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Techno-Economic Optimization of a Continuous Process for the Biodiesel Production from Waste Vegetable Oils

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ABSTRACT

A continuous process was designed and optimized at a conceptual stage for the biodiesel production from waste vegetable oils. Unlike previous studies, the process was optimized taking into account the technical and economic considerations, simultaneously, to find the optimum operating conditions for the commercial scale productions. The effect of major variables on the yield of the process was studied by modeling esterification and transesterification reactors. The mole fraction of free fatty acids (FFAs) in the feedstock, production rate, conversion and molar ratio of the reactants in both reactors were chosen as major variables. By considering the economic potential as the objective function of the process optimization, the optimum mole fraction of FFA was obtained as about 0.50 (24 wt %). Also, the optimum values of the conversion and molar ratio of the reactants in the esterification and transesterification reactors were found as 82-89 % (depending on the different production rates), 11:1 and 96 %, 8:1 respectively. It was found that the economic potential increases linearly as the production rate increases. Therefore, the production rate should be set at its maximum possible practical value. The break-even point at the optimum values of these variables, as mentioned above, occurs at the production rate of 157 ton/yr.

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1. Introduction

According to ASTM D6751-20a, biodiesel is produced from renewable lipid sources (such as vegetable oils, animal fats or kitchen

greases) as a mixture of different mono-alkyl esters of long chain fatty acids, for being used in diesel engines [1]. In addition to its pure form, a blend of biodiesel fuel with

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petroleum-based diesel fuel can also be used (B100, B75 or B20). It emits less carbon monoxide, particulate matter (e.g. smoke) and unburned hydrocarbons (e.g. soot) and almost no sulfur or aromatic components as compared to petrodiesel [2-4]. Thus, biodiesel has been commercially used in Austria, Italy, Germany and France since 1980 [5]. This fuel is traditionally produced through the transesterification of lipid materials with an alcohol such as methanol or ethanol in the presence of a catalyst to yield biodiesel and glycerin as byproduct [6, 7]. The low price of methanol compared to other alcohols has led to its greater use in the biodiesel production [8].

The high cost of biodiesel is the main difficulty and bottleneck in its current application. The price of biodiesel is about 3 to 5 times that of petrodiesel fuels. It is reported that approximately 75 % or more of the cost of this green fuel is due to the cost of raw materials [9]. So, the feedstock cost is the most influential factor in the biodiesel production, with the capital cost contributing only about 7 % to the biodiesel cost. Exploring the effective ways of reducing the biodiesel cost, especially the cost of raw materials, has become the focus of researches [10, 11]. Owing to this, the use of waste lipid sources, waste cooking oils, animal fats or the lipid extracted from algae instead of virgin oils seems to be a helpful and advantageous method to reduce the cost of raw materials [3, 12, 13]. But these materials include undesirable ingredients (such as free fatty acids (FFAs) and water), which increase the complexity of the required process and the final production costs. In this regard, Zhang et al. simulated four processes to produce biodiesel from virgin oils or waste cooking oils by the alkali or acid catalyzed

transesterification and assessed the economic feasibility of these processes [9]. Also, sensitivity analyses for these processes were carried out. Their findings revealed that the plant capacity and the prices of biodiesel and feedstock oil were the most effective factors on the economic viability of the biodiesel production. Further, the alkali catalyzed plant using virgin oils was the simplest process with the least required equipment. Although, it had the highest cost of raw materials. Despite the reduced cost of the feedstock in using waste lipids, it was the most complex process with the highest number of equipment components and requiring the addition of a pretreatment unit for the removal of FFA. Although the prior process had the least requirements for the biodiesel plant building, it had a high manufacturing cost, offsetting any economic advantage in terms of return on investment or the break-even price of biodiesel. They assumed waste cooking oil containing 6 wt % of FFA for producing biodiesel at the production rate of 8000 ton/yr. Tapasvi et al. developed a biodiesel process model based on the process engineering basic principles (e.g. mass and energy balances). This model can be used to compare the production of biodiesel from various vegetable oils. Accordingly, the model's outputs can be applied for performing the economic feasibility studies in the production of biodiesel from different feedstocks. Nonetheless, the mentioned model does not include the equipment sizing and costing calculations. Canakci et al. built a 190-liter batch pilot plant to produce biodiesel from high FFA feedstocks [15]. They used virgin oils, yellow greases with 9 wt % of FFA and brown greases with 40 wt % of FFA. Accordingly, they found the production costs of producing biodiesel from virgin oils,

yellow greases and brown greases as \$0.418, \$0.317 and \$0.241/L respectively. Their estimated costs do not include capital costs or a credit for the byproduct (i.e. glycerol) of the process. Their findings showed that the content of FFA had a very high impact on the process complexity, thus it is necessary to optimize the process conditions to realize the best feedstocks in the biodiesel production.

Suraj et al. investigated the effects of the content of FFAs on the biodiesel production yield as well as on the production methodology [16]. They used the alkali transesterification for the feedstocks having FFAs varying from 0.28 to 5 %. These researchers found that the production yield is about 95 % for oils having the FFA of below 2 %. However, it drops below 80 % for the feedstocks with the FFA of above 3.6 %, while the process fails for oils with the FFA of above 4.2 %.

