



Evaluation of hydrolysis–esterification biodiesel production from wet microalgae



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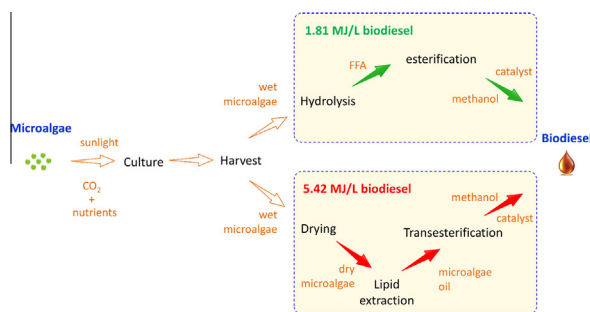
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HIGHLIGHTS

- Energy consumption of different microalgae biodiesel production routes is evaluated.
- Vapor recompression and heat integration are utilized to reduce energy consumption.
- Energy requirement of hydrolysis–esterification route is reduced to 1.81 MJ/L biodiesel.
- 3.61 MJ can be saved to produce per liter biodiesel by hydrolysis–esterification route.

GRAPHICAL ABSTRACT



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ABSTRACT

Wet microalgae hydrolysis–esterification route has the advantage to avoid the energy-intensive units (e.g. drying and lipid extraction) in the biodiesel production process. In this study, techno-economic evaluation of hydrolysis–esterification biodiesel production process was carried out and compared with conventional (usually including drying, lipid extraction, esterification and transesterification) biodiesel production process. Energy and material balance of the conventional and hydrolysis–esterification processes was evaluated by Aspen Plus. The simulation results indicated that drying (2.36 MJ/L biodiesel) and triolein transesterification (1.89 MJ/L biodiesel) are the dominant energy-intensive stages in the conventional route (5.42 MJ/L biodiesel). By contrast, the total energy consumption of hydrolysis–esterification route can be reduced to 1.81 MJ/L biodiesel, and approximately 3.61 MJ can be saved to produce per liter biodiesel.

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1. Introduction

Biofuel is a promising alternative of fossil fuels due to several advantages, sustainability, environmental friendly and good adaptability (Chen et al., 2015; Su et al., 2015). Among different biofuels,

biodiesel has attracted the most interest. However, the first and second generation biodiesel is difficult for commercial application owing to their influence on food security, instability and high production cost (Noraini et al., 2014; Rawat et al., 2013). In light of the challenge, microalgae have been considered as a more viable feedstock for biodiesel without displacing crops and land (Chisti, 2007; Alaswad et al., 2015).

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Generally, biodiesel production from microalgae includes culture, harvesting, drying, extraction and transesterification (Khoo et al., 2013; Bahadar and Khan, 2013). Although microalgae biodiesel production presents significant potential, it still has several challenges that must be overcome. Heretofore, cost is the main hurdle to commercialization of biodiesel product (Ma and Hanna, 1999; Song et al., 2015, 2016). Zhang et al. reported that biodiesel usually costs over 0.5 \$/L, compared to 0.35 \$/L for petroleum-based diesel (Zhang et al., 2003). The life-cycle assessment (LCA) by Lardon et al. indicated that high biodiesel from algae production cost was mainly caused by microalgae drying and lipid extraction, which accounted for up to 90% (Lardon et al., 2009). In addition, the presence of free fatty acids and water adversely causes saponification reaction during transesterification of triglycerides, which also causes additional energy input for pretreatment before reaction (Kusdiana and Saka, 2004a).

