

EXERGY ANALYSIS OF PALM OIL BIODIESEL PRODUCTION TECHNOLOGIES

ANALISIS EKSERGI PADA TEKNOLOGI PRODUKSI BIODIESEL KELAPA SAWIT

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ABSTRAK

Biodiesel merupakan bahan bakar alternatif yang dapat menggantikan bahan bakar diesel, karena sifatnya yang terbarukan dan ramah lingkungan. Biodiesel dapat diproduksi baik secara proses katalitik ataupun non-katalitik. Makalah ini membahas dua teknologi yang berbeda dalam memproduksi biodiesel kelapa sawit, yaitu proses katalitik yang menggunakan katalis basa dan proses non katalitik uap metanol superheated (superheated methanol vapor / SMV). Analisis eksergi dilakukan untuk membandingkan kedua teknologi tersebut. Sistem tertutup diasumsikan pada analisis eksergi, sedangkan eksergi kinetik dan potensial diabaikan. Hasil penelitian menunjukkan bahwa total efisiensi eksergi untuk proses non-katalitik SMV lebih rendah dibandingkan proses katalitik, yaitu sebesar 92,61% dan 95,37%, secara berurutan. Proses penguapan metanol memberikan kontribusi yang tinggi pada ireversibilitas (tidak mampu balik), yaitu sebesar 2802.07 kJ/kg biodiesel. Penerapan proses resirkulasi panas dapat meningkatkan efisiensi eksergi pada proses produksi biodiesel, terutama apabila metode SMV akan diterapkan. Ireversibilitas pada proses non-katalitik SMV lebih tinggi dibandingkan proses katalitik, karena kebutuhan suhu yang tinggi pada proses non-katalitik SMV. Oleh karena itu, perbaikan proses SMV sangat perlu dilakukan, terutama pada proses penguapan metanol, guna meningkatkannya efisiensi proses tersebut.

Kata kunci: minyak sawit, biodiesel, uap metanol superheated, katalis basa, analisis eksergi

ABSTRACT

Biodiesel becomes a promising substitution to petro-diesel fuel, since it is renewable and environmentally friendly. Biodiesel can be produced by catalytic or non-catalytic process. This paper discusses two different technologies in the palm oil biodiesel production, which is alkali-catalyzed and non-catalytic superheated methanol vapor (SMV) process. The exergy analysis was performed to compare those two technologies. Closed system was assumed for the exergy analysis, while kinetic and potential exergy were neglected. The result shows that the total exergy efficiency of non-catalytic SMV process was lower than the catalytic one, which was 92.61% and 95.37%, respectively. The methanol evaporation process contributed the highest irreversibility, which was 2802.07 kJ/kg biodiesel. The heat recirculation process could increase the exergy efficiency of biodiesel production, especially when SMV methods was adopted. The irreversibility of the non-catalytic SMV process was higher than the catalytic one, due to high temperature requirement of the non-catalytic SMV process. Therefore, the improvement of the SMV process was indispensable to be conducted, especially in the methanol evaporation process, to increase the efficiency of SMV process.

Keywords: palm oil, biodiesel, superheated methanol vapor, alkali-catalyzed, exergy analysis

INTRODUCTION

The global search for cleaner energy sources has led to the development of biodiesel. Biodiesel is a renewable energy source that could substitute fossil fuel. Biodiesel can be degraded easily (biodegradable), non-toxic, has a better cetane numbers than petroleum diesel, contains no sulfur and aromatic compounds thus the combustion emissions are more environmentally friendly and does not increase the accumulation of carbon dioxide in the atmosphere, thereby it can reduce the global warming effects (Sheehan *et al.*, 1998). One of the most important disadvantages of biodiesel is a lower energy output than fossil fuels and consequently requires greater quantities of energy to be consumed

in order to produce the same energy unit (Jaimes *et al.*, 2010).

Biodiesel can be produced by transesterification of natural oils or fats with short-chain alcohol, mainly methanol. Transesterification reaction can be performed with or without catalysts. Three types of catalysts, namely alkali, acid and enzyme catalyst, could be used in the transesterification process. Most of the methods on transesterification reaction are in the employing of alkali catalyst due to mild reaction conditions and high reaction rate. However, these methods have some drawbacks such as difficulties in the removal of the catalyst and the energy requirement for washing and purification of the product after transesterification process. Furthermore, oils

containing free fatty acids and/or water are incompletely transesterified using alkaline catalyst (Kusdiana and Saka, 2001).

