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Superstructure-based Design and Optimization of Batch Biodiesel Production Using Heterogeneous Catalysts

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Abstract. Biodiesel as a fuel comprised of mono alkyl esters of long chain fatty acids derived from renewable lipid feedstock, such as vegetable oil and animal fat. Biodiesel production is complex process which need systematic design and optimization. However, no case study using the process system engineering (PSE) elements which are superstructure optimization of batch process, it involves complex problems and uses mixed-integer nonlinear programming (MINLP). The PSE offers a solution to complex engineering system by enabling the use of viable tools and techniques to better manage and comprehend the complexity of the system. This study is aimed to apply the PSE tools for the simulation of biodiesel process and optimization and to develop mathematical models for component of the plant for case A, B, C by using published kinetic data. Secondly, to determine economic analysis for biodiesel production, focusing on heterogeneous catalyst. Finally, the objective of this study is to develop the superstructure for biodiesel production by using heterogeneous catalyst. The mathematical models are developed by the superstructure and solving the resulting mixed integer non-linear model and estimation economic analysis by using MATLAB software. The results of the optimization process with the objective function of minimizing the annual production cost by batch process from case C is $23.2587 million USD. Overall, the implementation a study of process system engineering (PSE) has optimized the process of modelling, design and cost estimation. By optimizing the process, it results in solving the complex production and processing of biodiesel by batch.

1. Introduction

Recently, to produce a biodiesel to replace the fossil fuels as a main energy is quite costly. Researchers have shown the biodiesel production is undergoing rapid and extensive technological reforms in industries and academia. The recent production of fossil fuels has reached up to 79% compared to other energy sources as shown in Figure 1 [1]. The demand or fossil fuel as a primary energy source is exceeding its production, due to rising consumption of fossil fuel energy up to 83% [2-3].

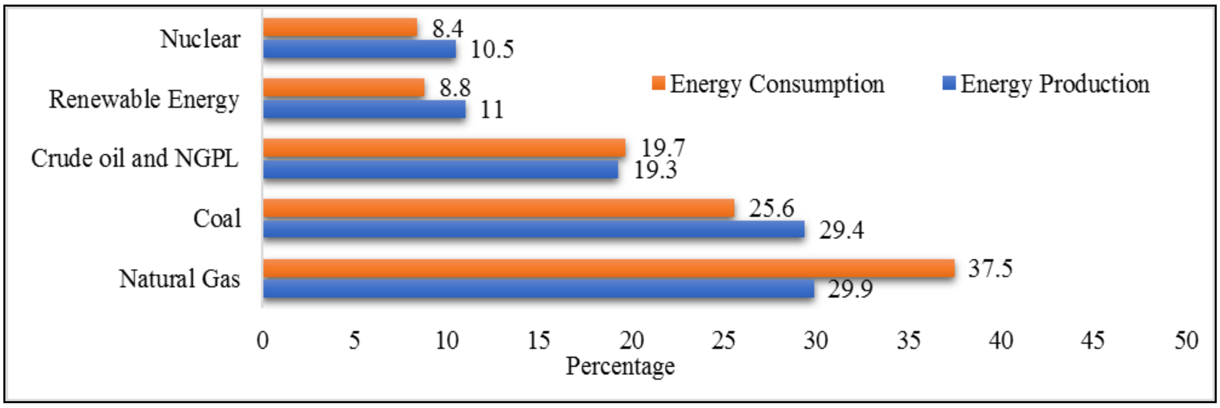

Figure 1: World primary energy production and consumption in November 2015 [2].

Biodiesel can be produced from material that contains fatty acids. Thus, animal fats and vegetable fats can be used as feedstocks for biodiesel production. The use of heterogeneous catalysts allows a more environmentally friendly process to be used for biodiesel production [4]. In other words, the use of calcium oxide as heterogeneous catalysts could enable the design of an efficient, continuous process and improve the economics of biodiesel production [5].

There are three cases produce biodiesel by using a base heterogenous catalyst, case A, case B and case C. The economic analysis is carried out to find the potential biodiesel production sold on the market based on 36000 tons. Zhang et al [12] and west et al [13] compare the economics of a biodiesel for producing approximately \$4.69 million and \$2.54 million. They conclude that in all cases the raw materials cost is the most important contribution to the unit production cost. The scope of study is three cases A, B and C for producing biodiesel by batch process using calcium oxide as a base heterogeneous catalyst and biodiesel production is 36000 tons per year and the mathematical models are solved by suitable solver and algorithms by MATLAB software.

