (AIT)

The annual net profit is the money gained or loosed resulting from revenues (A_R) after subtracting all associated costs. It can be calculated using Equation (9).

$$A_{NP} = A_R - COM \quad (9)$$

Taxation has a direct impact on the profits realized from building and operating a plant. The taxes on income (A_{IT}) vary according to national laws and regulations. For this study, the A_{IT} was assumed to be 30%. After deducting the income taxes from the annual net profit, the after tax net profit is obtained (A_{NNP}) as shown in Equation (10).

$$A_{NNP} = A_{NP} - A_{IT} \quad (10)$$

2.3.4.2. After tax rate of return on investment (ATROR)

For, the interest rate criterion, after tax rate of return on investment (ATROR) is used; which represents the rate at which money is made from fixed capital investment. The larger the ROI%, the more profitable the project. It can be calculated from Equation (11).

$$ATROR = \frac{(A_{NNP} - A_{DEP})}{C_{FC}} * 100 \quad (11)$$

2.3.4.3. Pay-back period (PBP)

It represents the time required, after start-up, to recover the fixed capital investment for the project. The shorter the PBP, the more profitable the project. It can be calculated from Equation (12).

$$PBP = \frac{C_{FC}}{A_{NNP}} \quad (12)$$

2.4. Sensitivity Analysis

A sensitivity analyses for the processes were performed to calculate the effect on the process variables that had some degree of uncertainty; and to figure out any operating conditions within each process that could be modified to improve the process.

The computer modeling results from HYSYS can be considered as experiments executed on computer. They are evidently different from traditional physical experiments but have been widely used in recent years. Usually, computer experiments provide an effective alternative to time-consuming or expensive physical experiments. For reaction conditions too difficult or costly to implement in practice, the computer experiment is a powerful tool for predicting system behavior.

2.4.1. Controlling factors

Aftertax rate of return on investment (ATROR) for the biodiesel plant was used as the performance criterion. It is related to many intermediate outputs, such as the total capital investment, total manufacturing cost and so forth. Although the quantities of these intermediate outputs were also available in this work, the aftertax rate of return provided the primary basis for the conclusions.

Aside from the chemical prices directly related to the economic calculations, some design variables affect the processes, such as the recovery rate of methanol, vacuum in the methanol recovery tower and vacuum in the biodiesel purification tower. Those factors were included in the sensitivity analysis study to measure their effect on the processes. In Process I for example, overall, eleven control variables (i.e. control factors) were found to affect the response variable (i.e., aftertax rate of return). They were: methanol recovery %, vacuum in methanol recovery tower, vacuum in biodiesel purification tower, the price of feed oil, the price of methanol, the price of co-solvent, the price of biodiesel, the price of glycerol, the price of catalyst, the price of neutralization agent and the price of the by-product salt form neutralization.

The control factors differ from one process to another. It depends on the type of catalyst and the removal process of catalyst from the system. In Process I, a liquid homogeneous catalyst is used which required using a neutralization agent to undergo a neutralization reaction to obtain a salt by-product; this increases the control variables to 11 factors. In Processes II, the catalyst used was solid heterogeneous which required removal by solid/liquid separator and no extra chemical was introduced into the system; this reduces the control variables to 8 factors. For Process III, there is no catalyst; which reduces the control variables to 8 factors. The

identification of control variables for each process is presented in **Table 7**.

2.4.2. Experimental design

A two-level fractional factorial design is a common screening tool to filter out insignificant variables without losing much important information. In this study, a two-level fractional factorial design with resolution IV was applied. In a resolution IV design, each main effect is at least confounded with one three-factor interaction. One special feature in this research is that several factors are chemical prices. In some cases, interactions between two chemical prices or interactions between one chemical price and another unrelated chemical property should be very small or zero. The description of all factors for Process I is listed in **Table 8**. Process I was chosen as the example because it contains the maximum number of variables; while the other processes have less control variables than Process I.

The setting of the levels of chemical prices was based on an assumption. If different price ranges were used, this would create some ambiguities in analyzing the practical significance of these factors. In other words, it would be difficult to clearly determine whether the significance of each chemical price factor is due to the price itself or to its wide price range. To avoid such ambiguities, the price of each chemical was arbitrarily set at the same price range (i.e., \$200/ton) for the sensitivity analyses. Thus, the final results would reflect the practical effect of each factor itself.