In order to eliminate the disadvantages resulted from the use of catalyst, non-catalytic transesterification methods have been proposed by many researchers: (1) supercritical methanol method, where the transesterification process is conducted at high temperature and high pressure (350° C, 43 MPa) (Kusdiana and Saka, 2001), (2) simultaneous reaction of transesterification and cracking (STING) method, which is a complex reaction of transesterification, pyrolysis, cracking and oxidation treated in supercritical methanol condition (Iijima *et al.*, 2004), and (3) superheated methanol vapor (SMV) method, where the transesterification process conducted in high temperature 290° C but in atmospheric pressure (Yamazaki *et al.*, 2007; Joelianingsih *et al.*, 2008).

Selection of the proper process in producing biodiesel becomes a crucial decision, not only because of its cost and efficiency, also the environmental impact factor in achieving technology sustainability. An accurate method that can be applied to assess technology sustainability of biodiesel production from crude palm oil (CPO) is exergy analysis. Exergy (extractable energy), by definition, is the maximum amount of work that can be done by a subsystem as it approaches thermodynamic equilibrium with its surroundings by a sequence of reversible processes (Bejan *et al.*, 1996).

The energy output/input ratio in biodiesel production life cycle can be an important factor for the feasibility evaluation of biodiesel production since higher energy content of the output compared to the energy content of the input means higher energy conversion efficiency. However, output/input ratio alone is not enough to indicate the conversion

effectiveness. There is a measure of availability of the energy input, as well as the output, which has to be considered in order to express the effectiveness. Besides, utilization of fossil energy as input to the energy production will jeopardize renewability of biodiesel itself. Measuring the renewability of an energy resource is also questionable if based only on energy balance stipulated by the first law of thermodynamics (FLT). Thereby, exergy analysis is indispensable for evaluation of the energy production.

Exergy is often confounded with energy. According to Dincer and Rosen (2007), energy analysis is the traditional method of assessing the way energy is used in some physical or chemical processes with transfer and/or conversion of energy. This usually entails performing energy balances and evaluating energy efficiencies. However, an energy balance provides no information on the quality degradation of energy or resources during a process.

The exergy method of analysis overcomes the limitations of the FLT. The concept of exergy is based on both the FLT and the Second Law of Thermodynamic (SLT). Exergy analysis clearly indicates the locations of energy degradation in a process and can therefore lead to improved operation or technology, also it can quantify the quality of heat in a waste stream. The main aim of exergy analysis is to identify meaningful (exergy) efficiencies and the causes and true magnitudes of exergy losses. Table 1 presents a general comparison of both energy and exergy (Dincer and Cengel, 2001).

Exergy is a measure of distance from thermodynamic equilibrium. It is not a conserved quantity (like energy) but it is possible to construct an exergy balance for any energy or materials transformation process, accounting for inputs, process losses, useful products and wastes (Ayres *et al.*, 1996).

Table 1. Comparison of energy and exergy

Energy	Exergy
<ul style="list-style-type: none"> • is dependent on the parameters of matter or energy flow only, and independent of the environment parameters. • has the values different from zero (equal to mc^2 of Einstein's equation). • is governed by the FLT for all the processes. • is limited by the SLT for all processes (incl. reversible ones). • is motion or ability to produce motion. • is always conserved in a process, so can neither be destroyed or produced. • is a measure of quantity only. 	<ul style="list-style-type: none"> • is dependent both on the parameters of matter or energy flow and on the environment parameters. • is equal to zero (in dead state by equilibrium with the environment). • is governed by the FLT for reversible processes only (in irreversible processes it is destroyed partly or completely). • is not limited for reversible processes due to the SLT. • is work or ability to produce work. • is always conserved in a reversible process, but is always consumed in an irreversible process. • is a measure of quantity and quality due to entropy.

Note: FLT= First Law of Thermodynamics; SLT = Second Law of Thermodynamics

The exergy of a system (relative to the assumed reference environment) depends on system temperature, pressure and composition; the first two contribute to thermo-mechanical exergy, and the third is the effect of composition to chemical exergy. Exergy analysis can identify areas in which technical and other improvements should be undertaken, and indicate the priorities, which should be assigned to conservation measures, efficiency improvements and optimizations. Exergy is an excellent concept to describe the utilization of energy and material resources in systems (Wall, 2011).