1.1 Superstructure

All potential alternatives in the processing network are represented by a schematic form, which is called the superstructure [6]. Hence, the superstructure contains all candidates for feasible and optimal processing pathways. In formulating the superstructure, all the potential raw materials and products are specified and then linked through a series of tasks (unit operations and/or unit processes) such that the raw materials get converted into the products. Systematic optimization techniques through a superstructure approach and modeling of MINLP problem for the biodiesel production process was carried out by [7] for obtaining an optimal processing route to produce biodiesel from microalgae biomass. By considering the selection of only one option from each processing stage, the current superstructure as shown in Figure 2, incorporates 192 possible combinations of processing pathways to produce biodiesel from microalga biomass. However, this number would change if allowed bypass of a processing stage or split of a process stream.

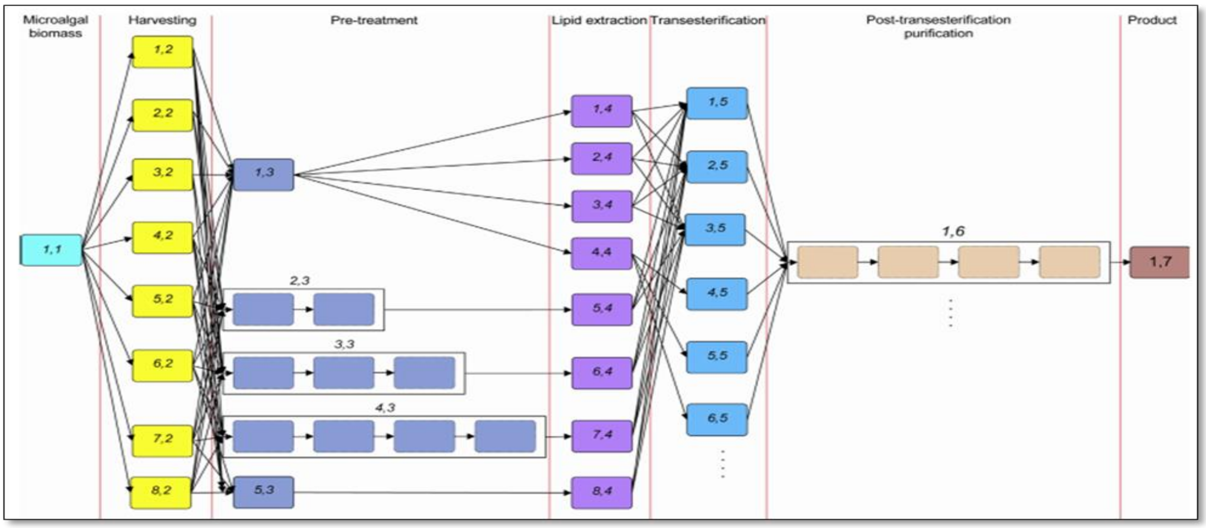

Figure 2: The developed superstructure for biodiesel production from microalga biomass [7].

The superstructure is described for the problem of optimal process synthesis for biogas production from organic and animal waste resulting in a mixed integer nonlinear programming (MINLP) problem [14]. A superstructure consisting of several alternative structures is developed for reactor separation recycle system and the interconnections are also considered. Different separation techniques, different types of reactors, different reactor configurations and feedstock, recycling, and bypass strategies are considered. The problem is then formulated as MINLP. An optimization model is developed based on the proposed superstructure, followed by the formulation of mathematical equations [10]. The mathematical formulation of the MINLP problem is then solved using the MATLAB application software packages.

2. Methodology

2.1 Case studies

Three different flow paths were studied by batch biodiesel production using heterogeneous catalysts from case A, case B and case C as shown in Figure 3, Figure 4 and Figure 5. The raw materials for the biodiesel production was an oil feed with free fatty acid and the catalyst used is CaO as heterogeneous catalysts. The reaction was carried out at a higher temperature (60-65°C). the molar ratio methanol to oil is 6:1 and the concentration CaO is 0.5% [9].

