Research Article

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Exergy analysis of conventional and hydrothermal liquefaction–esterification processes of microalgae for biodiesel production

Abstract: As fossil fuels were depleting at an alarming rate, the development of renewable energy has become necessary. One of the promising renewable energy to be used is biodiesel. The interest in using third-generation feedstock, which is microalgae, is rapidly growing. The use of third-generation biodiesel feedstock will be more beneficial as it does not compete with food crop use and land utilization. The advantageous characteristic which sets microalgae apart from other biomass sources is that microalgae have high biomass yield. Conventionally, microalgae biodiesel is produced by lipid extraction followed by transesterification. In this study, combination process between hydrothermal liquefaction (HTL) and esterification is explored. The HTL process is one of the biomass thermochemical conversion methods to produce liquid fuel. In this study, the HTL process will be coupled with esterification, which takes fatty acid from HTL as raw material for producing biodiesel. Both the processes will be studied by simulating with Aspen Plus and thermodynamic analysis in terms of energy and exergy. Based on the simulation process, it was reported that both processes demand similar energy consumption. However, exergy analysis shows that total exergy loss of conventional exergy loss is greater than the HTL-esterification process.

Keywords: biodiesel, microalgae, hydrothermal liquefaction, exergy, AspenPlus simulation

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1 Introduction

Nowadays, industrial development and population growth have stimulated high energy requirement for both transportation and electricity need [1]. In Indonesia, it is shown that energy consumptions in 2014 had reached 962 million tonnes of oil equivalent (MTOE), with 73% accounted for fossil fuel [2]. However, Indonesia's oil and coal reserves are depleting at an alarming rate [3]. From this standpoint, it is clear that renewable energy has significant influence in ensuring national energy security. This issue is in accordance with national government regulation which plans to increase renewable energy usage from 5% in 2005 to 25% in 2025 [4]. An attractive and robust renewable energy that can be implemented in Indonesia is biodiesel. Biodiesel is a methyl ester manufactured from transesterification of triglyceride and esterification of fatty acid.

Reactions, which result in biodiesel, can be carried out using various raw materials that include biodiesel from first-generation (G-1) and second-generation raw material (G-2), which cover edible and nonedible oil and waste [5]. However, both of them have several drawbacks, including competition with food requirements (G-1) and high impurity within the feedstock (G-2). In order to tackle those drawbacks, microalgae have received tremendous interest as relatively new biodiesel feedstock (third generation/G-3) [6]. Compared with other biomass sources, microalgae are more beneficial since its biomass productivity and oil/lipid content are high and can be cultivated without agricultural land [7]. Algae cultivation is also more advantageous due to its capability to be used for removing carbon dioxide and industrial wastewater treatment [8].

Among many microalgae species, *Botryococcus braunii* is one of the most potent microalgae in the development of biofuel. *Botryococcus braunii* is freshwater microalgae commonly found in ponds, open water space and other freshwater area [9]. *Botryococcus braunii* gains interest, especially for producing biodiesel, as it contains

relatively high content of lipid/oil (36–63%), depends on the amount of nitrogen supply during cultivation [10]. Pradana et al. [8] reported that *Botryococcus braunii* is able to produce 0.0187 g oil/g dry microalgae, which consists of several fatty acids including palmitic acid (43.06%), linolelaidic acid (8.60%), elaidic acid (43.06%) and stearic acid (5.29%). From this standpoint, it is clear that microalgae oil is one of the most suitable feedstock for producing biodiesel.

In order to utilize the oil content of microalgae, there are several methods that can be performed after cultivating the microalgae. In conventional process, harvested microalgae is proceeded through oil content extraction using chemical solvent and then transesterified into biodiesel [11]. However, in conventional process, the harvested microalgae concentration is usually very low due to excessive water content from harvesting process. In some cases, the harvested microalgae content is only 0.5–22%, depends on the method of harvesting [12]. Prior to the extraction process, water content needs to be set as minimum as possible.