Nowadays, computer programs are designed for each process. In the statistical analysis study of this research, Design Expert V7.0 was used as software to perform the study and to estimate the effecting variables. A 2_{IV}^{11-6} fractional factorial experimental design, involving 32 runs for each set of experiments, was used for Process I. The system description for each process is represented in **Table 9**.

After defining the model, the control variables and the response; the program randomly builds up runs. After that, the response values for different run conditions can be obtained and entered into the program. At this point, the analysis of variance table (ANOVA) can be easily completed. Lastly, if the P-value (Prob > F) is less than 0.05, the parameter can be considered as

significant; or in other words, the parameter has a major effect on the process.

3. Results and discussion

3.1. Technical Assessment

Simulation of the three different processes was performed using Aspen HYSYS simulator. A technical comparison of those processes is followed.

When comparing between the three types of processes used for biodiesel production in this study with using THF as a co-solvent (see

); the homogeneous alkali-catalyzed process (Process I), the heterogeneous alkali-catalyzed process (Process II) and the supercritical methanolysis process (Process III); we found that, the supercritical process (Process III) has the adverse reaction conditions with the highest conversion (98.5%). While Process II has the largest reactor volume (411.8 m³) due to its longest reaction time (360 min).

For the methanol recovery tower (T-100), Process I has the lowest methanol to oil molar ratio (4.5:1), which resulted in small amount of methanol needed to be recovered in T-100, thus decrease the vapor load inside the tower (11,431 kg/hr in Process I) and decrease the tower diameter (2.0 m in Process I). On the other hand, using 42:1 methanol to oil molar ratio in Process III resulted in increasing the load inside the tower (51,453 kg/hr in Process III) and eventually increasing the tower diameter (4.3 m in Process III).

For all processes, whether using a homogeneous catalyst, heterogeneous catalyst or no catalyst, it has no effect on the biodiesel/glycerol separator volume (V-100), as the processes have the same separator volume (0.3 m³) and high purity glycerol can be obtained (>95%).

Because of using homogeneous catalyst in Process I, a neutralization step is required to remove the catalyst from the final biodiesel product. On the other side, Process II does not require a neutralization step because the ease of separation of the heterogeneous catalyst using a filtration step; as well as Process III as no catalyst was used.

The neutralization reaction introduces extra water into the system which acts as a bipolar liquid and partially removed into the Glycerol stream; and thus, decreases its purity ($\approx 95\%$ for Process I instead of $\approx 99\%$ for the other processes).

In the biodiesel purification tower (T-200), the presence of a neutralization step before the tower in Process I introduce water into the system; which complicates the biodiesel purification. This resulted in the need for larger tower to obtain ASTM biodiesel. Thus a 3.8 m tower diameter is required in Process I. For the final biodiesel purity, the three processes were capable of producing biodiesel with a purity larger than 96.5% which complies with the ASTM and EN-14103 standards.

The total number of major processing units in each process is summarized in **Table 11**. The lowest number of units was Process I and II with 9 pieces of equipment. For the supercritical methanolysis Processes III, it is the most complex processes with 13 pieces of equipment respectively. This is due to the adverse reaction conditions required to conduct the reaction (i.e. reaction pressure and temperature). This increase in the number of equipment represents a potential increase in the cost of construction material.

3.2. Economic Assessment

Following the process simulation and design given in the previous section, the values of fixed capital cost, total manufacturing cost and after-tax rate of return for the processes were determined. A summary of the economic performance of each process is shown in **Figures (5, 6 & 7)** and **Tables (12, 13 & 14)**.

In **Table 12**, when comparing between the three types of processes; we found that the volumes of the transesterification reactor (R-100) are 9.2 m^3 , 411.8 m^3 and 220.9 m^3 respectively. Despite Process II has the highest transesterification reactor volume, Process III has the highest transesterification reactor cost ($\$0.07$ million for Process I, $\$1.53$ million for Process II and $\$1.98$ million for Process III). This is because of using high pressure (19,000 kpa) in Process III and

high methanol to oil molar ratio (42:1) which will cause increases in reactor thickness and reactor volume.

For the methanol recovery tower (T-100), Process I has the lowest methanol to oil molar ratio (4.5:1), which resulted in the need for smaller equipment sizes for Process I (the tower diameter equals 2.0 m in Process I, 2.7 m in Process II and 4.3 m in Process III). Thus, the cost of the T-100 for Process I is the lowest compared to the other two processes (\$0.54 million for Process I, \$0.67 million for Process II and \$1.64 million for Process III).