Exergy analysis enables calculating exergy of streams (mass or heat fluxes) and the destroyed exergy in different units included in the overall process to find energetic inefficiency (Portha *et al.*, 2008). Exergy of a system is divided into four components: kinetic exergy associated with relative motion; potential exergy associated with gravitational or electromagnetic field differentials; physical exergy from pressure and temperature differentials; and chemical exergy arising from differences in chemical composition (Szargut, 1988 cited in Ayres *et al.*, 1996; Kotas, 1995).

Several researchers have used exergy analysis to evaluate the production of biodiesel. Some studies evaluated the catalytic transesterification process (Talens *et al.*, 2007; Jaimes *et al.*, 2010; Peiro *et al.*, 2010). Tambunan *et al.* (2011) performed exergy analysis to assess heat recirculation in non-catalytic reaction of biodiesel production. The objective of this study was to compare catalytic and non-catalytic SMV methods of crude palm oil (CPO) based biodiesel production using exergy analysis as a tool.

MATERIAL AND METHODS

System Evaluation

For evaluating biodiesel production process technologies, two system methods are specified, that are alkali-catalyzed transesterification (catalytic process) and non-catalytic transesterification (SMV process). Transesterification is a reaction in which triglycerides is reacted with short-chain alcohols to form fatty acid methyl esters, known as biodiesel fuel. The stoichiometric ratio for the transesterification reaction requires three moles of methanol and one mole of triglyceride to yield three moles of fatty acid methyl ester and one mole of glycerol (Freedman *et al.*, 1986). Transesterification reactions can be performed with or without catalyst. The selection of catalyst depends on the amount of free fatty acid (FFA) present in the oils or fats. Alkali-catalyst is used for oils/fats with FFA content less than 5%, while acid-catalyst is used for oils/fats with FFA content more than 5% (Joelianingsih *et al.*, 2007). The following discussion describes the

catalytic and non-catalytic (SMV) transesterification process.

Catalytic Transesterification Process

Catalytic transesterification experiment was conducted in a facility owned by Center for Design Engineering and Technology System (Engineering Center), Agency for Assessment and Application of Technology (*Badan Pengkajian dan Penerapan Teknologi / BPPT*). The catalytic biodiesel production process started with the transesterification reaction, methanol recovery, methyl ester purification from the catalyst, and separation of glycerol as a byproduct. Figure 1 shows the process of catalytic transesterification to produce 1 ton palm oil biodiesel in Engineering Center.

Superheated Methanol Vapor of Non-catalytic Process (SMV)

The non-catalytic SMV data was obtained from previous research (Joelianingsih *et al.*, 2008; Furqon, 2011; Sekiguchi, 2012). The maximum output rate of FAME occurred at reaction temperature of 290°C (Yamazaki *et al.*, 2007). The process of non-catalytic SMV transesterification to produce 1 ton palm oil biodiesel is presents in Figure 2 (Joelianingsih, 2008).

This study concerned only on exergy analysis during the transesterification process at the biodiesel plant, and the analysis limited up to the conversion process without assessing the separation and methanol recovery process. The catalytic method utilized catalyst to accelerate the transesterification process. Therefore, it needs the washing process to purify the product from catalyst. This process also concerned of this study.

The exergy associated with a specified state of a system is the sum of two contributions: the thermomechanical contribution (physical exergy) and the chemical contribution (chemical exergy). A closed system was assumed both for catalytic and non-catalytic SMV processes, the kinetic and potential exergy were ignored. Schematic of transesterification process presents in Figure 3. The exergy balance for a closed system is developed by combining the closed system energy and entropy balances. The first step in deriving the exergy balance, multiply the entropy balance by the temperature T_0 and subtract the resulting expression from the energy balance, as in equation (1) (Moran and Shapiro, 2006):

$$\underbrace{\Delta U - T_0 \Delta S}_{\text{exergy change}} = \underbrace{Q \left(1 - \frac{T_0}{T}\right) - W}_{\text{exergy transfer}} - \underbrace{T_0 \sigma_g}_{\text{exergy destruction}} \dots (1)$$

The closed system exergy balance results as in equation (2)

