Iranian Journal of Chemical Engineering

Journal Homepage: www.ijche.com

pISSN: 1735-5397
eISSN: 2008-2355

Regular Article

Conceptual Design of a Batch Process for the Production of Biodiesel from High Free Fatty Acid Feedstocks

A. Mohammadi[1*], B. Ghobadian[2]

[1] *Department of Chemical Engineering, Faculty of Engineering, University of Qom, P.O. Box: 37161-46611, Qom, Iran*

[2] *Department of Agricultural Engineering, TarbiatModares University, P.O. Box: 14155-111, Tehran, Iran*

ARTICLE INFO

Article history:
Received: 2022-04-24
Accepted: 2022-08-10
Available online: 2022-08-10

Keywords:
Batch Process,
Biodiesel,
Conceptual Design,
Gantt Chart,
Optimization,
Process Cycle Time

ABSTRACT

A batch process was developed for the production of biodiesel from high free fatty acid feedstocks. The mixed-integer nonlinear programming (MINLP) problem, caused due to applying the hierarchical procedure together with Malone's algorithm for the conceptual design, was solved. Meanwhile, the optimum states of major process parameters such as the utilization of the process equipment, paralleling, splitting, and the merging of unit operations, the process cycle time (CT), and the combination of batch and continuous units were determined. Based on the present optimization study, the optimum value of the process cycle time and the optimum number of the esterification reactors in series were obtained as 3.257 h/batch and 3 stages respectively. The batch process was found to be suitable for a capacity of less than 260 tons/yr, while the continuous process was suitable for a capacity of greater production rates. The results showed that the production rate had a direct effect on the economic potential of the process and that it should be set at its maximum possible practical value. Also, the break-even point for the optimum state occurred at the production rate of 130 tons/yr.

DOI: 10.22034/ijche.2022.339186.1432 URL: http://www.ijche.com/article_154660.html

1. Introduction

Air pollution is a major global environmental problem. Since the diesel engines of heavy-duty vehicles emit a huge amount of NOx and particulate matter, a clean alternative fuel is highly demanded [1, 2]. Research into biofuels, as environmentally friendly fuels, have beengoing on for more than 100 years [3-6]. Among liquid biofuels, the biodiesel derived from renewable lipids is gaining acceptance and market share as the diesel fuel in Europe and the United States [7-10].

*Corresponding author:Mohammadi.a@qom.ac.ir (A. Mohammadi)

Nonetheless, the high price of biodiesel (about 3 to 5 times the price of petrodiesel) limited its commercial use. Approximately 60-95 % of the total production cost of biodiesel arises from the cost of its raw materials [11-13]. To solve this problem, the use of waste cooking oils or animal fats has been suggested. However, these cheaper feedstocks include undesirable components such as water and free fatty acids (FFA), which increase the process complexity and tribulation. Therefore, the use of these feedstocks requires simultaneous economic and technical optimization.

Only in a few studies it has been attempted to develop an optimal batch plant for producing biodiesel from waste materials such as used frying oils or animal fats. Canakci et al. built a 190-liter batch pilot plant, which could process these materials using an acid-catalyzed pretreatment stage followed by an alkaline catalyzed transesterification [14]. They reported the case studies of the pilot-scale production of biodiesel from virgin soybean oils and yellow and brown greases with 9 and 40 wt % of FFA respectively. Also, a pilot-scale production has been reported by Zhang for the production of biodiesel through the transesterification of the waste cooking oil plus an excess amount of methanol in the presence of sulfuric acid catalyst [15]. Unfortunately, the previous studies focused upon the use of the process operating conditions that were often similar to the chemist's recipe, while in the commercial-scale production, it is necessary to optimize the operating conditions taking into account the technical and economic considerations. Therefore, in this study, the emphasis was placed on the conceptual design of an optimal batch process with both economic and technical considerations. Eventually, this batch process was compared with an optimum continuous process based on the process profitability as a function of the production rate.

The conceptual design covers that stage in the evolution of a final design where enough information is available to enable the reliable estimates of capital and operating costs. This is different from the final stage of the chemical process design, where the specifications are exactly enough to enable purchasing the equipment and beginning the construction of plant equipment [16, 17]. The conceptual design is very complicated because the process of synthesis is very open-ended. Thus, the development of a general and systematic procedure for all possible chemical processes is impractical. Douglas presented a procedure for the conceptual design of chemical processes. His hierarchical algorithm considers different parts of the process in an order [16]. This algorithm is applicable for continuous processes in the absence of non-Newtonian fluids and solid phases. In principle, Douglas's methodology can also be applied to the batch process design, although there are significant problems, e.g. the interaction of the process design with scheduling and pieces of equipment that perform multiple duties.

Batch and continuous processes are both designed based on the same physical and chemical laws and use the same unit operations. However, they are fundamentally different in the nature of the process design and development. The batch processes are more complex and difficult than the continuous ones and a continuous process flowsheet enjoys a much simpler logic [18]. Nevertheless, the industry and academic community have found it very difficult to come to terms with the nature of the batch process design problem. Very little has been said about the systematic procedure for the conceptual design of the batch processes [19]. Some academic studies have been reported about the conceptual design of batch processes. A mathematical procedure and a super-structure model to improve the initial design of batch (or semicontinuous) processes have been reported by Balchen [20]. He used a mixed-integer nonlinear programming (MINLP) model to obtain the optimal process network. However, the most commonly used method is the systematic approach that has been developed by Malone [21]. Malone's approach considers various cycle times in the synthesis process steps (a reasonable assumption). Therefore, in the present study, the batch process was optimized using the procedure proposed by Malone.

2. Design and optimization algorithm

The selection of design variables is one of the most important steps in the conceptual design method. The variables must be independent and beget a tradeoff in the selected objective function with their changes. In this study, the economic potential (EP) was selected as the objective function of the process optimization.

EP = [Revenue] - [Raw materials costs + Equipment costs + Utility costs]

The dominant design variables for this process include the mole fraction of FFAs in the process feed, conversion and molar ratio of reactants in the esterification and transesterification reactors, batch scheduling, utilization of equipment, production rate, batch size (i.e. the amount of the final product made in one batch), process cycle time (CT), mode of the process (continuous, batch or semicontinuous), equipment merging and splitting, parallel or merged parallel units, intermediate storage tanks, and their optimum location. The optimum state (or value) of these variables can be determined by minimizing the total production costs or maximizing the economic potential. This process design has a complex optimization problem involving continuous variables (e.g. batch size or reaction conversion), integer or discrete variables (e.g. numbers of intermediate storage tanks or parallel units), and logical variables (e.g. intermediate storage position or combining procedure of batch and continuous unit operations). Therefore, it leads to an MINLP problem, which we tried to solve in the present study.

For simplicity, it is suitable to split this problem into two parts. In the first part, a continuous process (if possible) is designed and the optimum values of some design variables are determined. In the next part, this optimum continuous process is converted into a batch process. Then, all possible alternatives to this batch process are investigated to optimize other design variables. Considering Malone's procedure, the following steps were resulted for the conceptual design and optimization of a batch plant to produce biodiesel from multiple feedstocks such as waste cooking oils, animal fats (crude fats), or trapped greases (waste fats from the traps under kitchen drains).