Because of using homogeneous catalyst in Process I, a neutralization step is required to remove the catalyst from the final biodiesel product. This will add an extra cost of \$0.07 million for the total bare module cost.

Also, the adverse conditions used in Process III resulted in using more equipment to overcome the 42:1 methanol to oil molar ratio and 19,000 kpa pressure. Thus, supercritical methanolysis Process III has the highest total bare module cost between the co-solvent processes (\$1.36 million for Process I, \$2.87 million for Process II and \$4.92 million for Process III). On the other hand, Process I has the lowest total bare module cost due its normal conditions.

3.2.1. Total manufacturing cost

In **Table 13**, when comparing between the three types of processes; we found that the cost of feed oil equals \$43.96 million, \$41.24 million and \$ 40.61 million respectively (52%, 55% and 46% respectively). While the cost of make-up methanol equals \$4.71 million, \$5.27 million and \$7.57 million respectively (6%, 7% and 9% respectively). Process III has the highest make-up methanol cost due to the high methanol to oil molar ratio used (42:1).

For the utilities, the transesterification reaction conversions are 91%, 97% and 98.5% respectively, which indicates that Process I has the largest amount of superheated high pressure steam and eventually the highest cost (\$18.57 million, \$7.46 million and \$11.28 million respectively). Two more factors are affecting the utilities cost, the low pressure steam cost and the refrigeration water cost both used in T-100. The high methanol to oil molar ratio used in

Process III increases the load inside the tower and thus the amount and cost of the low pressure steam (\$1.42 million, \$2.71 million and \$4.93 million respectively); also increases the amount and cost of the refrigeration water in the condenser (\$0.50 million, \$1.32 million and \$4.17 million respectively).

Overall, Process II has the lowest total cost of manufacturing (\$82.20 million). Process III comes in the second place (\$90.07 million) due to the high methanol to oil molar ratio used. Finally, Process I has the highest total cost of manufacturing (\$94.81 million) due to its transesterification reaction conversion (91%) and the need for larger amount of superheated high pressure steam.

3.2.2. After-tax rate of return and payback period

According to **Table 14**, all processes achieve positive net profit after deduct the taxation. This is because the high revenue from selling the biodiesel product (approximately \$99.4 million). The homogeneous alkali-catalyzed Process I has the highest ATROR (513%) and the shortest payback period (0.19 year). This is due to its low capital investment (\$2.32 million); and the contribution of by-products (glycerol and K_3PO_4) on the total revenue (\$9.24 million and \$1.17 million respectively). On the other side, Process I has the lowest after tax net profit due to its high cost of manufacturing (\$94.81 million).

For Processes II and III, higher after tax net profit are obtained (\$18.20 million and \$12.40 million respectively); but on the expense of lower ATROR (417% and 160% respectively) and longer payback period (0.23 year and 0.59 year respectively).

3.3. Sensitivity Analysis

Sensitivity analyses were performed for all processes to determine the effect of process parameters on the ATROR. As mentioned before, to check the affecting parameters on each process, the analysis of variance table (ANOVA) must be obtained first. Lastly, if the P-value ($Prob > F$) is less than 0.05, the parameter can be considered as significant; or in other words, the parameter has a major effect on the process. The ANOVA table for each process is presented in **Table 15**.

The summary of sensitivity analyses' results is concluded in **Table 16**. In all processes, the methanol recovery percent has a major effect on the ATROR. The increase in the methanol recovery percent will result in an increase in the reboiler duty of the methanol recovery tower; thus, larger reboiler area will be needed and higher amount of steam. So, the FCI and the COM will be affected respectively; and finally, the ATROR.

Biodiesel purification tower vacuum pressure is a major effect in Process I and II. The slightest increase or decrease in it will result in change in the condenser and reboiler duties. Increasing the pressure to reach the atmospheric pressure will result in an increase in the temperature inside the tower. So, the temperature difference between the steam and the biodiesel mixture will be decreased; thus, a larger amount of steam will be needed and a larger heat transfer area for the reboiler to achieve the required biodiesel purity.

Process III is the only process that has the methanol recovery tower vacuum pressure as a major parameter. The use of large amount of methanol to oil molar ratio and large amount of co-solvent require large tower size and large condenser/reboiler sizes and duties. Therefore, the change in pressure inside the tower will indirectly affect the FCI and the COM.