Another process which can be chosen is hydrothermal liquefaction (HTL) due to its capability to produce biofuel from wet microalgae. HTL is one of the thermochemical routes of converting biomass into liquid fuel or bio-oil besides pyrolysis. HTL is relatively a more efficient process in terms of converting biomass into liquid fuel as compared to pyrolysis [13]. In addition, in HTL process, water content in harvested microalgae, which turns into subcritical water, acts as both reactant and medium [14]. Gai et al. [15] have confirmed that subcritical water allows hydrolysis reaction to occur, so that carbohydrate, protein and triglyceride contents in microalgae are hydrolyzed into their monomer, which are glucose, amino acid and fatty acid respectively. In this study, a new route of converting algae biomass into biodiesel utilizes fatty acid from HTL process with esterification. The proposed process is hypothetically created to examine its potency to become an alternative process of producing microalgal biodiesel. During this process, wet microalgae are processed using HTL to produce fatty acids, which are then converted into biodiesel using esterification reaction. The process of HTL-esterification was then compared with conventional process.

Exergy is one of the thermodynamic concepts which is able to examine process efficiency in a more comprehensive way [16]. Performing exergy analysis on similar process will be useful to justify the most energy efficient process configuration. The exergy analysis, which is developed from the second law of thermodynamics, allows to account for irreversibility of the process [17].

The objective of this study is to examine the potency of HTL-esterification to be an alternative and promising biodiesel production process. One of the most easiest and logical way is by comparing it with conventional biodiesel process from microalgae, which consumes a considerable amount of energy [18]. Exergy analysis will be more likely a suitable method to assess the efficiency of conventional biodiesel production process and the proposed process.

Simulation-based exergy analysis of biodiesel production has also been conducted by previous studies [17], which reported that in biodiesel production from *Jatropha curcas*, 95% of the raw material exergy content was destroyed during reaction. Another study by Ofori-Boateng et al. [19] showed simulation and exergy analysis of biodiesel plants from microalgae *Jatropha* using Aspen Plus. However, exergy analysis related to HTL is relatively limited, especially for integrated HTL-esterification process. From those standpoints, the objective of this study is to evaluate the proposed process via exergy analysis.

1.1 Thermodynamic analysis

Due to energy demand of both the hydrothermal and esterification processes, energy utilization needs to be done on the processes. Meanwhile, exergy analysis is a robust analysis based on the first and second law of thermodynamics to analyze an effective method of energy saving.

Furthermore, exergy analysis is used in thermodynamic basis to modify a process in order to achieve energy optimization. Exergy or available energy is a part of energy which can be converted into mechanical energy [20]. Exergy analysis would give information about quantity and quality of energy transformation in a system. It is because the second law of thermodynamics gives mathematical equation which states that every process will generate entropy [21]. Entropy generation within the process will lead to exergy destruction [22]. Mathematically, exergy change calculation is similar to ΔG^0 in which enthalpy is reduced due to entropy generation at ambient temperature ($T_0 = 298.15$ K) as mentioned in equation (1)

$$\Delta E = \Delta H - T_0 \cdot \Delta S \tag{1}$$

where E, H and T represent flow of exergy, enthalpy and entropy respectively.

Exergy analysis is able to be carried out in several methods. Budiman and Ishida [20] demonstrated that thermodynamic analysis using exergy concepts can be comprehensively performed by using energy utilization diagram. Hajjaji et al. [22] and Ofori-Boateng et al. [19],
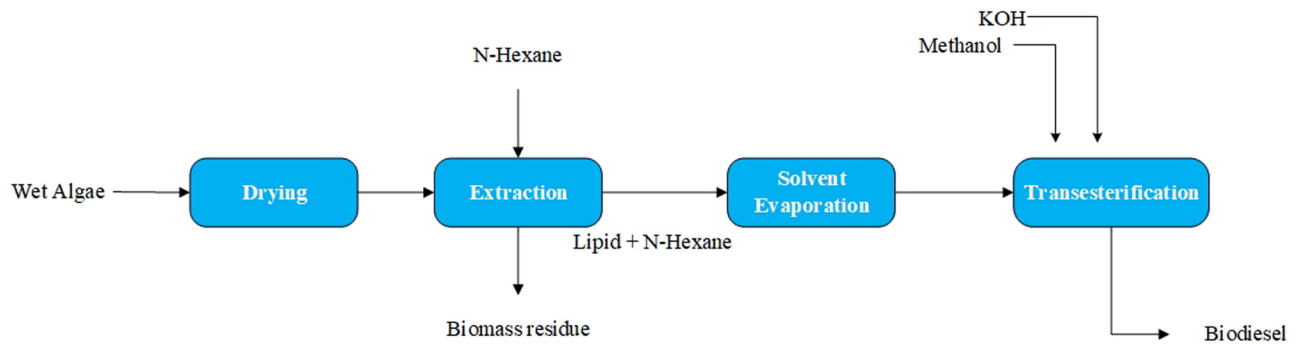
Figure 1: Biodiesel production block diagram via conventional process.