Nonetheless, the review of the literature shows that the operating conditions in all existing biodiesel production processes are similar to those of the chemist's recipe (i.e. laboratory scale production); while in the commercial scale production, it is necessary to optimize these conditions taking into account the technical and economic considerations. Therefore, in the present work, a continuous process for the production of biodiesel from high FFA feedstocks was optimally designed using a conceptual method and according to a technical and economic trade-off.

2. Computational method

The conceptual design is a strong and useful method for designing the chemical processes at the synthesis stage. The goal of a conceptual design is to select the process units and their possible interconnections and

to obtain the optimum values (or states) of the selected design variables. Thus, these problems are very open ended. They are difficult because many alternatives in the process (10^4 to 10^9) could be considered. In addition, prior experiences indicate that less than one percent of the solutions to the problem for new designs become commercialized [17]. Accordingly, there are many possibilities to be considered with only a small chance of success. Nonetheless, the major advantage of this method is that only a very small fraction of data is required to define a design or optimize the problem. Technical and economic feasibilities are also considered simultaneously. Further, the major variables with their effects and optimum values are determined.

In this methodology, the designer solves problems by first finding a very simple solution and then adding more details to the selected solution. In the present work, the suggested procedure by Douglas [17] and the general rules of thumb (heuristic methods) were used to eliminate undesirable alternatives in the process. However, sometimes it is necessary to design various alternatives and then to compare their Economic Potentials (EP) for the best process selection. The main advantages of Douglas's procedure include very quick decrease in the number of alternatives in the design and the step by step growth in the details and the complexities of the solution. In this study, EP was selected as the objective function of the process optimization. Here, this statement was defined as:

$$EP = [\text{Revenue}] - [\text{Raw Materials Costs} + \text{Equipment Costs} + \text{Utility Costs}]$$

The selection of the design variables is the fundamental step in Douglas's procedure. The

major design variables should be independent. Zhang et al. assessed the economic feasibilities of the four different continuous processes (including both alkali and acid catalyzed processes), using waste cooking oils or virgin oils as raw materials to produce biodiesel. Their finding reveals that the plant capacity and prices of the feedstock oil and biodiesel are the most significant factors affecting the economic viability of the biodiesel production [5]. Kasteren et al. reported the plant capacity, capital cost and the prices of the raw material and byproduct (i.e. glycerol) of the process as the most influencing key factors for the economic feasibility of the biodiesel production plant [18].

Unlike the previous studies, in the present work, the process production rate, conversion of transesterification and esterification reactors, molar ratio of raw materials at the inlet of transesterification and esterification reactors and finally content of the impurity (i.e. FFA) of the process feedstock were selected as the major design variables.

Multiple operating options are available for making biodiesel from different feedstocks. Many of these technologies can be practically combined to achieve the best operating option for selected raw materials. However, the choice of technology is a function of the type and quality of the feedstock, desired capacity, required fuel quality and alcohol and catalyst recovery subsystems [10]. In this research, first, the suggested methods for the biodiesel production, such as thermal cracking (pyrolysis), transesterification (alcoholysis), microemulsions, supercritical alcohol and cosolvent [10, 18, 19], were evaluated. As a result, the esterification of FFA in the presence of the homogeneous H_2SO_4 catalyst and the transesterification of waste oils or

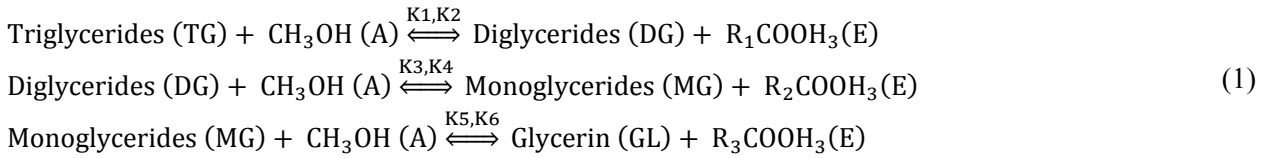
animal fats in the presence of the homogeneous NaOH catalyst were identified as the most promising method. The application of this method led to the maximum amount of biodiesel produced under the mild conditions of temperature and pressure and in the minimum required time [20]. As mentioned above, the mole fraction of FFA in the process feed (XFO), conversion and molar ratio of the reactants in the esterification reactor (XE and MRE), conversion and molar ratio of the reactants in the transesterification reactor (XT and MRT) and production rate of the process (PBC) were chosen as major design variables. These variables have global effects on the process. For example, increasing the reactor conversion increases the size of the reactor, resulting in the higher cost of the reactor. However, by increasing the reactor conversion, less unreacted materials appear at the reactor effluent stream. This means fewer loads are required for the separation section and consequently less expensive the separation is. This trade-off between the cost of the reactor and cost of separation determines the optimum value of the conversion. Similar trade-offs can also be explained for the molar ratio and other design variables. The main reason behind the selection of these variables lies certainly in their global effects.