For raw materials, the oil price and the methanol price have positive impact on all processes. As the raw materials contributes around 54-63% of the total cost of manufacturing. So, the change in their prices will affect the COM and consequently the ATROR. While for the products, the biodiesel price and the glycerol price have the most impact. As they both contributes around 90% and 8% of the total revenue respectively. So, the change in their prices will affect the after tax net profit and consequently the ATROR.

4. Conclusion

For a biodiesel production rate of 100,000 ton/year, three flowsheets for continuous homogeneous alkali-catalyzed, heterogeneous alkali-catalyzed and supercritical methanolysis processes (Process I, II and III) using virgin vegetable oil as the raw material were designed and simulated. From the technical assessment, all of these processes proved to be feasible for

producing a high quality biodiesel product and a top-grade glycerin (aka glycerol) by-product under reasonable operating conditions. However, each process type has its limitations.

The homogeneous alkali-catalyzed process (Process I) has low amount of process equipment and reasonable small sizes of transesterification and separation units. But on the other hand, the present of homogeneous catalyst in the process decreases the final purity of the glycerol by-product produced. The heterogeneous alkali-catalyzed process (Process II) is the simplest with the low amount of process equipment but larger transesterification unit size. This is due to the long reaction time with an average methanol to oil molar ratio. The supercritical methanolysis process (Process III) is the most complex processes with the largest amount of process equipment. The benefit of these processes is the shorter reaction time to produce high quality biodiesel. On the other hand, the adverse reaction conditions result in larger sizes of transesterification and separation units.

An economic assessment of the three different processes was also performed. In regard to fixed capital cost or total capital investment, Process I has the lowest value (\$2.32 million for TCI), which represents the lowest requirement for initial investment in building a new biodiesel plant. However, regarding total cost of manufacturing, Process I have high costs and became less attractive (\$94.81 million); while Process II has the lowest total manufacturing cost (\$82.20 million). The raw material costs were found to be the most important component of the total manufacturing cost for biodiesel production with a 54-63% share of the total cost of manufacturing.

On the basis of the after tax rate of return and the pay-back period, Process II has the highest after tax net profit (\$18.20 million) but with a lower ATROR (417%) and a longer biodiesel pay-back period (0.23 year). While Process I has the highest ATROR (513%) and the shortest pay-back period (0.19 year) with a lower after tax net profit equals \$10.54 million.

In conclusion, the homogeneous alkali catalyzed process to produce biodiesel from virgin vegetable oil is not only technically feasible but also economically viable. Also, heterogeneous

alkali-catalyzed process II can compete with process I with its narrow technical and economical parameters.

The results of the sensitivity analyses for these processes showed that methanol recovery percent, biodiesel purification tower vacuum pressure, price of feedstock oil, price of methanol, price of biodiesel and price of glycerol by-product were the major factors affecting the commercial viability of the biodiesel production.

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Availability of data and materials: The datasets generated and analyzed during the current study are available from the corresponding author on reasonable request through a material transfer agreement

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Ethics approval and consent to participate: Compliance with ethical standards was considered by informing participants about the aims and methods of the respective research. The participation in the survey was on a voluntary basis and anonymity of the participants is preserved— no inferences can be drawn from the answers to the individuals.