It can be conceived that avoiding microalgae drying and lipid extraction would be an effective alternative to save energy and

cost in the biodiesel production processes (Xu et al., 2011; Sathish and Sims, 2012; Takisawa et al., 2013a). Many efforts to eliminate these energy-intensive units have been put forward. In 2004, Kusdiana and Saka designed a two-step biodiesel production process from rapeseed oil (Kusdiana and Saka, 2004b). Hydrolysis and esterification were carried out under the subcritical state of water and methanol, respectively. They found that the hydrolysis–esterification route could convert rapeseed oil to fatty acid methyl esters (FAME) in considerably shorter reaction time and milder reaction condition than the direct supercritical methanol transesterification. In 2013, Takisawa et al. tested hydrolysis of wet microalgae and then esterified the hydrolysates under high water content (Takisawa et al., 2013b). The experiment results indicated that FAME yield by esterification of hydrolysates was increased by 181.7% compared to that by direct transesterification under the same amount of water content (80%). Although a large amount of research has been carried out to develop novel biodiesel production processes, literature

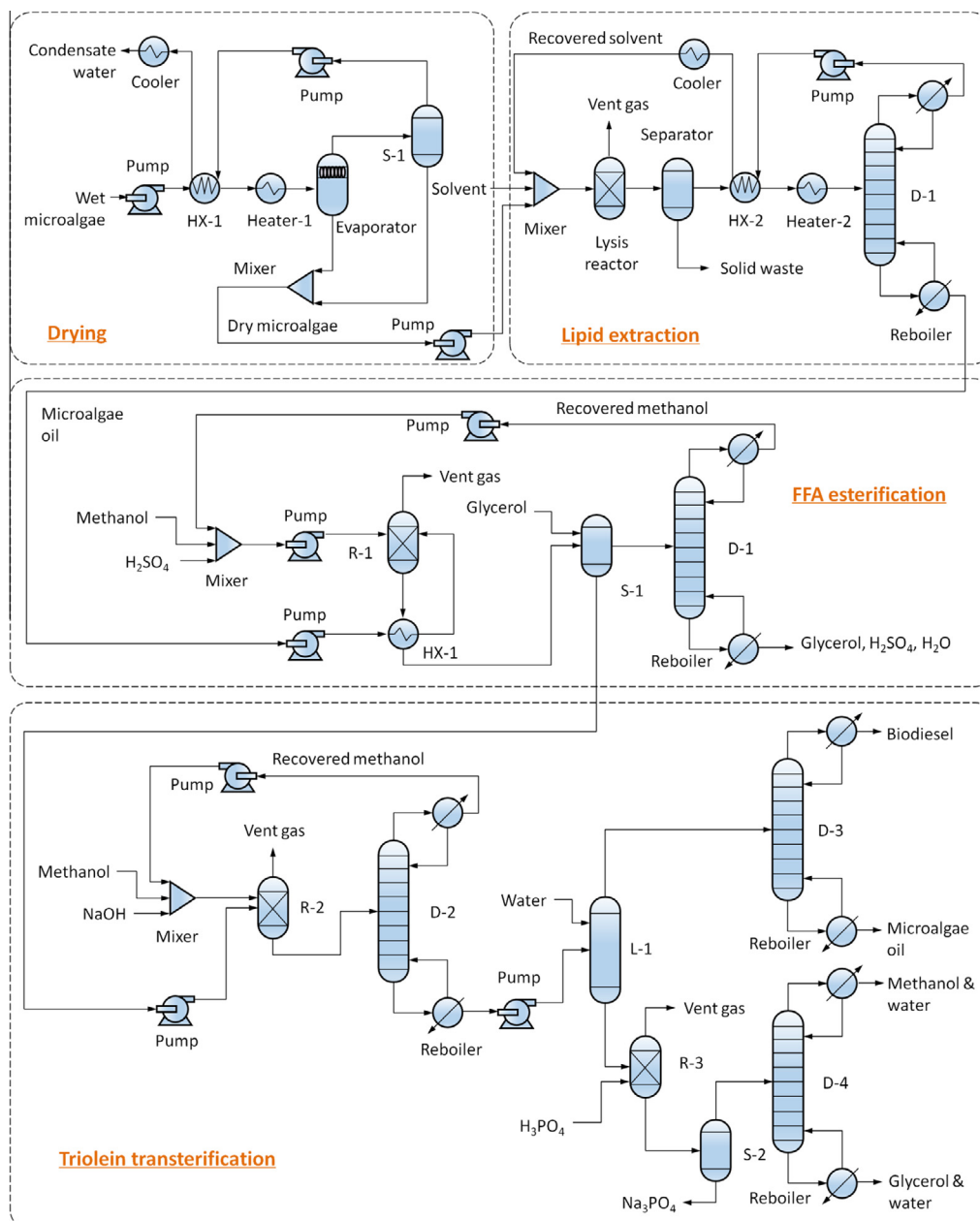


Fig. 1. Conventional biodiesel production process from microalgae by drying, lipid extraction, FFA esterification and triolein transesterification.

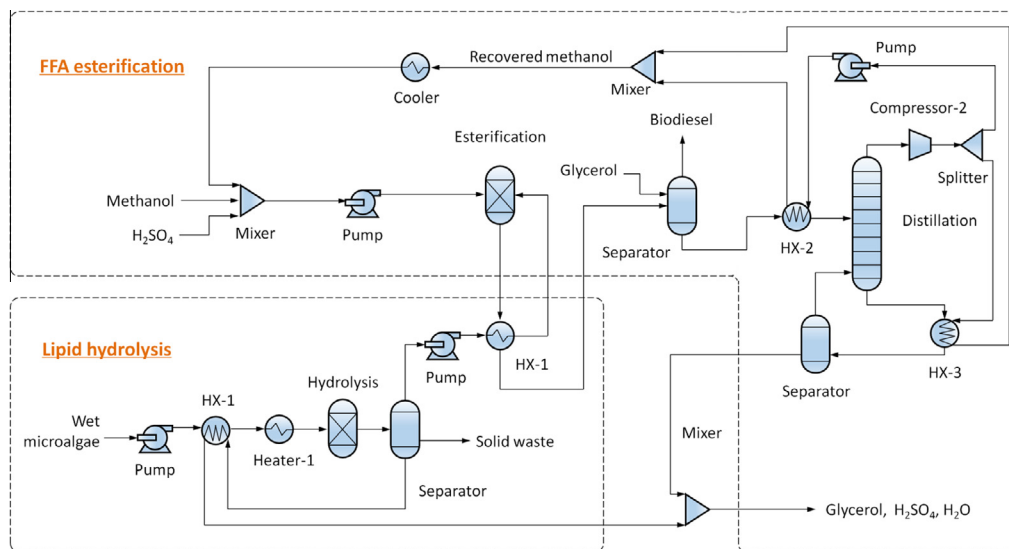


Fig. 2. Hydrolysis–esterification biodiesel production process from wet microalgae.

Table 1
Thermodynamic properties of dominant components involved in microalgae biodiesel production.

Properties	Wet microalgae				Methyloleate	Glycerol	Methanol	Hexane
	Triolein	Oleic acid	Phenylalanine	Sucrose				
Chemical formula	C ₅₇ H ₉₈ O ₆	C ₁₈ H ₃₄ O ₂	C ₉ H ₁₁ NO ₂	C ₁₂ H ₂₂ O ₁₁	C ₁₉ H ₃₆ O ₂	C ₃ H ₈ O ₃	CH ₃ OH	C ₆ H ₁₄
Molar mass (kg/kmol)	885.43	282.46	165.2	342.3	296.55	92.09	32.04	86.18
Freezing point (°C)	–	13.0	–	–	–20.0	17.8	–97.6	–
Flash point (°C)	–	–	153.1	375.4	92.4	160.0	11.0	–26.0
Density (kg/m ³)	916.0	895.0	1290.0	1580.5	873.0	1261.0	792.0	0.65
Boiling point (°C)	412.8	360.0	329.5	697.1	351.4	290.0	64.8	68.5
Critical temperature (°C)	588.8	507.85	–	–	490.85	452.85	239.43	–
Critical pressure (kPa)	1203.0	1390.0	–	–	1280.0	6687.4	8095.9	–

related to the techno-economic evaluation of these advanced strategies are relatively few.