Since esterification and transesterification reactions are reversible, the effects of the major design variables on the process yield were studied through modeling esterification and transesterification reactors. These reactor models are able to show the effect of the temperature, molar ratio of reactants, mixing intensity and residence time on the conversion and selectivity of the esterification and transesterification reactions. These models

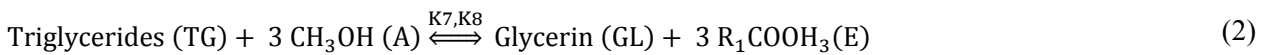
were prepared with the help of the MATLAB[®] software and other related software tools.

The esterification and transesterification reactors were modeled using the suggested

kinetics by Tesser et al. [21] and Nouredдини et al. [22] respectively. Nouredдини et al. reported the transesterification reaction of vegetable oils by the following three steps:



The overall reaction is as follows:

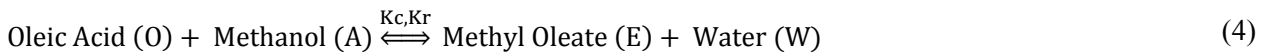


They suggested the following rate equations:

$$\begin{aligned} \frac{d[\text{TG}]}{dt} &= -K_1[\text{TG}][\text{A}] + K_2[\text{DG}][\text{E}] - K_7[\text{TG}][\text{A}]^3 + K_8[\text{GL}][\text{E}]^3 \\ \frac{d[\text{DG}]}{dt} &= K_1[\text{TG}][\text{A}] - K_2[\text{DG}][\text{E}] - K_3[\text{DG}][\text{A}] + K_4[\text{MG}][\text{E}] \\ \frac{d[\text{MG}]}{dt} &= K_3[\text{DG}][\text{A}] - K_4[\text{MG}][\text{E}] - K_5[\text{MG}][\text{A}] + K_6[\text{GL}][\text{E}] \\ \frac{d[\text{GL}]}{dt} &= K_5[\text{MG}][\text{A}] - K_6[\text{GL}][\text{E}] + K_7[\text{TG}][\text{A}]^3 - K_8[\text{GL}][\text{E}]^3 \\ \frac{d[\text{E}]}{dt} &= K_1[\text{TG}][\text{A}] - K_2[\text{DG}][\text{E}] + K_3[\text{DG}][\text{A}] - K_4[\text{MG}][\text{E}] + K_5[\text{MG}][\text{A}] - K_6[\text{GL}][\text{E}] + K_7[\text{TG}][\text{A}]^3 \\ &\quad - K_8[\text{GL}][\text{E}]^3 \\ \frac{d[\text{A}]}{dt} &= -\frac{d[\text{E}]}{dt} \end{aligned} \quad (3)$$

Based on their experimental data, Nouredдини et al. suggested a second order kinetic mechanism for the transesterification reaction. Also, the reaction rate constants and the activation energies have been determined

for all of the forward and reverse reactions. Also, Tesser et al. [21] studied the kinetics of oleic acid esterification with methanol in the presence of an acid catalyst.



They found that the mechanism of the esterification reaction is controlled initially by the mass transfer phenomena and then influenced by the kinetic phenomena [21]. They also reported the following rate equation by the assumption of the second order equilibrium reaction.

$$r = K_c x_O x_A C_{\text{cat}} \left(1 - \frac{1}{K_e} \frac{x_E x_W}{x_O x_A} \right) K_e = K_c / K_r \quad (5)$$

where C_{cat} and x denote the concentration of the catalyst and the mole fraction. Also, O, E, A and W subscripts show oleic acid, biodiesel, methanol and water respectively. Assuming an Arrhenius behavior, they

determined the kinetics and equilibrium constants.

As a result of the developed models, Table 1 shows the effect of the molar ratio of reactants on the maximum conversion and selectivity at the optimum temperature (60 °C) and mixing intensity in a single stage

reactor for esterification and transesterification reactions. A good agreement was observed between predicted and experimental results which have been reported by Tesser et al. [21] and Nouredini et al. [22].

Table 1

Maximum (or equilibrium) conversion and selectivity of esterification and transesterification reactions as a function of MRE and MRT at 60 °C.

MRE	$X_{E,Max}$ (or $X_{E,Equilibrium}$)	$S_{E,Max}$
1	0.52	1.000
11	0.93	1.000
21	0.95	1.000
31	0.96	1.000
41	0.97	1.000
MRT	XT_{Max} (or $XT_{Equilibrium}$)	$S_{T,Max}$
3	0.66	0.845
4	0.77	0.892
5	0.85	0.922
6	0.90	0.940
7	0.93	0.952
8	0.96	0.968
9	0.97	0.974

The results of these reactor models were applied to determine the optimum values of the design variables. For example, in order to get an optimum value of the molar ratio of the reactant, the present optimization procedure is able to change the reactor conversion from zero to the equilibrium conversion shown in Table 1, for each specific molar ratio. In case of the higher conversion ($x > x_{Equilibrium}$), the optimization algorithm chooses higher ratios until the optimum values of the conversion and molar ratio are achieved. The relationship between the required residence time and conversion ($\tau=F(x)$) can also be obtained by modeling the reactor. This, in turn, leads to

the estimation of the reactor volume (V) at a specific conversion:

$$V = (v)(\tau) \quad (6)$$

where v is the entrance volumetric flow (m^3/s).