which performed exergy analysis using Aspen Plus simulation, calculated exergy in every process streams to investigate exergy loss due to irreversibility and wasted stream. Basically, exergy flows in each process stream consist of physical, chemical and mixing exergy, as shown in equation (2) [19]:

$$Ex = Ex_{chem} + Ex_{phys} + Ex_{mix} \quad (2)$$

where Ex_{chem} is chemical exergy flows, while Ex_{phys} and Ex_{mix} are physical and mixing exergy flow respectively. The calculation of each term is listed using equations (3)–(5) [19]:

$$Ex_{chem} = M \cdot \left(x_{0,l} \sum_{i=1}^{n} x_{0,i} \cdot \varepsilon_{chem,i}^{0l} \right) \quad (3)$$

where $\varepsilon_{chem,i}^{0l}$ and M are the standard chemical exergy of pure components in phase and total molar flow rate [19].

$$Ex_{phys} = \left\{ M \left(x_l \left(\sum_{i=1}^{n} x_i H_i^l - T_0 \sum_{i=1}^{n} x_i S_i^l \right) \right) \right\} \quad (4)$$

where H_i and S_i are molar enthalpy and entropy of pure components.

Thermodynamic data used and the chemical exergy are obtained from Aspen Plus 8.6 database (version 8.6; AspenPlus; Aspentech) and chemical exergy calculator which perform calculation based on Gibbs free energy (exergoecology).

After calculating the exergy flow in every stream, calculation of exergy loss for every equipment is then carried out by using exergy balance. During this process, exergy loss or exergy gain will occur in every equipment. Exergy loss is present due to the irreversibility of the process, while irreversibility happened because of entropy generation. In general, the exergy loss can be calculated based on equation (5) [23]

$$\sum \Delta E_{in} = \sum \Delta E_{out} + I \quad (5)$$

where $\sum \Delta E_{in}$, $\sum \Delta E_{out}$ and I are the sum of exergy flow entering the system, the sum of exergy flow leaving the system and the exergy destroyed, respectively. Moreover,
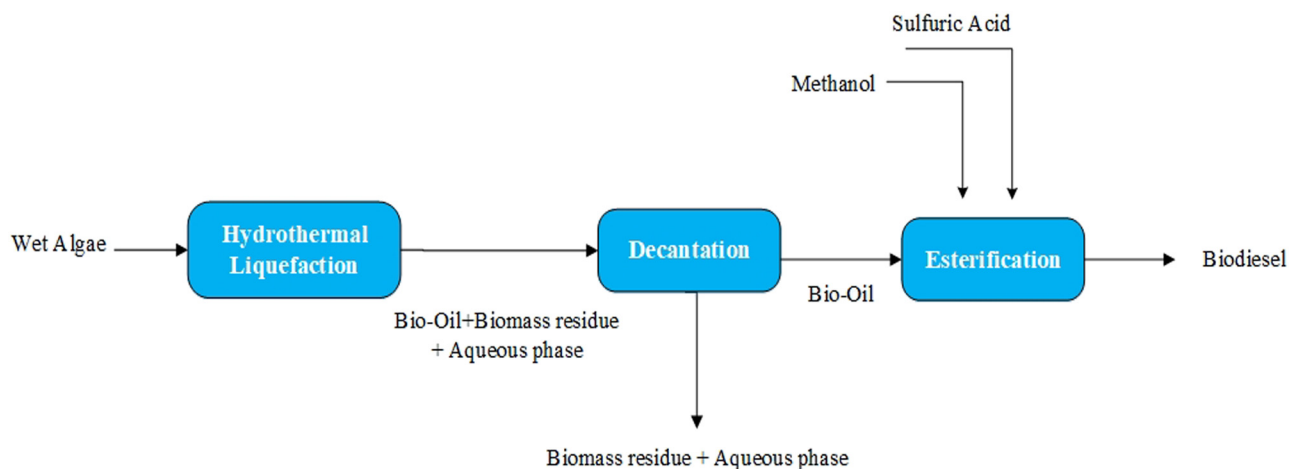