Competing interests: The authors declare no competing interests

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Figures

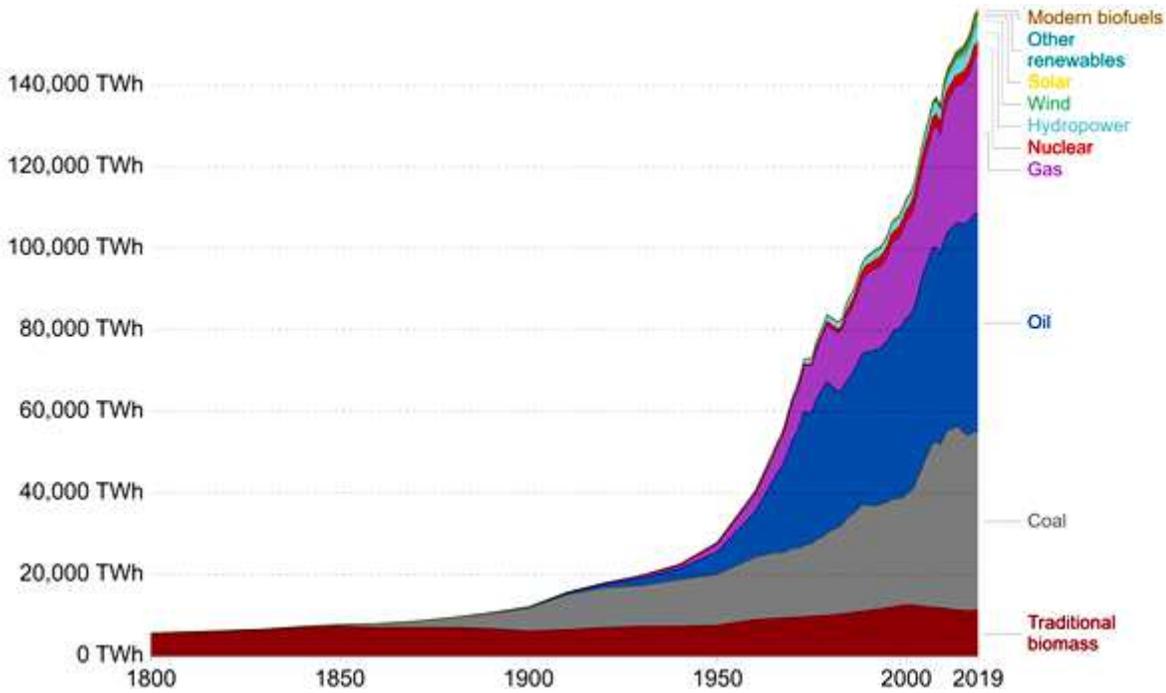


Figure 1

Global direct primary energy consumption from 1800 to 2019 [2]

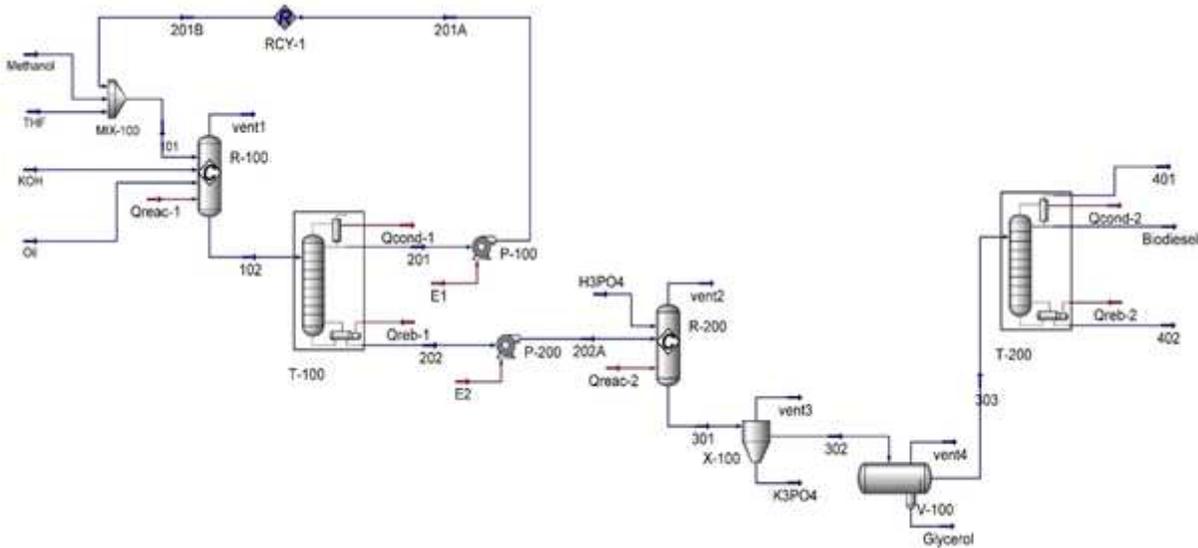


Figure 2

Homogeneous alkali-catalyzed process with THF as a co-solvent flowsheet on Aspen HYSYS