Step 1: a continuous process is designed and optimized. This section was carried out in the present authers' previous study [22]. Douglas's procedure was used for the continuous process design and optimization. For this purpose, the suggested methods for the production of biodiesel such as the thermal cracking, application of cosolvent, supercritical alcohol technology, transesterification, etc. [23, 12] were evaluated. As a result, the esterification of FFAs in the presence of acid catalysts (e.g. H_2SO_4) followed by the transesterification of oils (or fats) in the presence of alkali catalysts (e.g. NaOH) was identified as the most promising method. Also, it has been demonstrated that the transesterification reaction in the presence of an acid catalyst is about 4000 times slower than the same in the presence of an alkaline catalyst [24]. Thus, in the esterification reactor, triglycerides behave as inert components. So, in the present work, unlike in the traditional processes, the process feed was decided to enter into the separation section to remove the FFA from the triglycerides. Our findings showed that by making this change the size of the required esterification reactor and its capital and operating costs could be reduced, which were quite considerable for high FFA feedstocks. Also, by removing FFAs before the transesterification stage, the chance of soap formation in the presence of an alkali catalyst (such as NaOH or KOH) is highly reduced in the transesterification reactor. By considering EP as the objective function of the process optimization, the optimum mole fraction of FFA was obtained as about 50 %. Also, the results revealed that in the esterification and transesterification reactors, the optimum values of the conversion and molar ratio of reactants were 82-89 % (depending on the different production rates), 11:1 and 96 %, 8:1 respectively. It was found that EP increased linearly as the production rate increased. Therefore, the production rate should be set at its maximum possible practical value. The break-even point for the optimum values of the variables, as mentioned above, occurred at 157 tons/yr of the production rate. Figure 1 shows the obtained continuous process flowsheet, based on Douglas's procedure.

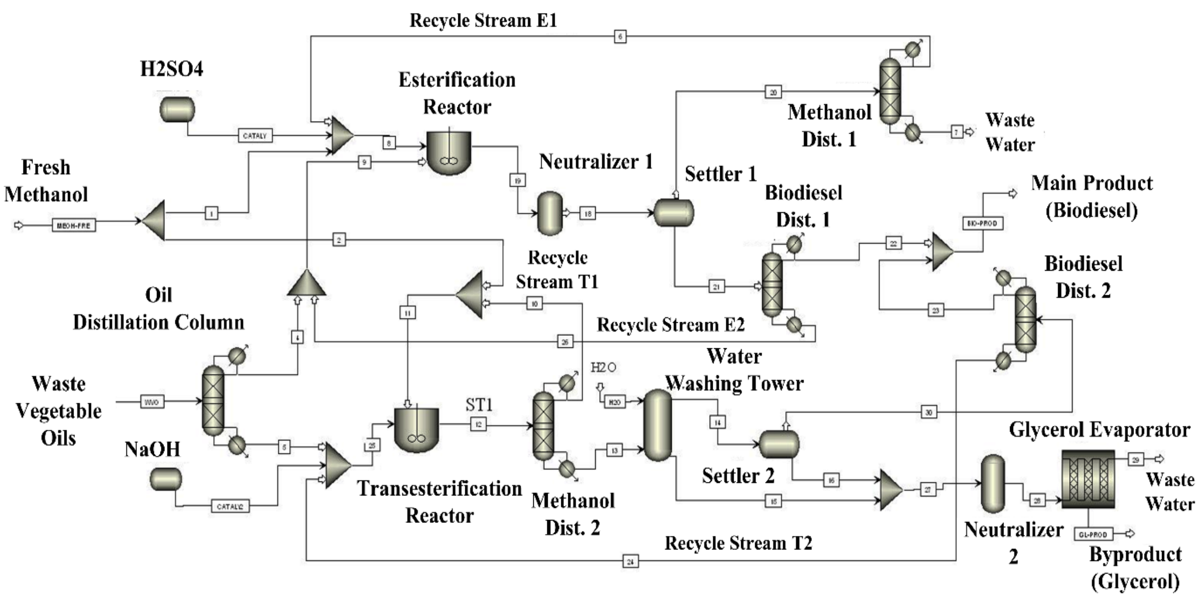

Figure 1. The optimum continuous process flowsheet.

Step 2: each continuous unit is replaced by a batch unit and the optimum value of the process CT is calculated by maximizing EP of the process or minimizing the total production costs.

The production process is a set of unit

operations assigned to each of them, different tasks of a given recipe. It is often convenient to operate the process cyclically, if it is used to produce a series of identical batches (a single product process as in the present case). The process CT is then the time between the completion of batches.

Step 3: the production of successive batches are overlapped to increase the utilization of equipment. At this step, the batch CT must be at least equal to required residence time of the longest unit operation. The rest of the equipment, except those of the limiting step, are then idle for some fraction of the batch cycle.

Step 4: merging of equipment is studied to optimize the overall utilization of the equipment.

Step 5: the parallel or merged parallel units are applied to optimize the process CT.

Step 6: the continuous and batch unit operations are combined to maximize the process EP.

Step 7: the splitting of equipment is investigated to optimize the process cycle time.

Step 8: the intermediate storage tanks are added to optimize the scheduling of batches.

For simplicity, all of the schedules considered in this study involved transferring the material from one operation to the storage tank or from the storage tank to a unit operation without any time delay. This is known as zero-wait transfer (ZWT) [25]. In addition, as mentioned above; the present batch process was designed as a single-product process. Therefore, the equipment do not need to be cleaned when changing from one batch to another. This act has a significant effect on the process CT (it means a batch process with higher profit). Also, another issue to be mentioned is that for the special case of the multiproduct plant that the process equipment need to be cleaned as the products are changed in the batch production system. This produces a significant amount of waste material from the process, leading to an environmental problem, which can decrease the process EP.

Gantt chart is one of the most commonly used tools in the batch process design and optimization. In this study, the Gantt chart is used as a type of bar chart as an equipment occupation diagram, in which time is the abscissa and the ordinate has an entry for each equipment item. Accordingly, it can show the configuration of units, utilization of equipment, process cycle time, required residence times, and also bottleneck unit.

3. Results and discussion

3.1. Continuous process design and optimization

The detailed design procedure and the optimum values of major design variables have been reported in the present authers' previous study [22].

3.2. Replacement of continuous units by batch units

The optimized continuous process, as a result of the previous step, was used in this step. It was assumed that the plant was able to process 2000 kg/day of waste cooking oils or animal fats (equivalent to 680 tons of biodiesel per year). Both batch and continuous processes are allowed to be used for such capacities [16]. So, the best mode of the process can be selected after a detailed design of these alternatives. The characteristics of the continuous process equipment were determined at the optimum values of design variables using the suggested process model in the present authers' previous study. Based on this model, the production rate of 680 tons/yr led to an EP of $302230/yr for the optimized continuous process. The specifications and prices of raw materials, products, and required utilities are listed in Table 1.