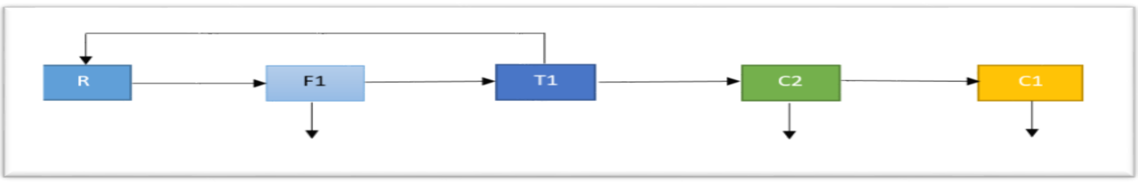

Figure 3: The pathway for case A

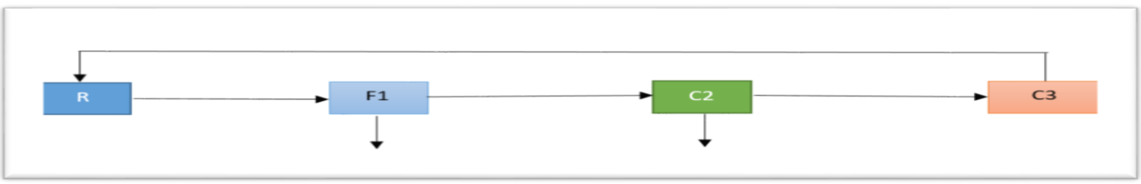

Figure 4: The pathway for case B

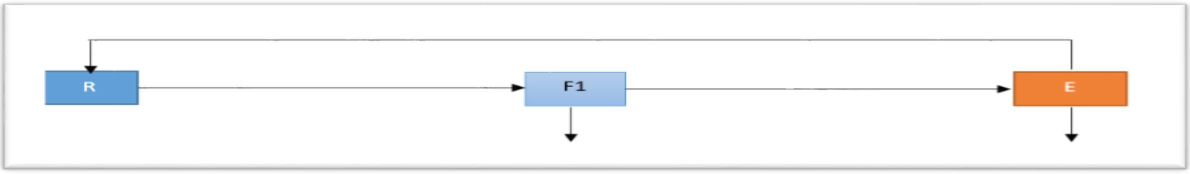

Figure 5: The pathway for case C

Figure 3 show the case A with flow process path. In this process, the oil was fed into the reactor (R) simultaneously with methanol for transesterification process by using CaO catalyst. The stream product flow into the filter (F) to remove the catalyst. After that, the stream product passed through a distillation (T1) column to separate and recycle the methanol. After distillation column phase (T1), the product stream passed through a settling tank (C2) to remove the glycerol. The final phase of this case the product stream passed through the hot water purification tank (C1) by using hot water to produce the FAMEs [15]. Figure 4 show the case B with flow process path. In this process, the incoming stream oil simultaneously with methanol was fed into the reactor (R) for transesterification process by using CaO catalyst. The stream product flow into the filter (F) to remove the catalyst. After that, the stream flow passed through into the settling tank (C2) to remove the glycerol. After the glycerol is remove, the stream product was passed through flash tank (C3) to remove the methanol to get the FAMEs [1].

Figure 5 show the case C with flow process path. In this process, the oil was fed into the reactor (R) simultaneously with methanol in transesterification process by using CaO catalyst. The stream product with catalyst passed through into the filter (F) to remove the heterogenous catalyst CaO. After that, the stream product passed through the evaporator (E) to separate the methanol and remove the glycerol to get the FAMEs [16]. Figure 6 shows the developed superstructure based on case study which consist the combination of case A, B and C. Each route superstructure has own processing biodiesel. R present as reactor, F1 present as filter, T1 present as distillation column, C1 hot water purification, C2 present as settling tank, C3 present as flash tank and E present as evaporator. The number 1 to 16 present as stream product flow for the mathematical expression model.