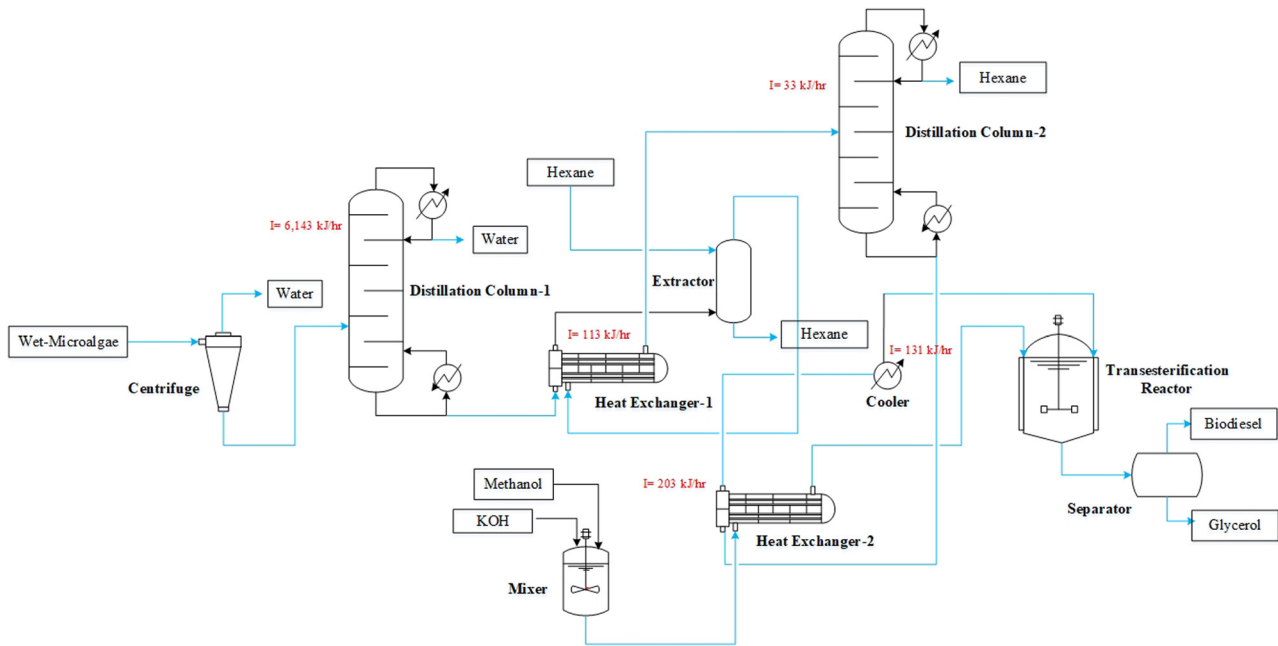**Figure 2:** Biodiesel production block diagram via HTL-esterification process.

Figure 3: Biodiesel production process flow diagram of conventional process.

the second law of thermodynamics states that irreversibility of a process is equal to or greater than zero, so that [23]:

$$I \geq 0 \qquad (6)$$

Therefore, the percentage of exergy loss for every equipment is obtained as follows [20]:

$$\psi = \frac{\sum \Delta E_{\text{out}}}{\sum \Delta E_{\text{in}}} \qquad (7)$$

or

$$\psi = 1 - \frac{I}{\sum \Delta E_{\text{in}}} \qquad (8)$$

2 Methodology

The objective of this study is to evaluate biodiesel production from microalgae with conventional process and HTL-esterification process. In this paper, Aspen Plus 8.6 software was used to simulate the process flow diagram as well as to provide data for the evaluation. The composition of *Botryococcus braunii* used in this simulation was taken from reference [8]. As the cultivation and harvesting are outside of the boundary of this study, the fresh feed for the process is started with wet microalgae.

The wet microalgae is then fed to the conventional process and HTL-esterification built using Aspen Plus equipment modules.

The Aspen Plus equipment modules enable user to resemble many processes in industry and considers equilibrium or rate-processes calculation rigorously. Both of the conventional and HTL-esterification simulations were developed from block diagrams shown in Figures 1 and 2.