Table 1

The costs of the raw materials, products, and utilities.

Items	Unit	Price
Chemicals		
Cooking oil (virgin, with 0.5-3 wt % FFAs)	$/ton	440
Waste cooking oil (yellow grease, ≤ 45 wt % FFAs)	$/ton	290
Waste cooking oil (brown grease, > 45 wt % FFAs)	$/ton	200
Biodiesel (99 mole % purity)	$/ton	500
Glycerin (85 wt % purity)	$/ton	730
Methanol (99 wt % purity)	$/ton	165
NaOH (catalyst)	$/ton	4000
H_2SO_4 (catalyst)	$/ton	60
Utilities		
Cooling water	$/m^3	0.07
Process water (washing water in WWT tower)	$/m^3	0.05
Steam (superheated, high pressure, 520 °C)	$/ton	12
Steam (superheated, medium pressure, 220 °C)	$/ton	8

At this step, each continuous unit was replaced by a batch unit. In batch processes, the determination of the batch size is the fundamental step for the sizing of requied equipment or EP estimation. The batch size is a function of the process CT or numbers of batches, where these variables are dependent on the required residence times of the each operation [18]. Also, the residence times are a function of the equipment characteristics such as their capacity. So, it is clear that there is a calculation loop and thus a trial and error calculation is inevitable. In the first trial, it was assumed that the required residence times of batch units could be calculated using the characteristics of continuous units. Meanwhile, some equations were derived for the estimation of the residence time. For example, Equation (1) was applied to calculate the required residence times of batch distillation columns as a function of feed and distillate specifications:

$$t_D = \left(\frac{F}{D_{av.}}\right)\left[1 - \exp\left(\left(\frac{-1}{\alpha - 1}\right) \times \left(\mathrm{Ln}\left(\frac{z}{x_w}\right) + \alpha\,\mathrm{Ln}\left(\frac{1 - x_w}{1 - z}\right)\right)\right)\right] \quad (1)$$

where F = the feed amount (mol), D_{av} = the average molar flow rate of distillate (mol/h), z = the light component mole fraction in the process feed, x_w = the light component mole fraction in the bottom product, and α is the relative volatility.

For modeling the batch distillation column, it was assumed that the batch distillation pots were charged initially with the mixture to be separated and that there was an outlet for the product to be collected (simple distillation configuration). The columns were operated using a constant reboiler duty strategy and started up with the cyclic operation technique. The cyclic operation technique was characterized by two modes of operation, called transient total reflux and stripping. During the total reflux portion of the cycle, liquid reflux was returned to the column but no product was withdrawn. Further, during the stripping portion of the cycle, the product was withdrawn but no reflux was returned to the column. Thus, the distillate product valve was open for a fixed period (t_O) to withdraw the distillate and was closed for a fixed time (t_C) to return the reflux to the column. Therefore, for a total batch operating time (t_D), the total opening time (t_{open}) for the distillate product valve can be given by the following equation [26].

$$t_{open} = \left(\frac{t_O}{t_O + t_C} \times t_D\right) = \left(\frac{t_D}{1 + R_{exp}}\right) \tag{2}$$

where R_{exp} is the reflux ratio setting. Assuming the continuous flow of the reflux and distillate rates throughout $t=t_O+t_C$, the average distillate rate can be expressed as:

$$D_{av.} = \left(\frac{t_O}{t_O + t_C} \times D\right) = \left(\frac{V_{exp} \times t_O}{t}\right) \tag{3}$$

where V_{exp} is the vapor rate into the condenser and D is the distillate rate, which is equal to V_{exp} when the valve is open. Also, the average reflux rate can be expressed as follows:

$$L_{av.} = \left(\frac{t_C}{t_O + t_C} \times L\right) = \left(\frac{V_{exp} \times t_C}{t}\right) \tag{4}$$

where L is the reflux rate, which is equal to V_{exp} when the valve is closed. Now, an average external reflux ratio over a period of time (t) can be defined as:

$$R_{av.} = \left(\frac{L_{av.}}{D_{av.}}\right) \tag{5}$$

Also, it was assumed that, in the washing tower, water was sprayed in a spherical form with an optimum (i.e. 3-6 mm) diameter [27]. The water particles are spherical and behave like rigid spheres. Therefore, the average velocity of free-falling can be estimated by the Stoke's law [28] as follows:

$$U_P = \left(\frac{d_P^2(\rho_P - \rho_m)}{18\ \mu_m} g\right) \tag{6}$$

where d_P = the diameter of the water particle, ρ_P = the density of water, ρ_m = the density of the mixture and μ_m = the viscosity of the mixture. Equation (7) was derived to estimate the required residence time in the washing step (t_w) as a function of the specification of the mixture, the tower's height (H_w), and the path diversion on the tower's trays.

$$t_w = \left(\frac{H_w}{1800\ U_P} + 0.5\right) \tag{7}$$

Modeling the esterification and transesterification reactors was used to estimate the required residence times in these reactors. The suggested kinetics by Tesser et al. [29] and Noureddini et al. [30] were used for these models. The temperature, molar ratio of the reactants, mixing intensity, and conversion were selected as the major variables and their effects on the required residence times were studied. The models were prepared with the help of the MATLAB® software and other related software tools. Noureddini et al. [30] reported the transesterification reaction of vegetable oils by the following three steps:

$$\text{Triglycerides (TG)} + \ CH_3OH\ (A) \overset{K1,K2}{\Longleftrightarrow} \text{Diglycerides (DG)} + \ R_1COOH_3(E)$$
$$\text{Diglycerides (DG)} + \ CH_3OH\ (A) \overset{K3,K4}{\Longleftrightarrow} \text{Monoglycerides (MG)} + \ R_2COOH_3(E) \tag{8}$$
$$\text{Monoglycerides (MG)} + \ CH_3OH\ (A) \overset{K5,K6}{\Longleftrightarrow} \text{Glycerin (GL)} + \ R_3COOH_3(E)$$

The overall reaction is as shown below:

$$\text{Triglycerides (TG)} + \ 3\ CH_3OH\ (A) \overset{K7,K8}{\Longleftrightarrow} \text{Glycerin (GL)} + \ 3\ R_1COOH_3(E) \tag{9}$$

They also suggested the following rate equations:

$$\begin{aligned}
\frac{d[TG]}{dt} &= -K_1[TG][A] + K_2[DG][E] - K_7[TG][A]^3 + K_8[GL][E]^3 \\
\frac{d[DG]}{dt} &= K_1[TG][A] - K_2[DG][E] - K_3[DG][A] + K_4[MG][E] \\
\frac{d[MG]}{dt} &= K_3[DG][A] - K_4[MG][E] - K_5[MG][A] + K_6[GL][E] \\
\frac{d[GL]}{dt} &= K_5[MG][A] - K_6[GL][E] + K_7[TG][A]^3 - K_8[GL][E]^3 \\
\frac{d[E]}{dt} &= K_1[TG][A] - K_2[DG][E] + K_3[DG][A] - K_4[MG][E] + K_5[MG][A] - K_6[GL][E] \\
&\quad + K_7[TG][A]^3 - K_8[GL][E]^3 \\
\frac{d[A]}{dt} &= -\frac{d[E]}{dt}
\end{aligned} \tag{10}$$

Also, Tesser et al. [29] studied the kinetics of the esterification of oleic acid with methanol in the presence of an acid catalyst.

$$\text{Oleic Acid (O)} + \ \text{Methanol (A)} \overset{Kc,Kr}{\Longleftrightarrow} \text{Methyl Oleate (E)} + \ \text{Water (W)} \tag{11}$$

They also reported the following rate equation by the assumption of the second-order equilibrium reaction.

$$r = K_c x_O x_A C_{cat.} \left(1 - \frac{1}{K_e}\frac{x_E x_W}{x_O x_A}\right) K_e = K_c/K_r \tag{12}$$

where C_{cat} and x denote the concentration of catalyst and 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.