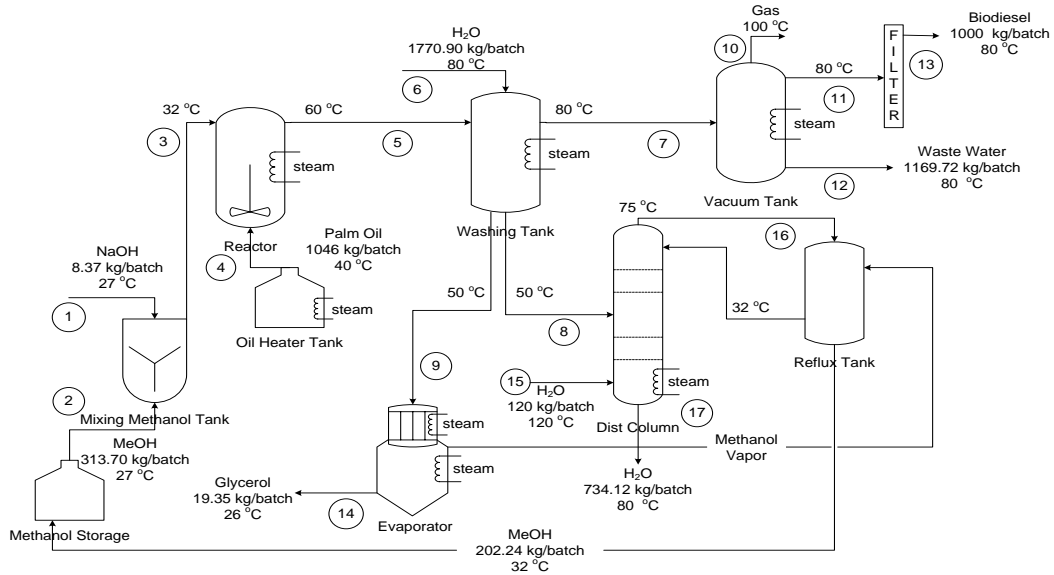


Figure 1. The alkali-catalyzed process of palm oil biodiesel production

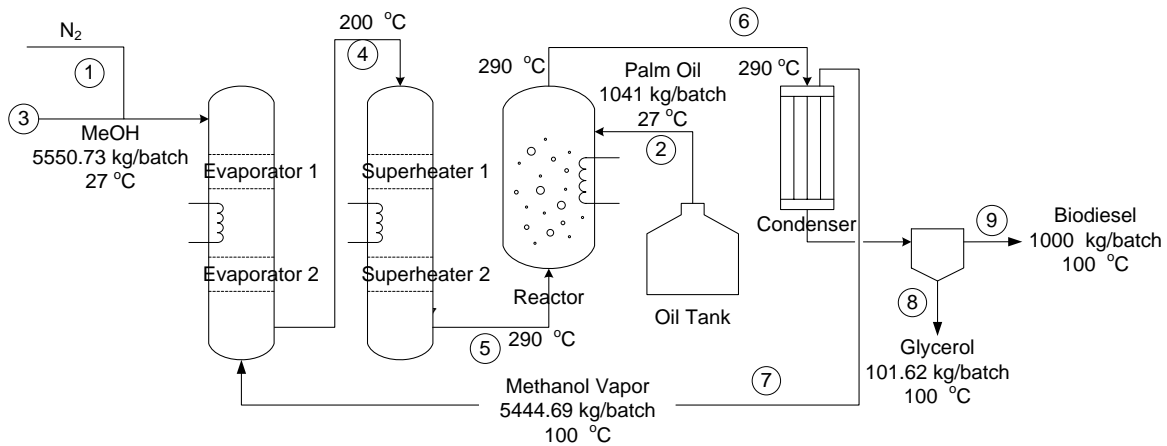


Figure 2. The superheated methanol vapor (SMV) process to produce 1 ton palm oil biodiesel

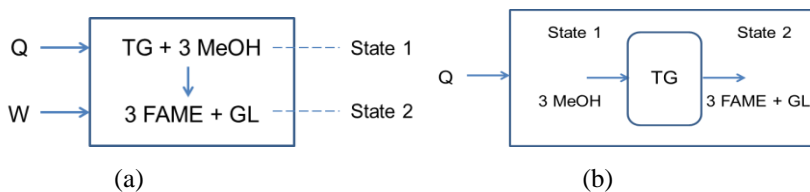


Figure 3. Schematic of transesterification process, (a) Catalytic process, (b) SMV process

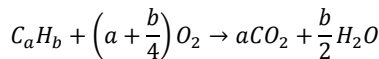
The equations (1) and (2) are the thermomechanical contribution of exergy, also called as physical exergy, where ΔB is the change in exergy between two states ($B_2 - B_1$). State 1 was in the form of triglyceride and methanol, state 2 was in the form of FAME and glycerol, which can be obtained by calculating its internal exergy.