In conventional process shown in Figure 1, biodiesel was produced from transesterification of lipid content in the microalgae. In this process, wet microalgae need to be dried up before entering lipid extraction. The water content of microalgae was reduced by centrifugation, which was followed by water evaporation. Typically, after water removal, dried microalgae was then fed to an extractor in which solvent will extract oil, leaving the microalgae biomass to become residue. The solvent was then evaporated so that the oil can be obtained, as depicted in Figure 1. Stream containing microalgae oil is then transesterified to produce methyl ester or biodiesel.

HTL, also known as subcritical water extraction, is one of the thermochemical conversion routes of biomass, which recently attracted attention due to its capability to proceed with wet biomass. The core of the HTL process lies in the utilization of water at subcritical condition which can act both as solvent for nonorganic components as well as reactant [14]. The needs for high pressure and temperature for producing subcritical water is one of the important parameters in designing HTL process. HTL yields residue, aqueous phase and bio-oil, which are produced from complex reaction [15]. In this simulation, bio-oil containing fatty acid was
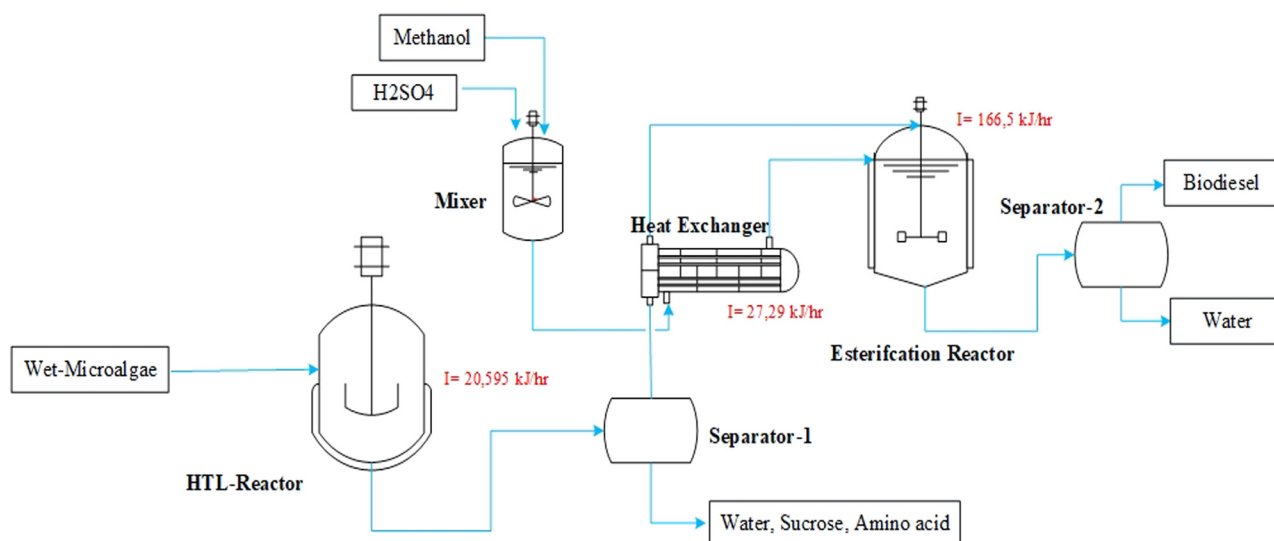
Figure 4: Biodiesel production process flow diagram of HTL-esterification process.

separated from its other constituents by phase separation. Simple description of HTL process is depicted in Figure 2. In this process, the effluent of HTL process that contained mixture of product was then fed into separator model in Aspen Plus using assumption that the separator was able to purify bio-oil from other constituents. In HTL-esterification process, instead of using lipid content of the microalgae as in the conventional process, biodiesel production was carried out via esterification that converted fatty acid found in bio-oil.

Although bio-oil consists of many organic compounds, it was assumed that the dominant compound was carboxylic acid/fatty acid. The produced carboxylic acid is then reacted with methanol in acidic condition to produce biodiesel.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results

Complete process flow diagram of conventional process is shown in Figure 3. Centrifuge used in the process was able to remove considerable amount of water content [13], yet further water evaporation is still needed to reduce water content of microalgae. Since there is significantly large boiling point difference between water and microalgae component, the distillation column is chosen. During solvent extraction, it is assumed that only triglyceride content is separated from the mixture.