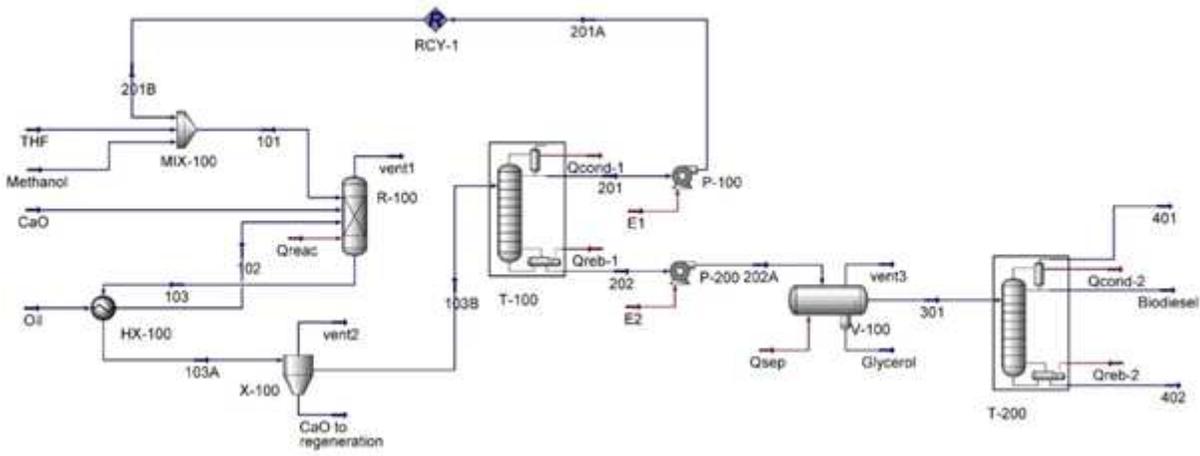


Figure 3

Heterogeneous alkali-catalyzed process with THF as a co-solvent flowsheet on Aspen HYSYS