Then, the process CT was determined using the Gantt chart. The estimated CT was applied to calculate the required batch size. Now, it is possible to calculate the required residence times as well as the process CT at the next iteration. The maximum absolute allowable error of the solution was selected as 10^{-3}. Finally, the optimum value of the process CT was found as 13.67 h/batch.

The process EP was estimated using Guthrie's correlations [16], although they were updated by applying Marshall and Swift's (M&S) cost index. For example, installed column cost ($) can be estimated as:

$$\text{Shell: } \left(\frac{M\&S}{280}\right) \times 101.9\ D_d^{1.066} H_d^{0.802} \times (2.18 + F_C) \tag{13}$$

$$\text{Tray: } \left(\frac{M\&S}{280}\right) \times 4.7\ D_d^{1.55} H_d \times F_C \tag{14}$$

where H_d and D_d are the tower's height (ft) and diameter (ft) respectively, and F_C is the correction factor as a function of the column pressure and required material of construction. Finally, the production rate of 680 tons/yr led to an EP of $(-229800)/yr for this batch process. Therefore, the change of process mode from continuous to batch decreased EP by 176 %. Figure 2 shows the Gantt chart of this stage.

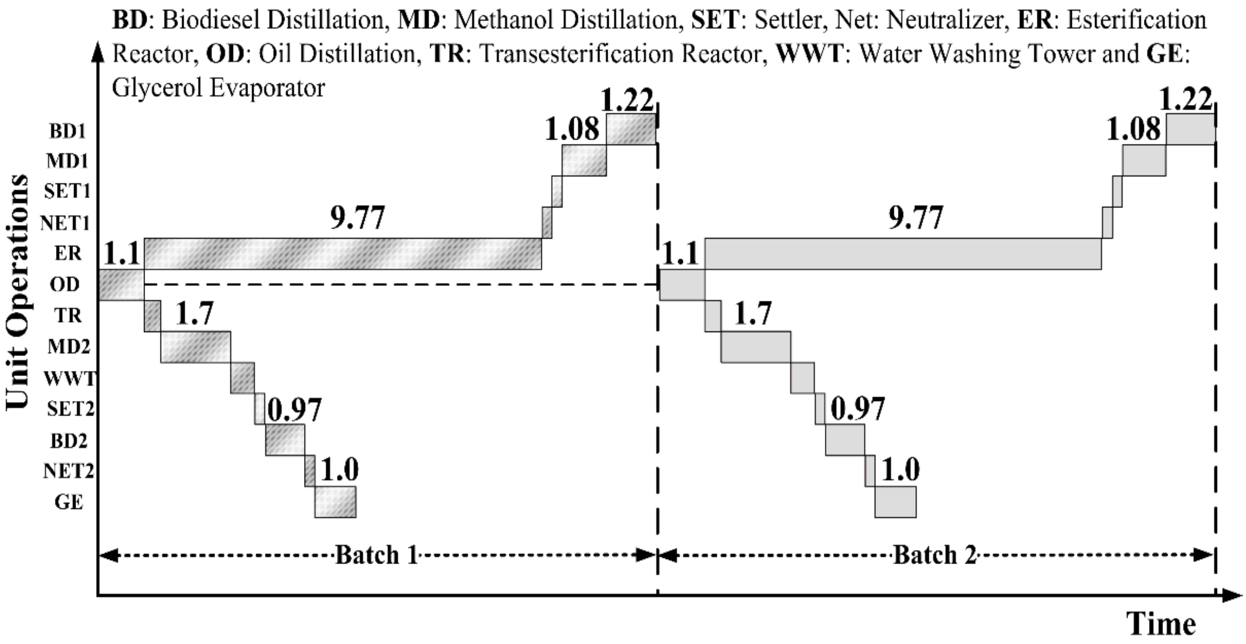

Figure 2. The Gantt chart of the batch process at a non-overlap state (the numbers indicate the required residence time for different units).

3.3. Overlapping technique

Figure 2 shows a sequential production schedule. At non-overlap status, the subsequent batches are only started once the previous batch is finished. This leads to the very poor utilization of the process equipment (CT=13.67 h/batch). It is well known that overlapping of subsequent batches can reduce the process CT. This is illustrated in Figure 3, where the subsequent batches are started as soon as the appropriate equipment becomes available. For overlapping batches, the process CT was decreased to 9.77 h/batch.

If a specified volume of production needs to be achieved over a given period, then the equipment in the process that used the overlapping batches (Figure 3) can in principle be 0.70 the size of the equipment for sequential production as shown in Figure 2. This change caused the increase in the process EP by 60 %. As a general rule of thumb, for the overlapping batches, the process CT is equal to the maximum required residence time of the process operations or the length of the longest step in the Gantt chart [20].

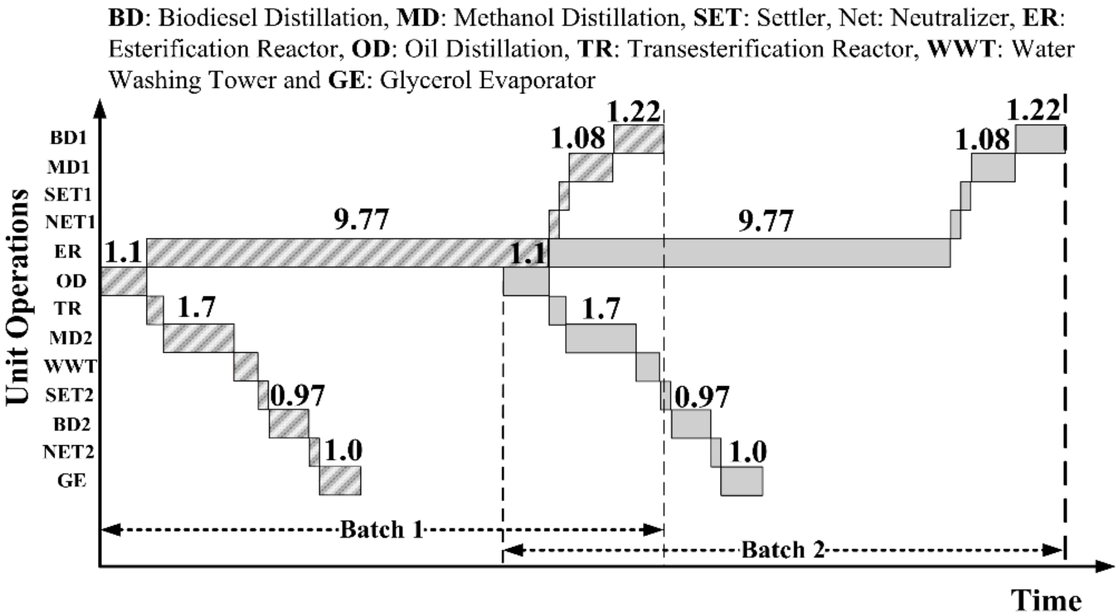

Figure 3. The Gantt chart of the batch process at the overlap state (the numbers indicate the required residence time for each unit).