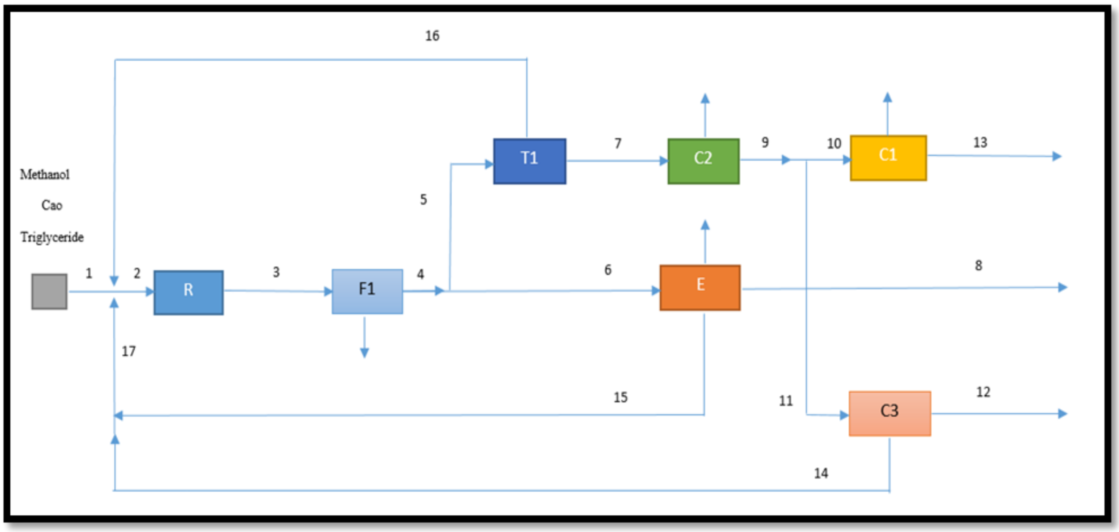

Figure 6: The developed superstructure for production biodiesel

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2.2 Modeling Mathematical Equation

The mathematical models can be formulated from the superstructure of alternatives as shown in equation as follows [10]:

- Material balance for separator and mixer in the reactor feed, the units separating and methanol recycling:

$$F_1 - F_A - F_C - F_D = 0$$
$$F_2 - F_{16} - F_{17} - F_1 = 0$$
$$F_{14} + F_{15} - F_{17} = 0$$
$$F_6 + F_5 - F_4 = 0$$
$$F_{10} + F_{11} - F_9 = 0 \quad (1)$$

- Component balance for mixer at input reactor:

$$F_1 \cdot x_{1,A} + F_{16} + F_{17} - F_2 \cdot x_{2,A} = 0$$
$$F_1 \cdot x_{1,C} - F_2 \cdot x_{2,C} = 0$$
$$F_1 \cdot x_{1,D} - F_2 \cdot x_{2,D} = 0 \quad (2)$$

- Component balance for the reactor:

$$F_2 \cdot x_{2,A} - F_3 \cdot x_{3,A} - A_1V_1 = 0$$
$$F_2 \cdot x_{2,D} - F_3 \cdot x_{3,D} - A_1V_1 = 0$$
$$- F_3 \cdot x_{3,B} - A_1V_1 = 0$$
$$- F_3 \cdot x_{3,E} - A_1V_1 = 0$$
$$F_2 \cdot x_{2,C} - F_3 \cdot x_{3,C} - A_1V_1 = 0$$
$$A_1 - 0.01 \cdot x_{3,A} \cdot x_{3,D} = 0 \quad (3)$$

The variable for the A_1 at reactor is 0.065 the reaction rate constant 2.5

- Component balance for each separation line:

$$F_{16} - F_3 \cdot x_{3,A} = 0$$
$$F_{B,2} - F_3 \cdot x_{3,B} = 0$$
$$F_{E,2} - F_3 \cdot x_{3,E} = 0$$
$$F_{14} - F_3 \cdot x_{3,A} = 0$$
$$F_{B,2} - F_3 \cdot x_{3,B} = 0$$
$$F_{E,2} - F_3 \cdot x_{3,E} = 0$$
$$F_{15} - F_3 \cdot x_{3,A} = 0$$
$$F_{B,2} - F_3 \cdot x_{3,B} = 0$$
$$F_{E,2} - F_3 \cdot x_{3,E} = 0 \quad (4)$$

Every path for line 1, line 2, and line 3 is in each case are A, B, and C.