Chemical exergy, B_{ch} , is the work that can be obtained by taking a substance at T_0 and P_0 , to the state defined by the environmental reference composition. It represents exergy that nature has spent or should have spent to create the resource, respectively the waste.

$$\underbrace{\Delta B}_{\text{exergy change}} = \underbrace{Q \left(1 - \frac{T_0}{T}\right)}_{\substack{\text{exergy transfer} \\ \text{accompanying heat}}} - \underbrace{W}_{\substack{\text{exergy transfer} \\ \text{accompanying work}}} - \underbrace{T_0 \sigma_g}_{\substack{\text{exergy destruction} \\ \text{accompanying irreversibility}}} \dots\dots\dots(2)$$

$$B_{ch} = \frac{\left[\bar{g}_f + \left(a + \frac{b}{4}\right) \bar{g}_{O_2} - a \bar{g}_{CO_2} - \frac{b}{2} \bar{g}_{H_2O(l)} \right] (T_0, P_0)}{\left\{ a B_{chCO_2} + \frac{b}{2} B_{chH_2O(l)} - \left(a + \frac{b}{4}\right) B_{chO_2} \right\}} \dots\dots\dots(3)$$

The chemical exergy in this study was approached by a chemical exergy of a hydrocarbon, C_aH_b, which reaction given by:



The chemical exergy of each element that contributed to the transesterification process can be calculated by the equation (3) (Bejan *et al.*, 1996; Moran and Shapiro, 2006). The specific Gibbs functions are evaluated at the temperature T₀ and pressure P₀ of the environment as in equation (4).

$$\bar{g}(T_0, P_0) = \bar{g}_f^0 + \left[\bar{g}(T_0, P_0) - \bar{g}(T_{ref}, P_{ref}) \right]$$

where \bar{g}_f^0 is the Gibbs function of formation. For the special case where T₀ and P₀ are the same as T_{ref} and P_{ref}, respectively, the second term on the right of Eq. 7 vanishes and the specific Gibbs function is just the Gibbs function of formation. Finally, note that the underlined term of Equation (3) can be written more compactly as -ΔG: the negative of the change in Gibbs function for the reaction, regarding each substance as separate at temperature T₀ and pressure P₀.

Exergy efficiency (second law of thermodynamics) in each subsystem can be written as in equation (5) (Cengel and Boles, 2007).

$$\eta = 1 - \frac{I}{B_1} = 1 - \frac{T_0 \Delta S_{gen}}{B_1} \dots\dots\dots(5)$$

where I is the irreversibility which is the multiplication of dead state temperature (T₀) and entropy generated by the process (ΔS_{gen}). B₁ is exergy at state 1 (kJ) in each subsystem.

Exergy is evaluated with respect to a reference environment. The reference ambient air is at 27°C and 100 kPa, for temperature and pressure, respectively.

RESULT AND DISCUSSION

Comparison of Exergy Efficiency of Catalytic and SMV Methods

The catalytic biodiesel production process utilized water by repetitive washing to purify product from catalyst; it made this process more wasteful of water. Biodiesel reaction with the catalyst has an advantage that the reaction can be run faster, while the disadvantages are the purification of the product requires longer process and the reaction

needs vigorous stirring due to the immiscible character oil with methanol (Kusdiana and Saka, 2001).

The non-catalytic SMV process has several advantages such as not requiring the removal of free fatty acid (FFA) by refining or pre-esterification. Esterification or transesterification reactions can take place in a reactor, thus oils with high FFA content can be used directly. In addition, the processes of separation and purification products become more simple and environmentally friendly, due to the absent of catalyst. However, non-catalytic processes normally require a higher operating temperature than the catalytic one and the reaction rate of biodiesel production is lower than that by catalytic process.