The HYSYSTM software was used for the estimation of physical and chemical properties. Vegetable oils or animal fats are a mixture of various types of triglycerides. For simplicity, Triolein ($C_{57}H_{104}O_6$) was chosen to represent waste cooking oil [10]. Accordingly, methyl oleate ($C_{19}H_{36}O_2$) and oleic acid ($C_{18}H_{34}O_2$) were taken as the resulting biodiesel (fatty acid methyl esters or

FAME) and FFA respectively. Such components as Triolein that are not available in the HYSYS™ component library were defined using Hypothetical Manager Tool in the HYSYS™ software. For this purpose, UNIFAC molecular structures were used as well as the empirical data reported in literatures [23]. Table 2 shows some of these physical properties. Finally, a good agreement was observed between the estimated properties and the experimental data.

The process flowsheet was determined according to the Douglas's algorithm for the Input/Output (IP/OP) structure, Recycle structure and Separation structure. Finally, Figure 1 shows the process flowsheet

obtained from the conceptual design based on Douglas's procedure.

For the process optimization, it was assumed that reactor conversions change from zero to the equilibrium conversion (see Table 1). Apparently, higher amounts of molar ratios ($MRE > 41$ and $MRT > 9$) had no sensible effect on the equilibrium conversions. Recycle streams (i.e. RT1, RT2, RE1 and RE2 streams in Figure 1) are required because of the excess methanol and unreacted Triolein and FFA. In case that optimum values determine very high conversion or stoichiometric molar ratios, the model process automatically eliminates these recycle streams.

Table 2
Physical properties of Triolein [23].

Property	Value
Molecular weight (g/mol)	885.45
Boiling point (°C)	
P=6.70 Pa	308
P=0.13 Pa	254
Density (g/cm ³)	
15 °C	0.9162
25 °C	0.9078
Viscosity (mPa.s)	
20 °C	65
30 °C	45
40 °C	33
50 °C	25
Specific heat capacity (J/g.K)	
80.4 °C	2.060
60.0 °C	2.000
Melting point (°C)	
Type α	-32.0
Type β'	-12.0
Type β	5.5
Heat of vaporization for 0.13-67 Pa (J/g)	209.3

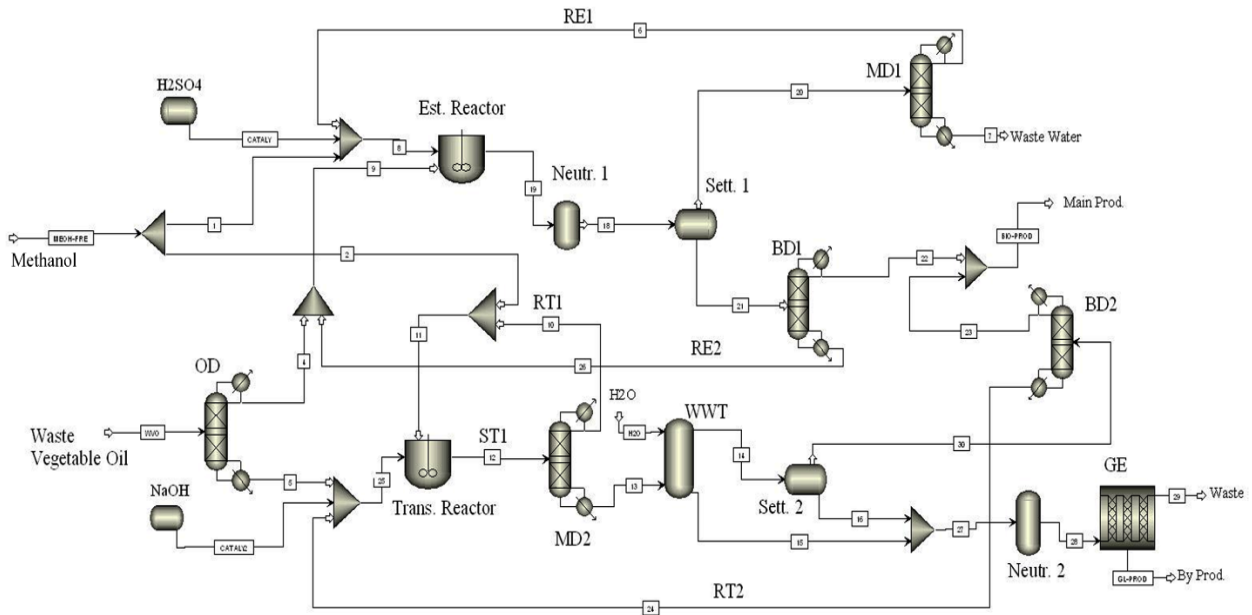


Figure 1. The process flowsheet obtained from the conceptual design based on Douglas’s procedure (BD: Biodiesel Distillation column; GE: Glycerol Evaporator; MD: Methanol Distillation column; Neutr.: Neutralizer; OD: Oil Distillation column; Sett.: Settler and WWT: Water Washing Tower).

The transesterification reactor output stream (ST1) has a high volumetric flow for the high unreacted methanol. So, in order to reduce the downstream equipment size, methanol was separated by the MD2 distillation column and then recycled into the transesterification reactor by the RT1 stream. For the removal of the catalyst, biodiesel and glycerol products and unreacted Triolein were washed in the water washing tower (WWT).