The objective of this study was to evaluate the techno-economic feasibility of hydrolysis–esterification biodiesel production process from wet microalgae. Energy and material balance of the proposed process is simulated. In order to make to a more accurate estimation, the performance of conventional biodiesel production process (including drying, oil extraction, pretreatment, triolein transesterification and biodiesel purification etc.) was also investigated. Finally, comparison between the hydrolysis–esterification and conventional processes was carried out.

2. Materials and methods

2.1. Conventional microalgae biodiesel production process

The typical biodiesel production process from microalgae is shown in Fig. 1. Generally, the harvested microalgae are first dried to concentrate the lipid. It is well known that additional heat is necessary to evaporate the moisture. After dehydration, chemical solvent is mixed with dried microalgae to extract the lipid. Then, excess solvent is recovered by distillation to avoid waste. The obtained microalgae oil mainly includes free fatty acid (FFA) and triolein. To avoid the negative reaction of saponification in biodiesel transesterification process, FFA should be removed by reacting with methanol under acid catalyst, namely esterification. After reaction, the excess methanol is recovered by distillation column. Finally, the obtained production from esterification (mainly triolein) is further converted into fatty acid methyl esters (FAME)

by transesterification under alkaline condition. In the transesterification section, three distillation columns are involved. Their functions are methanol recovery, biodiesel and glycerol purification (Song et al., 2015). In the whole biodiesel production process, two heaters (dryer and extraction column) and five reboilers (at the bottom of distillation columns) are utilized, which cause the high biodiesel production cost.

2.2. Hydrolysis–esterification biodiesel production process

Fig. 2 depicts the direct hydrolysis–esterification biodiesel production process. In order to avoid the high energy requirement caused by drying and oil extraction, triglycerides in the wet microalgae are first treated by hydrolysis reactor to produce fatty acid (FA). After hydrolysis, the reaction mixture is separated into aqueous, oil and solid phases by the phase separator. The oil phase (upper layer) consists mainly of FA, while the aqueous phase (middle layer) contains glycerol and water. The solid phase (down layer) includes carbohydrates and protein, etc. The separated oil mixture is then mixed with methanol and treated at supercritical condition to produce fatty acid methyl esters (FAME) through esterification reaction. Since the methanol is added in excess to facilitate the yield of FAME, the unreacted methanol is recovered by distillation column. It is worth noting that instead of condensation, the recovered methanol stream at the top of the distillation column is recompressed to elevate the exergy rate, and then exchanges heat with feed and bottom stream. Due to the upgrading of waste heat by vapor recompression, the sensible and latent heat associated with recovered methanol can be effectively circulated in the process (Kansha et al., 2009; Waheed et al., 2014).