Exergy is a measure of energy quality or energy availability to perform work, and the calculation uses environmental parameters as a reference. Exergy analysis included both exergy consumed in production processes due to energy and materials used. The differences between catalytic and non-catalytic SMV methods are conducted at the exergy transfer accompanying heat, since SMV method required high temperature in the process, and the exergy transfer accompanying work, since no mechanical work in the SMV method, hence the catalytic method utilized mechanical work in the mixing process of methanol and catalyst. Mass balances to produce 1 kg biodiesel in the catalytic and SMV process are shown in Table 2 and 3, respectively. Mechanical energy in catalytic process is 3.55 kJ/kg biodiesel.

Exergy balance analysis provides the amount of energy availability to run a process and also provides the irreversibility value at each unit. The change of exergy of a system will change exergy transfer and exergy destruction.

Table 4 represents the total exergy balance of palm oil biodiesel production. The result shows the total irreversibility of the non-catalytic SMV process was higher than the catalytic one due to high temperature requirement of the non-catalytic SMV process. Irreversibility represents the internal exergy loss in the process as the loss of quality of materials and energy due to dissipation (Prins *et al.*, 2003). The irreversibility is influenced by several factors, which are: the mass transfer between phases, environment temperature, and heat transfer. The heat recirculation is needed to reduce the irreversibility and to make the process more sustainable, especially if the SMV methods will be adopted.

The discrepancy amount of exergy change between catalytic and non-catalytic SMV methods was due to the difference of triglyceride and methanol consumption, and also the difference of glycerol production in the production of 1 kg biodiesel. The exergy change between two states can be evaluated based on its internal exergy (chemical exergy).

The chemical exergy in a material is the least possible amount of exergy that has to be consumed to create and maintain the chemical structure of the material in certain surroundings (Hovelius 1999). The catalyst in the catalytic process was assumed can be recycled after the washing process, so it was not taken into account in the chemical exergy. The result of chemical exergy balance of CPO biodiesel production presents in Table 5.

Figure 4 represents the total exergy efficiency of palm oil biodiesel production. The result shows the total exergy efficiency of the non-catalytic SMV process was lower than the catalytic one, again, due to high temperature requirement of the non-catalytic SMV process. Therefore, the improvement of the SMV process is indispensable to be conducted.

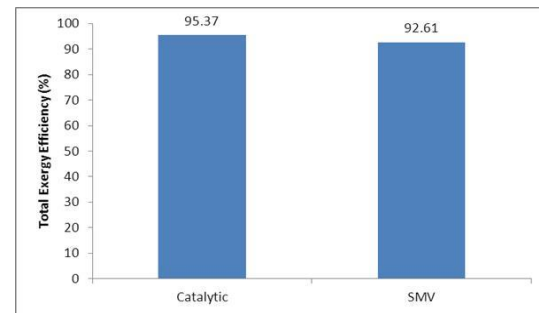


Figure 4. Total exergy efficiency to produce 1 kg biodiesel

Exergy Analysis of the Non-catalytic SMV Method

In order to identify the critical area in the transesterification process of non-catalytic SMV method, exergy analysis also conducted in each subsystem of the process being evaluated. Transesterification process in the non-catalytic SMV method accrued by passing methanol vapor up to superheated conditions (290°C) in reactor that has been loaded by palm oil and conditioned at a temperature of 290°C with *semi-batch* system.

Table 2. Mass balance to produce 1 kg biodiesel in the catalytic process

	NaOH		MeOH		CPO		ME		Gly	
	mass (kg)	temperature (K)	mass (kg)	temperature (K)	mass (kg)	temperature (K)	mass (kg)	temperature (K)	mass (kg)	temperature (K)
input	0.008	300	0.314	300	1.046	303	0	0	0	0
output	0.008	338	0.202	338	0.012	338	1.000	338	0.110	338

Table 3. Mass balance to produce 1 kg biodiesel in the SMV process

	MeOH		CPO		ME		Gly	
	mass (kg)	temperature (K)	mass (kg)	temperature (K)	mass (kg)	temperature (K)	mass (kg)	temperature (K)
input	5.551	308	1.041	308	0	0	0	0
output	5.445	563	0.001	563	1.000	563	0.107	563

Table 4. Total exergy balance to produce 1 kg biodiesel

	Exergy Change		Exergy transfer		Irreversibility
	state 1 (input) (kJ)	state 2 (output) (kJ)	input (kJ)	output (kJ)	
Catalytic	44146.66	42107.41	16.69	9.03	2046.90
SMV	43853.47	42034.49	3223.21	1563.35	3478.84