Before entering the transesterification reactor, hexane is separated in the second distillation column. For simulating reactors used in the process, block model of RStoic with operating condition obtained from reference is used [24]. The biodiesel product is then separated from glycerol, catalyst and remaining methanol using phase separator.

The process flow diagram of HTL-esterification process is shown in Figure 4. Based on Figure 4, it can be observed that HTL-esterification process is a relatively simpler process as compared to conventional. In this process, wet microalgae is directly converted in HTL reactor, in which water content will act as solvent and reactant at subcritical condition [14]. The distinct feature of HTL-esterification is the direct use of wet microalgae for feed stream, thus removing the need for water removal and extraction before reaction. Performing HTL at operating temperature from 95
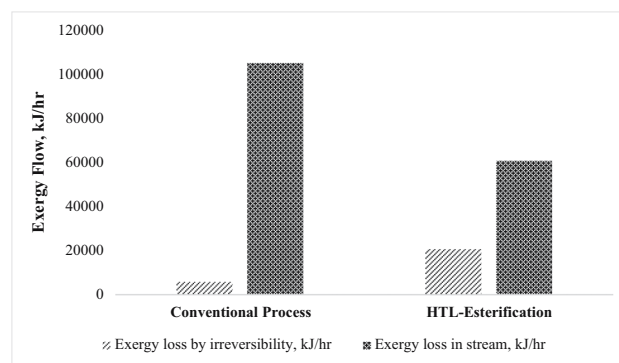

Figure 5: Biodiesel production process flow diagram of HTL-esterification process.
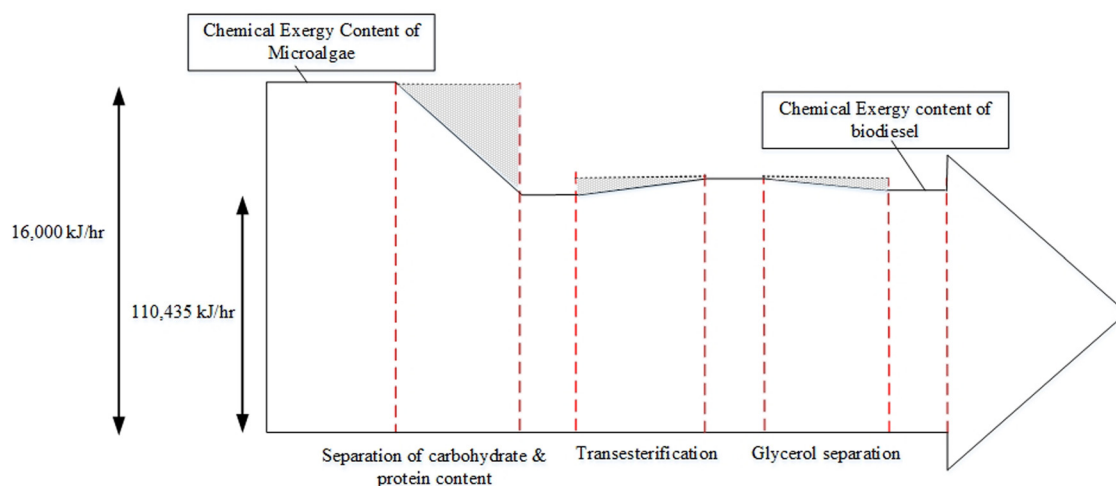
Figure 6: Biodiesel production process flow diagram of HTL-esterification process.

to 120°C allows the biopolymer content of the microalgae to hydrolyze into its monomer [15]. Therefore, it is expected that the triglyceride can be converted into fatty acid and glycerol. The fatty acid product is then separated from its aqueous phase by utilizing phase separation [20]. Esterification reaction simulation is performed based on the operating condition by Hidayat et al. [25]. After phase separation, the biodiesel product is collected.