After the separation of organic and aqueous phases, the organic phase (biodiesel and unreacted Triolein) enters the BD2 separation column producing biodiesel and the RT2

recycle stream. In order to concentrate the glycerol product, the aqueous phase (glycerol and washing water) enters the glycerol evaporator (GE). Similar interconnections can also be explained for the processing units in the esterification section of the production process.

After the general flowsheet determination, the stream and equipment characteristics were derived as a function of the selected design variables. For example, the following equations represent the molar flows of methanol recycle streams (mol/h) in the esterification and transesterification sections.

$$RE1 = \left(\frac{(PBC)(XFO)}{XFO + 3S_T(1 - XFO)} \right) \left[\frac{MRE}{X_E} - 1 \right] \quad (7)$$

$$RT1 = \left(\frac{(PBC)(1 - XFO)}{XFO + 3S_T(1 - XFO)} \right) \left[\frac{MRT}{X_T} - 3S_T \right]$$

where S_T denotes the selectivity of the transesterification reaction (Table 1). The similarity of these equations is noticeable. Also, Equation (8) shows the required

transesterification reactor volume (m^3) to get the desired conversion (X_T) for a specific molar ratio (MRT).

$$\text{TRV} = \left(\frac{(\text{PBC})(1 - \text{XFO})\tau_T}{(\text{XFO} + 3S_T(1 - \text{XFO}))} \right) \left[\frac{9.58 \times 10^{-4} + 4.0265 \times 10^{-5}(\text{MRT})}{\text{XT} + 9.67 \times 10^{-4}S_T} - 9.58 \times 10^{-4} \right] \quad (8)$$

where τ_T (as a result of the transesterification reactor model) is the required residence time to achieve the XT conversion. Meanwhile, the following major decisions were made in this conceptual design:

1. It has been demonstrated that in the presence of the acid catalyst, the transesterification reaction is about 4000 times slower than that of the alkaline one [24]. Thus, in the esterification reactor, Triolein behaves as an inert component. Owing to this, in the present investigation, in contrast to the traditional processes, the process feed was decided to enter into the separation section (Oil Distillation column, OD) in order to remove FFA from the Triolein feedstock. This will reduce the size and capital cost of the esterification reactor. This reduction in size and capital cost is quite considerable for high FFA feedstocks. Another advantage of such decision is that by removing the FFA before the transesterification reactor, the chance of soap formation in the presence of NaOH would be highly reduced [10].
2. All distillation column models, excluding OD, will have light key molar recovery and the distillate purity of 99 %. The maximum recommended level of FFA in the transesterification reactor entrance has been reported as 0.5-3 wt % [25, 26]. Therefore, the bottom product of the OD column has only 3 mol % (1 wt %) of FFA.
3. Biodiesel and glycerol are thermally decomposed above 250 °C and 150 °C respectively [10, 27]. Therefore, the

vacuum conditions were decided to be applied in some process unit operations to keep the temperature low enough.

4. Catalyst amounts were selected in the suggested amounts by Canakci [15]. In the present work, H₂SO₄ and NaOH were used as acidic and alkaline catalysts respectively.
5. The materials of construction (carbon steel or stainless steel) required for the main processing units were selected according to the content of acid or base in the process fluids.
6. Kramer's equation and the experimental data reported by Chuang [28], were applied in the water washing tower modeling.
7. Guthrie's correlations were used for the equipment costing [17]. Although, these equations were updated using Marshall and Swift (M&S) cost index.
8. Glycerol, a valuable byproduct, was decided to have 85 wt % of purity.

The size and cost of the equipments and also the stream characteristics were determined as the functions of the selected design variables. The production rate varied from 370 (910 ton/yr) to 4370 mol/h (10750 ton/yr). For further investigations [29], the lower bound was selected so that both batch and continuous processes will be allowed to be used for such capacities [17]. This will allow a comparison between the results of batch and continuous processes. The upper bound, however, was selected arbitrarily. In such capacities, only continuous processes are

suggested [17]. The FFA mole fraction in the process feed varied from 0.05 to 1.00.

Canakciet al. [15] used a 20:1 molar ratio of methanol to FFA for the esterification of yellow grease (FFA < 15 wt %) and a 40:1 molar ratio for the esterification of brown grease (FFA > 15 wt %). Zhang et al. [5] reported a 6:1 molar ratio of methanol to crude oil in the esterification of a feedstock with 6 wt % of FFA. Also, Lin et al. [30] used a 6:1 molar ratio of methanol to oil for the biodiesel production from crude rice bran oil. The main fatty acids of rice bran oil were composed of palmitic acid (16 %), oleic acid (41 %) and linoleic acid (38 %). The oil had an initial acid value of 40 mg KOH/g, corresponding to a FFA level of 20 wt %, which is far beyond the 1 % limit for the satisfactory transesterification reaction using the alkaline catalyst. In the present work, the molar ratio of methanol to FFA (MRE) was varied from 1:1 to 41:1. The lower ratio (i.e. 1:1) is the stoichiometric ratio in the esterification reaction, but 41:1 is the maximum ratio with a sensible increase in the esterification reaction conversion (Table 1). Also, by the assumption of a single stage reactor, the esterification conversion was varied from zero to XE_{Max} . According to Table 1, XE_{Max} is a function of the molar ratio of reactants in the esterification reactor (MRE).