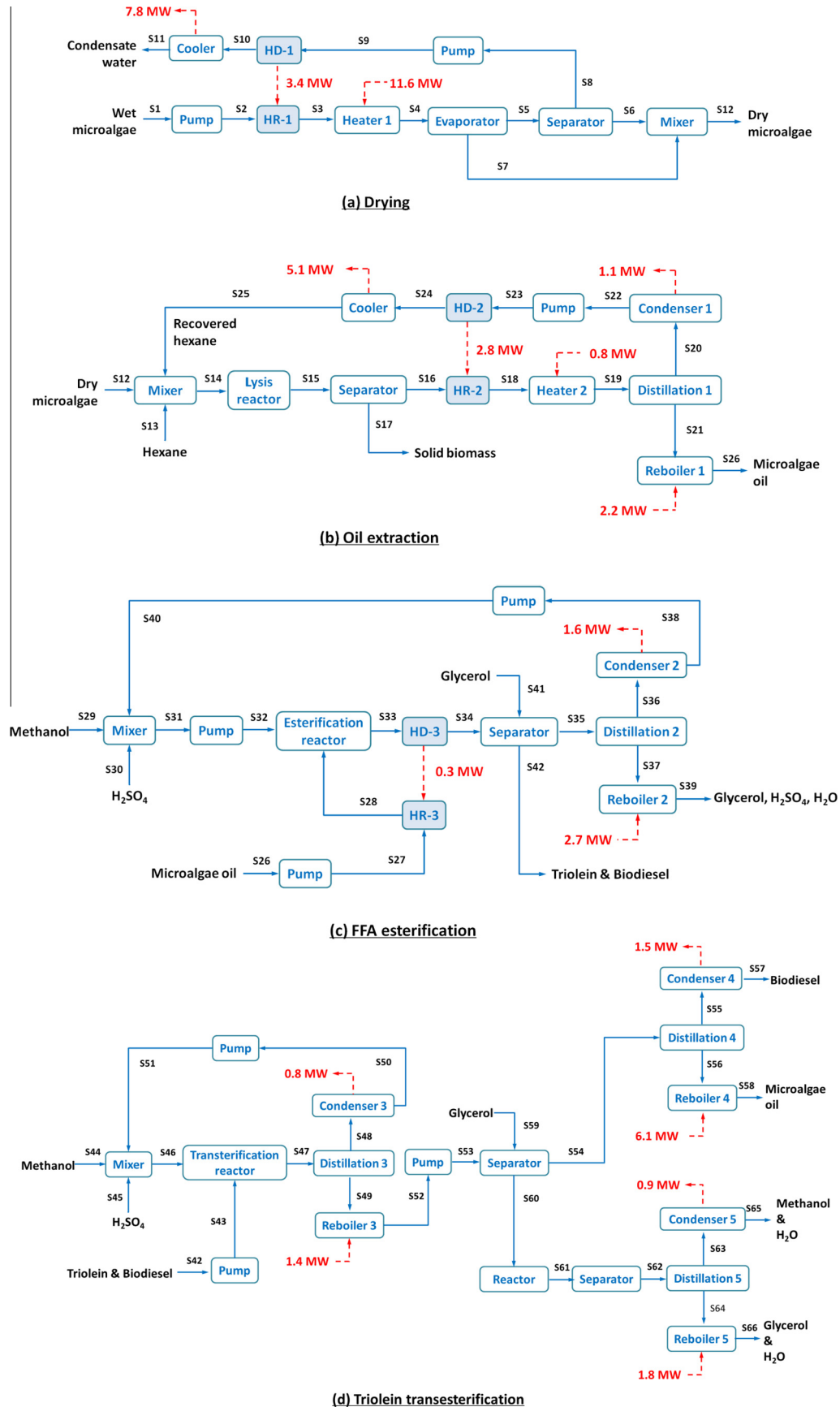


Fig. 3. Energy and material balance of conventional microalgae drying (a), oil extraction (b), esterification (c) and transesterification (d) for biodiesel production.

Table 2
Stream properties of drying and lipid extraction stage in the conventional biodiesel production process.