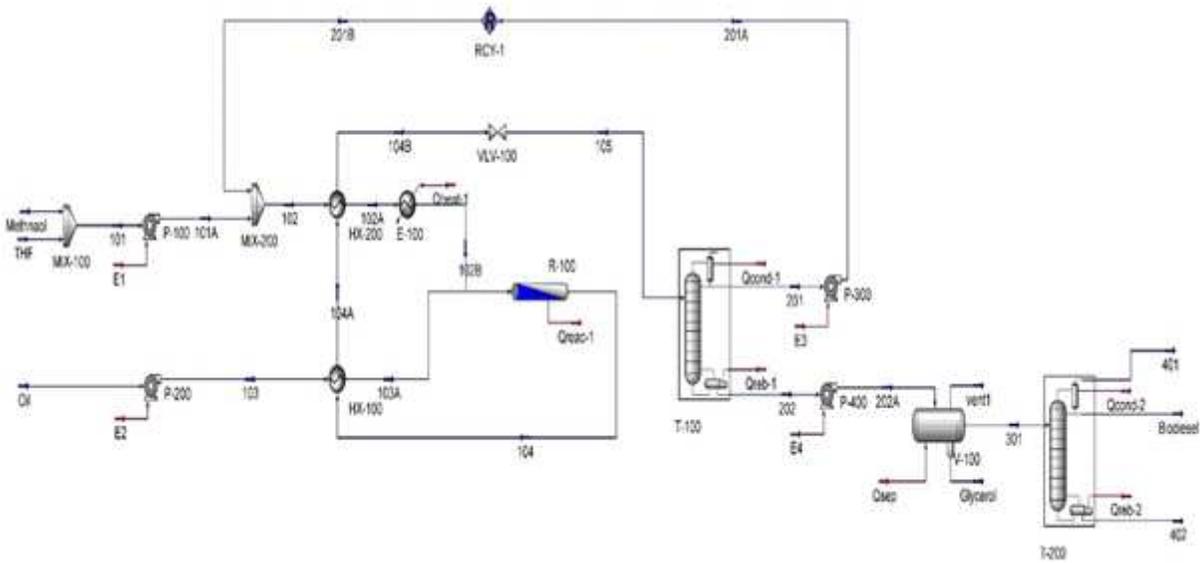


Figure 4

Supercritical methanol process with THF as a co-solvent flowsheet on Aspen HYSYS

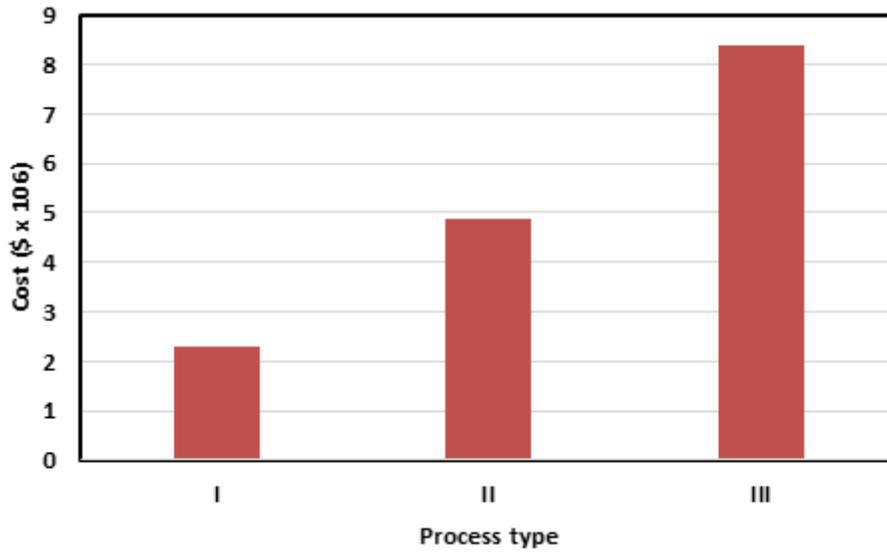


Figure 5

Total capital investment for each process

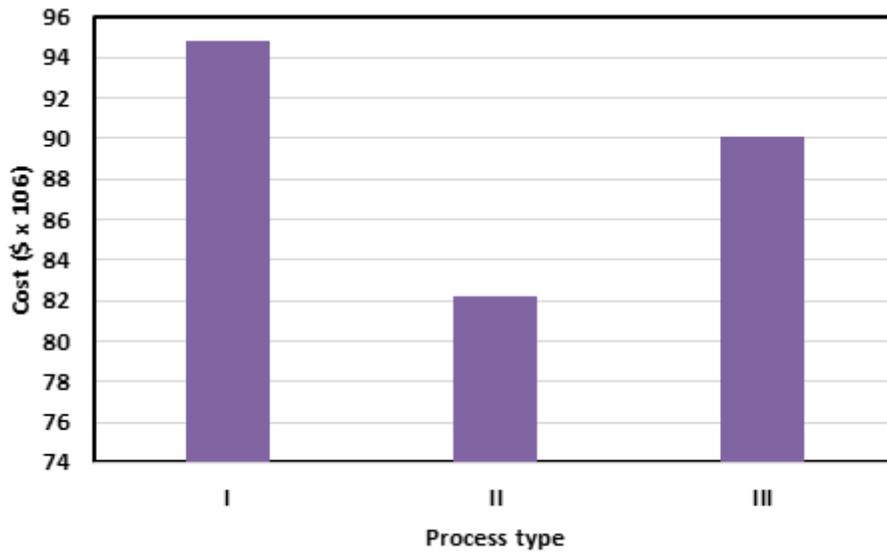


Figure 6

Total cost of manufacturing for each process

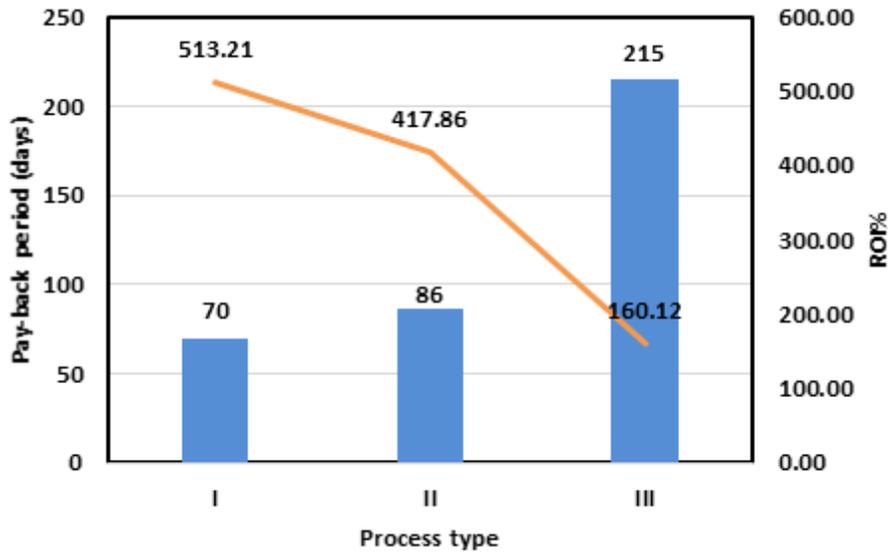


Figure 7

After tax rate of return and pay-back period for each process

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