The experimental studies reported different molar ratios of the reactants in the transesterification reactor [3, 7, 12, 19, 30-32]. The previously published studies used the same molar ratios in the commercial scale studies, while it is necessary to optimize this variable taking into account the technical and economic considerations. For example, Zhang et al. [9] used a 6:1 ratio for a commercial scale production (8000 ton/yr). But in the

present work, this variable (MRT) is varied from 3:1 to 9:1, where, the 3:1 ratio is the stoichiometric molar ratio and 9:1 is the maximum ratio with a sensible increase in the reactor conversion. For example, according to Table 1, the conversion is 93 % in a 7:1 ratio. This conversion rises to 96 % by increasing the molar ratio to 8:1. But by increasing the molar ratio to up to 9:1, the conversion increases only by 1 %. Finally, similar to the XE, the transesterification reactor conversion (XT) was varied from zero to XT_{Max} (see Table 1).

The process modeling and direct search procedure were used to search the optimum values of the selected design variables in the above mentioned 6D solution space. The present process model was also able to find the best process flowsheet, estimate the optimum conditions and determine the size and cost of the process equipments.

3. Results and discussion

Figure 2 shows the EP profile as a function of the production rate and FFA mole fraction.

The following points can be concluded from this figure:

1. The sensitivity of the EP to the production rate decreases in the high content of FFA. This is in agreement with the previously published data [5] that reveals that for a feedstock with 6 wt % of FFA, the production rate is an effective parameter in the process EP. However, as Figure 2 shows, it is expected that the effect of this parameter reduces at higher contents of FFA.
2. Kitchen drains include greases that their FFA content ranges from 50 to 100 wt % [10]. According to Figure 2, if these greases are blended with low FFA

feedstocks to produce a feed containing 50 mol % of FFA (24 wt %), the obtained feed would have an EP equal to that of the feedstocks with 10 mol % of FFA (it means using the cheaper feed with the higher profit).

3. The sensitivity of EP to FFA increases at higher contents of FFA (compare the slope of 5 curves for the range of the

mole fractions between 0.1 and 0.45 with the slope of these curves between 0.5 and 1.00).

4. The optimum value of XFO is insensitive to the production rate and appears always around 0.5.

5. The sensitivity of EP to the content of FFA decreases at lower production rates.

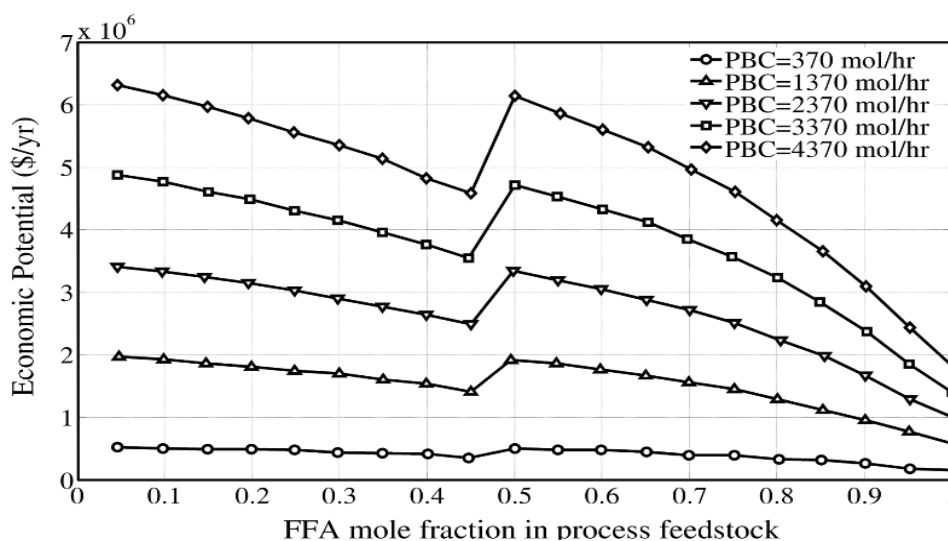


Figure 2. Economic potential as a function of the production rate (PBC) and FFA mole fraction.

After the process optimization, the following optimum conditions were found: the mole fraction of FFA, 0.50 (24 wt %); the esterification conversion, 82-89 % (depending on the different production rates); the molar ratio of reactants in the esterification reactor, 11:1; the transesterification conversion, 96 %; the molar ratio of reactants in the transesterification reactor, 8:1 and the maximum possible practical value for the process production rate. A similar optimum value of the production rate has been reported by Zhang [5] for the production of biodiesel from a feed containing 6 wt % of FFA. The optimum value of the mole fraction of FFA (XFO) in the present work shows that the best feedstocks can be located in the brown grease region (FFA > 15 wt %). This result is similar

to the previous results published by Canakci [15] where the estimated costs of the final product for this clean alternative fuel from virgin oils and yellow and brown greases were \$0.418, \$0.317 and \$0.241/L respectively.