4 Discussion

Based on the simulation, the comparison of energy consumption of both processes can be performed. In total, calculation showed that producing biodiesel via conventional process and HTL-esterification process has relatively similar energy consumption, which are 5.68 and 5.65 kW/kg respectively. It is reasonable since although the conventional process needs relatively high energy for water removal via centrifugation and distillation, the HTL-esterification process also demands considerable amount of energy to achieve the subcritical condition for the process.
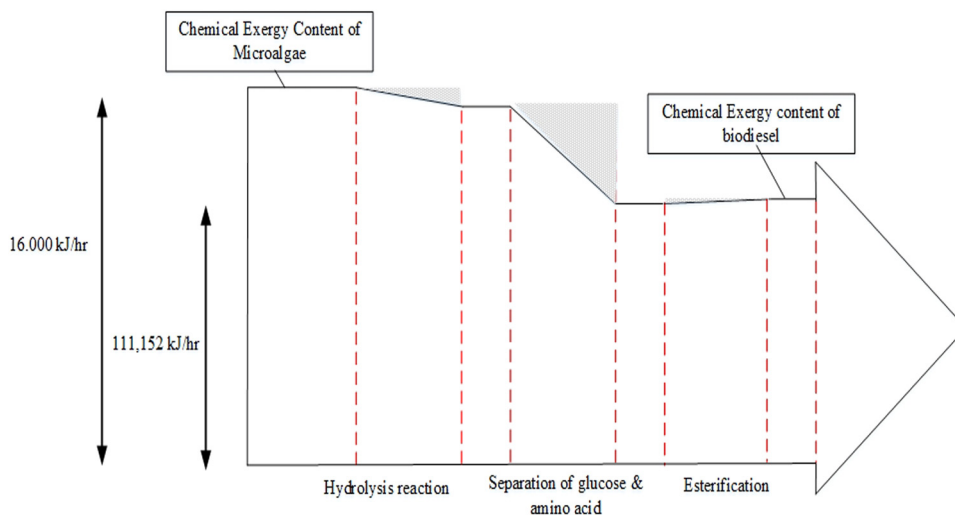
Besides the energy consumption of both processes, exergy analysis can also be performed on each process. Exergy analysis allows the investigation of the most inefficient process or equipment from overall process. In this simulation, exergy loss is categorized into internal exergy loss due to irreversibility and exergy loss due to component removal from stream [23]. Despite its simplicity, that categorization is able to give clearer exergy loss in each equipment as it is shown in Figures 3 and 4. The "I" letter

shown in Figures 3 and 4 indicate the exergy loss due to irreversibility or entropy generation, while other equipment without "I" has negligible exergy loss due to irreversibility. According to Figures 3 and 4, it is implied that high exergy loss due to irreversibility occurs in the equipment which is associated with heat transfer. Theoretically, it was also discovered that irreversibility in the process can be caused by several factors, including heat transfer over a finite temperature difference and friction [23]. However, in this simulation, exergy loss due to heat transfer is the dominant one.

Figure 5 gives overall comparison of exergy loss for both processes. It can be deduced that conventional process is significantly inefficient compared to HTL-esterification process. It is also observed that exergy which was carried by removed streams are higher compared to exergy loss due to irreversibility. In addition to that, Figure 5 also depicts that HTL-esterification process has higher irreversibility. This is possible since the HTL reactor consumes higher energy, thus providing heat transfer process leading to high exergy loss.

Simple Grassman diagram depicted in Figures 6 and 7 gives the information of chemical exergy change of microalgae during the process. According to both figures, approximately 30% of chemical exergy content of microalgae is lost during the process. It is also observed that the change of exergy content due to reaction is different for both processes. The hydrolysis reaction during HTL reduces the chemical exergy content (Figure 7). On the other hand, the transesterification and esterification reactions cause slight increase of chemical exergy content.

After comparing both conventional and HTL-esterification process, it is known that thermodynamic analysis of the process in terms of energy consumption does not tell

Figure 7: Biodiesel production process flow diagram of HTL-esterification process.

much, as the process only has slight difference of energy consumption. However, exergy analysis on both process reveals that chemical exergy recovery from microalgae in biodiesel products is approximately 70% for both conventional and HTL-esterification process. That finding implies that certain amount of exergy is lost during the process. Further investigation shows that exergy loss in the system consists of internal exergy loss in each unit operation due to irreversibility and exergy loss due to stream removal. Overall, it is justified that HTL-esterification offers greater potential for producing biodiesel compared to conventional process, due to its direct capability of utilizing wet microalgae, relatively simpler process and produces lower exergy loss in stream compared to conventional process.

5 Conclusion

From this study, it can be concluded that:
1. Approximately 30% of microalgae chemical exergy content is lost during conversion process to biodiesel.
2. Biodiesel production from microalgae using conventional process has higher overall exergy loss compared to HTL-esterification
3. Exergy loss due to irreversibility of heat transfer in HTL-esterification is higher compared to conventional process.

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