3.4. Merging of equipment

Most of the techniques in the batch process optimization are applied to increase the utilization of the process equipment, of which the merging is the most commonly used method that leads to a significant decrease in the capital investment for the process. The merging of operations into the same equipment could be considered to replace the connections through space with the connections through time. Unit operations are merged when the operations are not limiting the process CT and also have similar size factors and mechanical specifications (such as the material of construction) [16, 18]. In this study, the size factor was defined as the capacity required for each unit per unit amount of the final product. The following alternatives were investigated to study the effect of this technique on the process scheduling.

Merging of esterification and transesterification reactors

Esterification and transesterification reactors satisfy the required merging conditions. Meanwhile, it is necessary to use an intermediate storage tank to adjust the performance of unit operations. It was observed that two different effective factors changed EP. Increasing the process CT from 9.77 to 10.19 h/batch caused a decrease in EP, whereas, on the other hand, the improvement in the utilization of reactors led to an increase in EP as well. Finally, this alternative decreased EP by 3.33 %.

Merging of the washing tower with BD2 column

Merging of the washing tower with BD2 column increased EP by 12.04 %, meanwhile the process CT remained constant.

Merging of MD1 and MD2 columns

Despite the increase in the process CT, this design alternative increased EP by 182 %.

3.5. Combination of batch and continuous units

In the next step, it was tried to optimize the batch process performance by a combination of the batch and continuous units. To do so, the following alternatives were studied. In practice, most batch processes are made up of a series of batch and semicontinuous units. A semicontinuous unit runs continuously with periodic startups and shutdowns. It is noteworthy to mention that this technique decreases the process flexibility and increases its complexity. Although, the present work was done at the conceptual stage, therefore the combination of batch and continuous units had no sensible effect on the screening of process alternatives. For the detailed design of a batch process, the complexity and flexibility of the studied process should be considered.

Continuous performance of MD1 and MD2 columns

The merging of MD1 and MD2 was studied in the previous section. For the continuous performance of these columns, it was necessary to give up the merging assumption. As mentioned above, the merging of these distillation columns increased EP by 182 %. But, the continuous performance of these columns increased EP by 230 %. So, it was suitable to give up the merging of MD1 and MD2 columns.

Continuous performance of WWT and BD2 columns

Similarly to the above case, this is also necessary to give up the merged state of the columns. It was found that the continuous mode of these unit operations decreased the process EP by 2 %.

Continuous performance of the glycerol evaporator

The continuous performance of the glycerol evaporator decreased EP by 3.3 %.

Continuous performance of the BD1 column

The continuous performance of the BD1 column increased EP by 87.5 %.

Continuous performance of ER and TR reactors

The continuous performance of ER and TR reactors also decreased EP by 15.7 and 17.43 % respectively.

Continuous performance of the OD column

The continuous performance of the OD column increased EP by 7.9 %.

In principle, it is necessary to locate the intermediate storage tanks to adjust the batch and continuous unit operations. Intermediate storage tanks for liquids should not be designed to operate with less than 10 % of inventory at minimum or more than 90 % full at maximum [25]. So, in this study, the volume ratio of liquid to the vessel was selected as 0.75 and the installed costs of tanks were assumed in the estimation of EP. Figure 4 shows the Gantt chart of this step of the batch process design. So far, the optimum value of EP was found as $222020/yr.

In the industrial practice, because of the startup and shutdown complications, it is preferred that distillation columns operate in the continuous mode. Similarly, according to our findings, the process EP was more profitable when the distillation columns ran in continuous mode.

3.6.Equipment splitting

The equipment splitting technique is applied to decrease the effect of the bottleneck step on the process CT or process scheduling. The splitting technique increases the number of the process equipment (leading to lower EP). Nonetheless, it also leads to a decrease in the process CT or the required batch size (it means a higher EP). Thus, there is a technical and economic trade-off. Therefore, the optimization of this subproblem is unavoidable.

BD: Biodiesel Distillation, **MD**: Methanol Distillation, **SET**: Settler, Net: Neutralizer, **ER**: Esterification Reactor, **OD**: Oil Distillation, **TR**: Transesterification Reactor, **WWT**: Water Washing Tower and **GE**: Glycerol Evaporator

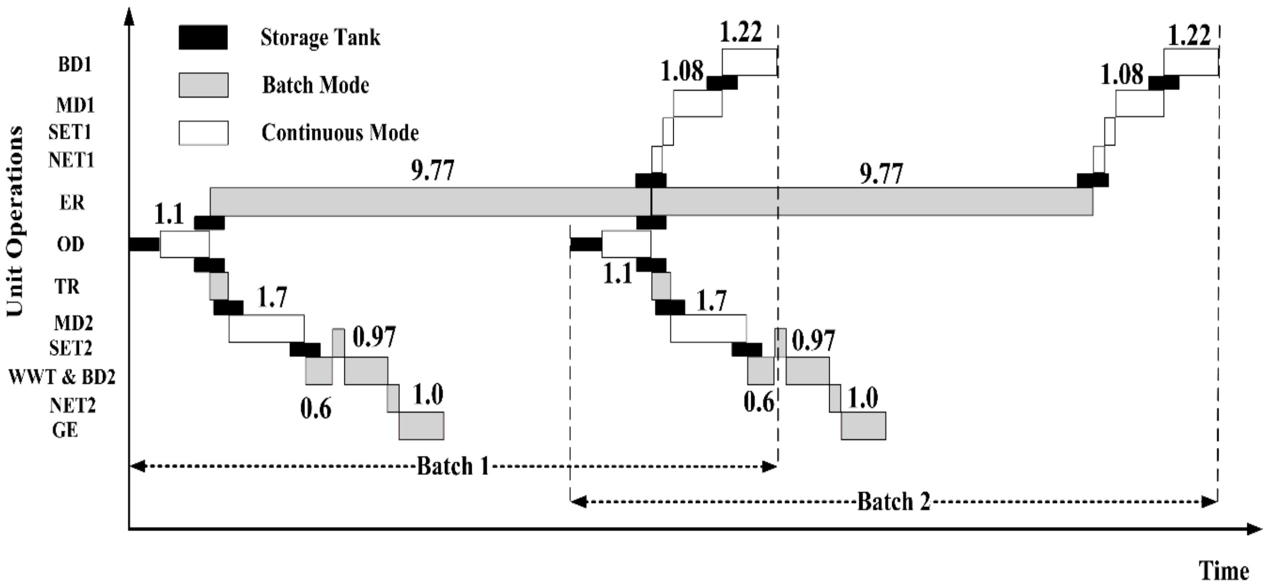

Figure 4. The effect of the combination of batch and continuous units on the configuration of the process equipment (the numbers indicate the required residence times for different units).