- Total mole fraction:

$$x_{1,D} + x_{1,C} + x_{1,A} = 1$$
$$x_{2,D} + x_{2,C} + x_{2,A} = 1$$
$$x_{3,E} + x_{3,B} + x_{3,C} + x_{3,A} = 1$$
$$x_{4,B} + x_{4,E} + x_{4,A} = 1$$
$$x_{5,B} + x_{5,E} + x_{5,A} = 1$$
$$x_{6,B} + x_{6,E} + x_{6,A} = 1 \quad (5)$$

For the overall reaction include this case, A is methanol, B is biodiesel, C is catalyst CaO, D is oil feed and E is glycerol. The total annual cost of biodiesel production, C_T is given as follows:

The total cost of production:

$C_T = C_f + C_v$

With:

$pce = \Sigma cx$
$f_1 = 0.4$
$f_2 = 0.7$
$f_3 = 0.2$
$f_4 = 0.1$
$f_7 = 0.15$
$f_{10} = 0.3$
$f_{11} = 0$
$f_{12} = 0.1$
$ppc = pce \times (1 + f_1 + f_2 + f_3 + f_4 + f_7)$;
$fcc = ppc \times (1 + f_{10} + f_{11} + f_{12})$
$wc = fcc \times 0.05$
$C_r = -$
$C_m = 0.05 \times fcc$
$C_{mm} = 0.1 \times C_m$
$C_u = -$
$C_l = 160000$
$C_o = 0.5 \times C_l$
$C_{lab} = 0.3 \times C_l$
$C_c = 0.06 \times fcc$
$C_i = 0.01 \times fcc$
$C_f = C_m + C_o + C_{lab} + C_c + C_i$
$C_v = C_r + C_{mm} + C_u$

With f_1, f_2, f_3, f_4, f_7, f_{10}, f_{11}, f_{12} is construction equipment factors, piping, instrumentation, electrical, storage, design, engineering, contractor cost and unexpected costs. Ppc, pce, wc, fcc, they are physical plant costs, the purchase equipment cost, work cost and fixed cost. Meanwhile, C_r, C_m, C_{mm}, C_u, C_l, C_o, C_{lab} C_c, C_i, C_f, C_v and C_T, is raw material cost, maintenance cost, waste treatment cost, utility cost, reliance cost, overhead plant, laboratory cost, modal cost, insurance cost, production equipment, variable production cost and annual production cost. The mathematical model from equation is problematic for the MNLP because it consists continues variables and binary with objective function and non-linear constraints. Constraints from (2), (3), and (4) are non-linear, for (1) and (5) is linear constraints. Due to the objective function and constraints is non-linear, then the function f(x) and the solution will have considered as the local optimum if the optimization algorithm is used.

2.3 Summary of Production Cost

The estimated cost is based on the design, and the costs are such as equipment cost, fixed and variable capital cost, fixed and variable production cost. To perform a cost analysis, several type data are required to develop a cost analysis. That includes equipment that is required to design an optimum route for a biodiesel plant such as heat exchanger, methanol tank, biodiesel tank, wash tank, separator, evaporators, filters, reactors and flash tanks. Besides that, data such as the size of an equipment capacity also need to be included to produce 36,000 tons. Only one process of analysis is in the batch biodiesel process using heterogeneous catalyst. All the design equipment is based on the conceptual design of chemical processes from McGraw-Hill book [8].

The estimated cost for the annual production biodiesel on 36000 tons to determine the potential biodiesel production. Table 1 shows the summary of the economic analysis for the biodiesel production. There are several costs that are not included, for example the overhead cost, research and development and shipping cost, it is because to estimate the initial cost. The estimation of production costs can be concluded from the representative values given in the Table 2.

Table 1: Summary of Production Cost [8].