Stream No.	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S16	S18	S19	S20	S21	S22	S24	S26	
Temperature (°C)	25	25	102	180	180	180	180	180	180	180	180	180	25	25	59	69	91	91	70	68	361	
Pressure (kPa)	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101	101
Mole flow rate (kmol/h)	1000	1000	1000	1000	902	2	98	900	900	900	900	100	1150	1266	1266	1266	1167	19	1167	1167	1167	19
Composition (wt.%)																						
Oleic acid	0.001	0.001	0.001	0.001	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.010	0.000	0.004	0.004	0.004	0.000	0.050	0.000	0.000	0.000	0.050
H ₂ O	0.910	0.910	0.910	0.910	0.998	0.001	0.101	0.998	0.998	0.998	0.998	0.099	0.000	0.013	0.013	0.013	0.014	0.000	0.014	0.014	0.014	0.000
Hexane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.909	0.909	0.909	0.986	0.000	0.986	0.986	0.986	0.000
Sucrose	0.015	0.015	0.015	0.015	0.000	0.000	0.152	0.000	0.000	0.000	0.000	0.149	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Phenylalanine	0.055	0.055	0.055	0.055	0.002	0.999	0.546	0.002	0.002	0.002	0.002	0.555	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Triolein	0.019	0.019	0.019	0.019	0.000	0.000	0.191	0.000	0.000	0.000	0.000	0.187	0.000	0.074	0.074	0.074	0.000	0.950	0.000	0.000	0.000	0.950

2.3. Materials

The wet microalgae is represented by *Chlorella* sp., and its composition is assumed as lipid (2%), carbohydrates (1.5%), proteins (5.5%) and water (91%) (Becker, 2007; Kanda and Li, 2011; Phukan et al., 2011). Microalgae oil includes free fatty acids (FFAs, 5%) and triolein (95%). FFAs are represented by oleic acid. Proteins and carbohydrates are represented by L-phenylalanine and sucrose, respectively. Fatty acid methyl esters (FAME) are represented by methyloleate. In the conventional biodiesel process, hexane is selected as solvent for oil extraction. Sulfuric acid and sodium hydroxide are used as catalyst for esterification and transesterification reaction, respectively. By contrast, catalyst involved in the hydrolysis-esterification process is only sulfuric acid.

2.4. Methods

Microalgae culture and harvesting are not considered in this work since they are necessary in the both processes. The main processing units for the microalgae biodiesel production routes include dryer, distillation columns, heat exchangers, pumps, mixers, separators. Mixers were used for blending solvents with biomass. Heaters were utilized for heating and cooling streams. Heat exchangers were used to recover the waste heat generated in the process. Pumps were used for moving liquid streams. Separation of liquid/solid phases was carried out using separators. The production capacity was chosen taking into account the necessary oil amount to produce 100,000 ton/year of third generation biodiesel, which corresponds to an approximate lipid flow of 104,000 ton/year (Peralta-Ruiz et al., 2013).

Aspen plus is used to simulate the energy and material balance of conventional and hydrolysis-esterification processes. The procedures for process simulation mainly involve defining chemical components, selecting a thermodynamic model, determining plant capacity, choosing proper operating units and setting up input conditions (composition, flow rate, temperature and pressure) (Zhang et al., 2003). The nonrandom two liquid (NRTL) thermodynamic method is used to calculate the mixture properties based on functional-groups that constitute the components. Except triolein, most of components are available in the component library. The density, boiling point, critical temperature, pressure, and volume can be determined from the work of Lee et al. (2011). The properties of dominant components are summarized in Table 1.

To simplify the complexity of simulation, the following assumptions are made: (1) The mode of heat exchange is counter-current in all heat exchangers. (2) The minimum temperature approach in all heat exchangers is set at 10 °C. (3) The isentropic efficiency of the compressors and pumps is assumed to be 80%. (4) The heat and pressure loss during the biodiesel production process are assumed to be negligible. (5) In order to facilitate understanding, the heat exchanger (HX) is assumed to consist of two parts: heat donor (HD) and heat receptor (HR). The dryer is assumed to consist of heater and evaporator. (6) Dried microalgae has a moisture content of 10 wt.%. (7) The flow rate of wet microalgae is 1000 kmol/h.

3. Results and discussion

3.1. Energy and material balance

3.1.1. Conventional biodiesel production process

The energy and material balance of conventional biodiesel production process (including microalgae drying, lipid extraction, esterification, transesterification and purification units) is simulated and shown in Fig. 3. The detail streams information of different units is listed in Tables 2–4. In the drying stage (Fig. 3a), the

Table 3
Stream properties of FFA esterification stage in the conventional biodiesel production process.