According to Figure 4, the esterification reactor is the bottleneck step in the process scheduling. So, it is necessary to determine the optimum required splitting number of this reactor. The optimum size ratio for the mixed reactors in series is found in general to be dependent on the kinetics of the reaction and the conversion as well. As a general rule, for first-order reactions (n=1), equal size reactors are the best. For the reaction order $n > 1$, the smaller reactor should come first. But for $n < 1$, the larger one should come first. However, the advantage of the minimum size system over the equal size system is quite small, only a few percent at most [31]. So, the overall economic and technical considerations would nearly always recommend using the equal size units. This was one of the major decisions for the investigation of the reactor splitting in the present study. Accordingly, at this step, the process CT was found as the residence time of the esterification reactor divided by the number of reactors in series. Table 2 shows the results of this subproblem. According to this table, the optimum number of the stages of esterification reactors in series was found to be three. Also, Figure 5 shows the Gantt chart for the process after the application of the splitting technique.

Table 2

The effect of the esterification reactor splitting on the process cycle time (CT) and process EP.

Number of esterification reactor in series	CT (h/batch)	EP ($/yr)
1	9.77	247030
2	4.89	252647
3	3.26	253490
4	2.44	253300

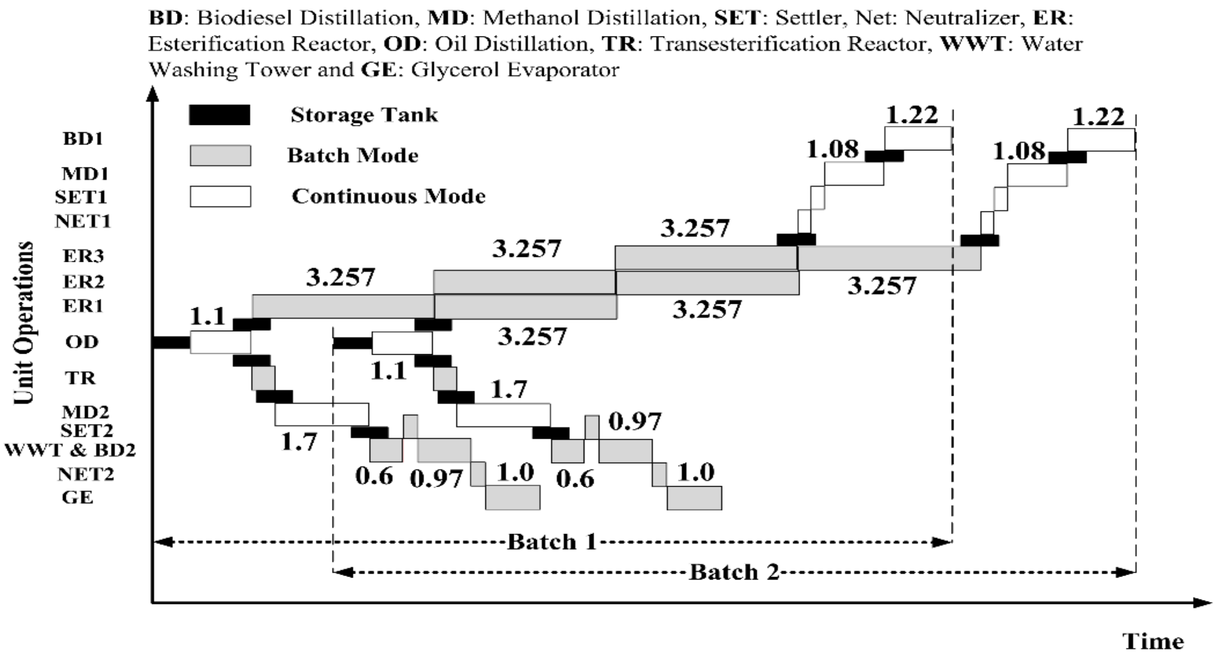

Figure 5. The effect of the esterification reactor splitting on the configuration of the process equipment (the numbers indicate the required residence times for different units).

3.7. Parallel and merged parallel units

Similarly to the splitting technique, the application of paralleling technique leads to a technical and economic trade-off. As a general rule of thumb, chemical batch processes use at most three parallel units [16]. The esterification reactor was the bottleneck step of CT or the process scheduling (see Figure 5). As mentioned above, the process contained batch and continuous unit operations, connected by intermediate storage tanks. Owing to this, here, the application of the paralleling technique caused a local change in the size of the equipment (not a global effect). Therefore, it was observed that the addition of parallel units had a moderate effect on EP. Finally, the present process model revealed that the paralleling technique decreases the process EP by 2.3 %.

3.8. Intermediate storage

In batch (or semicontinuous) processes, when each unit operation (batch and/or continuous) is connected in a series, the outlet stream from the prior unit directly becomes the inlet flow to the next unit. Therefore, the variations in the required residence time and/or batch size in a specific unit affect the batch size of the whole process and also the operation schedule. Thus, these variations may cause serious problems, so it is necessary to readjust the operation schedules and/or the batch sizes of other batch units.

It is the most effective action to install an intermediate storage tank between the batch-batch and batch-continuous units [32]. By installing storage tanks between these units, the outlet streams from the precedent units are stored in the tanks and do not instantly enter other units following the storage tanks. In other words, the installed storage tank can neutralize any influence due to the difference in the operation mode that may occur in the previous batch or continuous units. In addition, the storage tanks act as dampers and prevent the propagation of such undesirable influences on the units following each tank. The estimations of the cost and size of intermediate storage tanks and their effects on the process scheduling were previously investigated in section 3.5.

Figure 6 shows the final optimum batch (or semicontinuous) process flowsheet to produce biodiesel from high FFA feedstocks. As a result of the optimum batch (or semicontinuous) process model, it was observed that the production rate of 680 tons/yr led to an EP of about \$253490/yr. As mentioned earlier (see section 3.2.), the continuous process has an EP of about \$302230/yr for the same production rate. Therefore, the continuous process was preferred to the batch (or semicontinuous) process at this production rate.