Cost	Typical Values
Variable Cost	From flow-sheets
1. Raw materials	10 per cent of item
2. Miscellaneous materials	From flow-sheet
3. Utilities	Usually negligible
4. Shipping and packaging	
Sub-total A	
Fixed costs	
5. Maintenance	5-10 per cent of fixed capital
6. Operating labor	From manning estimates
7. Laboratory costs	20-23 per cent of 6
8. Supervision	20 per cent of item (6)
9. Plant overheads	50 per cent of item (6)
10. Capital charges	10 per cent of the fixed capital
11. Insurance	1 per cent of the fixed capital
Sub-total B	2 per cent of the fixed capital
Direct production costs A + B	
12. Sales expense	
13. General overheads	
14. Research and development	
Sub-total C	20-30er cent of the direct production cost
Annual production cost = A + B + C	

3. Result and Discussion

3.1 Economic analysis

The superstructure consists three pathway case A, case B and case C. The mathematical equation is created based on the superstructure consists linear and nonlinear constraints. From that constraints and economic analysis is solved by using MATLAB software. The economic analysis is carried out to determine the potential biodiesel production sold on the market. In this economic analysis if to find out the annual production biodiesel on 36000 tons.

Table 2: The estimation annual cost production

No	Detail cost	Typical value
1	Total amount cost of equipment	PCE
	f_1 Equipment erection	0.4
	f_2 Piping	0.7
	f_3 Instrumentation	0.2
	f_4 Electrical	0.1
	f_5 Buildings, process	-
	f_6 Utilities	-
	f_7 Storages	0.15
	f_8 Site development	-
	f_9 Ancillary buildings	-
	PPC = PCE $(1 + f_1 + \ldots + f_9)$	952,884
2	Total physical plant	PPC
	f_{10} Design and Engineering	0.3
	f_{11} Contractor's fee	-
	f_{12} Contingency	0.1
	Fixed capital = PPC $(1 + f_{10} + f_{11} + f_{12})$	611,637
3	Variable production cost	
	Raw material	21,642,000
	Waste treatment	10,000
	Utility	23,110
	Packaging and shipping	-
	Subtotal-A	22,723631
4	Fixed production cost	
	Maintenance	103,000
	Operator cost	160,000
	Laboratory	40,000
	Supervision	
	Plant overhead	80,000
	Capital charge	124,000
	Insurance	21,000
	Subtotal-B	528,000
5	Direct cost, A+ B	23,251,631
	Selling expenses	-
	Overhead	-
	Research and development	-
	Subtotal-C	-
6	The annual production cost, A+ B + C	24,364,631

Based on the Table 2, the estimated annual cost production of this study is a bit too high in the range $25 million. The annual cost is high because the main contribute is the raw materials purchased is about 87% of the total annual cost production biodiesel to 36000 tons per year [9]. However, the cost of raw material cannot be avoided, especially the price from oil feed and catalyst. For production, 8000 tons of raw material per year would cost $4.69 million from zhang and $2.54 from west. As for this study, it was discovered that the cost of raw material was nearly $24 million. [12-13]. The difference price raw material cost is because the plant capacity for both their research is small, their produce biodiesel per year only 8000 tons.

Figure 7 and Figure 8 are showing the function value and bar chart is plotted from the optimization. Figure 7 is showing the function value for each calculation. During the optimization, the function value is monitored to make sure the function is solved for each iteration. Figure 8 show the value variable is changed to small at 18-55, this variable changing has a limit from one upper limit and zero lower limit. The variable at 1 to 18 has the different upper limit and its value is much higher.