Stream No.	S27	S28	S29	S30	S32	S33	S35	S38	S39	S41	S42
Temperature (°C)	25	59	25	25	25	70	25	64	295	25	25
Pressure (kPa)	101	101	101	101	101	101	101	101	101	101	101
Mole flow rate (kmol/h)	19	19	58	10	88	88	87	56	31	20	19
Composition (wt.%)											
Oleic acid	0.050	0.050	0.000	0.000	0.012	0.000	0.000	0.000	0.000	0.000	0.000
H ₂ O	0.000	0.000	0.000	0.000	0.000	0.012	0.012	0.000	0.034	0.000	0.000
H ₂ SO ₄	0.000	0.000	0.000	1.000	0.114	0.114	0.115	0.000	0.322	0.000	0.000
Methanol	0.000	0.000	1.000	0.000	0.669	0.657	0.643	0.999	0.000	0.000	0.000
Glycerol	0.000	0.000	0.000	0.000	0.000	0.000	0.230	0.001	0.644	1.000	0.000
Triolein	0.950	0.950	0.000	0.000	0.205	0.205	0.000	0.000	0.000	0.000	0.950
FAME (biodiesel)	0.000	0.000	0.000	0.000	0.000	0.012	0.000	0.000	0.000	0.000	0.050

Table 4
Stream properties of triolein transesterification stage in the conventional biodiesel production process.

Stream No.	S44	S45	S46	S47	S50	S52	S54	S57	S58	S59	S60	S62	S65	S66
Temperature (°C)	25	25	25	75	64	102	25	344	345	25	25	25	64	185
Pressure (kPa)	101	101	101	101	101	101	101	101	101	101	101	101	101	101
Mole flow rate (kmol/h)	81	18	126	145	27	118	53	52	1	55	120	102	29	73
Composition (wt.%)														
Oleic acid	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H ₂ O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H ₂ SO ₄	0.000	1.000	0.143	0.124	0.000	0.152	0.000	0.000	0.000	0.000	0.150	0.000	0.000	0.000
Methanol	1.000	0.000	0.857	0.391	1.000	0.252	0.000	0.000	0.000	0.000	0.249	0.282	0.999	0.002
Glycerol	0.000	0.000	0.000	0.118	0.000	0.145	0.000	0.000	0.000	1.000	0.601	0.718	0.001	0.998
Triolein	0.000	0.000	0.000	0.006	0.000	0.007	0.016	0.001	1.000	0.000	0.000	0.000	0.000	0.000
FAME (biodiesel)	0.000	0.000	0.000	0.361	0.000	0.444	0.984	0.999	0.000	0.000	0.000	0.000	0.000	0.000