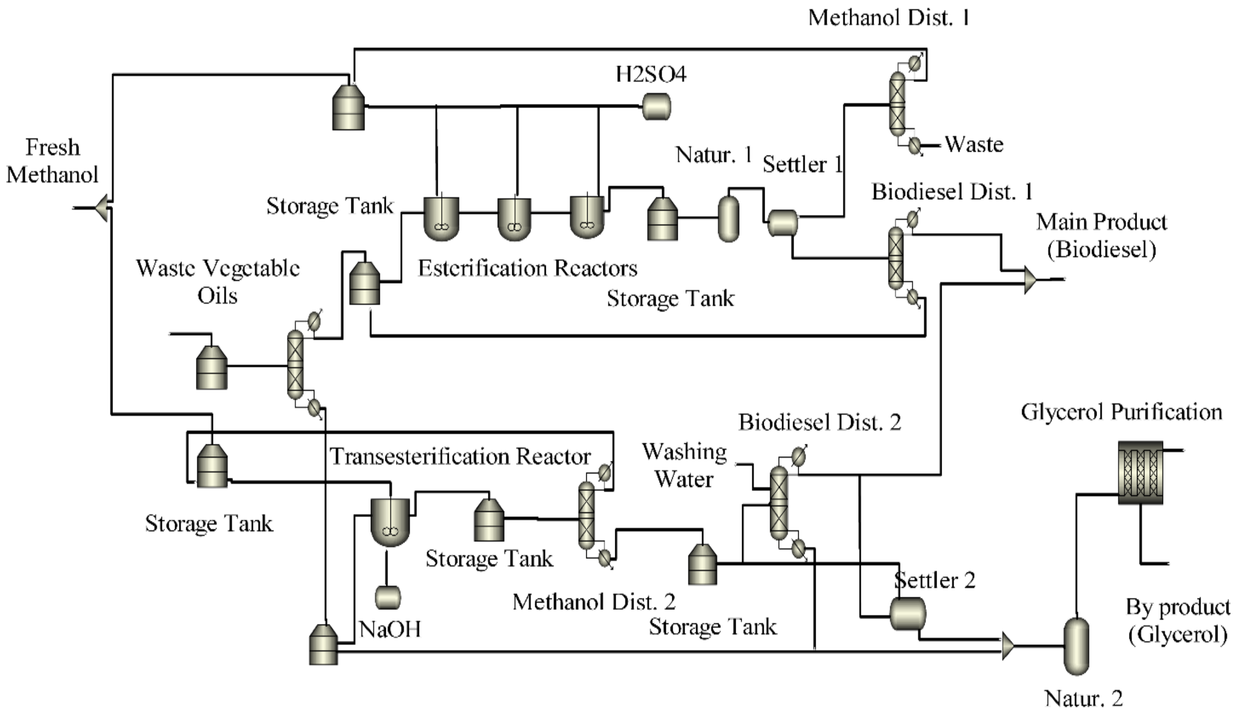

Figure 6. The optimum batch (or semicontinuous) process flowsheet.

Results for costing the main equipment of the process has been summarized in Table 3.

To annualize the costs of equipment, a capital charge factor (CCF) was defined as:

$$\mathrm{CCF} = \frac{[0.25(1+\mathrm{i})^4 + 0.295\mathrm{i} - 0.298](1+\mathrm{i})^{\mathrm{N}} - 0.225\mathrm{i} + 0.048}{0.676[(1+\mathrm{i})^{\mathrm{N}} - 1]} \tag{15}$$

where iand N denote the interest rate and the equipment operating life [16]. In the present design calculations, for i =0.15 and N =13, we let CCF = 0.333 yr^{-1}.

Table 3

The annualized equipment costs (as a function of plant capacity).

Equipment type	**Annualized equipment costs ($/yr)**				
Plant capacity (tons/yr)	823	3047	5270	7494	9718
Esterification Reactor (ER)	12,362	27,931	39,291	59,871	70,386
Transesterification Reactor (TR)	2,156	4,872	6,854	8,534	10,033
Methanol distillation column #1 (MD1)	18,210	53,414	84,192	111,707	138,801
Biodiesel distillation column #1 (BD1)	22,125	61,770	95,048	117,613	144,359
Oil distillation column (OD)	7,934	22,322	34,483	45,622	56,113
Methanol distillation column #2 (MD2)	34,134	97,137	150,898	200,426	247,265
Water washing tower (WWT)	10,365	10,365	10,365	10,365	10,365
Biodiesel distillation column #2 (BD2)	1,387	4,023	6,306	8,428	10,448
Glycerin evaporator (GE)	2,081	2,676	3,042	3,296	3,523

Figure 7 shows the dependence of the process EP on the production rate in the continuous and batch processes. As a general heuristic rule, chemical processes having capacities of greater than 4540 tons/yr are usually continuous whereas, plants having capacities of less than 454 tons/yr are normally batch types [16]. For other rates, the best process mode (batch or continuous) is selected after the detailed design of both batch and continuous alternatives. Nonetheless, for the production of biodiesel (based on the esterification-transesterification technique), the batch process was found to be suitable for a capacity of less than 260 tons/yr, while the continuous process was suitable for the capacities of greater production rates.

It can be seen that EP increased linearly as the production rate increased. Therefore, the process capacity should be set at its maximum possible practical value. Also, in the present batch (or semicontinuous) plant, the break-even point for the optimum values of design variables occurred at the production rate of 130 tons/yr. We found that for continuous process, this point occurred at the production rate of 157 tons/yr. It is noteworthy that the optimum batch process contained considerable numbers of distillation columns (see Figure 6). Because of startup and shutdown complexities, it is preferred that distillation columns operate in the continuous mode. Similarly, as mentioned above, the continuous performance of distillation columns showed better performance in the process optimization and also the process scheduling. Therefore, the synthesized optimum batch process inherently had a semicontinuous mode. This is the main reason for the small difference between the break-even points of the optimum batch and continuous processes.

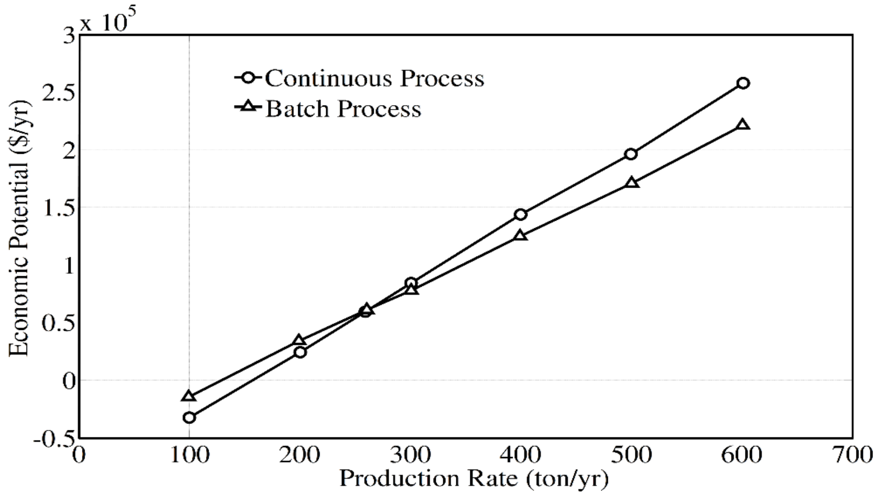

Figure 7. The economic potential of the optimum batch and continuous processes as a function of the process production rate.