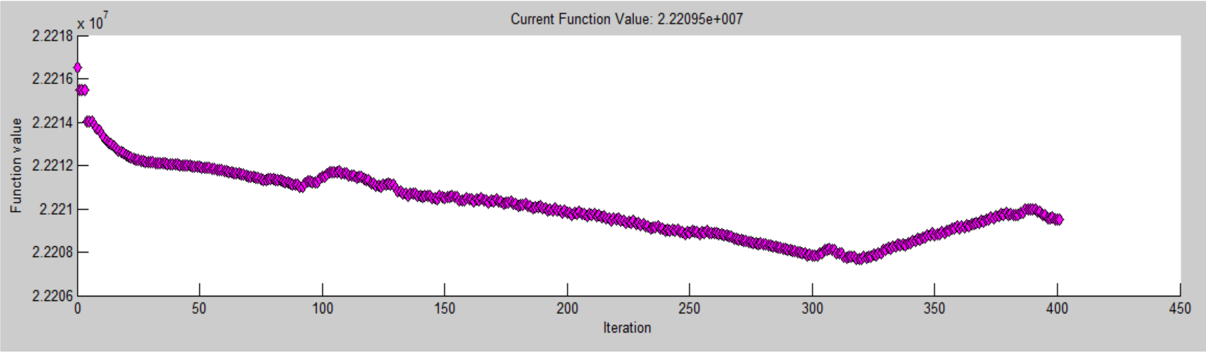

Figure 7: The function value against iteration

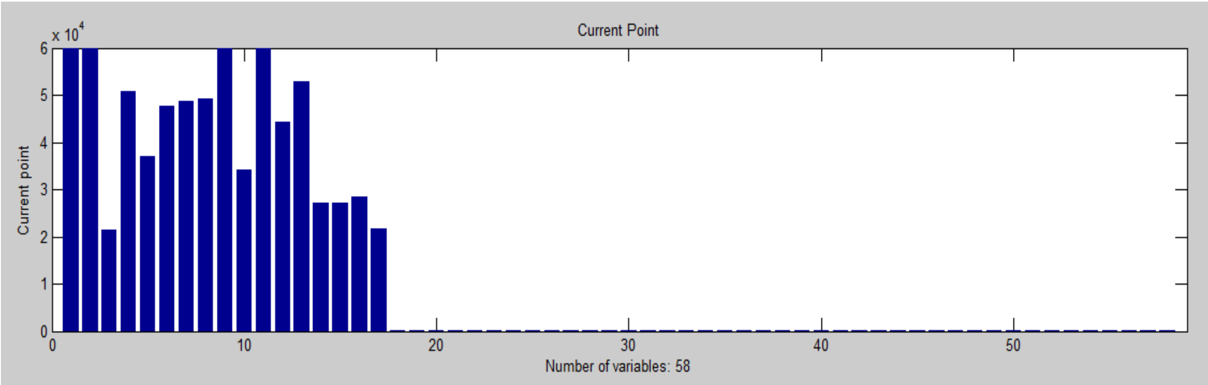

Figure 8: Value variable in bar chart

Based on that graph shown in figure 9, the most minimum annual cost biodiesel production by using heterogenous catalysts CaO is case C, by following case B and case A. Case A is the highest cost production because the contribution purchase cost of equipment. Based on this result, the synthesis reactor recycling-separator for proses biodiesel production is conducted and MINLP model equation can be solved for this synthesis.

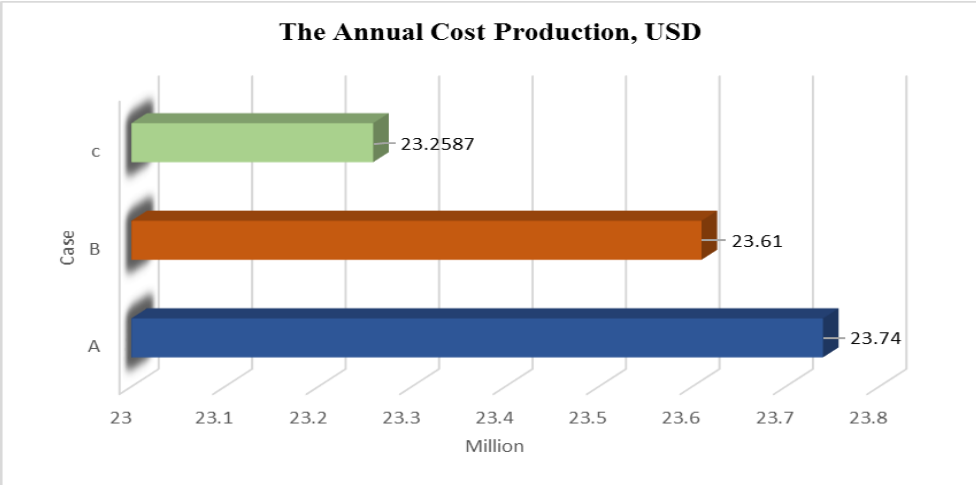

Figure 9: The total cost production for each case

4. Conclusion

Based on this study, the minimum annual cost biodiesel production by batch process from case C is \$23.2587 million. From the aspect of industry, the optimization find the optimum pathway, also the minimum cost and may be beneficial for sustainable development due to the lower consumption. Overall, this study has successfully implement the process system engineering (PSE) to optimize the design and cost estimation.

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