In the present work, a single stage esterification reactor was employed and the optimum value of XE was obtained as 82-89 % (depending on the different production rates). Canakci et al. used a two stage reactor and an intermediate water removal for the production of biodiesel from yellow and brown greases [15]. They reported the 95 and 98 % conversion of esterification for yellow and brown greases respectively. Also, Zhang et al. [9] published a 100 % conversion for the esterification reaction in

their simulation. Similarly, they also used a two stage reactor for a feed containing 6 wt % of FFA.

In the present model, the optimum value of MRE was found as 11:1, while Canakci et al. [15] used 20:1 and 40:1 ratios for yellow and brown greases respectively. Nonetheless, Zhang et al. [9] used a 6:1 molar ratio of methanol to crude oil for the esterification reaction. They applied a two-stage reactor for a feed containing 6 wt % of FFA. As mentioned in section 1, in the previous studies, the operating conditions of the process were similar to a thoes of the chemist's recipe, while in the commercial scale production, it is necessary to optimize these conditions taking into account the technical and economic considerations. The optimum values claimed in the present research were found with paying due attention to the operating conditions in the industrial scale. This is the main difference of the present research and the previous studies [3-5, 9, 10, 14, 15, 30, 33] and also the main reason for the difference between the present and already reported optimum values for the selected design variables.

It is noteworthy to mention that according to Table 1, for a transesterification conversion more than 90 % and a 6:1 ratio of MRT, a

multi stage reactor is required. Therefore, it is impossible to obtain a conversion more than 90 % with a 6:1 MRT in a single stage reactor [22]. These results are similar to the previous results published by Sheehan [33]. Their model assumed a two-stage reactor scheme, consistent with the design of Kansas City facility; in which 90 % conversions were achieved at each stage (the overall conversion was equal to 99 %). Nonetheless, Zhang et al. [9] used 96 % and 6:1 for XT and MRT respectively, to simulate a single stage transesterification reactor. The optimum values of the respective variables in the present study were found as 96 % and 8:1.

In order to understand the sensitivity of each design variable, it was tried to fix five variables and change the sixth. Figures 2 to 5 show the sensitivity of all six variables. As Figure 3 shows, the relationship between EP and the production rate is completely linear. This result has a good agreement with the previous results published by West [34]. Therefore, the production rate should be set at its maximum possible practical value. Also, this figure reveals that the break-even point at the optimum values of the design occurs at the production rate of 157 ton/yr and that production at the rates lower than this value has no economic benefit.

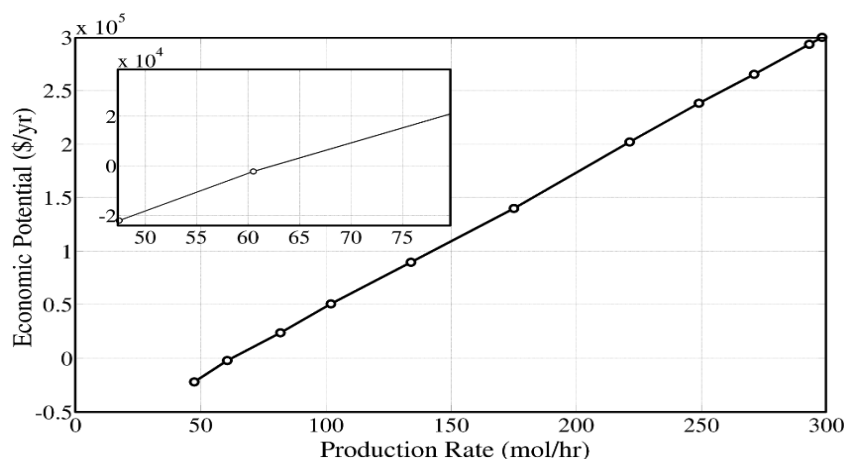


Figure 3. Economic potential as a function of the production rate.

Also, as shown in Figure 4, increasing the transesterification conversion from 95 to 96 % does not require a change in the molar ratio as it has not reached to the equilibrium conversion. However, for increasing the conversion from 96 % to 97 %, it is required to increase the molar ratio from 8:1 to 9:1, due to the fact that the equilibrium conversion (96 %) is to be passed. This, in turn, causes a sharp fall in EP at that region.

ratio (MRT) from 8:1 to 7:1, the transesterification conversion decreases by 3.13 %, while by increasing the molar ratio from 8:1 to 9:1, the conversion increases only by 1 % (see Table 1). Therefore, increasing MRT is more effective on EP than decreasing it around the optimum region. The similar behavior can also be explained for the conversion and molar ratio in the esterification reactor (i.e. XE and MRE).