4.Conclusions

In the present work, a batch process was conceptually designed and optimized to produce biodiesel from high FFA feedstocks with techno-economic considerations. The results showed that, unlike in the traditional processes, methanol, biodiesel, and oil distillation columns should be operated in the continuous mode, whereas the glycerol evaporator and esterification and transesterification reactors are preferred to operate in the batch mode. Also, the optimum number of the stages of esterification reactors in series was found to be three. As a result, it is concluded that in the production of biodiesel (using the esterification-transesterification methods), the batch process is suitable for capacities less than 260 tons/yr while the continuous process is suitable for capacities greater than 260 tons/yr. Also, for this batch (or semicontinuous) plant, the break-even point for the optimum values of major design variables occurred at the production rate of 130 tons/yr.

References

[1] Takumi, I. and Torii, Sh., "Characteristics of stable biodiesel emulsion fuel with the aid of lipophilic surfactant, polyglycerol polyricinoleate (PGPR)", *International Journal of Green Energy*, **17** (14), 946 (2020).

[2] Morris, R. E., Pollack, A. K., Mansell, G. E. and Lindhjem, Y. J., "Impact of biodiesel fuels on air quality and human health", National Renewable Energy Laboratory (NREL), Annual Report, Report number: NREL/SR-540-33798, (2003).

[3] Rafael, L. and Juan, A. M., Advances in biodiesel production processes and technologies, 1st ed., Woodhead Publishing Limited, Cambridge, UK, p. 74 (2012).

[4] Sahu, G., Das, L. M., Sharma, B. K. and Naik, S. N., "Pilot plant study on biodiesel production from karanja and jatropha oils", *Asia-Pac. J. Chem. Eng.*, **6** (1), 38 (2011).

[5] Suthar, K., Dwivedi, A. and Joshipura M., "A review on separation and purification techniques for biodiesel production with special emphasis on jatropha oil as a feedstock", *Asia-Pac J. Chem. Eng.*, **14** (5), e2361 (2019).

[6] Basha, S. A., Gopal, K. R. and Jebaraj,

S., "A review on biodiesel production, combustion, emissions and performance", *Renewable and Sustainable Energy Reviews*, **13** (6), 1628 (2009).

[7] Takase, M. and Essandoh, P. K., "Two-step biodiesel production using high free fatty acid containing pig fat", *International Journal of Green Energy*, **18** (4), 381 (2021).

[8] Kavitha, M. S. and Murugavelh, S., "In situ acid catalyzed transesterification of biodiesel production from sterculiafoetida oil and seed", *International Journal of Green Energy*, **16** (15), 1465 (2019).

[9] Demirbuş, A., "Biodiesel fuel from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterification and other methods: A survey", *Energy Conversion and Management*, **44** (13), 2093 (2003).

[10] Khan, N., Maseet, M. and Basir, S. F., "Synthesis and characterization of biodiesel from waste cooking oil by lipase immobilized on genipin cross-linked chitosan beads: A green approach", *International Journal of Green Energy*, **17** (1), 84 (2020).

[11] Zhang, Y., Dube, M. A., McLean, D. D. and Kates, M., "Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis", *Bioresour. Technol.*, **90** (3), 229 (2003a).

[12] Gerpen, J. V., Shanks, B. and Pruszko, R., "Biodiesel production technology", National Renewable Energy Laboratory (NREL), Annual Report, Report number: NREL/SR-510-36244, (2004).

[13] Lin, L., Ying, D., Chaitep, S. and Vittayapadung, S., "Biodiesel production from crude rice bran oil and properties as fuel", *Applied Energy*, **86** (5), 681 (2009).

[14] Canakci, M. and Gerpen, J. V., "A pilot plant to produce biodiesel from high free fatty acid feedstocks", *Transactions of the ASAE*, **46** (4), 945 (2003).

[15] Zhang, Y., Dubé, M. A., McLean, D. D. and Kates, M., "Biodiesel production from waste cooking oil: 1. Process design and technological assessment", *Bioresour. Technol.*, **89** (1), 1 (2003b).

[16] Douglas, J. M., Conceptual design of chemical processes, 1st ed., McGraw-Hill Book Co., Singapore, p. 568 (1988).

[17] Fair, J. R., "Book review: conceptual design of distillation systems", *AIChE Journal*, **49** (9), 2452 (2003).

[18] Sharrat, P. N., Handbook of batch process design, 1st ed., Blackie Academic and Professional, London, UK, p. 26 (1997).

[19] Hoyle, W., Pilot plant and scale up of chemical processes, 1st ed., The Royal Society of Chemistry Press, Cambridge, UK, p. 15 (1997).

[20] Balchen, J. G., Dynamics and control of chemical reactors, distillation columns and batch processes, Selected Papers from the 3rd IFAC Symposium, 1st ed., Pergamon Press, New York, USA, p. 45 (1993).

[21] Malone, M. F. and Iribarren, O., "A systematic procedure for batch process synthesis", *78th AICHE Annual Meeting*, Chicago, USA (1985).

[22] Mohammadi, A. and Ghobadian, B., "Techno-economic optimization of a continuous process for biodiesel production from waste vegetable oils", *Iranian Journal of Chemical Engineering (IJChE)*, **18** (4), 21 (2022).

[23] Fangrui, M. and Hanna, M. A.,

"Biodiesel production: a review", *Bioresour. Technol.*, **70** (1), 1 (1999).

[24] Sendzikiene, E., Makareviciene, V., Janulis, P. and Kitrys, S., "Kinetics of free fatty acids esterification with methanol in the production of biodiesel fuel", *Eur. J. Lipid Sci. Technol.*, **106** (12), 831 (2004).

[25] Smith, R., Chemical process design and integration, 1st ed., John Wiley & Sons, Barcelona, Spain, p. 9 (2005).

[26] Mujtaba, I. M., Batch distillation design and operation, 1st ed., Imperial College Press, London, UK, p. 25 (2004).

[27] Couper, W., Penney, R., Fair, J. R. and Walas, S. M., Chemical process equipment selection and design, 3rd ed., Elsevier Publishing, Oxford, UK, p. 111 (2012).

[28] Treybal, R. E., Mass transfer operations, 3rd ed., McGraw Hill, Singapore, p. 142 (2001).

[29] Tesser, R., Serio, M. D. and Natasi, M., "Kinetics of oleic acid esterification with methanol in the presence of triglycerides", *Ind. Eng. Chem. Res.*, **44** (21), 7978 (2005).

[30] Noureddini, H. and Zhu, D., "Kinetics of transesterification of soybean oil", *J. Am. Oil Chem. Soc.*, **74** (11), 1457 (1997).

[31] Levenspiel, O., Chemical reaction engineering, 3rd ed., John Wiley and Sons, New York, USA, p. 134 (1991).

[32] Takamatsu, T., Hashlmoto, I., Hasebe, S. and O'Shlma, M., "Design of a flexible batch process with intermediate storage tanks", *Ind. Eng. Chem. Process Des. Dev.*, **23**, 40 (1984).