Table 5. Chemical exergy balance to produce 1 kg biodiesel

Catalytic	State 1 (kJ)	State 2 (kJ)	SMV	State 1 (kJ)	State 2 (kJ)
CPO	41645.77		CPO	41460.18	
Methanol (l)	2500.88		Methanol (g)	2393.30	
Biodiesel		40014.60	Biodiesel		40014.60
glyserol		2092.81	glyserol		2019.89

Evaporator works to increase the methanol temperature and change it to vapor phase, further the temperature of methanol steam upgraded to the level of superheated in the superheater sub-systems. In reactor occurred the reaction between palm oil in the liquid phase with methanol in the superheated vapor phase at a temperature of 290°C. As a result of the exothermic nature of the reaction, the reactor also got the addition of heat energy from the chemical reaction of biodiesel formation. Mass balances to produce 1 kg biodiesel in each subsystem of the SMV process are shown in Table 6 – 8.

Table 6. Mass balance to produce 1 kg biodiesel in evaporator of the SMV process

	Evaporator 1		Evaporator 2	
	MeOH		MeOH	
	mass (kg)	temperature (K)	mass (kg)	temperature (K)
input	5.55	308	5.55	423
output	5.55	423	5.55	473

Table 7. Mass balance to produce 1 kg biodiesel in superheater of the SMV process

	Superheater 1		Superheater 2	
	MeOH		MeOH	
	mass (kg)	temperature (K)	mass (kg)	temperature (K)
input	5.55	473	5.55	523
output	5.55	523	5.55	563

The analysis result of exergy balance of the non-catalytic SMV process shows that the methanol evaporation process in the evaporator 1 contributed the highest irreversibility compare to other processes (Table 9). The evaporator 1 works to transform methanol into a vapor phase. The different temperature levels and mass transfer between phases were the main source of irreversibility in evaporator. It can be said that evaporator is the key component for improvements.

Joelianingsih (2008) proposed the substitution of evaporator, and superheated function

Table 8. Mass balance to produce 1 kg biodiesel in reactor of the SMV process

	MeOH		CPO		ME		Gly	
	mass (kg)	temperature (K)	mass (kg)	temperature (K)	mass (kg)	temperature (K)	mass (kg)	temperature (K)
input	5.55	563	1.041	308	0	0	0	0
output	5.44	563	0.001	563	1.00	563	0.107	563

Table 9. The exergy balance of SMV method to produce 1 kg biodiesel

	Exergy Input (kJ)	Exergy Output (kJ)	Ireversibility (kJ)
Evaporator 1	3802.72	1000.64	2802.07
Evaporator 2	434.52	343.54	90.98
Superheater 1	701.44	590.22	111.22
Superheater 2	863.26	777.91	85.35
Reactor	1501.91	1162.95	338.96

in the SMV process by four heat exchangers. The heat balance of the biodiesel production process was determined using HYSYS software. The simulation result showed that heat recirculation by heat exchangers could reduce about 55% of energy consumption in biodiesel production with the SMV method. Tambunan *et al.* (2012) performed heat recirculation in the SMV process. The results presented that heat recovery in the SMV process could increase about 18% of energy ratio in biodiesel production. Those methods, which performed by Joelianingsih (2008) dan Tambunan *et al.* (2012), can be implemented in order to reduce the irreversibility and to increase the exergy efficiency of SMV methods.

CONCLUSIONS AND RECOMMENDATION

Conclusions

Exergy analyses of the palm oil biodiesel production technologies were accomplished in this study. The exergy analysis result shows that the exergy efficiency of non-catalytic SMV method was lower than the catalytic method. This condition occurred because the irreversibility of the non-catalytic SMV process was higher than the catalytic one due to high temperature requirement of the non-catalytic SMV process. Heat recirculation is needed to increase the exergy efficiency of both methods and to make the process more sustainable, especially if the SMV methods will be adopted. The improvement of overall process in the SMV methods is required, especially in the methanol evaporation process to reduce the irreversibility and increase the exergy efficiency. Exergy analysis is a useful concept for improving the efficiency of biodiesel production.

Recommendation

The exergy analysis in this study was limited up to the conversion process. Therefore, in the future study, the exergy analysis should be performed up to the return of unreacted methanol.

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