Figure 5 shows that by decreasing the molar

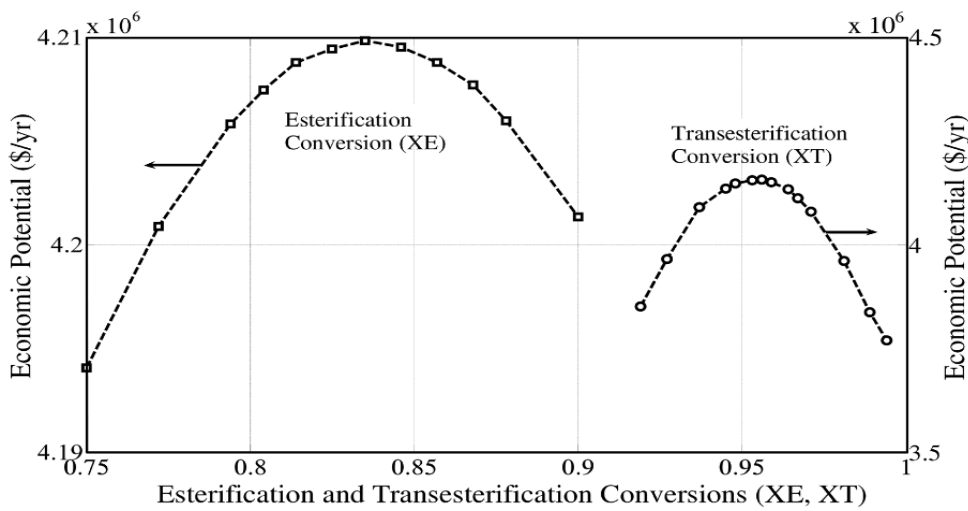


Figure 4. Economic potential as a function of esterification (\square) and transesterification (\circ) conversions.

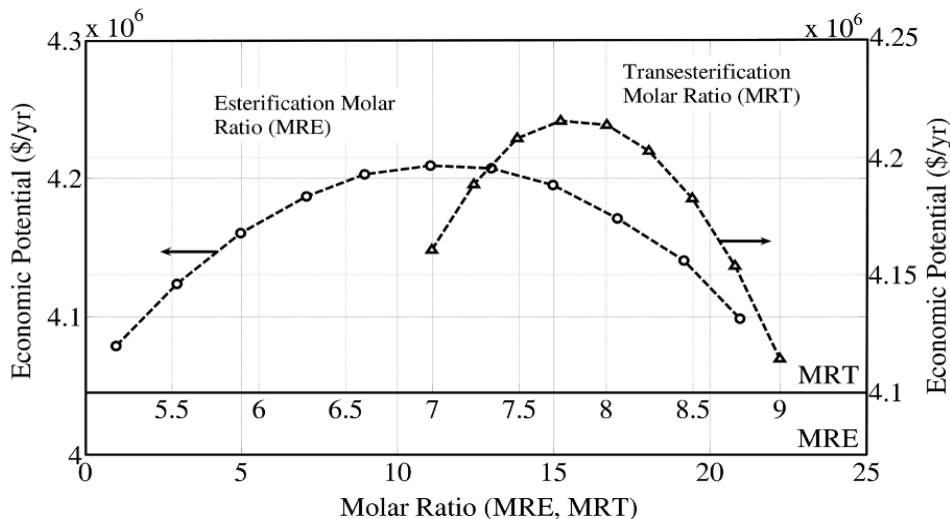


Figure 5. Economic potential as a function of esterification (\circ) and transesterification (Δ) molar ratios.

4. Conclusions

Cheaper feedstocks for the biodiesel production include undesirable impurities

such as FFA that increase the complexity of the process. Thus, these materials require techno-economic optimizations. In the

previous studies, the operating conditions of the process were similar to those of the chemist's recipe, while in the commercial scale production, it is necessary to optimize these conditions taking into account the technical and economic considerations. In the present research, a continuous process for producing biodiesel from high FFA feedstocks was optimally designed at the conceptual stage. Firstly, the suggested procedure by Douglas [17] and the general rules of thumb (heuristic methods) were used to eliminate undesirable alternative processes. Then, by considering the economic potential as an objective function, the optimum mole fraction of FFA was obtained about 0.50. Also, the results revealed that in esterification and transesterification reactors, the optimum value of conversion and molar ratio of reactants were found as 82-89 % (depending on the different production rates), 11:1 and 96 %, 8:1 respectively. The relationship between EP and production rate was completely linear. Therefore, the maximum possible practical value of the production rate was obtained as the optimum value of the process production rate. Also, a proper conformity between the present study and the previously published results indicates the accuracy of the conceptual approach (Douglas's procedure) to the process design at the synthesis stage. Further, it is necessary to optimize the operating conditions of the process taking into account the technical and economic considerations in the commercial scale production.

Nomenclature

EP	Economic potentials [$\$/\text{yr}^{-1}$].
MRT	Molar ratio of the reactants in the transesterification reactor.
MRE	Molar ratio of the reactants in the esterification reactor.

PBC	process production rate [mol h^{-1}].
S_E	Selectivity of the esterification reaction.
S_T	Selectivity of the transesterification reaction.
TRV	Transesterification reactor volume [m^3].
V	Reactor volume [m^3].
XE	Conversion of the esterification reaction.
XFO	FFA mole fraction in the process feedstock.
XT	Conversion of the transesterification reaction.

Greek variables

τ	Reactor residence time [s].
v	Entrance volumetric flow [m^3s^{-1}].

Abbreviations

A	Alcohol, Methanol.
BD	Biodiesel Distillation column.
DG	Diglycerides.
E	Methyl Esters, Methyl oleate or Biodiesel.
FFA	Free Fatty Acids.
GE	Glycerin Evaporator.
GL	Glycerin.
MD	Methanol Distillation column.
MG	Monoglycerides.
M&S	Marshall and Swift cost index.
O	Oleic acid.
OD	Oil Distillation column.
TG	Triglycerides.
W	Water.
WWT	Water Washing Tower.

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