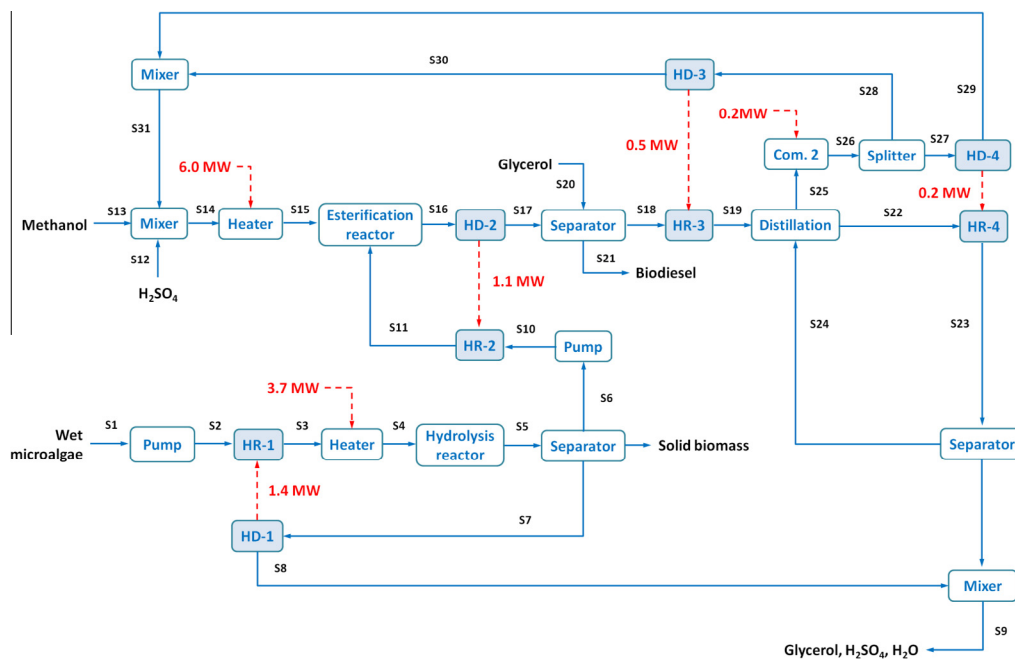


Fig. 4. Energy and material balance of hydrolysis–esterification biodiesel production process from microalgae.

wet microalgae (S3) is firstly heated by Heater-1 (11.6 MW). To recover the waste condensate heat (3.4 MW), the vapor product (S9) of separator exchanges heat with wet microalgae (S2). Due to the low exergy rate of S9, the performance of heat exchanger 1 (HX-1) is not optimal. Thus, 7.8 MW condensate heat is wasted in the cooling process. In the oil extraction stage (Fig. 3b), the energy consumption is mainly caused by distillation treatment, including two parts. First, Heater-2 (0.8 MW) is used to heat the mixture of microalgae oil and solvent (S18). The other part is the

heat requirement (2.2 MW) of reboiler to evaporate the extraction agent (S21). For heat recovery, the top product (recovered hexane, S22) is exchanged with oil mixture (S16) to reuse part of the waste heat (2.8 MW). In addition, most of condensate heat is wasted by the condenser (1.1 MW) and cooler (5.1 MW). In the esterification stage (Fig. 3c), the FFA in the oil mixture (S28) reacts with methanol (S32) in the esterification reactor, and part of reaction heat (0.3 MW) is recovered by heat exchanger-3 (HX-3) to heat microalgae oil (S27). The product (S35) is further purified by distillation

2.36 and 0.62 MJ/L biodiesel, respectively. Meanwhile, owing to the high FFA content in the microalgae oil, the pretreatment of converting FFA into FAME is also necessary. The energy consumption caused by esterification is around 0.55 MJ/L biodiesel. Finally, the triolein in the microalgae oil is transferred into FAME by transesterification reaction, which consumes 1.89 MJ/L biodiesel. Therefore, the total energy consumption of conventional process is 5.42 MJ/L biodiesel. By contrast, the energy-intensive sections (such as drying and oil extraction) are avoided in the hydrolysis–esterification process. The total energy consumption (1.81 MJ/L biodiesel) is attributed to hydrolysis and FFA esterification, which are 0.68 and 1.13 MJ/L biodiesel. Compared to the conventional microalgal biodiesel production method, the energy consumption of hydrolysis–esterification process can be reduced by 62.78%, which means 3.61 MJ can be saved to produce per liter biodiesel.

4. Conclusion

In this study, the feasibility analysis of hydrolysis–esterification biodiesel production process from microalgae was investigated and compared with conventional route (*i.e.* drying, lipid extraction, esterification and transesterification). Energy and material analysis indicated that the high energy requirement (5.42 MJ/L biodiesel) of conventional route is mainly contributed to the drying and transesterification stages, 2.36 and 1.89 MJ/L biodiesel, respectively. By contrast, the energy consumption of hydrolysis–esterification process was reduced to 1.81 MJ/L biodiesel, which equals to 33.39% that of conventional process.

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